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Equilibria in moderately concentrated aqueous hydrogen fluoride solutions

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Abstract

Hydrogen and fluoride ion molalities have been estimated potentiometrically in HF/H_2O mixtures up to 10 mol% HF (c. 6 mol kg^{-1} HF) at 298 K using the galvanic cells:

$$Ag/AgCl|KCl(m_1),\ HF(m_2)|PbClF/Pb\ \text{(two-phase amalgam)} \qquad (1)$$

$$Pt/H_2|KCl(m_1),\ HF(m_2)|AgCl/Ag \qquad (2)$$

The data show progressive solvation of F^- by HF to form first HF_2^- and then $H_2F_3^-$; this association is directly responsible for the rapid rise in acidity as the analytical HF concentration rises above 1 molal. No evidence was found for any significant further association of HF with F^- at molalities below 6.

Introduction

In a previous paper [1] we reported potentiometric data on fluoride ion activities in HF/H_2O mixtures in the HF molality range 0–6. In that work, the hydrogen ion concentrations were estimated from known acidity functions and conductivity measurements. New experimental measurements have now been made that include reliable potentiometric hydrogen ion activity determinations, providing the basis for a considerably more accurate determination of some relevant equilibrium constants.

Experimental

All chemicals used were obtained and purified as previously described [1]. The hydrogen and silver/silver chloride electrodes were prepared according to Farrell and McTigue [2], and the lead/lead chlorofluoride electrode was made following the method of McTigue and Verity [3].

The galvanic cells were constructed from four 20-mm diameter cylindrical compartments drilled in a solid Perspex block. This material was found to be unaffected by 10 M HF over the period during which the experiments were carried out. The electrodes were held in the electrolyte via Teflon plugs fitted to a standard B14 socket. The hydrogen electrode, the lead/lead chlorofluoride electrode and the silver/silver chloride electrode occupied three of the compartments while the fourth was used as a presaturator for the hydrogen gas used for the hydrogen electrode. The composite cell was kept in a darkened air thermostat at 298 ± 0.02 K. Emf measurements were made with a calibrated Keithley 192 programmable multimeter. As before [1], in order to obtain stable and reproducible emf measurements, it was necessary to protect the lead/lead chlorofluoride electrode from light, oxygen and vibration. The cell was kept oxygen-free by initially flushing with O_2-free nitrogen, deoxygenating all solutions with presaturated N_2 and keeping it closed during all measurements, apart from the continuous hydrogen input. Cells were routinely allowed to equilibrate for at least 24 h, although the emf usually stabilised within 5 h and remained constant for at least 2 d after that time.

Results and discussion

The emfs of cells 1 and 2 above are given by [1]:

$$E_1 = -0.6068 - 0.01285 \ln\left(\frac{m_{F^-}\gamma_{F^-}}{m_{Cl^-}\gamma_{Cl^-}}\right) \qquad (3)$$

$$E_2 = 0.2223 - 0.02569 \ln(m_{H^+}m_{Cl^-}\gamma_{H^+}\gamma_{Cl^-}) \qquad (4)$$

where E_2 is the emf value of cell 2 corrected to the standard state hydrogen pressure of 1 bar and $\gamma_\pm$ is

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TABLE 1. Emfs of galvanic cells 1 and 2

