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PROBLEMS IN THE AQUEOUS CHEMISTRY OF CERIUM(III) FLUORIDE AND LANTHANUM(III) FLUORIDE

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(Thesis)

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I. INTRODUCTION

It has long been known that tripositive rare-earth ions form insoluble gelatinous fluorides in aqueous hydrofluoric acid solutions. Aside from some early work on the composition of these fluorides,[1-3] there are no quantitative data in the chemical literature on the subject.

In this investigation a method for the determination of the solubilities of the rare-earth trifluorides has been developed. It was necessary first to measure the extent of complexing of iron(III) by fluoride ion. These data were utilized to investigate the solubilities of cerium(III) fluoride and lanthanum(III) fluoride and the extent of complexing of cerium(III) and lanthanum(III) by fluoride ion. A calorimetric determination of the heat of precipitation of cerium(III) fluoride was also carried out.

Results from similar experiments involving gadolinium are used in discussing trends in the extent of complexing by fluoride ion and in the solubility of the trifluorides through the lanthanide series.

II. THE COMPLEXING OF IRON(III) BY FLUORIDE IONS IN AQUEOUS SOLUTION: FREE ENERGIES, HEATS AND ENTROPIES.

A number of workers have investigated the extent of association of ferric ions and fluoride ions by a variety of methods.[4-8] If one knows the equilibrium quotients for the various complexing reactions of ferric ion and fluoride ion, it is possible to investigate the extent of complexing of some other cation by measuring the potential of the ferrous-ferric half cell as a function of the hydrofluoric acid concentration and the concentration of the cation in question.[7-10] It is also possible to use a ferrous-ferric concentration cell to determine the solubility of a metal fluoride.

It is the purpose of this investigation to determine the equilibrium quotients for the fluoride complexes of iron(III) as a function of temperature at an ionic strength of 0.50.[7,9] These values will then be used in determining the solubility of several rare-earth fluorides.

Experimental

The Cell. The concentration cell B-C is shown in Figure 1 (half-cell A is used in the determination of the extent of fluoride complexing of other metal cations and will be discussed in Chapter III). The containers and caps were made from 5 cm ground glass joints. The inside of the containers as well as the stirrers were coated with "Tavern" paraffin to prevent hydrofluoric acid from reacting with the glass.[8] Half-cells B and C were joined by a 1.6M sodium perchlorate-agar-agar salt bridge in an effort to minimize junction potentials.[7] A carbon dioxide atmosphere was maintained over the solutions to

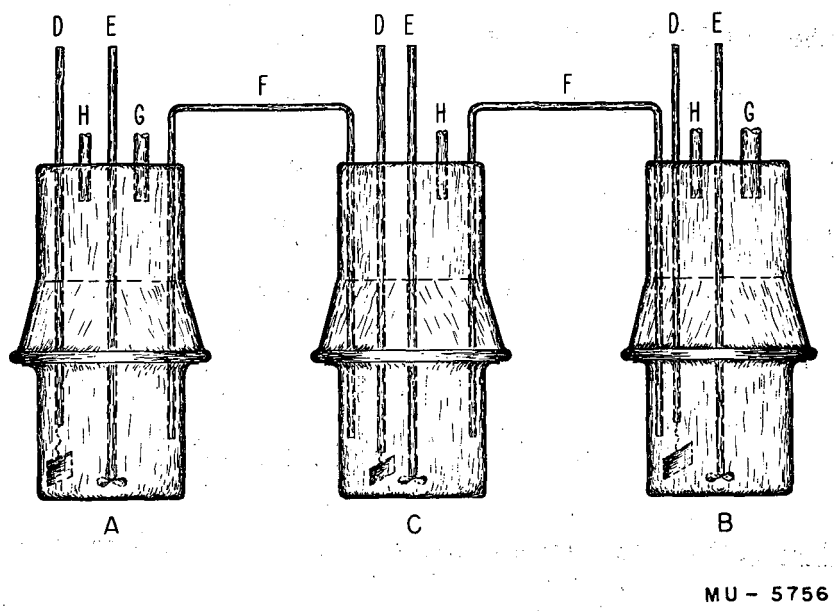

Fig. 1

A, B and C = Containers
D = 2 cm x 2 cm platinum electrodes
E = stirrers
F = Agar-Agar salt bridges
G = Inlet for pipetting NaF
H = CO_2 inlet

Concentration Cells A-C and B-C.

prevent air oxidation of iron(II). Electrodes made from spectroscopically pure platinum sheet and wire were stored in distilled water when not in use. Standard sodium fluoride solution was added to half-cell B by means of calibrated, "dri-filmed" micropipets.

The potential of the cell was measured by a Rubicon type B, high precision potentiometer with a D.C. spotlight galvanometer (sensitivity 0.009 μa/mm, period 3.2 sec and critical damping resistance 830 ohms) for indication of the null point. The potentiometer was checked against a standard cell from time to time during an experiment.

Procedure. Experiments were carried out at 25.00 ± 0.01° C and 35.00 ± 0.02° C. Before each run the assembled cells and the stock solutions were brought to the temperature of the experiment. The ground glass joints were sealed with "Lubriseal" to prevent thermostat water from entering the containers.

One hundred ml aliquots of stock solution containing the desired concentrations of ferrous perchlorate, ferric perchlorate, perchloric acid and sodium perchlorate were pipetted into half-cells B and C. The stirrers were activated, and the potential of half-cell B was measured with respect to reference half-cell C.

After the small initial potential (usually less than 0.20 mv) had become constant, aliquots of standard sodium fluoride solution were added to half-cell B. The potential E_{B-C} became constant (within 0.02 mv) very shortly after each addition. The stirrers were left on both while adding sodium fluoride solution and while reading the potential.

Experimental Results

The variation of potential with $(\Sigma F^-)_B$ for cell B-C at 25° C and 35° C as well as the initial concentrations of perchloric acid, ferrous perchlorate and ferric perchlorate are given in Tables 1 and 2. In all the runs sodium perchlorate was used to make the total ionic strength 0.50. E_{B-C} = measured potential after each addition of sodium fluoride minus the initial potential.

$(V_B)_i$ = initial volume in half-cell B. V_B = volume in half-cell B after adding sodium fluoride.

