

# The Activity Coefficients of Hydrofluoric Acid in Water from 0 to 35 °C

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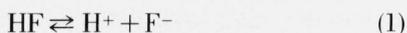
The mean stoichiometric activity coefficients of hydrofluoric acid in aqueous solutions have been calculated from measurements of electrolytic conductivity, the electromotive forces of galvanic cells without liquid junction, and the freezing-point depression. Values obtained from freezing-point depressions were converted to values for 25 °C using known values of the heats of dilution and apparent molal heat capacities of aqueous solutions of hydrofluoric acid of various concentrations. It is also shown that values for the concentrations of the various ionic species in hydrofluoric acid, namely,  $H^+$ ,  $F^-$ ,  $HF_2^-$ , and  $HF$  depend on the functions used to represent the ionic activity coefficients whereas values of the mean activity,  $a_{H^+}a_{F^-}$ , are independent of such functions. Values of the pH of various concentrations of hydrofluoric acid are given for temperatures of 0 to 35 °C; these, likewise, are nearly independent of activity-coefficient function used to obtain values for the ionic concentrations.

Key words: Activities of HF; equilibrium constant of HF dissociation; ionic concentrations in HF; pH values of HF.

During the critical evaluation of the activity coefficients of hydrofluoric acid under the National Standard Reference Data Program certain facts were uncovered that seemed worth presenting. These facts constitute this paper.

## 1. Dissociation of Hydrofluoric Acid

The degree of dissociation of hydrofluoric acid in aqueous solution is controlled by the two equilibria:



and



with the first one more significant at molal or molar concentrations below 0.001. The equilibrium constants for these reactions are given, respectively, by:

$$K = \frac{a_{H^+} a_{F^-}}{a_{HF}} = \frac{m_{H^+} m_{F^-} \gamma_{H^+} \gamma_{F^-}}{m_{HF} \gamma_{HF}} \quad (3)$$

and

$$k = \frac{a_{HF} a_{F^-}}{a_{HF_2^-}} = \frac{m_{HF} m_{F^-} \gamma_{HF} \gamma_{F^-}}{m_{HF_2^-} \gamma_{HF_2^-}} \quad (4)$$

where  $a$ ,  $m$ , and  $\gamma$  denote, respectively, the activity, molal concentration, and activity coefficient of the species denoted by the subscripts. Values of  $K$  and

$k$  may be determined from conductivity or emf measurements.

### 1.1. Conductivity Measurements

Values of  $K$  and  $k$  may be obtained from conductivity measurements as follows [1].<sup>1</sup> Let  $y$  and  $y_3$  be ratios, respectively, of the concentration unit of  $F^-$  and  $HF_2^-$  to the stoichiometric concentration,  $C$ , mol  $kg^{-1}$ , of HF and assume, as a start, that all activity coefficients are unity. Then,

$$K = \frac{Cy(y+y_3)}{(1-y-2y_3)} \cong Cy(y+y_3) \quad (5)$$

and

$$k = \frac{Cy(1-y-2y_3)}{y_3} \cong \frac{Cy}{y_3} \quad (6)$$

For the simplified versions of eqs (5) and (6),  $(1-y-2y_3)$  is set equal to unity.

Now the observed equivalent conductance,  $\Lambda$ , of HF is given approximately by:

$$\Lambda = y\Lambda_0 + y_3\lambda_0 \quad (7)$$

where  $\Lambda_0$  is the sum of the limiting equivalent conductances of  $H^+$  and  $F^-$  and  $\lambda_0$  is the sum of the limiting equivalent conductances of  $HF_2^-$  and  $H^+$ . Solving the

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

simplified versions of eqs (5) and (6) for  $y$  and  $y_3$  and substituting in eq (7) gives:

$$\Lambda(1+C/k)^{1/2} = (\Lambda_0 \sqrt{K})/\sqrt{C} + (\lambda_0 \sqrt{K}/k) \sqrt{C}. \quad (8)$$

This equation may be converted to a linear form by multiplying by  $\sqrt{C}$ , adding and subtracting  $C\Lambda_0 \sqrt{K}/k$  to the right side, dividing by  $(1+C/k)^{1/2}$ , squaring both sides, and simplifying. This procedure [1] gives:

$$C\Lambda^2 = \Lambda_0^2 K + [2\lambda_0/\Lambda_0 - 1 + (1 - \lambda_0/\Lambda_0)^2 / (1 + k/C)] \Lambda_0^2 K/k. \quad (9)$$

The term  $(1 - \lambda_0/\Lambda_0)^2 / (1 + k/C)$  becomes negligible at low concentrations and approaches asymptotically the limit  $(1 - \lambda_0/\Lambda_0)^2$  at high concentrations. Hence, this term may be neglected when  $\lambda_0/\Lambda_0$  is sufficiently close to unity to render  $(1 - \lambda_0/\Lambda_0)^2$  negligible with respect to  $(2\lambda_0/\Lambda_0 - 1)$ . Accordingly, eq (9) reduces to

$$C\Lambda^2 = \Lambda_0^2 K + C(2\Lambda_0\lambda_0 - \Lambda_0^2)K/k. \quad (10)$$

