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# Ionization of Hydrofluoric Acid at 25 °C\*

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The ionization constant,  $K_1$ , for the reaction  $HF \rightleftharpoons H^+ + F^-$  was calculated on the basis of potentiometric measurements in the cell Ag; AgCl, Cl<sup>-</sup>, F<sup>-</sup>||LaF<sub>3</sub>||NaF, HCl, H<sub>2</sub>O|KCl(Satd.), Hg<sub>2</sub>Cl<sub>2</sub>; Hg at 25 °C. A least squares procedure was applied to the experimental data yielding a best estimate for  $K_1$  of  $5.85 \times 10^{-4}$  with a standard error of  $0.03 \times 10^{-4}$ .

Key words: Hydrofluoric acid; ionization constant; lanthanum fluoride electrode; least squares procedure; potentiometric measurements.

### 1. Introduction

The chemical properties of dilute aqueous solutions of hydrofluoric acid are described [1, 2, 3]<sup>1</sup> by the equilibria

$$HF \rightleftharpoons H^+ + F^-; K_1 = \frac{(H^+)(F^-)}{(HF)}$$
 (1)

$$F^- + HF \rightleftharpoons HF_{\overline{2}}; K_2 = \frac{(HF_{\overline{2}})}{(F^-)(HF)}$$
 (2)

in which parentheses indicate activities of the various chemical species. Most of the evidence for the presence of the various species involved in the above equilibria has been obtained from studies [3, 4] at high constant ionic strengths. Unfortunately, the values for the apparent equilibrium constants derived from such studies are of limited use.

Thermodynamic values of  $K_1$  and  $K_2$  have been reported on the basis of potentiometric [5, 6] or conductance measurements [7]. However, there are uncertainties in the values of the constants originating from the graphical approximations [5, 6] used in the calculations, or from the assumptions regarding the species responsible for the transport of current [7].

The present investigation was prompted by the observation of small but consistent discrepancies between the values of fluoride ion activities obtained with a lanthanum fluoride membrane electrode and those calculated on the basis of the reported ionization constants of hydrofluoric acid. Potentiometric measurements were made in the ternary system NaF-HCl-H<sub>2</sub>O. The use of the thermodynamic value of  $K_1$  derived from such measurements eliminated the discrepancy between measured and calculated fluoride ion activities. The least squares procedure used in the present study obviates the uncertainties inherent to graphical methods and permits the estimation of errors on a sound statistical basis.

# 2. Experimental Methods and Procedures

# 2.1. NaF-HCl-H<sub>2</sub>O Systems

All the chemicals used in the present study were reagent grade. Stock solutions of sodium fluoride were prepared by weighing the salt which was dried at 100 °C for 24 h; the salt was dissolved with conductivity water in borosilicate volumetric flasks and immediately transferred to polyethylene bottles for storage. The systems used in the potentiometric measurements were made by taking 100 ml of sodium fluoride solutions of suitable concentrations and adding various aliquots of standard hydrochloric acid. In this way it was possible to obtain systems with a wide concentration range in both sodium fluoride and hydrochloric acid. The estimated standard error in the concentrations of sodium fluoride and hydrochloric acid was  $\pm 1.3$  percent of the amount present.

#### 2.2. Potentiometric Measurements

The cell used in these measurements may be schematically represented by

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

Ag; AgCl, Cl<sup>-</sup>(0.1), F<sup>-</sup>(0.1) | |LaF<sub>3</sub> | |test solution | KCl(satd.), Hg<sub>2</sub>Cl<sub>2</sub>; Hg.