Table 1

Temperature = 25.00 ± 0.01° C μ = 0.50

	$(\Sigma F^-)_B \times 10^4$ (moles/l)	E_{B-C} (mv)	V_B (ml)
Run I			
(ΣH_i^+) = .04946 M	3.78	13.83	105.0
(ΣFe_i^{+2}) = 6.338 x 10^{-4} M	7.55	26.32	105.1
(ΣFe_i^{+3}) = 4.277 x 10^{-4} M	11.31	36.65	105.1
$(V_B)_i$ = 104.9 ml	15.07	45.17	105.2
	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
Run II			
(ΣH_i^+) = 0.09443 M	2.48	6.38	105.1
(ΣFe_i^{+2}) = 6.338 x 10^{-4} M	4.94	12.46	105.3
(ΣFe_i^{+3}) = 4.277 x 10^{-4} M	9.84	23.09	105.7
$(V_B)_i$ = 104.9 ml	14.71	31.86	106.1
	26.94	48.26	106.3
	39.12	60.16	106.5
	51.25	69.66	106.7
	63.34	77.88	106.9
	75.39	85.20	107.1

Table 1 (cont.)

	$(\Sigma F^-)_B \times 10^4$ (moles/l)	E_{B-C} (mv)	V_B (ml)
Run III			
$(\Sigma H_i^+) = .09246$ M	2.38	6.41	110.1
	4.75	12.43	110.3
$(\Sigma Fe_i^{+2}) = 6.050 \times 10^{-4}$ M	9.46	22.95	110.7
	14.13	31.58	111.1
$(\Sigma Fe_i^{+3}) = 4.083 \times 10^{-4}$ M	25.88	47.68	111.3
	37.59	59.51	111.5
$(V_B)_i = 109.9$ ml	49.26	68.96	111.7
	60.88	77.01	111.9
	72.47	84.23	112.3
Run IV			
$(\Sigma H_i^+) = .09490$ M	8.31	17.95	110.0
	16.47	32.05	110.2
$(\Sigma Fe_i^{+2}) = 9.09 \times 10^{-4}$ M	24.32	42.66	110.3
	33.76	58.87	110.5
$(\Sigma Fe_i^{+3}) = 6.133 \times 10^{-4}$ M	44.22	62.01	110.6
	54.53	69.58	110.8
$(V_B)_i = 109.9$ ml	73.25	81.61	111.1

Table 2

Temperature = 35.00 ± 0.02° C $\mu = 0.50$

	$(\Sigma F^-)_B \times 10^4$ (moles/l)	E_{B-C} (mv)	V_B (ml)
Run I			
$(\Sigma H_i^+) = .0975$ M	3.94	10.06	100.0
	7.88	18.83	100.1
$(\Sigma Fe_i^{+2}) = 6.717 \times 10^{-4}$ M	11.82	26.42	100.1
	15.74	32.94	100.2
$(\Sigma Fe_i^{+3}) = 4.367 \times 10^{-4}$ M	19.66	38.65	100.3
	27.49	48.17	100.4
$(V_B)_i = 99.9$ ml	37.95	58.37	100.6
	48.37	66.95	100.8
	58.75	74.25	101.0
	69.09	80.74	101.2
	89.64	91.92	101.6

Table 2 (cont.)

	$(\Sigma F^-)_B \times 10^4$ (moles/l)	E_{B-C} (mv)	V_B (ml)
Run II			
$(\Sigma H_i^+) = 0.0957$ M	3.94	12.38	100.0
	7.88	21.90	100.1
$(\Sigma Fe_i^{+2}) = 2.635 \times 10^{-4}$ M	11.82	29.61	100.1
	15.74	36.15	100.2
$(\Sigma Fe_i^{+3}) = 1.748 \times 10^{-4}$ M	19.66	41.77	100.3
	30.14	54.08	100.5
$(V_B)_i = 99.9$ ml	40.59	63.68	100.7
	50.99	71.55	100.9
	61.36	78.35	101.1
	81.96	90.06	101.5
Run III			
$(\Sigma H_i^+) = 0.0975$ M	2.10	5.26	100.1
	4.19	10.57	100.3
$(\Sigma Fe_i^{+2}) = 6.717 \times 10^{-4}$ M	6.28	15.48	100.5
	10.17	23.63	100.6
$(\Sigma Fe_i^{+3}) = 4.367 \times 10^{-4}$ M	14.06	30.63	100.7
	24.48	45.40	100.9
$(V_B)_i = 99.9$ ml	34.86	56.50	101.1
	45.19	65.57	101.3
Run IV			
$(\Sigma H_i^+) = 0.05975$ M	0.78	2.50	100.0
	2.89	9.62	100.2
$(\Sigma Fe_i^{+2}) = 6.717 \times 10^{-4}$ M	4.99	16.27	100.4
	8.89	27.48	100.5
$(\Sigma Fe_i^{+3}) = 4.367 \times 10^{-4}$ M	12.78	36.77	100.5
	16.68	44.69	100.6
$(V_B)_i = 99.9$ ml	20.56	51.43	100.7
	31.00	66.03	100.9
	42.40	77.57	101.1
	51.77	87.27	101.3
	62.09	95.73	101.5

Table 2 (cont.)

	$(\Sigma F^-)_B \times 10^4$ (moles/l)	E_{B-C} (mv)	V_B (ml)
Run V			
$(\Sigma H_i^+) = .1060$ M	1.50	3.80	109.9
	6.34	14.96	110.0
$(\Sigma Fe_i^{+2}) = 6.050 \times 10^{-4}$ M	13.44	28.32	110.1
	22.42	40.71	110.3
$(\Sigma Fe_i^{+3}) = 4.083 \times 10^{-4}$ M	30.70	49.87	110.5
	43.68	61.05	110.6
$(V_B)_i = 109.9$ ml	63.94	74.89	111.0
	76.99	82.40	111.2
Run VI			
$(\Sigma H_i^+) = .05645$ M	4.57	14.69	105.0
	13.21	38.76	105.1
$(\Sigma Fe_i^{+2}) = 6.338 \times 10^{-4}$ M	20.06	51.91	105.2
	27.03	62.54	105.3
$(\Sigma Fe_i^{+3}) = 4.277 \times 10^{-4}$ M	34.18	71.30	105.5
	43.16	81.12	105.6
$(V_B)_i = 104.9$ ml	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

Analysis of Results

The experimental results may be systematically interpreted by considering the following equilibria:

$$Fe^{+3} + HF = FeF^{+2} + H^+ \qquad K_1 \qquad (1)$$

$$FeF^{+2} + HF = FeF_2^+ + H^+ \qquad K_2 \qquad (2)$$

$$FeF_2^+ + HF = FeF_3 + H^+ \qquad K_3 \qquad (3)$$

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

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

The K's are equilibrium quotients, for example:

$$K_1 = \frac{(FeF^{+2})_B \, (H^+)_B}{(Fe^{+3})_B \, (HF)_B}$$

where $(\ \ )_B$ signifies concentration in moles/l in half-cell B.