Introducing corrections for the ionic activity coefficients,<sup>2</sup>  $\gamma_c$ , and changes in ionic mobility with concentration,  $b$ , in eq (10) leads to [1]

$$\left(\frac{\gamma_c \Lambda}{b}\right)^2 \frac{C}{(1 - \Lambda/\Lambda_0)} = \Lambda_0^2 K + \frac{(2\Lambda_0\lambda_0 - \Lambda_0^2)K}{k} \left(1 - \frac{\Lambda}{\Lambda_0}\right) C, \quad (11)$$

where  $(1 - \Lambda/\Lambda_0)$  gives an approximation for the unionized portion of the solute. Furthermore, approximate values of  $\gamma_c$  and  $b$  are given, respectively, by:

$$\log \gamma_c = -A_c \sqrt{C\Lambda/\Lambda_0} \quad (12)$$

and

$$b = 1 - (B_1\Lambda_0 + B_2) \Lambda_0^{-1} \sqrt{C\Lambda/\Lambda_0} \quad (13)$$

where  $A_c$ ,  $B_1$ , and  $B_2$  are constants given by:

$$A_c = \left(\frac{2\pi N}{1000}\right)^{1/2} \frac{e^3}{(4\pi\epsilon_0)^{3/2} 2.302585 k^{3/2}} \left(\frac{1}{T^{3/2}\epsilon^{3/2}}\right) \quad (14)$$

$$B_1 = \frac{e^2}{6\epsilon kT (1 + \sqrt{0.5})} \left(\frac{8\pi N e^2}{(4\pi\epsilon_0)^2 1000\epsilon kT}\right)^{1/2} \quad (15)$$

$$B_2 = \frac{F^2}{3\pi\eta N} \left(\frac{8\pi N e^2}{(4\pi\epsilon_0)^2 1000\epsilon kT}\right)^{1/2} \quad (16)$$

in which  $N$  is Avogadro's constant ( $6.02252 \times 10^{26}$  kmol<sup>-1</sup>),  $e$  is the elementary charge ( $1.60210 \times 10^{-19}$  C),  $k$  is Boltzmann's constant ( $1.38054 \times 10^{-23}$  J/K),  $T$  is the Kelvin temperature,  $\epsilon$  is the dielectric constant of water,  $\eta$  is the viscosity of water, and  $\epsilon_0$  is the per-

mittivity of free space ( $8.85417 \times 10^{-12}$  C<sup>2</sup>J<sup>-1</sup>m<sup>-1</sup>). Using these values, concentrations are expressed in kmol m<sup>-3</sup> and equivalent conductances in m<sup>2</sup>Ω<sup>-1</sup>. Numerical values, however, remain the same as normally used in the cgs system of units.

A plot of the left side of eq (11) against  $c(1 - \Lambda/\Lambda_0)$  gives a straight line. The intercept at  $c(1 - \Lambda/\Lambda_0) = 0$  gives  $\Lambda_0^2 K$  and the slope of the line the value of  $(2\Lambda_0\lambda_0 - \Lambda_0^2)K/k$ . Accordingly  $K$  and  $k$  may be evaluated if values of  $\Lambda_0$  and  $\lambda_0$  are known.

Data on the conductivity of hydrofluoric acid at 25 °C have been reported by Deussen [2], Fredenhagen and Wellmann [3], Thomas and Maass [4], Ellis [5], and Erdey-Grúz, Majthényi, and Kugler [6]. Thomas and Maass reported their values to only one significant figure and the data of Erdey-Grúz et al. were lower than those of the others. The data of Deussen, Fredenhagen and Wellmann, and Ellis agreed to within 0.1 in the equivalent conductance and were accepted. Measurements of  $\Lambda$  were made at 16 and 20 °C by Roth [7] and Hill and Sirkar [8]. The data of Hill and Sirkar were very much lower than those of Roth and were inconsistent with the data obtained by other experimenters at other temperatures. Deussen [2] and Hill and Sirkar [8] made measurements at 0 °C; the data of the latter showed erratic changes with concentration. The data of Hill and Sirkar at 0, 16, and 20 °C were, therefore, not considered.

Since HF shows complex dissociation,  $\Lambda_0$  values could not be obtained from  $\Lambda$  values on extrapolation to  $c=0$ . Accordingly,  $\Lambda_0$  for HF at 25 °C was obtained from the known values of  $\Lambda_0$  of 126.39, 105.43, and 426.06 Ω<sup>-1</sup> m kequiv<sup>-1</sup>, respectively, for NaCl [9], NaF [6], and HCl [10] using the Kohlrausch law of the independent migration of ions (the literature data, were, in each case, converted to absolute ohms using the factor: 1 international ohm = 1.000495 absolute ohms); this procedure gave 405.10 Ω<sup>-1</sup> m kequiv<sup>-1</sup> for  $\Lambda_0$  for HF at 25 °C. Wooster [1] gave 225 and 404 Ω<sup>-1</sup> m kequiv<sup>-1</sup> for  $\Lambda_0$  at 0 °C and 25 °C, respectively. Using the ratio 405.10/404 (at 25 °C), his value at 0 °C becomes 225.69 Ω<sup>-1</sup> m kequiv<sup>-1</sup>. From a linear plot of  $\Lambda_0$  against  $1/T$  354.29, 365.85, and 377.26 Ω<sup>-1</sup> m kequiv<sup>-1</sup> were obtained for  $\Lambda_0$  at 16, 18, and 20 °C, respectively. Wooster [1] obtained 437 and 275.4 Ω<sup>-1</sup> m kequiv<sup>-1</sup> for  $\lambda_0$  at 25 °C and 0 °C, respectively. On converting to absolute ohms and from a  $(\lambda_0 - 1/T)$  plot, 276.15, 383.08, 395.62, 407.99, and 438.19 Ω<sup>-1</sup> m kequiv<sup>-1</sup> were obtained for  $\lambda_0$  at 0, 16, 18, 20, and 25 °C, respectively [11]. Using these values for  $\Lambda_0$  and  $\lambda_0$ , known values of  $A_c$  [11] and  $B_1$  [10] and  $B_2$  [10] and data for  $\Lambda$  cited above, eq (11) was used to obtain the values of  $K$  and  $k$  given in table 1. Plots of  $(\gamma_c \Lambda/b)^2 (c/(1 - \Lambda/\Lambda_0))$  against  $c(1 - \Lambda/\Lambda_0)$  are shown in figure 1. Line A is obtained if no corrections are made for activity coefficients or changes in ionic mobilities with concentration, i.e.,  $(\gamma/b)^2$  is unity. Line B is obtained if corrections are made for activity coefficients and line C if both types of corrections are made. Values of  $K$  and  $k$  are obtained from line C. Plots at the other temperatures were similar to that of figure 1. Although the concentration unit used in the