The lanthanum fluoride membrane electrode has been described in the literature [8, 9] and its Nernstian behavior was confirmed in our laboratories. The calomel electrode was encased in a polytetrafluoroethylene (PTFE) jacket; only the fibre tip was in direct contact with the test solution. This precaution was indispensable to obtain reproducible measurements. The measurements were made with a commercially available pH meter (claimed relative accuracy  $\pm 0.1$  mV). Polyethylene beakers containing the solutions and the electrodes were thermostated in a water bath at  $25 \pm 0.05$  °C. The solutions were constantly stirred with magnetic stirrers except during the measurement. Precautions were taken to minimize evaporation and contamination with the atmosphere. A reading was considered to represent equilibrium conditions when the EMF remained constant, within  $\pm 0.1$  mV for about 20 min. A minimum of three such readings were obtained for each system. For the purpose of calculations a conservatively estimated standard error of 0.15 mV was adopted. Measurements of pH with glass and calomel electrodes were made only on the standard sodium fluoride solutions (pH values above 6.2). No reliable measurements of pH could be obtained in the NaF-HCl-H<sub>2</sub>O systems, presumably because of the attack of hydrofluoric acid on the glass electrode. The ionic strengths of all the systems were in the range of 0.008 to 0.03 M.

# 3. Calculative Procedures

As mentioned in the introduction, discrepancies were observed in this study between the measured fluoride ion activities,  $(F^{-})_m$ , and those calculated,  $(F^{-})_c$ , on the basis of the available ionization constants for hydrofluoric acid. In the next two sections, details will be given concerning the methods used to derive these activities. The statistical procedure used for the estimation of  $K_1$ , on the basis of the potentiometric measurements reported here, will be given in section 3.3.

# 3.1. Calculation of Fluoride Ion Activities

Fluoride ion activities in the systems NaF-HCl-H<sub>2</sub>O were calculated from the cubic equation

$$(\mathbf{F}^{-})_{c}^{3} \left\{ \frac{K_{2}}{K_{1}f_{1}f_{2}} \right\} + (\mathbf{F}^{-})_{c}^{2} \left\{ \frac{2K_{2}[\mathbf{H}]_{T}}{K_{1}f_{2}} + \frac{1}{K_{1}f_{1}} - \frac{K_{2}[\mathbf{F}]_{T}}{K_{1}f_{2}} \right\} + (\mathbf{F}^{-})_{c} \left\{ \frac{[\mathbf{H}]_{T}}{K_{1}} + \frac{1}{f_{1}f_{3}} - \frac{[\mathbf{F}]_{T}}{K_{1}} \right\} - \frac{[\mathbf{F}]_{T}}{f_{3}} = 0$$
(3)

in which  $[F]_T$  and  $[H]_T$  represent total concentrations of sodium fluoride and hydrochloric acid respectively, and  $f_i$  represent molar ionic activity coefficients; in this paper subscripts 1, 2, 3 and 4 refer to the species  $F^-$ ,  $HF_{\overline{2}}$ ,  $H^+$ , and  $OH^-$ , respectively. In the present calculations it was assumed that  $f_1 = f_2$  and that the activity coefficient for the undissociated species, HF, was unity. The values for  $K_1$  and  $K_2$  reported by Broene and DeVries were used in eq (3) to calculate the fluoride ion activity in the ternary system.

The ionic strength, I, in the systems considered here is defined by

$$I = 0.5 \left\{ \left[ \mathrm{Na^{+}} \right] + \frac{(\mathrm{H^{+}})}{f_{3}} + \frac{K_{w}}{(\mathrm{H^{+}})f_{4}} + \frac{(\mathrm{F^{-}})}{f_{1}} + \frac{K_{2}(\mathrm{H^{+}})(\mathrm{F^{-}})^{2}}{K_{1}f_{2}} + \left[ \mathrm{Cl^{-}} \right] \right\}$$
(4)

in which  $[Na^+]$  is the sodium ion concentration, equal to  $[F]_T$ ;  $[Cl^-]$  is the chloride ion concentration, equal to  $[H]_T$ , and  $K_w$  is the ionization constant of water  $(1.008 \times 10^{-14} [10])$ .