m_2 (mol kg^{-1})	m_1 (mol kg^{-1})	$-E_1$ (V)	E_2 (V)	m_{H^+} (mol kg^{-1})	m_{F^-} (mol kg^{-1})	a_{HF}
0.050	0.05664	0.5780	0.4343	0.00690	0.00598	0.0414
0.085[a]	0.04428	0.5827	–	0.00972[b]	0.00675	0.0729[c]
0.106	0.05844	0.5795	0.4198	0.01182	0.00693	0.0815
0.160	0.05545	0.5834	0.4150	0.01505	0.00889	0.1332
0.173[a]	0.04651	0.5850	–	0.01565[b]	0.00848	0.1432[c]
0.218	0.05710	0.5838	0.4089	0.01863	0.00945	0.1744
0.251	0.05674	0.5841	0.4063	0.02080	0.00964	0.1983
0.252[a]	0.04374	0.5868	–	0.02051[b]	0.00918	0.2030[c]
0.305	0.05561	0.5848	0.4033	0.02385	0.00998	0.2347
0.390	0.05466	0.5854	0.3993	0.02853	0.01021	0.2863
0.474	0.03999	–	0.4008	0.03643	–	0.3856
0.537	0.04723	0.5883	0.3934	0.04170	0.01108	0.4518
0.646	0.05764	0.5858	0.3875	0.04320	0.01103	0.4656
0.732	0.04638	0.5885	0.3897	0.04949	0.01102	0.5298
0.794	0.05047	–	0.3846	0.05604	–	0.5975
0.827[a]	0.04667	0.5887	–	0.0571[b]	0.01135	0.6243[c]
0.888	0.05169	0.5872	0.3812	0.0630	0.01108	0.6668
1.046	0.04716	0.5884	0.3780	0.0789	0.01111	0.8099
1.109[a]	0.04730	0.5876	–	0.0777[b]	0.01056	0.8880
1.110	0.05403	–	0.3745	0.0795	–	0.8900
1.193	0.05831	–	0.3679	0.0969	–	0.9833
1.298	0.05702	0.5858	0.3678	0.0993	0.01091	1.0043
1.404	0.07198	–	0.3592	0.1124	–	1.042
1.544	0.05873	–	0.3627	0.1194	–	1.136
1.617[a]	0.04754	0.5879	–	0.1204[b]	0.01087	1.185[c]
1.900	0.04064	0.5885	0.3681	0.1404	0.00956	1.226
1.981	0.05521	0.5864	0.3563	0.1675	0.01098	1.649
2.047[a]	0.04730	0.5864	–	0.1624[b]	0.00962	1.477[c]
2.969[a]	0.04626	0.5840	–	0.2727[b]	0.007805	2.162[c]
2.999	0.07308	0.5784	0.3341	0.3121	0.007723	2.114
4.948	0.06566	0.5791	0.3187	0.6026	0.007030	4.050
4.990[a]	0.07430	0.5757	–	0.633[b]	0.006550	4.148[c]
6.003	0.05459	0.5802	0.3129	0.8439	0.006144	5.512
6.089[a]	0.08750	0.5732	–	0.8660[b]	0.006341	5.550[c]

[a] Data from ref. 1.
[b] Calculated using eqn. (7).
[c] Calculated using eqn. (12).

the appropriate mean molal activity coefficient. The hydrogen ion molality has been calculated from:

$$m_{H^+} = \frac{1}{\gamma_\pm^2 m_{Cl^-}} \exp\left\{-\frac{E_2 - 0.2223}{0.02569}\right\} \tag{5}$$

using an iterative procedure in which $\gamma_\pm$ was equated to the known mean activity coefficients of HCl(aq.) [4] as a function of ionic strength, with the initial ionic strength being equated to m_1 ($= m_{K^+}$) and subsequently evaluating the molal ionic strength as:

$$I = m_{K^+} + m_{H^+} \tag{6}$$

The value of I was then used to estimate $\gamma_\pm$ from which a new value of m_{H^+} was calculated and the process continued until I and m_{H^+} remained unchanged. An excellent smooth relationship between m_{H^+} and m_2 resulted which was well represented by the expression:

$$\ln m_{H^+} = -2.6665 + 1.0633x + 0.01959x^2 \tag{7}$$

where

$$x = \ln m_2 \tag{8}$$

This relation was used to calculate m_{H^+} as a function of m_2, the HF analytical molality, for the data on cell 1 from ref. 1. These data are included in Table 1.

The fluoride ion molality was then evaluated as:

$$m_{F^-} = \frac{m_{Cl^-}\gamma_{Cl^-}}{\gamma_{F^-}} \exp\left\{-\frac{E_1 + 0.6068}{0.01285}\right\} \tag{9}$$

where $m_{Cl^-} = m_1 = m_{K^+}$ and $\gamma_{Cl^-}/\gamma_{F^-}$ was estimated using the known ratio [4] of the square of the mean activity coefficients of KCl and KF, which is given by:

$$\gamma_\pm^2(\text{KCl})/\gamma_\pm^2(\text{KF}) = \gamma_{Cl^-}/\gamma_{F^-} = 1 - 0.1112I \tag{10}$$

where I is the ionic strength determined from eqn. (6) above. Finally, the HF activity, a_{HF}, referred to infinite dilution in water, was calculated from the relation:

$$a_{\mathrm{HF}}=\frac{m_{\mathrm{H^+}}m_{\mathrm{F^-}}\gamma_{\mathrm{H^+}}\gamma_{\mathrm{F^-}}}{K_a}$$
$$=K_a^{-1}\exp\left\{-\frac{2E_1+E_2+0.9913}{0.02569}\right\} \qquad (11)$$

where K_a is the acidity constant of HF. This activity was found to be well represented by the expression:

$$a_{\mathrm{HF}}=0.8895m_2-0.4067m_2^2-0.2960m_2^3 \qquad (12)$$

The experimental quantities $m_{\mathrm{H^+}}$, $m_{\mathrm{F^-}}$ and a_{HF}, as determined from eqns. (5), (9) and (11), are given in Table 1 and have been used to calculate constants for the equilibria in concentrated HF solutions. The relevant equilibria and corresponding equilibrium expressions are:

$$\mathrm{HF} \rightleftharpoons \mathrm{H^+}+\mathrm{F^-} \qquad K_a=\frac{m_{\mathrm{H^+}}m_{\mathrm{F^-}}\gamma_{\pm}^2}{a_{\mathrm{HF}}} \qquad (13)$$

$$\mathrm{HF}+\mathrm{F^-} \rightleftharpoons \mathrm{HF_2^-} \qquad K_1=\frac{m_{\mathrm{HF_2^-}}}{a_{\mathrm{HF}}m_{\mathrm{F^-}}} \qquad (14)$$

$$\mathrm{HF}+\mathrm{HF_2^-} \rightleftharpoons \mathrm{H_2F_3^-} \qquad K_2=\frac{m_{\mathrm{H_2F_3^-}}}{a_{\mathrm{HF}}m_{\mathrm{HF_2^-}}} \qquad (15)$$

In writing the above equilibrium expressions (14) and (15), it has been assumed that the activity coefficients of $\mathrm{F^-}$, $\mathrm{HF_2^-}$ and $\mathrm{H_2F_3^-}$ are all the same. This is unlikely to be true, particularly at high ionic strengths and it is a limitation on the accuracy of the results of this work. Applying the charge balance principle, we obtain:

$$m_{\mathrm{H^+}}=m_{\mathrm{F^-}}+m_{\mathrm{HF_2^-}}+m_{\mathrm{H_2F_3^-}} \qquad (16)$$

$$\left(\frac{m_{\mathrm{H^+}}}{m_{\mathrm{F^-}}}-1\right)=R-1=K_1a_{\mathrm{HF}}+K_1K_2a_{\mathrm{HF}}^2 \qquad (17)$$

where R is the ratio of the molalities of the hydrogen and fluoride ions. Equation (17) has been used to analyse our data. The left-hand side of the equation can be calculated directly from hydrogen and fluoride ion molalities calculated using eqns. (5) and (9) and the constants K_1 and K_2 are then determined by a standard curve-fitting procedure using the HF activities obtained from eqn. (12) for all values of m_2 less than 1.5 mol kg^{-1}. The experimental data and the fitted quadratic are shown in Fig. 1.

This gives a value of 5.13 ± 0.1 for K_1 and 0.50 ± 0.1 for K_2; these values can then be used with the known acidity constant of HF (K_a at 298 K = 6.84×10^{-4} [5–7]) to calculate the molalities of all species in solution as a function of the analytical HF molality over the whole molality range studied. The quantity R, and hence $m_{\mathrm{H^+}}/m_{\mathrm{F^-}}$, was calculated from eqn. (17) and the product $m_{\mathrm{H^+}}m_{\mathrm{F^-}}$ from eqn. (13). The $\gamma_{\pm}^2$ term in eqn. (13) was evaluated by combining the HCl mean activity coefficients with the ratio $\gamma_{\mathrm{Cl^-}}/\gamma_{\mathrm{F^-}}$ from eqn. (10) to take account of the difference between the activity coefficients of the chloride ion and the fluoride ion in solutions containing significant amounts of the potassium ion. The results obtained are shown in Figs. 2, 3 and 4. The fit with the experimental data is within experimental error at HF analytical molalities up to 2; beyond 2, the $\mathrm{H^+}$ molality is slightly underestimated while the $\mathrm{F^-}$ molality is overestimated. The lack of a perfect fit above 2 molal is not surprising bearing in mind the difficulties of allowing for the activity coefficients at high ionic strengths of both the ions and molecules

