[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA RADIATION LABORATORY AND THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Complexing of Iron(III) by Fluoride Ions in Aqueous Solution: Free Energies, Heats and Entropies

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RECEIVED OCTOBER 20, 1955

The potential of the ferrous–ferric half-cell has been studied as a function of hydrofluoric acid concentration at 15, 25 and 35°. Equilibrium quotients and free energy, heat and entropy changes at an ionic strength of 0.50 are calculated for the reactions: $Fe^{+3} + HF = FeF^{+2} + H^+$, $FeF^{+2} + HF = FeF_2^+ + H^+$ and $FeF_2^+ + HF = FeF_3 + H^+$.

In order to investigate the fluoride complexing of sundry cations[1–3] as a function of temperature using the "ferri"[4,5] method, it was necessary to extend the work of Dodgen and Rollefson[5] with iron to 15 and 35°.

The experimental technique used in the present investigation of the fluoride complex ions of iron(III) is essentially the same as theirs.[5] Several experiments were also carried out at 25°, the results of which deviated slightly from those of the above investigators.

Experimental

The cell, solutions and potentiometer circuit used in these experiments have been described previously.[1,6] Experiments were carried out at 15, 25 and 35°.

Before each run the assembled cell and the stock solutions were brought to the temperature of the experiment. One-hundred-milliliter aliquots of stock solution containing the desired concentrations of $Fe(ClO_4)_2$, $Fe(ClO_4)_3$, $HClO_4$ and $NaClO_4$ were pipetted into each half-cell. The stirrers were activated and after observing the small initial potential (usually less than 0.2 mv.) standard sodium fluoride solution was added to one half-cell. The potential of the cell was read after each addition. The stirrers were left on both while adding sodium fluoride and reading the potential. The potential became constant to within 0.02 mv. approximately one minute after each addition.

The variation of potential with total fluoride concentration at 15, 25 and 35° as well as the initial concentrations of $HClO_4$, $Fe(ClO_4)_2$ and $Fe(ClO_4)_3$ are given in Table I for a typical run at each temperature. In all runs the initial compositions of the two half-cells were the same. Sodium perchlorate was used to bring the initial ionic strength to 0.50. The half-cell to which fluoride was added is designated as "B" and the other as "C." The measured potential after each addition of sodium fluoride minus the initial potential is designated as "E." The total fluoride concentration in half-cell B is (ΣF^-). The equal initial volumes in the half-cells is V_i; V is the volume in half-cell B after adding sodium fluoride. The total initial concentrations are designated with the symbol "Σ" and the subscript "i."

Several experiments were run at each temperature with varying hydrogen ion concentrations and with smaller ferrous and ferric concentration changes. The initial conditions and the range of fluoride concentration are given in Table II. In each experiment anywhere from seven to eighteen e.m.f. determinations were made at different fluoride concentrations. The complete data may be found in references 6 and 12.

Analysis of Results

The experimental results may be interpreted by considering the following equilibria

$$Fe^{+3} + HF = FeF^{+2} + H^+ \qquad Q_1 \qquad (1)$$

$$FeF^{+2} + HF = FeF_2^+ + H^+ \qquad Q_2 \qquad (2)$$

$$FeF_2^+ + HF = FeF_3 + H^+ \qquad Q_3 \qquad (3)$$

$$HF = H^+ + F^- \qquad Q_{HF} \qquad (4)$$

$$Fe^{+3} + H_2O = FeOH^{+2} + H^+ \qquad Q_H \qquad (5)$$

The Q's are equilibrium quotients, for example

$$Q_1 = \frac{(FeF^{+2})(H^+)}{(Fe^{+3})(HF)}$$

where ( ) signifies concentration in moles/l.