The activity of hydrogen ion appearing in eq (4) was calculated from

$$(\mathrm{H}^{+}) = [\mathrm{H}]_{T} / \left( \frac{1}{f_{3}} + \frac{(\mathrm{F}^{-})_{c}}{K_{1}} + \frac{K_{2}(\mathrm{F}^{-})_{c}^{2}}{K_{1}f_{2}} \right).$$
(5)

The ionic activity coefficients were calculated from the Debye-Hückel equation

$$f_i = \exp\left(-2.303AZ_i^2 \sqrt{I}/(1 + Ba_i \sqrt{I})\right)$$
(6)

in which A and B are temperature dependent constants,  $Z_i$  is the valence of the *i*th ion and  $a_i$  is its ion size parameter.<sup>2</sup>

The calculations were performed by an iterative procedure in which initial values of unity were taken for all  $f_i$ ; approximate solutions for eqs (3) and (5) and their substitution into eq (4) yielded an approximate value of I which was then used to obtain  $f_i$  from eq (6). The new values of  $f_i$  were cycled in a similar fashion until convergence in the value of I, which required from 3 to 4 cycles.

#### 3.2. Measured Fluoride Ion Activities

Fluoride ion activities,  $(F^{-})_{s}$ , for the standard sodium fluoride solutions were calculated from the quadratic equation

$$(\mathbf{F}^{-})_{s}^{2}\left\{\frac{2K_{2}(\mathbf{H}^{+})}{K_{1}f_{2}}\right\} + (F^{-})_{s}\left\{\frac{1}{f_{1}} + \frac{(\mathbf{H}^{+})}{K_{1}}\right\} - [\mathbf{F}]_{T} = 0. \quad ^{3}(7)$$

In the pH range of these solutions (6.2 to 6.8), differences of up to 30 percent in the values of  $K_1$  and  $K_2$ do not affect the calculated fluoride ion activities in the standard sodium fluoride solutions. Standard curve was obtained by least squares fitting of the equation

$$E_s = a + b \log (\mathbf{F}^-)_s \tag{8}$$

<sup>&</sup>lt;sup>2</sup> The values used for A and B in eq (6) were 0.5115 and 0.3291 × 10<sup>8</sup> [11], respectively. The ion size parameters were  $a_1 = a_2 = a_4 = 3.5 \times 10^{-8}$  cm and  $a_3 = 9 \times 10^{-8}$  cm [12]. <sup>3</sup> This equation is used instead of equation (3) because the values for (H<sup>+</sup>) are readily obtained from pH determinations in the standard solutions.

in which  $E_s$  represents potential measurements of the standard solutions and a and b are the parameters to be estimated. In table 1 typical results for the potential measurements in standard sodium fluoride solutions are given. The concentrations of the standard solutions covered a range  $1 \times 10^{-1}$  to  $2.5 \times 10^{-5}$  molar in sodium fluoride. When eq (8) was fitted to the data in table 1, the best estimates of the parameters obtained were  $a = -173.032 \pm 0.176$  and  $b = -57.9066 \pm 0.0610$ . Frequent checks were made to ascertain the invariability of these parameters; these were found to be constant for the course of the experiments reported in this paper.

 
 TABLE 1. Electromotive force measurements for the standard sodium fluoride solutions

Standard number	$[\operatorname{NaF}]_T \times 10^3 \\ \operatorname{mol.} 1^{-1}$	$\begin{array}{c} \text{Log } (\mathrm{F}^{-})_{s} ^{\mathrm{a}} \\ \text{mol. } 1^{-1} \end{array}$	$E_s \\ mV$
1 2 3	$   \begin{array}{r}     100.0 \\     75.0 \\     50.0 \\     25.0   \end{array} $	-1.118 -1.231 -1.392 1.670	-108.4 -101.6 -92.4 76.1
4 5	25.0 10.0	-1.670 -2.046	-76.1 -54.6
6 7 8 9	$     \begin{array}{r}       7.50 \\       5.00 \\       2.50 \\       1.00 \\       5.00 \\       7.00 \\       $	-2.105 -2.335 -2.627 -3.016	-48.0 -37.8 -20.7 1.5
$     \begin{array}{c}       11 \\       12 \\       13 \\       14     \end{array}   $	0.500 .250 .100 .750 .0250	$ \begin{array}{r} -3.313 \\ -3.612 \\ -4.015 \\ -4.137 \\ -4.627 \end{array} $	18.8 35.8 59.2 67.1 94.9

<sup>a</sup> Activities of standard sodium fluoride solutions were calculated from eq (7). Linear least squares fitting of eq (8) yielded the best estimates of parameters a ( $-173.032\pm0.176$ ) and b ( $-57.9066\pm0.0610$ ).