<sup>2</sup> Corrections for ionic activity coefficients are introduced by using  $K/\gamma_c$  for  $K$ ; no correction is needed for  $k$  since the activity coefficients cancel in eq (4). Corrections for the ionic mobility are introduced by using  $\Lambda = b(\gamma\Lambda_0 + \gamma_3\lambda_0)$  instead of the approximate eq (7) which is based on the limiting equivalent conductances.

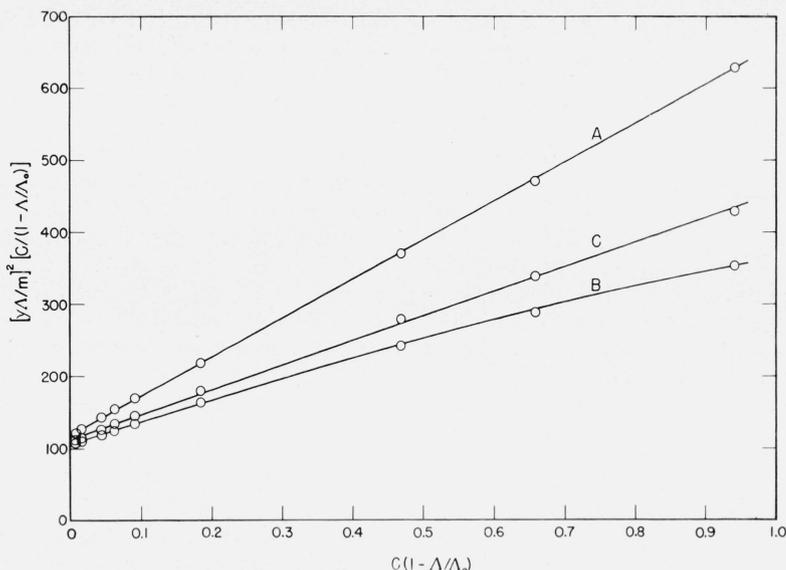


FIGURE 1. Plots used to obtain values for  $K$  and  $k$  governing the dissociation of HF.

- A. No corrections made for activity coefficients or changes in ionic mobilities with concentration.  
 B. Corrections made for activity coefficients.  
 C. Corrections made for activity coefficients and changes in ionic mobilities with concentration.

TABLE 1. Constants,  $K$  and  $k$ , for the equilibria governing the dissociation of hydrofluoric acid<sup>a</sup>

$t$	$\Lambda_0$	$\lambda_0$	$A_c$	$B_1$	$B_2$	$K$	$k$
°C	$\Omega^{-1} m \text{ equiv}^{-1}$	$\Omega^{-1} m \text{ equiv}^{-1}$	$m^{3/2} \text{ kmol}^{-1/2}$	$m^{3/2} \text{ kmol}^{-1/2}$	$\Omega^{-1} m^{3/2} \text{ kmol}^{-1/2}$	$\text{mol kg}^{-1}$	$\text{mol kg}^{-1}$
0	255.69	276.15	0.4918	0.2211	29.82	0.00109	0.413
16	354.29	383.08	.5038	.2266	48.48	.000782	.362
18	365.85	395.62	.5054	.2272	51.06	.000755	.355
20	377.26	407.99	.5072	.2280	53.72	.000731	.347
25	405.10	438.19	.5116	.2300	60.64	.000684	.381

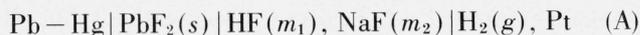
<sup>a</sup> On the SI the unit for  $K$  and  $k$  is  $\text{kmol m}^{-1}$ .

conductivity measurements was  $\text{mol l}^{-1}$ , because of the experimental uncertainties it is assumed here that  $K$  and  $k$  can be expressed in units of  $\text{mol kg}^{-1}$ .

Wooster [1] obtained  $0.000689$  and  $0.320 \text{ mol l}^{-1}$  for  $K$  and  $k$ , respectively, using older conductance data in international ohms. Davies and Hudleston [12], by combining data on the anodic transference number and the equivalent conductances of HF, obtained  $0.213 \text{ mol l}^{-1}$  for  $k$  at  $25^\circ\text{C}$ . However, they made no corrections for activity coefficients or the variation of the ionic mobilities with concentration. When these corrections are made, their data yield  $0.333 \text{ mol l}^{-1}$ , if the value of  $K$ , obtained here, is used. This value is still considerably lower than that obtained with later conductance data.