TABLE I

DATA FOR TYPICAL RUNS AT DIFFERENT TEMPERATURES

(μ = 0.50)

	$(\Sigma F^-) \times 10^4$, moles/l.	E, mv.	V, ml.
14.97 ± 0.03°	9.08	39.88	110.2
$(\Sigma H_i^+) = 0.01838\ M$	18.10	71.56	110.4
$(\Sigma Fe_i^{+2}) = 2.315 \times 10^{-4}\ M$	27.13	92.82	110.6
$(\Sigma Fe_i^{+3}) = 5.866 \times 10^{-4}\ M$	36.12	109.75	110.8
V_i = 110.0 ml.	45.08	124.30	111.0
	54.00	136.99	111.2
	62.86	148.78	111.4
	71.73	159.50	111.6
	80.52	169.60	111.8
	89.38	179.40	112.0
	98.09	188.88	112.2
	106.79	197.90	112.4
25.00 ± 0.01°	3.78	13.83	105.0
$(\Sigma H_i^+) = 0.04946\ M$	7.55	26.32	105.1
$(\Sigma Fe_i^{+2}) = 6.338 \times 10^{-4}\ M$	11.31	36.65	105.1
$(\Sigma Fe_i^{+3}) = 4.277 \times 10^{-4}\ M$	15.07	45.17	105.2
V_i = 104.9 ml.	18.83	52.57	105.3
	28.77	68.22	105.5
	38.68	80.24	105.7
	48.55	90.28	105.9
	68.18	107.32	106.3
	87.66	121.46	106.7
	107.0	133.84	107.1
	126.2	144.98	107.5
35.00 ± 0.02°	4.57	14.69	105.0
$(\Sigma H_i^+) = 0.05645\ M$	13.21	38.76	105.1
$(\Sigma Fe_i^{+2}) = 6.338 \times 10^{-4}\ M$	20.06	51.91	105.2
$(\Sigma Fe_i^{+3}) = 4.277 \times 10^{-4}\ M$	27.03	62.54	105.3
V_i = 104.9 ml.	34.18	71.30	105.5
	43.16	81.12	105.6
	56.93	93.39	105.8
	79.95	110.34	106.2
	104.3	125.56	106.6
	119.8	134.17	106.9
	133.4	141.51	107.1

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(2) R. E. Connick and M. Tsao, THIS JOURNAL, **76**, 5311 (1954).

(3) Complexing of Sc^{+3} by fluoride ion, to be published.

(4) C. Brosset and G. Orring, *Svensk. Kem. Tid.*, **55**, 101 (1943).

(5) H. W. Dodgen and G. K. Rollefson, THIS JOURNAL, **71**, 2600 (1949).

(6) J. W. Kury, University of California Radiation Laboratory Report, UCRL-2271, July, 1953.

TABLE II

CONDITIONS FOR INDIVIDUAL EXPERIMENTS ($\mu = 0.50$)

14.97°

$(\Sigma\text{Fe}_i^{+3}) = 5.866 \times 10^{-4}\ M$, $(\Sigma\text{Fe}_i^{++}) = 2.315 \times 10^{-4}\ M$

Run	(ΣH_i^+), M	Highest (ΣF^-), M
1	0.0944	0.028
2	.0437	.022
3	.01838	.011
4	.00994	.009

Run	(ΣH_i^+), M	Highest (ΣF^-), M	$(\Sigma\text{Fe}_i^{++}) \times 10^{+4}$, M	$(\Sigma\text{Fe}_i^{+3}) \times 10^{+4}$, M
		25.00°		
1	0.04946	0.0126	6.338	4.277
2	.09443	.0075	6.338	4.277
3	.09246	.0072	6.050	4.083
4	.09490	.0073	9.09	6.133
		35.00°		
1	0.0975	0.0090	6.717	4.367
2	.0957	.0082	2.635	1.748
3	.0975	.0045	6.717	4.367
4	.05975	.0062	6.717	4.367
5	.1060	.0077	6.050	4.083
6	.05645	.0133	6.338	4.277

Both Brosset and Gustaver[7] and Babko and Kleiner[8] were able to interpret their experimental data on the complexing of iron(III) with fluoride by assuming the presence of such species as FeF^{+2}, FeF_2^+, FeF_3, FeF_4^- and $\text{FeF}_6^=$. Dodgen and Rollefson[5] discuss the nature of the complex fluoride ions present in solutions similar to ours. Based upon their conclusions we have assumed the presence of FeF^{+2}, FeF_2^+ and FeF_3 and are able to account for our experimental results.