Fluoride ion activities in the systems NaF-HCl-H<sub>2</sub>O were obtained from the potential measurements,  $E_m$ , by the use of equation

$$(\mathbf{F}^{-})_{m} = \exp((2.303 \ (E_{m} - a)/b)).$$
 (10)

Estimations of the variances,  $\sigma^2_{(F^-)m}$ , were obtained from Ref. [13]

$$\sigma_{(\mathbf{F}^{-})m}^{2} = (2.303 \ (\mathbf{F}^{-})_{m})^{2} \cdot \sigma_{\log (\mathbf{F}^{-})m}^{2}$$
(11)

in which

$$\sigma_{\log (\mathbf{F}^{-})m}^{2} = \frac{\sigma_{s}^{2}}{b^{2}} \left\{ \frac{1}{i} + \frac{1}{j} + \frac{(E_{m} - \bar{E}_{s})^{2} \cdot \sigma_{b}^{2}}{b^{2} \sigma_{s}^{2}} \right\}.$$
 (12)

In eq (12), *i* and *j* are the number of measurements per sample and the number of points in the standard curve respectively;  $\overline{E}_s$  is the mean value of the potential measurements for the standard curve, and  $\sigma_b^2$  is the variance in the parameter *b* as obtained from the least squares fitting of eq (8).

The calculated standard errors,  $\sigma_{(F^-)m}$ , for all the systems lay between 0.65 and 0.70 percent of the measured activity.

# 3.3. Least Squares Procedure for Estimation of the Equilibrium Constants

This procedure entails the simultaneous adjustment of the weighted observables -i.e.,

$$[\mathbf{F}]_T$$
,  $[\mathbf{H}]_T$ , and  $(\mathbf{F}^-)_n$ 

- and the determination of two parameters which yield best estimates of  $K_1$  and  $K_2$ . The main features of the method follow the general least squares adjustment discussed by Deming [14] and they are similar to those reported in connection with the calculation of diffusion coefficients [15]. The adjustment of the observables was made subject to the condition function  $\phi$ ,

$$\boldsymbol{\phi} = \bar{n}_m - \bar{n}_c = 0. \tag{13}$$

In eq (13),  $\bar{n}_m$  is defined by

$$\bar{n}_m = \frac{[\mathbf{F}]_T - (\mathbf{F}^-)_m / f_1}{[\mathbf{H}]_T}$$
(14)

and it is a function often used in ion association studies [3, 16]. The term  $\bar{n}_c$  is an alternative definition involving the equilibrium constants  $K_1$  and  $K_2$ ,

$$\bar{n}_{c} = \left\{ \frac{(\mathbf{F}^{-})_{m}/K_{1} + 2K_{2}(\mathbf{F}^{-})_{m}^{2}/K_{1}f_{2}}{1/f_{3} + (\mathbf{F}^{-})_{m}/K_{1} + K_{2}(\mathbf{F}^{-})_{m}^{2}/K_{1}f_{2}} \right\}.$$
(15)

The weights of the observables were calculated from

$$W_{\rm obs} = \frac{\sigma_{\rm int}^2}{\sigma_{\rm obs}^2} \tag{16}$$

in which  $\sigma_{obs}$  is the standard deviation for the observable in question and  $\sigma_{int}$  is an arbitrary constant conveniently selected for calculating purposes. The aim of the procedure is to compute adjustments of the observables and the corrections for the initial estimates of the equilibrium constants in such a way that

$$\phi([\mathbf{F}]_T^*, [\mathbf{H}]_T^*, (\mathbf{F})_m^*, k_1, k_2) \approx 0$$
(17)

in which  $k_1$  and  $k_2$  are the final estimates of the equilibrium constants and the starred quantities represent adjusted observables. The adjustment of the observables is done subject to the criterion that the weighted sum of squares of the residuals (observed value adjusted value) be a minimum.