## 1.2. Electromotive Force Measurements

$K$  and  $k$  for HF may also be obtained from the electromotive forces (emfs) of cells of the type:



used by Broene and DeVries [13] where  $s$ =solid,  $m$ =molality,  $g$ =gas, and the vertical lines indicate the interface between distinct phases. Broene and DeVries used a 5 percent amalgam. The emf of this cell, as a function of  $m$ , is given by:

$$E = E^0 + \frac{2.303RT}{2F} \log m_{\text{H}^+} m_{\text{F}^-} \gamma_{\text{H}^+} \gamma_{\text{F}^-} \quad (17)$$

$$E = E^0 + \frac{2.303RT}{2F} \log m_{\text{H}^+} (m_2 + m_{\text{H}^+} - m_{\text{HF}_2^-}) \gamma_{\text{H}^+} \gamma_{\text{F}^-} \quad (18)$$

or

$$E = E^0 + \frac{2.303RT}{2F} \log h \quad (19)$$

where  $h$  denotes  $m_{\text{H}^+} (m_2 + m_{\text{H}^+} - m_{\text{HF}_2^-}) \gamma_{\text{H}^+} \gamma_{\text{F}^-}$  and  $E^0$  denotes the standard potential of the  $\text{Pb}-\text{Hg}$  (5%),  $\text{PbF}_2$ , F- electrode; this value was determined at  $15^\circ\text{C}$  (0.3346 V),  $25^\circ\text{C}$  (0.3445 V), and  $35^\circ\text{C}$  (0.3551 V) by Ivett and DeVries [14] (their values were converted here to absolute volts using the factor: 1 international volt = 1.0003384 absolute volts). Now the two equilibrium constants, as given by eqs (3) and (4) may be expressed as:

$$K = \frac{m_{\text{H}^+} (m_2 + m_{\text{H}^+} - m_{\text{HF}_2^-}) \gamma_{\text{H}^+} \gamma_{\text{F}^-}}{(m_1 - m_{\text{H}^+} - m_{\text{HF}_2^-}) \gamma_{\text{HF}}} = \frac{h}{m_1 - m_2 - 2m_{\text{H}^+} + h / (m_{\text{H}^+} \gamma_{\text{H}^+} \gamma_{\text{F}^-})} \quad (20)$$

$$k = \frac{(m_1 - m_{\text{H}^+} - m_{\text{HF}_2^-}) (m_2 + m_{\text{H}^+} - m_{\text{HF}_2^-}) \gamma_{\text{H}^+} \gamma_{\text{F}^-}}{m_{\text{HF}_2^-} \gamma_{\text{HF}_2^-}}$$

$$= \frac{\left(m_1 - m_2 - 2m_{H^+} + \frac{h}{m_{H^+}\gamma_{H^+}\gamma_{F^-}}\right) \left(\frac{h}{m_{H^+}\gamma_{H^+}\gamma_{F^-}}\right)}{m_2 - m_{H^+} - h/(m_{H^+}\gamma_{H^+}\gamma_{F^-})} \quad (21)$$

In the second expression of eq (20),  $\gamma_{HF}$  is taken equal to 1 while in the second expression of eq (21),  $\gamma_{HF}\gamma_{F^-}/\gamma_{HF_2}$  is taken equal to 1. For each acid-salt solution there are two equations like (20) and (21) with four unknowns:  $K$ ,  $k$ ,  $m_{H^+}$ , and  $\gamma_{H^+}\gamma_{F^-}$ . Broene and DeVries [13] reduced the number of unknowns to three by assuming that the mean activity coefficient of NaF in the HF-NaF solutions was the same as that found by Ivett and DeVries [14] for NaF alone. Broene and DeVries then inserted various values of  $m_{H^+}$  (obtained approximately from eq (18)) in eq (20) and (21) and calculated the corresponding  $K$  and  $k$  values. They then plotted the values of  $K$  against the corresponding  $k$ . Since they had studied four HF-NaF mixtures they had four straight lines.  $K$  and  $k$  were given by the point where the four lines intersected. The same process could be accomplished by iteration, using various values of  $m_{H^+}$  until the same value is obtained for  $K$  and for  $k$  at the concentrations studied.

Broene and DeVries [13] obtained 0.000793, 0.000671, and 0.000564 mol kg<sup>-1</sup> for  $K$  at 15, 25, and 35 °C, respectively, and 0.254, 0.259, and 0.231 mol kg<sup>-1</sup> for  $k$  at 15, 25, and 35 °C, respectively (they actually gave values for the reciprocal for  $k$ ). Their values for  $K$  agree closely with the conductivity data but their  $k$  value is lower than that obtained from conductivity data. However, in treating their data they assumed that the solubility of PbF<sub>2</sub> in HF-NaF was negligible and that the liquid-junction potential between the solution saturated with PbF<sub>2</sub> and the solution not so saturated could be neglected. It is for these reasons that the conductivity values for  $K$  and  $k$  are considered preferable.

## 2. Activities and Activity Coefficients of HF

The mean ionic activity,  $(a_{\pm})_i$ , and the mean ionic activity coefficient of HF are given, respectively, by:

$$(a_{H^+}a_{F^-})_i^{1/2} = (a_{\pm})_i = (\gamma_{\pm})(m_{\pm})_i \quad (22)$$

and

$$(\gamma_{H^+}\gamma_{F^-})_i^{1/2} = \frac{(a_{\pm})_i}{(m_{H^+}m_{F^-})_i^{1/2}} = \frac{(a_{\pm})_i}{(m_{\pm})_i} \quad (23)$$

Now  $(m_{\pm})_i = (m_{\pm})_s$ , where  $s$  = stoichiometric, only if HF were completely dissociated.

Broene and DeVries [13] calculated the activity coefficients of various stoichiometric concentrations of HF from measurements of the emf of the cell:



where the symbols have the same significance as given above. In this case Broene and DeVries corrected for the solubility of PbF<sub>2</sub> in HF [15, 16, 17] and calculated the liquid-junction potential for the junction of

the solution saturated with PbF<sub>2</sub> and the one free of PbF<sub>2</sub> using the Henderson [18] equation. The  $E^0$  values for the Pb-Hg, PbF<sub>2</sub>, F<sup>-</sup> electrode, determined by Ivett and DeVries, and listed above were used.