The equations necessary for the numerical evaluation of Q_1, Q_2 and Q_3 will now be developed. From stoichiometric considerations we obtain

$$(\Sigma\text{F}^-) = (\text{HF}) + (\text{F}^-) + (\text{FeF}^{+2}) + 2(\text{FeF}_2^+) + 3(\text{FeF}_3) \qquad (6)$$

$$(\Sigma\text{Fe}^{+3}) = (\text{Fe}^{+3}) + (\text{FeOH}^{+2}) + (\text{FeF}^{+2}) + (\text{FeF}_2^+) + (\text{FeF}_3) \qquad (7)$$

$$(\Sigma\text{Fe}^{+3})_\text{C} = (\text{Fe}^{+3})_\text{C} + (\text{FeOH}^{+2})_\text{C} \qquad (8)$$

The reference half-cell C has been designated by the subscript "C," while for simplicity B has been left undesignated. The potential of the concentration cell B-C is given by

$$E = -\frac{RT}{\mathfrak{F}} \ln \frac{(\text{Fe}^{+3})(\text{Fe}^{+2})_\text{C}}{(\text{Fe}^{+2})(\text{Fe}^{+3})_\text{C}} \qquad (9)$$

One obtains from equation 9

$$(\text{Fe}^{+3})_\text{C} = (\text{Fe}^{+3})_\text{C} \frac{V_\text{i}}{V} e^{-\mathfrak{F}E/RT} \qquad (10)$$

Combining equilibrium expression (5) and equation 8, one obtains

$$(\text{Fe}^{+3})_\text{C} = \frac{(\Sigma\text{Fe}^{+3})_\text{C}}{1 + Q_\text{H}/(\text{H}^+)_\text{C}} \qquad (11)$$

also

$$(\Sigma\text{Fe}^{+3}) = \frac{V_\text{i}}{V} (\Sigma\text{Fe}^{+3})_\text{C} \qquad (12)$$

Combining (10), (11) and (12), we obtain

$$\frac{(\Sigma\text{Fe}^{+3})}{(\text{Fe}^{+3})} = \left\{1 + \frac{Q_\text{H}}{(\text{H}^+)_\text{C}}\right\} e^{\mathfrak{F}E/RT} \qquad (13)$$

Combining equilibrium expressions (1)–(4) with equation 7 one obtains

$$\frac{(\Sigma\text{Fe}^{+3})}{(\text{Fe}^{+3})} - 1 - \frac{Q_\text{H}}{(\text{H}^+)} = Q_1 \frac{(\text{HF})}{(\text{H}^+)} + Q_1Q_2 \frac{(\text{HF})^2}{(\text{H}^+)^2} + Q_1Q_2Q_3 \frac{(\text{HF})^3}{(\text{H}^+)^3} \qquad (14)$$

With the justifiable approximation that

$$\left\{1 + \frac{Q_\text{H}}{(\text{H}^+)}\right\} = \left\{1 + \frac{Q_\text{H}}{(\text{H}^+)_\text{C}}\right\} \qquad (15)$$

we can combine equations 13 and 14 to obtain

$$\left\{1 + \frac{Q_\text{H}}{(\text{H}^+)}\right\} \{e^{\mathfrak{F}E/RT} - 1\} = Q_1 \frac{(\text{HF})}{(\text{H}^+)} + Q_1Q_2 \frac{(\text{HF})^2}{(\text{H}^+)^2} + Q_1Q_2Q_3 \frac{(\text{HF})^3}{(\text{H}^+)^3} \qquad (16)$$