The procedure is an iterative one in which new estimates of the equilibrium constants are substituted as initial estimates until their values converge to a constant value. Also, it allows one to calculate the standard errors in the final estimates of the equilibrium constants.

Although the calculations based upon this procedure are of a general nature and permit the estimation of best values (in the least squares sense) for  $K_1$  and  $K_2$ , in the concentration ranges used here, there was significant information only about  $K_1$ . For this reason, a fixed value of 3.86 for  $K_2$  [5] was adopted and the least squares procedure was applied to estimate  $K_1$ . As shown in section 5, the best estimate for  $K_1$  derived from the present data is relatively insensitive to substantial variations in the value of  $K_2$ .

In the iterative procedure described in this section, each new estimate of  $K_1$  was used to recalculate the ionic species distribution, ionic strength, and activity coefficients. The total number of cycles, using  $K_1 = 6.71 \times 10^{-4}$  as an initial estimate, was from 6 to 7, over the whole concentration range.

# 4. Results

The measured fluoride ion activities together with concentrations of sodium fluoride and hydrochloric acid are shown in table 2.

The quantity R (5th column of table 2) is defined as  $R = (F^{-})_m/(F^{-})_c$ , i.e., the ratio of the fluoride ion activity measured with the lanthanum fluoride membrane electrode to the activity calculated from eq (3) in section 3.1. The equilibrium constants given by Broene and DeVries [5] were used for this calculation. It is apparent that as the concentration of hydrochloric acid increases relative to that of sodium fluoride the value of R departs substantially from unity. As indicated in the Discussion, the most probable cause for the departure of R from unity is the value of  $K_1$  used in the calculation of  $(F^{-})_c$ . Similar calculations were made using the value of  $K_1$  reported here (table 3); the ratio in this case is represented by  $R^*$ . last column of table 2. The values of  $R^*$  are in general close to unity; their departure from unity are anticipated on the basis of the experimental errors in the observables.

Adjusted values of the concentrations for sodium fluoride, hydrochloric acid and measured fluoride ion activities are given in table 3 together with the ionic strength calculated from these adjusted quantities. A comparison with table 2 shows that the adjustments were very small and well within experimental errors in the measurements. The values for  $K_1$  given in column 6 of table 3 were obtained for each individual system using the activities calculated from adjusted observables in eq (1). For this purpose an iterative procedure was used in which an initial distribution of ionic species was obtained from the values of adjusted observables and the best estimate of  $K_1$  obtained from the least squares adjustment; the ionic strength was recalculated and a new value for  $K_1$  was obtained from eq (1); this process was recycled until convergence in the value of the constant.

The near constancy for the value of  $K_1$  in all the systems and the closeness of these values to that of the overall estimate of  $K_1$  further substantiates the soundness of the statistical treatment of the data.

The best estimate of  $K_1$  as obtained from the least squares adjustment on 46 systems is given at the bottom of column 6 in table 3. The calculation of the error associated with this value (sect. 3.3) takes into consideration all the experimental errors in the observables. Thus, the small magnitude of the error in  $K_1$ reflects the reliability of the experimental data and the validity of the physical model, eqs (1) and (2).

The function  $\bar{n}_m$  is plotted against the logarithm of the fluoride ion concentration in figure 1. The points in the figure appear to describe a smooth function; however, since the ionic strength was not the same in all the systems, trends in families of points are discernible