Both Brosset and Gustaver[5] and Babko and Kleiner[6] 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 $FeF_6^{\equiv}$. Dodgen and Rollefson[7] 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 were satisfactorily able to explain our experimental results.

The equations necessary for the numerical evaluation of K_1, K_2 and K_3 will now be developed. From stoichiometric considerations we obtain:

$$(\Sigma F^-)_B = (HF)_B + (F^-)_B + (FeF^{+2})_B + 2(FeF_2^+)_B + 3(FeF_3)_B \qquad (6)$$

$$(\Sigma Fe^{+3})_B = (Fe^{+3})_B + (FeOH^{+2})_B + (FeF^{+2})_B + (FeF_2^+)_B + (FeF_3)_B \qquad (7)$$

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

The potential of the concentration cell B-C is given by:

$$E_{B-C} = -\frac{RT}{\mathcal{F}} \ln \frac{(Fe^{+3})_B \, (Fe^{+2})_C}{(Fe^{+2})_B \, (Fe^{+3})_C} \qquad (9)$$

Now if we let V_i equal the initial volumes in half-cells B and C and let V equal the volume in half-cell B after addition of sodium fluoride solution, we obtain from equation (9):

$$(Fe^{+3})_B = (Fe^{+3})_C \, \frac{V_i}{V} \, e^{-\mathcal{F}E/RT} \qquad (10)$$

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

$$(Fe^{+3})_C = \frac{(\Sigma Fe^{+3})_C}{1 + \frac{K_H}{(H^+)_C}} \tag{11}$$

also:

$$(\Sigma Fe^{+3})_B = \frac{V_i}{V} (\Sigma Fe^{+3})_C \tag{12}$$

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

$$\frac{(\Sigma Fe^{+3})_B}{(Fe^{+3})_B} - 1 - \frac{K_H}{(H^+)_C} = \left\{1 + \frac{K_H}{(H^+)_C}\right\} \left\{e^{\mathcal{F}E/RT} - 1\right\} \tag{13}$$

Combining equilibria expressions (1) - (4) with equation (7) one obtains:

$$\frac{(\Sigma Fe^{+3})_B}{(Fe^{+3})_B} - 1 - \frac{K_H}{(H^+)_B} = K_1 (HF/H^+)_B + K_1K_2(HF/H^+)_B^2 + K_1K_2K_3(HF/H^+)_B^3 \tag{14}$$

With the justifiable assumption that:

$$\left\{1 + \frac{K_H}{(H^+)_B}\right\} = \left\{1 + \frac{K_H}{(H^+)_C}\right\} \tag{15}$$

we can combine equations (13) and (14) to obtain:

$$\left\{1 + \frac{K_H}{(H^+)_B}\right\} \left\{e^{\mathcal{F}E/RT} - 1\right\} = K_1 (HF/H^+)_B + K_1K_2(HF/H^+)_B^2 + K_1K_2K_3(HF/H^+)_B^3 \tag{16}$$

Also by using equilibria expressions (1) - (5) and equations (6) and (7) we obtain:

$$(HF/H^+)_B = \frac{1}{K_{HF} + (H^+)_B} \left\{(\Sigma F^-)_B - (\Sigma Fe^{+3})_B + (Fe^{+3})_B (1 + K_H/(H^+)_B) - K_1K_2(Fe^{+3})_B (HF/H^+)_B^2 - 2 K_1K_2K_3(Fe^{+3})_B (HF/H^+)_B^3\right\} \tag{17}$$

Remembering that:

$$(H^+)_B = \frac{(\Sigma H^+)_B}{1 + (HF/H^+)_B} \tag{18}$$

and

$$(Fe^{+3})_B = \frac{(\Sigma Fe^{+3})_B}{(e^{\mathcal{F}E/RT})\ (1 + K_H/(H^+)_B)} \tag{19}$$

we are able to solve equations (16) and (17) for K_1, K_2 and K_3 by successive approximations.

Neglecting terms containing K_1, K_2 and K_3, we obtain a first approximation for the ratio $(HF/H^+)_B$ from equation (17). These values are then used with estimated K's to obtain a better set of $(HF/H^+)_B$ values from equation (17).

As seen from equation (16), we are able to obtain better values for K_1, K_2 and K_3 by plotting the quantity

$$Y = (H^+/HF)_B \left\{1 + \frac{K_H}{(H^+)_B}\right\} \left\{e^{\mathcal{F}E/RT} - 1\right\} \text{ vs.}$$

$(HF/H^+)_B$ at low $(HF/H^+)_B$ and the quantity

$$Z = \left[\left\{1 + \frac{K_H}{(H^+)_B}\right\}\left\{e^{\mathcal{F}E/RT} - 1\right\} (H^+/HF)_B\ (1/K_1) - 1\right] (H^+/HF)_B$$

vs. $(HF/H^+)_B$ at high $(HF/H^+)_B$. In Figure 2, Y is plotted vs. $(HF/H^+)_B$. The intercept and slope of the resulting straight line are equal to K_1 and K_1K_2 respectively. In Figure 3, Z is plotted vs. $(HF/H^+)_B$. Here the intercept and slope of the resulting straight line are equal to K_2 and K_2K_3 respectively. This procedure was repeated until consistent values for K_1, K_2 and K_3 were obtained.

In the above treatment we have made the justifiable assumptions that:

(a) $1 + K_H/(H^+)_B = 1 + K_H/(H^+)_C$

(b) There is no complexing of iron(II) by fluoride ion.[7]

(c) $(HF_2^-)_B$ can be neglected.

(d) There is no complexing of iron(II) and iron(III) by perchlorate ion.

(e) Hydrolysis of iron(II) is negligible.

The values used for K_{HF} and K_H are given in Table 3.[8]

Table 3

	25° C	35° C
K_H	1.9×10^{-3}	3.2×10^{-3}
K_{HF}	1.23×10^{-3}	1.01×10^{-3}

The final values of K_1, K_2 and K_3 from each run are presented in Table 4.