It is most interesting that Broene and DeVries obtained their values of the activity coefficients of HF by first calculating the activities of H<sup>+</sup> and F<sup>-</sup> using their values for  $K$  and  $k$  and the Güntelbrug's [19] modification of Debye-Hückel equation

$$\log \gamma_{\pm} = -A\sqrt{I}/(1 + \sqrt{I}) \quad (24)$$

for the activity coefficient. In eq (24),  $I$  represents the ionic strength; they did not state the value of  $A$  they used. They reported their activity coefficients as stoichiometric ones which they calculated from  $\gamma = (a_{H^+}a_{F^-})^{1/2}/m$  where  $m$  is the stoichiometric molality. Actually, they did not need to use this procedure involving values of  $K$  and  $k$ , since the stoichiometric activity coefficients may be calculated directly from the observed emfs of cell (B) using the equation:

$$E = E^0 + \frac{2.303RT}{2F} \log a_{H^+}a_{F^-} + E_j \quad (25)$$

or

$$E = E^0 + \frac{2.303RT}{2F} \log m_{H^+} (m_{F^-} + m') \gamma_{H^+}\gamma_{F^-} + E_j \quad (26)$$

where  $m'$  = molality of the fluoride ion arising from the solubility of PbF<sub>2</sub> in HF and  $E_j$  denotes the liquid-junction potential. Values of  $(\gamma_{H^+}\gamma_{F^-})^{1/2}$  or  $\gamma_{\pm}$ , obtained directly from the emfs of cell B by eq (26), with and without Henderson [18] corrections for  $E_j$ , are given, respectively, in the second and third columns of table 2 and compared with those calculated by Broene and DeVries from their  $K$  and  $k$  values. In obtaining the direct emf values, the values were read from a curve of  $\gamma_{\pm}$  (obtained from the emfs) versus  $\sqrt{m_{HF}}$ , neglecting  $m'$  in the plot; if  $m'$  were used agreement between calculated and observed  $\gamma_{\pm}$ 's was obtained only above 0.03 molal. It will be noted that the Henderson equation gives an overcorrection for  $E_j$  for the dilute solutions. Hamer and Acree [20] have shown that this is frequently the case; in the Henderson equation concentrations rather than activities are used. On the other hand, the direct values obtained from the emf data without  $E_j$  corrections agree closely with those calculated by Broene and DeVries as well as those calculated from conductivity data. The close agreement between the data of Broene and DeVries and the conductivity data shows that the value of  $\gamma_{\pm}$  is insensitive to the value of  $k$  (the emf and conductivity values for  $K$  agree closely whereas the  $k$  values differ by about 30 percent); this follows since  $\gamma_{\pm}$  is for the H<sup>+</sup> and F<sup>-</sup> ions and does not include the activity coefficient of the HF<sub>2</sub><sup>-</sup> ion.

Anthony and Hudleston [21] measured the freezing-point depression of HF solutions from 0.025 to 4.14 molal and Parker [22] gave values for the apparent

TABLE 2. Comparison of stoichiometric mean activity coefficients of hydrofluoric acid at 25 °C obtained from electromotive force, conductivity, and freezing point and heat of dilution data.

<i>m</i>	Electromotive Force			Conductivity <sup>c</sup>	Freezing point and heats of dilution
	Emf with <i>E<sub>j</sub></i> corrections <sup>a</sup>	Emf without <i>E<sub>j</sub></i> corrections <sup>a</sup>	Broene and DeVries <sup>b</sup>		
mol/kgH <sub>2</sub> O					
0.001	0.822	0.543	0.544	0.547	0.542
.002	.658	.449	<sup>a</sup> (0.431)	.433	.455
.003	.557	.387	.371	.373	(0.406)
.005	.436	.313	.300	.304	.340
.007	.365	.264	(0.263)	.264	(0.300)
.01	.295	.219	.224	.227	.259
.02	.195	.162	(0.166)	.166	.188
.03	.157	.138	.136	.136	(0.154)
.05	.119	.108	.106	.108	.116
.10	.079	.076	.077	.0778	.079
.20	.055	.055	(0.055)	.0554	.053
.30	.045	.045	.044	.0450	.043
.50	.035	.035	<sup>c</sup> .031	.0351	.033
1.0	.025	.025	.024	.0248	.024
2.0				.0174	.0178
3.0				.0141	.0147
4.0				.0121	.0131

<sup>a</sup> All values were read from a smooth curve of emf data versus *m*<sup>1/2</sup>.

<sup>b</sup> Using the *K* and *k* values of Broene and De Vries [13].

<sup>c</sup> Using the *K* and *k* values obtained herein.

<sup>d</sup> Values in parentheses were read from a smooth curve of data versus *m*<sup>1/2</sup>.

<sup>e</sup> Apparently in error; 0.034 is a better value.

molal heat capacity and the heats of dilution of HF from 0 to 22.753 molal. The stoichiometric osmotic coefficient,  $\phi$ , of HF at 25 °C may be obtained from these data by the eqs [23, 24, 25]:

$$\nu\lambda m\phi = \left(1 + \frac{\bar{L}_1}{\Delta H_f^0}\right)\theta + \left(1/T_f - \frac{\Delta C_f^0}{2\Delta H_f^0} + \frac{\bar{L}_1}{T_f\Delta H_f^0} - \frac{\bar{J}_1}{2\Delta H_f^0}\right)\theta^2 + \left(1/T_f^2 - \frac{2\Delta C_p^0}{3T_f\Delta H_f^0} + \frac{\Delta b}{6\Delta H_f^0} + \frac{\bar{L}_1}{T_f^2\Delta H_f^0} - \frac{2\bar{J}_1}{3T_f\Delta H_f^0}\right)\theta^3 + \dots \quad (27)$$

where

$\nu$  = number of ions in one molecule of solute = 2

$\lambda$  = molal freezing-point depression = 1.860 ± 0.001 K/kg mol<sup>-1</sup> for H<sub>2</sub>O

$m$  = molality

$\bar{L}_1$  = relative partial molal enthalpy of solvent at *T*  
 $\Delta H_f^0$  = heat of fusion of pure water = 6009.48 J mol<sup>-1</sup> (1436.3 cal mol<sup>-1</sup>)

$\theta$  = freezing-point depression = *T<sub>f</sub>* - *T*

*T<sub>f</sub>* = freezing point of pure solvent; 273.15 K for H<sub>2</sub>O.