TABLE 2. Unadjusted measurements in the system  $NaF - HCl - H_2O$  at 25 °C

System number	$[\mathbf{F}]_T  imes 10^3$ mol. 1 <sup>-1</sup>	$[H]_T \times 10^3$ mol. 1 <sup>-1</sup>	$(F^{-})_m \times 10^3$ mol. 1 <sup>-1</sup>	R <sup>a</sup>	$R^{* a}$
$\begin{array}{c}1\\2\\3\\4\\5\end{array}$	$\begin{array}{c} 0.499 \\ .499 \\ .499 \\ .499 \\ .498 \\ .498 \end{array}$	$\begin{array}{c} 0.504 \\ 1.02 \\ 1.52 \\ 2.03 \\ 2.53 \end{array}$	0.318 .222 .168 .133 .110	0.97 .95 .94 .92 .91	$1.01 \\ 1.02 \\ 1.02 \\ 1.02 \\ 1.01$
6 7 8 9 10	.497 .497 .496 .496 .495	3.04 3.54 4.04 4.54 5.04	.0938 .0819 .0724 .0648 .0584	.91 .90 .90 .89 .89	$1.01 \\ 1.01 \\ 1.01 \\ 1.01 \\ 1.01 \\ 1.00$
$11 \\ 12 \\ 13 \\ 14 \\ 15$	.999 .998 .997 .996 .995	$\begin{array}{c} 0.508 \\ 1.02 \\ 1.52 \\ 2.03 \\ 2.53 \end{array}$	.701 .508 .389 .305 .249	.98 .96 .94 .93 .91	$1.01 \\ 1.00 \\ 1.01 \\ 1.01 \\ 1.00$
16 17 18 19 20	.994 .993 .992 .991 .990	3.04 3.54 4.04 4.54 5.04	.209 .180 .158 .136 .124	.90 .90 .89 .86 .87	$1.00 \\ 1.00 \\ 1.00 \\ 0.97 \\ .98$
21 22 23 24 25	$\begin{array}{c} .990 \\ 4.99 \\ 4.98 \\ 4.97 \\ 4.96 \end{array}$	5.29 1.02 2.03 3.04 4.04	.119 3.77 2.97 2.29 1.74	.87 .99 .97 .96 .93	.99 1.00 0.98 .98 .97
26 27 28 29 30	4.95 4.94 4.93 4.92 4.91	5.04 6.04 7.03 8.02 9.00	$\begin{array}{c} 1.33 \\ 1.04 \\ 0.846 \\ 0.696 \\ .586 \end{array}$	.92 .92 .93 .92 .92	.98 .99 1.02 1.02 1.03
$31 \\ 32 \\ 33 \\ 34 \\ 35$	4.90 9.88 9.85 9.83 9.80	9.98 6.04 7.52 8.51 9.98	.504 3.86 3.05 2.40 1.93	.92 .93 .94 .88 .92	$1.03 \\ 0.95 \\ .97 \\ .92 \\ .99$
36 37 38 39 40	9.79 9.76 9.74 9.71 9.69	$11.0 \\ 12.4 \\ 13.4 \\ 14.8 \\ 15.8$	$1.50 \\ 1.28 \\ 1.03 \\ 0.927 \\ .771$	.85 .91 .85 .92 .86	$\begin{array}{c} .92 \\ 1.00 \\ 0.94 \\ 1.02 \\ 0.96 \end{array}$
41 42 43 44 45	9.66 9.62 9.57 9.52 9.48	17.2 19.6 21.9 24.2 26.5	.710 .570 .477 .407 .355	.92 .92 .91 .91 .91	$1.03 \\ 1.04 \\ 1.04 \\ 1.03 \\ 1.03 \\ 1.03$
46	9.43	28.8	.315	.91	1.04

"For the definition of R and  $R^*$ , see section 4.

TABLE 3. Adjusted measurements in the system NaF-HCl-H<sub>2</sub>O, ionic strength, and ionization constant of hydrofluoric acid at 25 °C

sodium fluoride and hydrochloric acid and the calculation of ionic activity coefficients would be questionable.