Table 4

Temperature = 35.00 ± 0.02° C

Run	K_1	K_2	K_3
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
Average	178	10.0	1.0

Temperature = 25.00 ± 0.01° C

Run	K_1	K_2	K_3
1	184	11.1	1.0
2	185	10.1	
3	183	10.2	
4	184	10.0	
Average	184	10.3	1.0

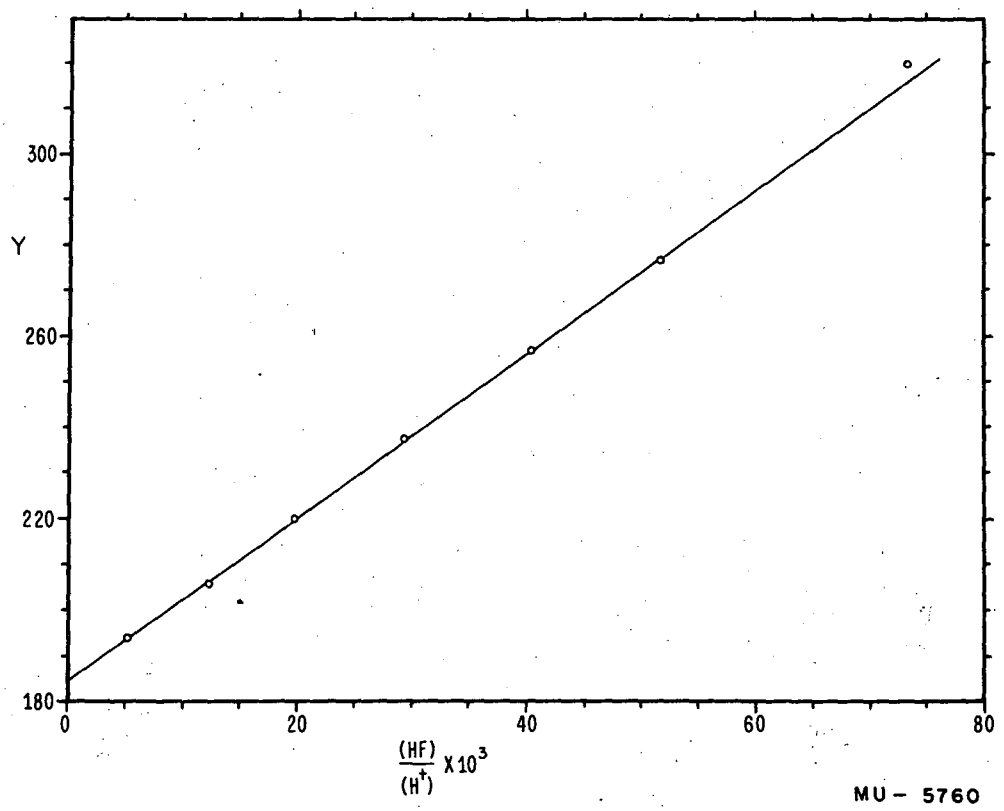

Fig. 2

Graphical method for obtaining K_1 and K_2 using data of Run IV at 25° C.

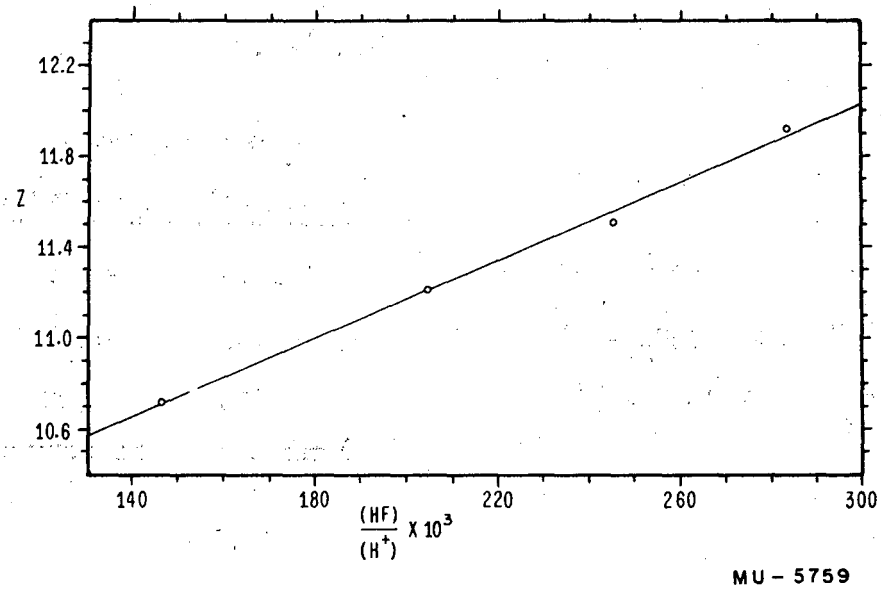

Fig. 3

Graphical method for obtaining K_3 using data of Run VI at 35° C.

These results were combined with those of Tsao[8] at 15° C and by using the thermodynamic relations:

$$\Delta F = -RT \ln K$$

$$\frac{d(R \ln K)}{d(1/T)} = -\Delta H$$

$$\Delta S = \frac{\Delta H - \Delta F}{T}$$

we were able to calculate ΔF, ΔH and ΔS for reactions (1), (2) and (3) (Table 5).

Table 5

	ΔF_{298} (kcal/mole)	ΔH_{298} (kcal/mole)	ΔS_{298} (eu.)
$Fe^{+3} + HF = FeF^{+2} + H^+$	-3.09	-0.65	8.2
$FeF^{+2} + HF = FeF_2 + H^+$	-1.39	-1.21	0.6
$FeF_2^+ + HF = FeF_3 + H^+$	0.00	0.00	0

III. CERIUM(III) FLUORIDE

It has long been known that tripositive rare-earth ions form gelatinous precipitates in aqueous fluoride solution. Even though these sparingly soluble rare-earth fluorides play an important part in many fields of chemistry, there is only a small amount of quantitative data in the chemical literature on the subject.

It is the purpose of this investigation to determine the nature and extent of the various equilibria involved in the aqueous chemistry of cerium(III) fluoride. In the following sections we will treat the complexing of cerium(III) by fluoride ion, the solubility product of cerium(III) fluoride and the heat of precipitation of cerium(III) fluoride.

A. The Complexing of Cerium(III) by Fluoride Ions in Aqueous Solution.

In order to determine the solubility of cerium(III) fluoride in acid solutions it is necessary to know the nature of the ionic species formed. Preliminary experiments indicated that one must consider not only the species Ce^{+3}, F^- and HF but also possible complex fluorides of cerium(III). This might be expected since Mayer[11] has reported the existence of CeF^{+2}.