$\Delta C_f^0 = \Delta \bar{C}_f - \bar{J}_1$  where  $\Delta \bar{C}_f = \Delta a + \Delta bT_f = (\Delta \bar{C}_p)_{T_f}$  where  $\Delta \bar{C}_p$  is the difference between the partial molal heat capacity of the solvent in the solution and the molal heat capacity of the solid solvent.

$\bar{J}_1$  = relative partial molal heat capacity of solvent at constant pressure at *T*

*b* = coefficient in  $\Delta \bar{C}_f = \Delta a + \Delta bT_f$ .

The mean activity coefficient of HF is then obtained from  $\phi$  by the relation:

$$\ln \gamma = (\phi - 1) + \int_0^m (\phi - 1) d \ln m. \quad (28)$$

Values of  $\gamma$  so calculated are given in the last column of table 2. The agreements with the emf and conductivity data are generally good when one considers the uncertainties in the heat data for HF.

### 3. Ionic and Molecular Species in HF

Broene and DeVries in calculating  $\gamma_{\pm}$  from  $(a_{H^+}a_{F^-})^{1/2}/m$  used the Güntelberg equation for ionic activity coefficients in obtaining values for  $a_{H^+}$  and  $a_{F^-}$  from the emf data. One may ask, therefore, if their values for  $\gamma_{\pm}$  did not depend on this choice and would be different if another expression had been used for the ionic activity coefficient. The concentrations but not the activities of the ionic species would differ, since from eq (25)

$$\log a_{H^+}a_{F^-} = \frac{E - E^0 - E_j}{2.303RT/2F}. \quad (29)$$

$a_{H^+}a_{F^-}$  is a constant for each stoichiometric concentration of HF. This may be shown in another way, as follows:

According to the equilibria given by eq (3) and (4), values of  $m_{H^+}$ ,  $m_{F^-}$ ,  $m_{HF_2^-}$  and  $m_{HF}$  and the corresponding ionic activities can be obtained from *K* and *k* only by selecting some function to represent the activity coefficients,  $\gamma_{H^+}$ ,  $\gamma_{F^-}$ ,  $\gamma_{HF_2^-}$ , and  $\gamma_{HF}$  (in accord with convention, the last one may be taken equal to 1). In other words, values of  $m_{H^+}$ , etc., for any stoichiometric molality, *m*, of HF differ for each function selected to represent the  $\gamma$ 's. On the other hand,  $(a_{H^+}a_{F^-})$  will be the same, regardless of the function selected for the  $\gamma$ 's, since  $(a_{H^+}a_{F^-})^{1/2} = K^{1/2}$ .

To illustrate, seven different theoretical equations [11], namely, those of Debye-Hückel limiting law, Güntelberg, extended Güntelberg, Davies, Scatchard, extended Scatchard, and Bjerrum are used to calculate the molalities of all species in HF. In all of these calculations values for the ionic strength, *I*, are needed. The ionic strength is given by

$$I = (m_{H^+} + m_{F^-} + m_{HF_2^-})/2 = my + my_3. \quad (30)$$

Combining eqs (5) and (6), eq (31) results:

$$\frac{K(1 - y - 2y_3)}{m\gamma^2} = y^2 \left[ 1 + \frac{m}{k(1 - y - 2y_3)} \right]. \quad (31)$$

The activity coefficient term is evaluated:

$$\gamma = \text{one of 7 functions of } I \text{ or } my + my_3. \quad (32)$$

Values of  $\gamma$ , or  $m_{F^-}/m$ , are obtained from eqs (31) and (32) by iteration. Iteration is necessary since  $\gamma$  depends on an a priori knowledge of  $\gamma$ . As a start  $\gamma$  is assumed to be unity in the  $\gamma$  function;  $\gamma$  thus obtained from eq (31) is then substituted in eq (32) to get a new value of  $\gamma$  which is then used in eq (31) to get a new value of  $\gamma$  and so on. Values of  $\gamma_3$ , or  $m_{HF_2^-}/m$  are then obtained from eq (6) and  $m_{H^+}$  from  $y + y_3$ . The molality of the undissociated HF is then obtained from values of  $\gamma_3$ ,  $y + y_3$ , and  $m$ . In table 3, these values are given for  $m = 1$ , for illustration. It will be noted that the values of  $H^+$ ,  $F^-$ , etc., differ for each  $\gamma$  function but that all  $\gamma$  functions lead to the same value for the product:  $(m_{H^+}m_{F^-})^{1/2}(\gamma_{H^+}\gamma_{F^-})^{1/2}$  or  $a_{\pm}$ . Furthermore, each one equals  $a_{\pm}$  as obtained from  $(a_{H^+}a_{F^-})^{1/2}/m$  obtained directly from the emf measurements. These same principles obtain for other stoichiometric concentrations of HF, and for brevity are not given here. It is important to note that stoichiometric activity coefficients of HF given by  $(a_{H^+}a_{F^-})^{1/2}/m$  are independent of a choice of  $\gamma$  function.