System	$[F]_T^* \times 10^3$	$[H]_T^* \times 10^3$	$(\mathbf{F}^{-})_{m}^{*}  imes 10^{3}$	$I \times 10^{3}$	$K_1 \times 10^4$
number	mol. $1^{-1}$	mol. $1^{-1}$	mol. $1^{-1}$	mol. $1^{-1}$	mol. $1^{-1}$
1	0.502	0.503	0.318	0.830	5.85
2	.503	1.02	.222	1.25	5.85
3	.502	1.51	.168	1.69	5.85
4	.500	2.02	.133	2.17	5.85
5	.500	2.53	.110	2.65	5.85
6	499	3.03	0937	3.14	5.85
7	499	3 53	0818	3.63	5.85
ç i	407	4.03	0723	4.19	5.05
0	.497	4.03	.0725	4.12	5.05
10	.490	4.54	.0040	4.01	5.65
10	.494	5.05	.0584	5.10	5.85
11	1.00	0.508	.700	1.24	5.85
12	0.996	1.02	508	1.55	5.85
13	999	1.52	389	1.00	5.85
14	.996	2.03	305	2 35	5.85
15	.990	2.00	240	2.00	5.05
15	.993	2.33	.249	2.00	5.05
16	.992	3.04	.209	3.26	5.85
17	.990	3.55	.180	3.73	5.85
18	.989	4.05	158	4.21	5.85
19	974	4.61	137	4.69	5.84
20	078	5.00	194	5.18	5.85
20	.970	5.09	.124	5.10	5.05
21	.981	5.33	.119	5.42	5.85
22	4.97	1.02	3.77	5.13	5.87
23	4.92	2.04	2.98	5.33	5.86
24	4 91	3.06	2 29	5.61	5.86
25	4.01	4.07	1.74	6.01	5.85
20	<b>T.</b> 91	4.07	1.17	0.01	5.05
26	4.91	5.07	1.33	6.54	5.85
27	4.92	6.05	1.04	7.21	5.85
28	4.95	7.01	0.845	7.96	5.85
29	4.95	7.98	695	8.79	5.85
30	4.94	8.95	.585	9.65	5.85
21	4.02	0.02	500	10.5	5.05
31	4.93	9.92	.503	10.5	5.85
32	9.65	6.12	3.87	10.7	5.86
33	9.75	7.57	3.05	11.1	5.86
34	9.60	8.65	2.41	11.5	5.84
35	9.75	10.0	1.93	12.3	5.85
36	9.59	11.2	1.50	12.9	5.84
37	9.75	12.4	1.28	13.9	5.85
38	0.57	12.4	1.20	14.7	5.00
30	0.76	14.7	0.026	15.0	5.04
39	9.70	14.7	0.920	15.9	5.65
40	9.58	10.0	.772	10.8	5.85
41	9.73	17.1	.709	18.0	5.85
42	9.71	19.4	.569	20.3	5.85
43	9.67	21.7	.476	22.5	5.85
44	9.61	24.0	.406	24.7	5.85
45	9.56	26.3	.354	26.9	5.85
46	9.52	28.5	.314	29.2	5.85
			9.7	5.05 . 0.	

 $k_1 = 5.85 \pm 0.03 \times 10^{-1}$ 

<sup>a</sup> Best estimate for  $K_1$  and its standard error as obtained by least squares procedure. Fixed value of  $K_2 = 3.86$ .

in this plot. The maximum value of the  $\bar{n}_m$  was 0.922; reliable information on the value of  $K_2$  can be obtained only from systems with  $\bar{n}_m$  values in the neighborhood of 1.5; this would require high concentrations of

#### 5. Discussion

The lack of agreement between the calculated fluoride ion activities and the measurements reported here must be attributed to the value of the constant  $K_1$ used in the calculations and not to the measurements, because: (a) the specific fluoride electrode used in this investigation displays a normal behavior in standard solutions at relatively high pH as well as in acidic solution [6, 8]; (b) the contribution of liquid junction potential<sup>3</sup> to the potential measurements in the standard NaF solutions and the dilute NaF-HCl-H<sub>2</sub>O systems should be approximately constant since identical cells and dilute solutions were used in this study; the standard curves, equation (8), should absorb this contribution and it should not be reflected in the fluoride ion activities,  $(F^{-})_m$ , obtained from eq (10); (c) the highest ionic strength in the present systems was 0.0292 M; for this reason the Debye-Hückel theory eq (6), used in the calculations, should be quite adequate for the calculation of  $f_i$ ; (d) the relatively low standard errors in the observables vouch for the quality of the experimental data.