The experimental technique used to investigate the nature and extent of this complexing of cerium(III) is based upon the competition for fluoride ion between cerium(III) and iron(III) in an iron(II)-iron(III) concentration cell.

Experimental

The Cells. The two concentration cells A-C and B-C are shown in Figure 1 and have been described in Chapter II.

Procedure. All experiments were carried out at 25.00 ± 0.01° C and at an ionic strength of 0.50. Before each run the assembled cells and the stock solutions were brought to the temperature of the experiment.

One hundred ml. aliquots of stock solution containing the desired concentrations of ferrous perchlorate, ferric perchlorate, perchloric acid and sodium perchlorate were pipetted into half-cells A, B and C. A known volume of standard cerous perchlorate - perchloric acid solution was added to half-cell A. An equal volume of sodium perchlorate - perchloric acid solution, equivalent to the cerous solution in total ionic strength and in acid concentration, was added to half-cells B and C.

The stirrers were activated and the potentials of half-cells A and B were measured with respect to reference half-cell C. After the small initial potentials had become constant, aliquots of standard sodium fluoride solution were added to half-cells A and B. The potential E_{B-C} became constant very shortly after each addition (Chapter II). This was also true for E_{A-C} at low total fluoride concentrations in half-cell A. At high total fluoride concentrations though, E_{A-C} began to drift downward due to the slow precipitation of cerium(III) fluoride. Several runs were made with half-cell A in the path of a beam of light. The noticeable onset of this downward drift in E_{A-C} approximately coincided with the appearance of a Tyndall beam.

Experimental Results

The initial conditions for each run as well as the variation of potential with total fluoride concentration for cells A-C and B-C are given in Table 6. The ferrous ion and ferric ion concentrations for each run were approximately 5×10^{-4} M.

Table 6

Temperature = 25.00 ± 0.01° C μ = 0.50

	$(\Sigma F^-)_A \times 10^4$ (moles/l)	E_{A-C} (mv)	V_A (ml)	$(\Sigma F^-)_B \times 10^4$ (moles/l)	E_{B-C} (mv)
Run I					
$(Ce_i^{+3})_A$ = 0.004207 M	3.32	9.91	105.0	3.32	10.67
	6.64	19.73	105.1	6.64	20.80
$(H_i^+)_A$ = 0.05659 M	9.95	28.41	105.2	9.95	29.80
	13.26	35.84	105.2	13.26	37.54
$(V_i)_A$ = 104.9 ml	16.56	41.93	105.3	16.56	44.24
	25.41	55.62	105.5	19.86	50.16
				23.16	55.44
Run II					
$(Ce_i^{+3})_A$ = 0.004340 M	3.32	7.52	105.0	3.32	8.09
	6.63	14.82	105.1	6.63	15.57
$(H_i^+)_A$ = 0.0987 M	9.94	21.37	105.2	9.94	22.28
	13.24	27.09	105.2	13.24	28.18
$(V_i)_A$ = 104.9 ml	16.54	32.13	105.3	16.54	33.44
	19.84	36.65	105.4	19.84	38.16
	23.13	40.76	105.5	23.13	42.43
	26.41	44.48	105.5	26.41	46.32
	29.69	47.83	105.6	29.69	49.91
	32.97	50.89	105.7	32.97	53.21
	36.24	53.62	105.8		
Run III					
$(Ce_i^{+3})_A$ = 0.001785 M	3.42	10.78	102.0	3.42	11.31
	6.83	21.45	102.1	6.83	21.87
$(H_i^+)_A$ = 0.05073 M	10.23	30.84	102.2	10.23	31.55
	13.63	38.87	102.2	13.63	39.88
$(V_i)_A$ = 101.9 ml	17.03	45.76	102.3	17.03	47.05
	20.42	51.75	102.4	20.42	53.33
	23.80	57.04	102.5	23.80	58.92
	27.19	61.6	102.5	27.19	63.95
Run IV					
$(Ce_i^{+3})_A$ = 0.00829 M	3.13	8.69	110.0	3.13	10.28
	6.26	17.80	110.1	6.26	20.18
$(H_i^+)_A$ = 0.05614 M	9.39	25.70	110.2	9.39	28.89
	12.51	32.30	110.2	12.51	36.47
$(V_i)_A$ = 109.9 ml	15.62	37.94	110.3	15.62	43.05
	18.74	42.71	110.4		

Analysis of Results

In Figure 4, E_{B-C} and E_{A-C} (up to the point of precipitation) are plotted as a function of the total fluoride concentration. The fact that the two curves are not identical, and also that one does not observe a Tyndall beam in half-cell A over this range, indicates the presence of complex fluorides of cerium(III).

It is possible to interpret the experimental results satisfactorily by assuming the species CeF^{+2}. The equilibria in question are:

$$Fe^{+3} + HF = FeF^{+2} + H^+ \qquad K_1 \qquad (20)$$

$$FeF^{+2} + HF = FeF_2^+ + H^+ \qquad K_2 \qquad (21)$$

$$Fe^{+3} + H_2O = FeOH^{+2} + H^+ \qquad K_H \qquad (22)$$

$$HF = H^+ + F^- \qquad K_{HF} \qquad (23)$$

$$Ce^{+3} + HF = CeF^{+2} + H^+ \qquad K_3 \qquad (24)$$

where the K's are equilibrium quotients, for example:

$$K_3 = \frac{(CeF^{+2})_A \ (H^+)_A}{(Ce^{+3})_A \ (HF)_A} \qquad (25)$$

Concentration in moles/l in half-cell A is represented by $(\ \ )_A$. The values of K_1, K_2, K_H and K_{HF} at 25° C used in these calculations are given in Tables 3 and 4 (Chapter II).

We shall now define $\Delta(\Sigma F^-)$ as:

$$\Delta(\Sigma F^-) = (\Sigma F^-)_{E_{A-C}} - (\Sigma F^-)_{E_{B-C}} \qquad (26)$$

where $E_{A-C} = E_{B-C}$. Because half-cells A and B have the same (ΣH_i^+), (ΣFe_i^{+3}) and (ΣFe_i^{+2}), $\Delta(\Sigma F^-)$ is a measure of the fluoride ions complexing cerium(III).