Also, by using equilibrium expressions (1)–(5) and equations 6 and 7 we obtain

$$\frac{(\text{HF})}{(\text{H}^+)} = \frac{1}{Q_\text{HF} + (\text{H}^+)} \left\{ (\Sigma\text{F}^-) - (\Sigma\text{Fe}^{+3}) + (\text{Fe}^+)^3 \left(1 + \frac{Q_\text{H}}{(\text{H}^+)}\right) - Q_1Q_2(\text{Fe}^{+3}) \frac{(\text{HF})^2}{(\text{H}^+)^2} - 2Q_1Q_2Q_3(\text{Fe}^{+3}) \frac{(\text{HF})^3}{(\text{H}^+)^3} \right. \qquad (17)$$

Neglecting H^+ from ferric hydrolysis

$$(\text{H}^+) = \frac{(\Sigma\text{H}^+)}{1 + \frac{(\text{HF})}{(\text{H}^+)}} \qquad (18)$$

From equations 13 and 15

$$(\text{Fe}^{+3}) = \frac{(\Sigma\text{Fe}^{+3})}{(e^{\mathfrak{F}E/RT})\left(1 + \frac{Q_\text{H}}{(\text{H}^+)}\right)} \qquad (19)$$

We are able to solve equations 16 and 17 for Q_1, Q_2 and Q_3 by successive approximations.

Neglecting terms containing Q_1, Q_2 and Q_3, we obtain a first approximation for the ratio $(\text{HF})/(\text{H}^+)$ from equation 17. These values are then used with estimated Q's to obtain a better set of $(\text{HF})/(\text{H}^+)$ values from equation 17.

As seen from equation 16, we are able to obtain values for Q_1, Q_2 and Q_3 by plotting[9] the quantity

$$Y = \frac{(\text{H}^+)}{(\text{HF})} \left\{1 + \frac{Q_\text{H}}{(\text{H}^+)}\right\} \{e^{\mathfrak{F}E/RT} - 1\}$$

vs. $(\text{HF})/(\text{H}^+)$ at low $(\text{HF})/(\text{H}^+)$ and the quantity

$$Z = \left[\left\{1 + \frac{Q_\text{H}}{(\text{H}^+)}\right\} \{e^{\mathfrak{F}E/RT} - 1\} \frac{(\text{H}^+)}{(\text{HF})_{Q_1}} - 1\right] \frac{(\text{H}^+)}{(\text{HF})}$$

vs. $(\text{HF})/(\text{H}^+)$ at high $(\text{HF})/(\text{H}^+)$. This procedure was repeated until consistent values for Q_1, Q_2 and Q_3 were obtained.

In the above treatment it has been assumed that the pertinent activity coefficient ratios remained constant at the nearly constant ionic strength of the experiments. Following Dodgen and Rollefson's[5] reasoning, complexing of ferrous ion was taken to be negligible. The hydrolysis of ferrous ion[10] and the formation of HF_2^-[11] are too small to be detected. Any complexing by perchlorate ion would be absorbed in the equilibrium quotients.

The values of Q_HF and Q_H used in the calculations

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(7) C. Brosset and B. Gustaver, *Svensk. Kem. Tidskr.*, **54**, 185 (1942).

(8) A. Babko and K. Kleiner, *J. Gen. Chem.* (*U.S.S.S.R.*), **17**, 1259 (1947).

(9) I. Leden, *Z. physik. Chem.*, **188**, 160 (1941).

(10) D. L. Leussing and I. M. Kolthoff, THIS JOURNAL, **75**, 2476 (1952).

are given in Table III. The values for Q_{HF} at 15 and 35° were calculated from the 25° value using the temperature dependence for this equilibrium at zero ionic strength measured by Broene and DeVries.[11] The value at 25° was determined experimentally[12] for an ionic strength of 0.50 ($NaClO_4$, $HClO_4$) by measuring the hydrogen ion concentration spectrophotometrically, using the indicator Tropeolin 00, in solutions containing sodium fluoride and hydrofluoric acid. The value is estimated to be accurate to at least 6%.