Although both the values of  $K_1$  and  $K_2$  are involved in the calculations of the fluoride ion activity, only the former affects the value of  $(F^{-})_{c}$  in the experimental ranges reported here. Indeed, when the value of  $K_1$  obtained from the least squares procedure was used to calculate the fluoride ion activity, the discrepancies were eliminated (see values for  $R^*$  in table 2). In this connection it is pertinent to mention that, whereas forty-two values of R (out of forty-six) are significantly different from unity at the 0.05 confidence level, only four values of  $R^*$  are significantly different from unity. For the significance test (two sided normal test), the error in  $(F^{-})_m$  was obtained as explained in section 3.2 and the error in  $(F^-)_c$  was obtained by propagation [17] in eq (3).

The generalized least squares procedure described in section 3.3 can be applied to the present data for the simultaneous estimation of the equilibrium constants. When this was done, the best estimates for  $K_1$  and  $K_2$  were  $5.91 \pm 0.04 \times 10^{-4}$  and  $8 \pm 2$ , respectively. Whereas the value of  $K_1$  obtained in this fashion is in reasonably good agreement with that reported in table 3, the estimate for  $K_2$  is substantially different from that used in the reported calculations. This is a clear indication that the experimental data are inadequate for the estimation of a reliable value for  $K_2$ . Such a limitation is to be anticipated on the basis of the values of  $\bar{n}_m$  calculated from the experimental data and plotted in figure 1. In physical terms, the experimental systems are essentially defined by the

 $<sup>^{\</sup>rm a}$  The type of cells used in this study have a liquid junction formed by a contact between saturated KCI in the reference electrode and the test solution. A liquid junction potential arises because of the different nature of the electrolytes at the two boundaries of the junction [Bates, R. G., Determination of pH Theory and Practice, Chapter 3 (John Wiley and Sons, Inc., New York, New York, 1965)].



 $\label{eq:Figure 1. Plot of $\bar{n}_m$ versus -log $[F^-]_m$.}$  Experiments with similar ionic strengths are represented by the same symbol.

equilibrium given in eq (1). For this reason substantial changes in the value of  $K_2$  should not affect significantly the best estimate of  $K_1$ .

Broene and DeVries reported [5] a value of  $6.71 \times 10^{-4}$ for  $K_1$ , obtained from EMF measurements using a lead fluoride electrode. The calculations involved graphical approximations. In addition, the solubility of lead fluoride is sufficient [18] to open to question their measurements at least in the most dilute systems. Ellis reported [7] a value,  $6.60 \times 10^{-4}$ , for  $K_1$  calculated from conductance data. In his calculations, Ellis had to make questionable assumptions regarding the ionic species responsible for the current transport. Recently, Vanderborgh has reported [6] a value of  $6.46 \times 10^{-4}$ for  $K_1$ , calculated from EMF measurements using a lanthanum fluoride membrane electrode. This value was obtained by extrapolation to zero ionic strength of apparent equilibrium constants at finite ionic strengths. However, the plot used for this purpose (fig. 1 in refence [6]) is in error. The values for the apparent equilibrium constants given by Vanderborgh (table 1 in reference [6]) are plotted against the square root of the ionic strength in figure 2; the full line is a least squares fit of this data. It is apparent that the intercept of this line,  $pK_1 = 3.21 \pm 0.03$ , which corresponds to a value of  $K_1 = 6.17 \pm 0.43 \times 10^{-4}$ , is in reasonable agreement with the value of  $K_1$ ,  $5.85 \pm 0.03 \times 10^{-4}$ , reported here. Furthermore, if the point corresponding to  $\sqrt{I}=0.224$  in figure 2 is disregarded then the remaining three points extrapolate even closer to the value obtained in the present study at zero ionic strength (shown by the open square). This agreement substantiates the validity of the assumption used in this study regarding the liquid junction potential since in both Vanderborgh's and the present investigation the potential measurements were made using comparable cells except that the liquid junction potentials were eliminated in his study by a special experimental design.



FIGURE 2. Plot of pK<sub>1</sub> versus square root of ionic strength. •, points from table 1 of reference [6];  $\Box$ ,  $pK_1=3.23$  corresponding to the value  $K_i=5.85$  $\times 10^{-4}$  reported in this paper.

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