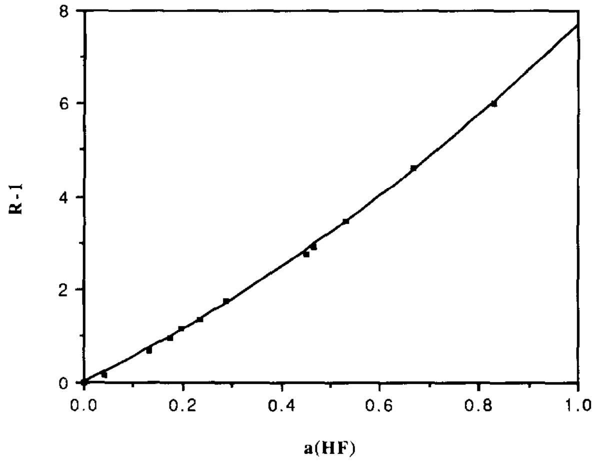

Fig. 1. Plot of $R-1$ versus HF activity. The full line represents the equation $R-1=5.13a_{\mathrm{HF}}+2.57a_{\mathrm{HF}}^2$.

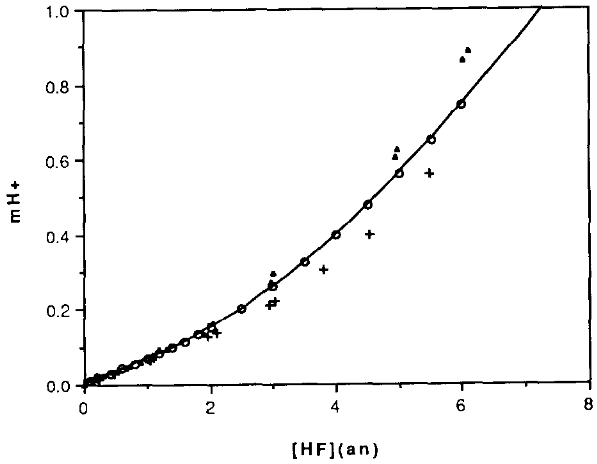

Fig. 2. The full line is the calculated hydrogen ion molality using the experimentally determined values of K_1 and K_2, and a K_a value of 6.84×10^{-4}. The small triangles show the experimental molalities from this work (Table 1), the crosses the molalities estimated from the electrical conductivities of the HF solutions, and the circles show the calculated molalities.

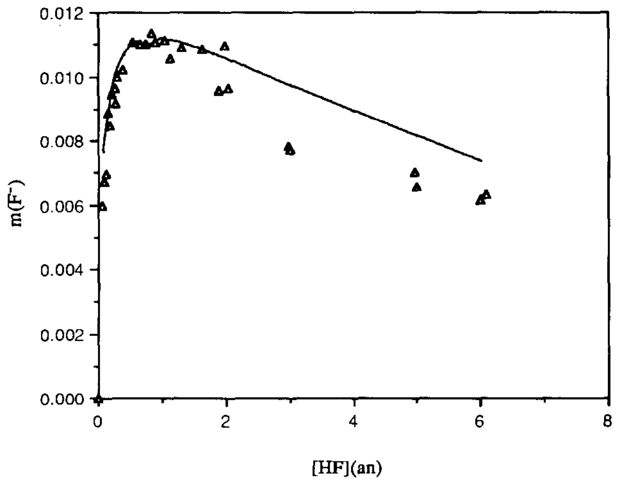

Fig. 3. The full line is the calculated fluoride ion molality using the experimentally determined values of K_1 and K_2, and a K_a value of 6.84×10^{-4}; the open triangles are the experimental values from Table 1.