Stoichiometric considerations give:

$$(\Sigma Ce^{+3})_A = (Ce^{+3})_A + (CeF^{+2})_A \tag{27}$$

$$\Delta(\Sigma F^-) = (CeF^{+2})_A \tag{28}$$

Combination of equations (25), (27) and (28) yields:

$$\frac{\Delta(\Sigma F^-)}{(\Sigma Ce^{+3})_A - \Delta(\Sigma F^-)} = K_3 \, (HF/H^+)_A \tag{29}$$

If we plot $(HF/H^+)_A$ vs. $\frac{\Delta(\Sigma F^-)}{(\Sigma Ce^{+3})_A - \Delta(\Sigma F^-)}$, we should obtain a straight line of slope K_3 and intercept zero (Figure 5). In order to do this we must know $(HF/H^+)_A$ as a function of E_{A-C}. Since $(\Sigma Fe_i^{+3}) = (\Sigma Fe_i^{+3})_B$, $(\Sigma Fe_i^{+2})_A = (\Sigma Fe_i^{+2})_B$ and $(\Sigma H_i^+)_A = (\Sigma H_I^+)_B$, the quantity $(HF/H^+)_A = (HF/H^+)_B$ when $E_{A-C} = E_{B-C}$. We can thus calculate $(HF/H^+)_A$ from equation (16).

The experimentally determined values of K_3 are given in Table 7.

Table 7

Temperature = 25.00 ± 0.01° C

Run	K_3
I	1.5
II	1.7
III	1.4
IV	1.7
Average	1.6

Since $\Delta(\Sigma F^-)$ as well as $(HF/H^+)_A$ are small in the experimental range necessarily employed, their uncertainties are relatively large. The resulting uncertainty in K_3 is estimated to be 15%.

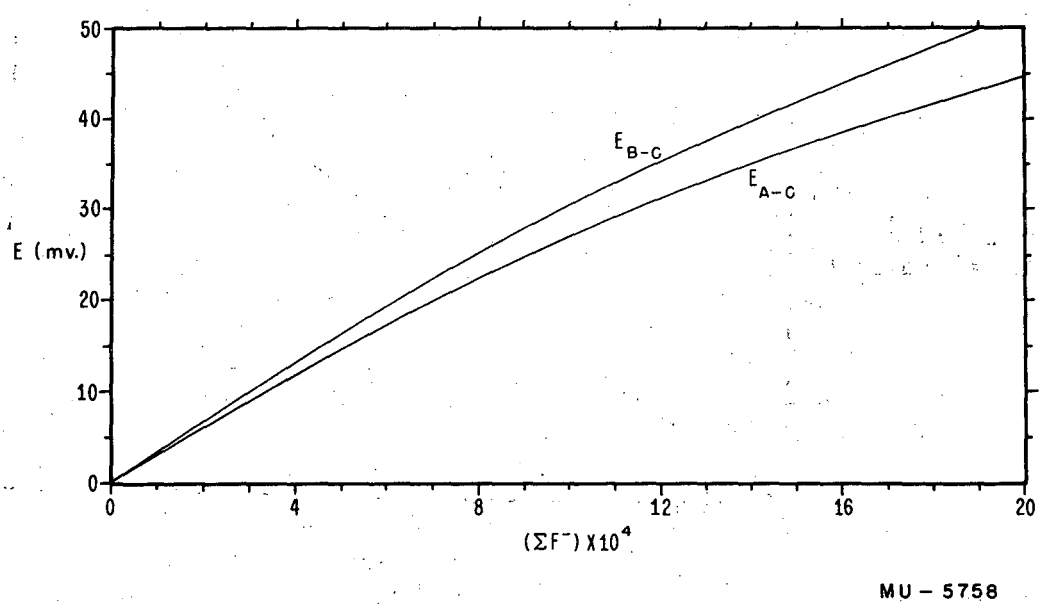

Fig. 4

The variation of potentials of cells B-C and A-C with total fluoride concentration for Run IV.

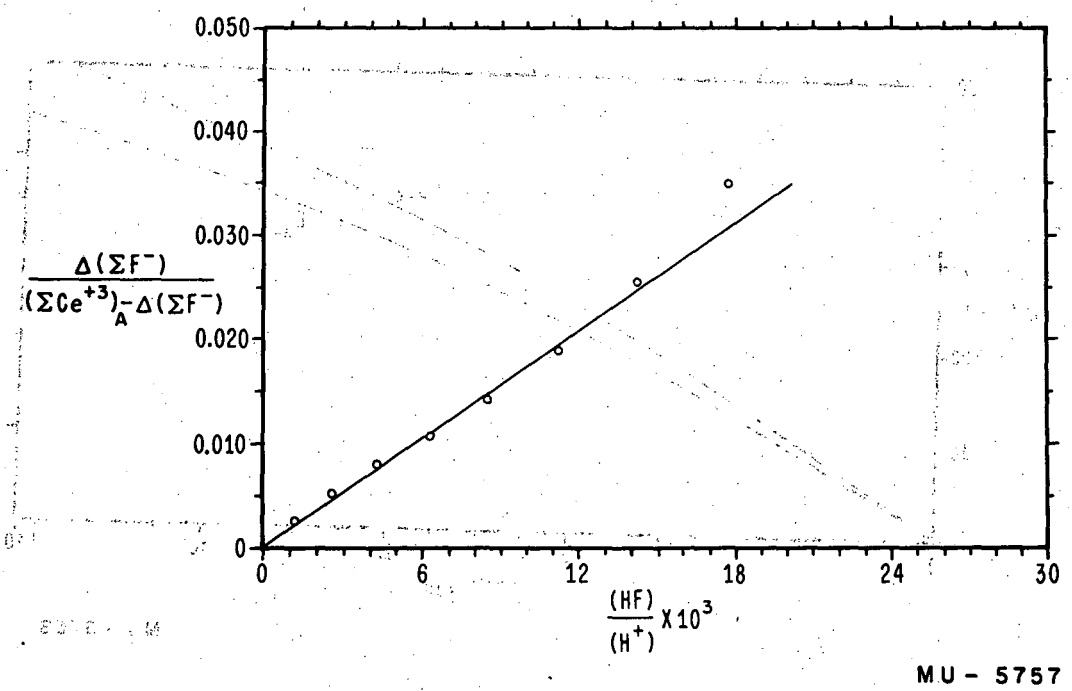

Fig. 5

Graphical method for obtaining K_3 using data of Run IV.