Another interesting fact is that the pH of the solution as given by  $\log m_{H^+}\gamma_{H^+} = \log m_{H^+}\gamma_{\pm}$  is practically independent of the  $\gamma$  function selected. This comes about from the ionic equilibria for HF and is quite dif-

ferent from what would be obtained for a completely dissociated acid, such as HCl. To illustrate, the pH of 1 molal HCl as calculated by the seven theoretical  $\gamma$  functions is given in the last column of table 3. It is evident that the spread in pH values for HCl is 0.523, whereas for HF it is only 0.003.

For completeness,  $\gamma_{\pm}$ ,  $a_{\pm}$ , pH, and ionic and molecular (HF) concentrations for various stoichiometric concentrations of HF are given in table 4. Also, for completeness,  $\gamma_{\pm}$  and pH of various stoichiometric concentrations of HF were calculated at 0 °C using the  $K$  and  $k$  values listed in table 1. These quantities are given in tables 5 and 6, respectively. In these tables data are also listed for temperatures between 0 and 25 °C and at 30 and 35 °C. Values between 0 and 25 °C were obtained by interpolation while those above 25 °C were obtained by extrapolation. Values of  $\gamma_{\pm}$  in parentheses were obtained from emf measurements by Broene and DeVries [13] and are given for comparison. Also values of the concentration of the ionic and molecular species in various stoichiometric concentrations of HF, as calculated using the limiting law of Debye and Hückel, are given for 0 °C and 25 °C in tables 7 and 8, respectively. Values at intermediate temperatures may be obtained by interpolation. These are relative values since some function other than the Debye-Hückel limiting law for activity coefficients would give a better estimate of their magnitude (see table 3).

TABLE 3. Molalities of the ionic species and undissociated HF in 1 molal (stoichiometric) HF at 25 °C, including data on ionic strength, mean ionic activity coefficient, mean ionic activity, and pH based on various theoretical functions of the ionic activity coefficient,  $\gamma_{H^+}\gamma_{F^-}$

Activity coefficient function	$m_{H^+}$	$m_{F^-}$	$m_{HF_2^-}$	$m_{HF}$	$I$	$\gamma_{\pm} = (\gamma_{H^+}\gamma_{F^-})^{1/2}$	$a_{\pm}$	pH	pH (1 m HCl)
Debye-Hückel.....	0.06059	0.01807	0.04252	0.8969	0.06059	0.7486	0.0248	1.343	0.292
Güntelberg (ext.) <sup>a</sup> .....	.05726	.01700	.04026	.9025	.05726	.7964	.0248	1.341	.590
Güntelberg.....	.05723	.01699	.04024	.9025	.05723	.7969	.0248	1.341	.593
Bjerrum.....	.05680	.01685	.03995	.9033	.05680	.8034	.0248	1.341	.630
Davies.....	.05647	.01675	.03973	.9038	.05647	.8085	.0248	1.340	.815
Scatchard (ext.) <sup>a</sup> .....	.05615	.01665	.03951	.9043	.05615	.8135	.0248	1.340	.687
Scatchard.....	.05611	.01663	.03948	.9044	.05611	.8142	.0248	1.340	.690

<sup>a</sup>Extended or modified equation.

TABLE 4. Molalities of the ionic species and undissociated HF in various stoichiometric molalities of HF at 25 °C, including data on ionic strength, mean ionic activity coefficient, mean ionic activity, and pH based on the Debye-Hückel limiting law for ionic activity coefficients

<i>C</i>	$m_{H^+}$	$m_{F^-}$	$m_{HF_2^-}$	$m_{HF}$	<i>I</i>	$\gamma_{\pm} = (\gamma_{H^+}\gamma_{F^-})^{1/2}$	$a_{\pm}$	$a_{\pm}$ (Broene & DeVries)	pH
0.001	0.000562	0.000562	0.00000064	0.000437	0.000562	0.9725	0.000547	0.000544	3.26
.002	.000899	.000897	.00000258	.001098	.000899	.9653	.000867	.....	3.06
.003	.001167	.001161	.00000557	.001828	.001167	.9606	.00112	.00113	2.95
.005	.001602	.001588	.00001410	.003384	.001602	.9540	.00152	.00150	2.82
.007	.001963	.001938	.00002549	.005011	.001963	.9492	.00185	.....	2.73
.01	.002428	.002381	.00004702	.007525	.002428	.9437	.00227	.00224	2.64
.02	.003649	.003501	.0001489	.01620	.003649	.9314	.00333	.....	2.47
.05	.006236	.005602	.0006342	.04313	.006236	.9113	.00539	.0053	2.25
.10	.009696	.007869	.001827	.08848	.009696	.8906	.00778	.0077	2.06
.20	.01556	.01058	.004983	.1795	.01556	.8636	.0111	.0132	1.87
.50	.03202	.01467	.017348	.4506	.03202	.8102	.0176	.0155	1.59
1.0	.06059	.01807	.04252	.8969	.06059	.7486	.0248	.0240	1.34
2.0	.1255	.02221	.1033	1.771	.1255	.6593	.0348	.....	1.08
3.0	.2016	.02558	.1760	2.622	.2016	.5897	.0423	.....	0.93
4.0	.2901	.02886	.2612	3.449	.2901	.5308	.0486	.....	0.81

TABLE 5. Stoichiometric mean activity coefficients of aqueous solutions of hydrofluoric acid