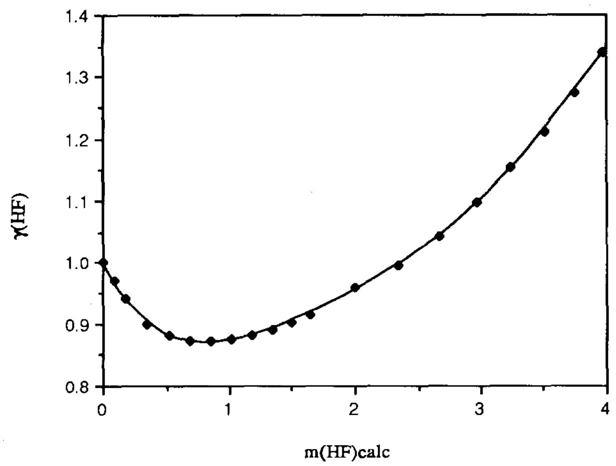

Fig. 4. Plot of the experimentally determined molal activity coefficient of molecular HF as a function of molecular HF molality calculated using the experimental values of K_1 and K_2.

present; furthermore, the possibility exists of significant HF–HF (see below) and HF–Cl^- association. Such factors provide the most likely explanation for the discrepancies between the model and the data in the analytical HF molality range of 2–6 mol kg^{-1}. Indeed, the inclusion of a significant equilibrium constant for the species $H_3F_4^-$ to improve the fit leads to physically impossible (negative!) values of the free HF molality, suggesting that $H_3F_4^-$ and $H_4F_5^-$ only become important at higher HF analytical molalities.

Our value of 5.1 ± 0.1 for K_1 is greater than that determined by Broene and De Vries [5] and Kresge and Chiang [6] (4.0 ± 0.1 in both cases) but agrees with the values of Davies and Hudleston [8] (4.7 ± 0.3) and Baumann [6] (5.0 ± 0.2). There is no obvious reason for the discrepancy between the two sets of results and resolution of the problem must await further work. We can find no earlier reliable reports of a determination of K_2.

One interesting consequence of the results was uncovered when the calculated free HF molalities were compared with the experimental HF activities to give the activity coefficient of free molecular HF as shown in Fig. 4. One obvious interpretation of the initial reduction in the activity coefficient with increasing HF molality is some association of HF molecules into dimers and it is possible that under these conditions the observed behaviour is related largely to HF–HF interactions. The increasing activity coefficient at higher molalities and ionic strengths may be due to the rapidly growing importance of the normal salting out of the uncharged molecule as well as to the progressive lowering of the water activity with the accompanying reduction in the degree of solvation of HF. The accepted values of the acidity constant have been based on the presumption [5–7] that molecular HF in dilute solutions behaves ideally, a view supported by early freezing point depression measurements that appeared to rule out appreciable HF association [9]. We now believe that this assumption needs to be checked, possibly by way of a potentiometric study using a wide range of ionic strengths and HF molalities to clarify the situation. Unfortunately, there is a difficulty in choosing an appropriate electrode system to sense the fluoride ion; the lead/lead fluoride system is unsatisfactory at low fluoride ion activity as the data of Broene and De Vries [5] clearly showed, while our lead/lead chlorofluoride system [1] requires the presence of chloride ions. Careful studies with an LaF_3 membrane electrode would seem to be the best option.

Conclusions

1. The behaviour of aqueous HF solutions can be satisfactorily described in terms of the three equilibria shown in eqns. (13)–(15) with $K_a=6.84\times10^{-4}$ mol kg^{-1}, $K_1=5.13\pm0.1$ kg mol^{-1} and $K_2=0.50\pm0.1$ kg mol^{-1}, and the empirically determined relationship (12) between analytical HF molality and the HF activity. The fit with the experimental data is excellent in the range $0\leqslant m_2\leqslant2$ mol kg^{-1} and fair in the range $2\leqslant m_2\leqslant6$ mol kg^{-1}. It must be remembered that the estimation of ionic activity coefficients becomes decreasingly reliable at ionic strengths above 0.1 mol kg^{-1} as does the assumption that the activity coefficients of all anionic fluoride species are identical. However, there is no convincing alternative to these estimates and assumptions at present.

2. Although there is no doubt [1] that fluoride ions associate with HF molecules up to at least the species

$H_4F_5^-$ at high HF molalities, there is no compelling evidence that there are appreciable amounts of ions of complexity beyond $H_2F_3^-$ up to analytical HF molalities of *c.* 6 where the model described above is still a fair approximation.

3. There is circumstantial evidence for appreciable HF–HF interactions at fairly low molalities of molecular HF. Although our estimates of the HF activity coefficients depend on our calculated values of the molecular HF molality, the low molality data seem reasonably reliable. We conclude that previous assumptions that molecular HF behaves ideally at low molalities need to be checked.

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