B. The Solubility of Cerium(III) Fluoride

It was at first hoped that it would be possible to determine the solubility of cerium(III) fluoride in the same manner as Dodgen and Rollefson[7] had determined that of thorium(IV) fluoride. Preliminary experiments showed though, that under these conditions cerium(III) fluoride precipitated slowly and even after 24 hours, equilibrium was not attained. The rate of dissolution of solid cerium(III) fluoride was also found to be slow. Since, as shown by Tsao,[8] the potential of the iron(II)-iron(III) concentration cell containing hydrofluoric acid is not stable over long periods of time, we were not able to use these direct methods.

An indirect cell method which enabled us to approach the equilibrium

$$CeF_3 \cdot 1/2\ H_2O_{(s)} + 3H^+ = Ce^{+3} + 3HF + 1/2\ H_2O \qquad K_s \qquad (30)$$

from both sides was adopted. Various solutions (some initially containing solid cerium(III) fluoride, perchloric acid and sodium perchlorate; others, cerous perchlorate, sodium fluoride, perchloric acid and sodium perchlorate) were equilibrated by shaking in a constant temperature bath for periods up to two weeks. Aliquots from these solutions were analyzed for total fluoride concentration by using an iron(II)-iron(III) concentration cell. Several of the solutions initially containing solid cerium(III) fluoride were also analyzed spectrophotometrically for cerium(III).

Experimental

Apparatus. Two-hundred-fifty-ml polyethylene bottles with polyethylene screw caps were used to equilibrate solid cerium(III) fluoride with various stock solutions. The filled bottles were sealed with paraffin,

mounted in a constant temperature bath at 25.0 ± 0.1° C and were mechanically shaken. Aliquots from these equilibrated mixtures were analyzed using the concentration cell A-C described in Chapter II (see Figure 1).

Procedure

Method 1. To approach the equilibrium represented by equation (30) from the side of solid cerium(III) fluoride, freshly precipitated $CeF_3 \cdot 1/2\ H_2O_{(s)}$ was added to various sodium perchlorate-perchloric acid stock solutions. The total ionic strength of these solutions was 0.50. The freshly precipitated $CeF_3 \cdot 1/2\ H_2O_{(s)}$ was prepared by adding sodium fluoride solution to aqueous cerous perchlorate and perchloric acid. After being centrifuged and washed, the moist $CeF_3 \cdot 1/2\ H_2O_{(s)}$ was transferred to a polyethylene bottle containing about 125 ml of sodium perchlorate-perchloric acid stock solution. This solution was placed in a constant temperature bath and shaken. It was found by varying the time of shaking, that in all cases equilibrium was reached in less than seven days.

The equilibrium solutions were analyzed as follows: A 100 ml aliquot was taken from the polyethylene bottle and added to half-cell A. An equal amount of the original perchloric acid-sodium perchlorate stock solution was added to half-cell C. The stirrers were activated, and after 30 minutes one ml of a ferrous perchlorate-ferric perchlorate-perchloric acid stock solution was added first to half-cell C and then to half-cell A. The potential E_{A-C} was read as a function of time. Since the solution in half-cell A still contained a small amount of colloidal cerium(III) fluoride, the potential increased slowly. The

experiments described in Chapters II and III-A show that the fluoride complexing of iron(III) is rapid. Thus the true potential, E°_{A-C}, could be obtained by extrapolating the measured E_{A-C} back to zero time. These extrapolations were usually less than 0.10 mv. E_{A-C} as a function of time is given for Run 11 in Table 8.

Table 8

Time (min)	E_{A-C} (mv)
0.00	(20.61) extrap.
1.40	20.69
2.25	20.74
3.10	20.78
3.90	20.85

Method II. In order to approach the equilibrium represented by equation (30) from the opposite side, stock solutions containing perchloric acid, sodium perchlorate, and cerous perchlorate were prepared with a total ionic strength of 0.50. Known amounts of standard sodium fluoride solution were added to 125 ml aliquots of these solutions contained in polyethylene bottles. The bottles were then placed in a constant temperature bath at 25.0 ± 0.1° C. and agitated for 7 days.

The equilibrium solutions were analyzed in a manner identical to that described in Method I. However, for use in half-cell C, the original perchloric acid-sodium perchlorate-cerous perchlorate stock solution had to be diluted to compensate for the volume of sodium fluoride solution added to the equilibrated solution.

Method III. Several of the solutions which had been equilibrated with freshly precipitated cerium(III) fluoride were analyzed spectrophotometrically for cerium(III). The saturated solution was centrifuged and the ultra-violet adsorption spectra of the supernatant was determined on a Cary recording spectrophotometer. A one cm fused quartz adsorption cell was used for all the optical density measurements. The adsorption blank was determined by using the original perchloric acid-sodium perchlorate stock solution.

Experimental Results

Method I. The experimental conditions and results for Method I are presented in Table 9. Sodium perchlorate was used in all the runs to keep μ, the total ionic strength, constant. V_P is the volume of equilibrated solution added to half-cell A. V_A is the final volume of solution in half-cell A. $(\Sigma Fe^{+3})_A$, $(\Sigma Fe^{+2})_A$ and $(\Sigma H^+)_A$ are respectively the total iron(III), iron(II) and hydrogen ion concentrations in half-cell A. $(\Sigma H^+)_P$ is the total hydrogen ion concentration in the equilibrated solution.

Table 9

Temperature = 25.0 ± 0.1° C $\mu = 0.5$

V_A = 100.95 ml

V_P = 99.95 ml

$(\Sigma Fe^{+3})_A = 5.111 \times 10^{-4}$ M

$(\Sigma Fe^{+2})_A = 3.902 \times 10^{-4}$ M

Run	$(\Sigma H^+)_A$ (moles/l)	$(\Sigma H^+)_P$ (moles/l)	E°_{A-C} (mv)
1	0.0964	0.0961	25.7
2	0.0964	0.0961	25.3
3	0.0726	0.0721	25.8
4	0.0726	0.0721	24.0
5	0.0488	0.0480	23.8
6	0.0488	0.0480	22.2
7	0.0726	0.0721	25.8
8	0.0488	0.0480	24.5

Method II. The experimental conditions and results for Method II are presented in Table 10. Sodium perchlorate was used in all the runs to keep the total ionic strength constant. V_P, V_A, $(\Sigma Fe^{+3})_A$, $(\Sigma Fe^{+2})_A$, $(\Sigma H^+)_A$ and $(\Sigma H^+)_P$ have the same significance as in Table 9. $(\Sigma F_i^-)_P$ and $(\Sigma Ce_i^{+3})_P$ are respectively the initial total fluoride concentration and the initial total cerium(III) concentration in the equilibrated solution.