TABLE III

HYDROLYSIS QUOTIENTS FOR FERRIC ION AND IONIZATION QUOTIENTS FOR HF ($\mu = 0.50$)

	15°	25°	35°
Q_H	1.18×10^{-3}	1.9×10^{-3}	3.2×10^{-3}
Q_{HF}	1.42×10^{-3}	1.23×10^{-3}	1.01×10^{-3}

The value of Q_H at 25° and an ionic strength of 0.5 is that used in references 1, 2 and 5; it is in excellent agreement with the recent results of Milburn and Vosburgh.[13] The value at 15° was obtained[12] spectrophotometrically using molar extinction coefficients for Fe^{+3} and $FeOH^{++}$ taken from the work of Olson and Simonson.[14] It could be in error by 15%. The 35° value was extrapolated from the 15 and 25° values.

The final values of Q_1, Q_2 and Q_3 are presented in Table IV and in Table V are given ΔF, ΔH and ΔS for reactions (1) and (2) and ΔF for reaction (3) at 25° and an ionic strength of 0.50. Because of the relatively large uncertainty in Q_3, values of ΔH and ΔS for reaction (3) have not been tabulated. It is to be noted that the value of Q_3 at 15° is more reliable than the others because the fraction of iron converted to the third complex was greatest in these experiments.

The values for Q_1, Q_2 and Q_3 at 25° of 184, 10.3 and 1.0, respectively, compare well with those reported by Dodgen and Rollefson,[5] *i.e.*, 189, 10.4 and 0.58, except for Q_3, which is highly uncertain in both cases.

TABLE IV

EQUILIBRIUM QUOTIENTS FOR FLUORIDE COMPLEXING OF FERRIC ION ($\mu = 0.50$)

Run	Q_1	Q_2	Q_3
	15°		
1	191.5	10.7	0.84
2	194	12.0	0.95
3	192	11.8	1.09
4	192	11.5	0.95
Mean value	192 ± 1	11.5 ± 0.4	1.0 ± 0.1
	25°		
1	184	11.1	1.0
2	185	10.1	
3	183	10.2	
4	184	10.0	
Mean value	184 ± 1	10.3 ± 0.4	1.0
	35°		
1	178	9.7	
2	175	9.7	
3	179	10.6	
4	179	10.3	
5	178	9.5	
6	178	10.2	1.0
Mean value	178 ± 1	10.0 ± 0.4	1.0

TABLE V

THERMODYNAMIC QUANTITIES FOR FLUORIDE COMPLEXING OF FERRIC ION AT $\mu = 0.50$

	ΔF_{298}, kcal./mole	ΔH_{298}, kcal./mole	ΔS_{298}, e.u.
$Fe^{+3} + HF = FeF^{+2} + H^+$	−3.09	−0.65	8.2
$FeF^{+2} + HF = FeF_2^+ + H^+$	−1.38	−1.2	0.6
$FeF_2^+ + HF = FeF_3 + H^+$	~0.0		

Using the entropy of ionization of HF at 25°[15] and estimating the value at an ionic strength of 0.50 to be −22.0 e.u., the values for the entropy of complexing of ferric ion by fluoride ions (at μ = 0.50) are obtained

$F^- + Fe^{+3} = FeF^{+2}$ ΔS = 30 e.u.

$F^- + FeF^{+2} = FeF_2^+$ ΔS = 23 e.u.

These entropies compare closely with those for the corresponding reactions of aluminum ion[16] which are 32 and 26 e.u., respectively. The corresponding value for the third complex of ferric ion was not fixed accurately by these experiments, but the data are not inconsistent with a value of 18 e.u. found for the aluminum ion.[16]

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