<i>m</i>	<i>t</i> , °C												
	0	5	10	15	15	18	20	25	25	30	35	35	
<i>mol/kgH<sub>2</sub>O</i>													
0.001	0.624	0.609	0.593	0.578	<sup>a</sup> (0.573)	0.569	0.562	0.547	(0.544)	0.532	0.516	(0.515)	
.002	.505	.491	.477	.462	.....	.454	.448	.434	.....	.419	.405	.....	
.003	.440	.427	.413	.400	(0.395)	.393	.387	.373	(0.371)	.360	.347	(0.347)	
.005	.366	.354	.342	.328	(0.320)	.322	.316	.304	(0.300)	.292	.280	(0.280)	
.007	.320	.309	.297	.287	.....	.280	.276	.264	.....	.253	.241	.....	
.01	.276	.266	.256	.247	(0.241)	.241	.237	.227	(0.224)	.217	.207	(0.208)	
.02	.205	.197	.190	.182	.....	.177	.174	.167	.....	.159	.152	.....	
.05	.134	.129	.124	.118	(0.115)	.115	.113	.108	(0.106)	.102	.0976	(0.097)	
.10	.0968	.0930	.0892	.0854	(0.083)	.0831	.0816	.0778	(0.077)	.0740	.0702	(0.070)	
.20	.0690	.0665	.0635	.0610	.....	.0595	.0580	.0555	.....	.0530	.0500	.....	
.50	.0438	.0420	.0404	.0386	(0.034)	.0376	.0370	.0352	(0.031)	.0334	.0318	(0.028)	
1.0	.0309	.0297	.0285	.0272	(0.026)	.0266	.0260	.0248	(0.024)	.0236	.0224	(0.022)	
2.0	.0217	.0208	.0200	.0191	.....	.0186	.0183	.0174	.....	.0165	.0157	.....	
3.0	.0175	.0168	.0161	.0155	.....	.0151	.0148	.0141	.....	.0134	.0127	.....	
4.0	.0150	.0144	.0139	.0133	.....	.0130	.0128	.0122	.....	.0116	.0111	.....	

<sup>a</sup> Values in parentheses, Broene & DeVries [13].

TABLE 7. Relative ionic and molecular species in aqueous solutions of hydrofluoric acid at 0 °C (based on Debye-Hückel limiting law for activity coefficients)

TABLE 6. pH of aqueous solutions of hydrofluoric acid

<i>m</i> , °C	0	5	10	15	18	20	25	30	35
0.001	3.21	3.22	3.23	3.24	3.25	3.25	3.26	3.27	3.29
.002	2.99	3.01	3.02	3.03	3.04	3.05	3.06	3.08	3.09
.003	2.88	2.89	2.91	2.92	2.93	2.94	2.95	2.97	2.98
.005	2.74	2.75	2.77	2.78	2.79	2.80	2.82	2.83	2.85
.007	2.65	2.66	2.68	2.70	2.71	2.71	2.73	2.75	2.76
.01	2.56	2.57	2.59	2.61	2.62	2.62	2.64	2.66	2.67
.02	2.38	2.40	2.42	2.43	2.44	2.45	2.47	2.49	2.51
.05	2.15	2.17	2.19	2.21	2.22	2.23	2.25	2.26	2.28
.10	1.97	1.99	2.01	2.03	2.04	2.05	2.06	2.08	2.10
.20	1.78	1.80	1.82	1.84	1.85	1.85	1.87	1.89	1.91
.50	1.50	1.52	1.54	1.55	1.56	1.57	1.59	1.60	1.62
1.0	1.26	1.28	1.30	1.31	1.32	1.33	1.34	1.36	1.38
2.0	1.01	1.02	1.04	1.05	1.06	1.07	1.08	1.10	1.11
3.0	0.85	0.87	0.90	0.91	0.91	0.91	0.93	0.94	0.95
4.0	.74	.76	.77	.78	.79	.80	.81	.83	.84

<i>m</i>	H <sup>+</sup>	F <sup>-</sup>	HF <sub>2</sub> <sup>-</sup>	HF
	Moles per 1000 grams of solvent			
0.001	0.0006423	0.0006418	0.00000555	0.0003571
.002	.0010536	.0010512	.000002403	.0009440
.003	.0013845	.0013792	.000005377	.001610
.005	.0019263	.0019121	.00001417	.003060
.007	.0023783	.0023521	.00002617	.004596
.01	.0029603	.0029111	.00004927	.006990
.02	.004494	.004333	.0001609	.015345
.05	.007796	.007084	.0007117	.04149
.10	.012040	.009968	.002073	.08589
.20	.019284	.013545	.005739	.17498
.50	.039426	.019084	.020342	.44023
1.0	.074271	.023810	.050461	.87527
2.0	.15358	.029700	.12388	1.7225
3.0	.24705	.034547	.21250	2.5405
4.0	.35623	.039339	.31689	3.3269

TABLE 8. *Relative ionic and molecular species in aqueous solutions of hydrofluoric acid at 25 °C*

(based on Debye-Hückel limiting law for activity coefficients)

<i>m</i>	H <sup>+</sup>	F <sup>-</sup>	HF <sub>2</sub> <sup>-</sup>	HF
	Moles per 1000 grams of solvent			
0.001	0.0005624	0.0005618	0.000000644	0.0004370
.002	.0008992	.0008966	.000002584	.001098
.003	.0011667	.0011612	.000005570	.001828
.005	.0016018	.0015877	.00001410	.003384
.007	.0019633	.0019378	.00002549	.005011
.01	.0024277	.0023807	.00004702	.007525
.02	.0036494	.0035005	.0001489	.01620
.05	.0062360	.0056018	.0006342	.04313
.10	.0096962	.0078689	.0018273	.08848
.20	.015561	.010578	.0049828	.17946
.50	.032015	.014667	.017348	.45064
1.0	.060594	.018066	.042523	.89688
2.0	.12547	.022210	.10326	1.7713
3.0	.20161	.025576	.17604	2.6224
4.0	.29006	.028856	.26120	3.4487

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