Table 10

Temperature = 25.0 ± 0.1° C

μ = 0.5

V_A = 100.95 ml

V_P = 99.95 ml

Run	$(\Sigma Fe^{+3})_A \times 10^4$ (moles/l)	$(\Sigma Fe^{+2})_A \times 10^4$ (moles/l)	$(\Sigma H^+)_A$ (moles/l)	$(\Sigma H^+)_P$ (moles/l)	$(\Sigma F_i^-)_P \times 10^3$ (moles/l)	$(\Sigma Ce_i^{+3})_P \times 10^3$ (moles/l)	E°_{A-C} (mv)
9	5.111	3.902	0.1056	0.1054	4.128	4.384	14.0
10	5.111	3.902	0.1056	0.1054	4.128	4.384	13.6
11	3.709	3.873	0.1036	0.1031	10.20	4.463	20.6
12	3.709	3.873	0.1036	0.1031	10.20	4.463	18.7
13	3.709	3.873	0.0644	0.0635	7.685	3.586	18.1
14	3.709	3.873	0.0454	0.0442	3.881	3.615	12.8

Method III. The experimental conditions and results for Method III are presented in Table 11. $(Ce^{+3})_P$ is the spectrophotometrically-determined concentration of cerium(III) in the equilibrated solution.

Table 11

Temperature = 25.0 ± 0.1° C

μ = 0.5

Run	$(\Sigma H^+)_P$ (moles/l)	$(Ce^{+3})_P \times 10^4$ (moles/l)
15	0.0961	4.25
16	0.0721	3.13
17	0.0480	2.24

Analysis of Results

$CeF_3 \cdot 1/2\ H_2O_{(s)}$. To analyze the solubility data it is necessary to know the nature of the solid phase present. In the literature it is reported that freshly precipitated, hydrated cerium(III) fluoride has the composition $CeF_3 \cdot 1/2\ H_2O$.[1,12] The approximate data of Scott[13] on the hydration of the cerium group fluorides agrees with this. We shall write our equilibria in terms of $CeF_3 \cdot 1/2\ H_2O_{(s)}$.

Several samples of $CeF_3 \cdot 1/2\ H_2O$ were prepared by adding hydrofluoric acid to acidic cerous nitrate solutions. After air drying at room temperature, powder diffraction patterns were taken using CuKα x-rays. The patterns obtained using hydrated cerium(III) fluoride were apparently identical to those obtained using anhydrous cerium(III) fluoride. This was also found to be the case for the diffraction pattern given by a sample of freshly precipitated cerium(III) fluoride still in contact with its supernatant solution. From x-ray diffraction data on anhydrous cerium(III) fluoride,[14] it is seen that vacancies existing in the crystal lattice are able to accomodate molecules of water without appreciably changing the rest of the structure. This phenominon has been reported for aluminum(III) fluoride.[15] In this case it is also the hemihydrate which has approximately the same crystal structure as the anhydrous fluoride.

In both the equilibrated mixtures used for the solubility measurements and the final solution obtained from the calorimetric experiments, solid $CeF_3 \cdot 1/2\ H_2O$ was present in the form of finely divided particles. The average size of these colloidal particles was estimated with an optical microscope to be about 2 microns.

Equilibria in Question. In analyzing the data it is necessary to consider the following equilibria:

$$Fe^{+3} + HF = FeF^{+2} + H^+ \qquad K_1 \qquad (31)$$

$$FeF^{+2} + HF = FeF_2^+ + H^+ \qquad K_2 \qquad (32)$$

$$Fe^{+3} + H_2O = FeOH^{+2} + H^+ \qquad K_H \qquad (33)$$

$$HF = H^+ + F^- \qquad K_{HF} \qquad (34)$$

$$Ce^{+3} + HF = CeF^{+2} + H^+ \qquad K_3 \qquad (35)$$

$$CeF_3 \cdot 1/2\ H_2O_{(s)} + 3H^+ = Ce^{+3} + 3HF + 1/2\ H_2O \qquad K_s \qquad (36)$$

$$CeF_3 \cdot 1/2\ H_2O_{(s)} = Ce^{+3} + 3F^- + 1/2\ H_2O \qquad K_s' \qquad (37)$$

The K's are equilibrium quotients, for example:

$$K_s = \frac{(Ce^{+3})_P\ (HF)_P^3}{(H^+)_P^3} \qquad (38)$$

$$K_s' = (Ce^{+3})_P\ (F^-)_P^3 = K_s\ K_{HF}3 \qquad (39)$$

where $(\ )_P$ signifies concentration in moles/l in the equilibrated solution. The values used for K_1, K_2, K_H, K_{HF} and K_3 at 25° C are found in Tables 3, 4 and 7.

Calculation of K_s and K_s'

Method I. K_s' can be calculated from the experimental results of Method I in the following manner:

As was seen in Chapter III-A, we are able to calculate the quantity $(HF/H^+)_A$ since we know E^o_{A-C}, $(\Sigma H^+)_A$, K_1, K_2 and K_H (equation 16). Using equations (17), (18) and (19) and remembering that half-cell A contains CeF^{+2}, we obtain:

$$(\Sigma F^-)_A - (CeF^{+2})_A = (HF/H^+)_A \left\{ \frac{(\Sigma H^+)_A}{1 + (HF/H^+)_A} + K_{HF} \right\} + (\Sigma Fe^{+3})_A$$

$$- \frac{(\Sigma Fe^{+3})_A}{e^{\mp E/RT}} + \frac{(\Sigma Fe^{+3})_A \; K_1 K_2 \; (HF/H^+)_A^2}{e^{\mp E/RT} \; (1 + K_H/(\Sigma H^+)_A)} \qquad (40)$$

Since $CeF_3 \cdot 1/2\ H_2O_{(s)}$ dissolves slowly under the conditions of this experiment, it is valid to assume that a 1% volume change and the addition of a small amount of iron(III) does not cause any more cerium(III) fluoride to dissolve. Therefore stoichiometric considerations yield:

$$\frac{V_A}{V_P} (\Sigma F^-)_A = (\Sigma F^-)_P \qquad (41)$$

$$\frac{V_A}{V_P} \left\{ (Ce^{+3})_A + (CeF^{+2})_A \right\} = (Ce^{+3})_P + (CeF^{+2})_P \qquad (42)$$

$$(\Sigma F^-)_P = 3(Ce^{+3})_P + 3(CeF^{+2})_P \qquad (43)$$

$$(\Sigma F^-)_P = (F^-)_P + (HF)_P + (CeF^{+2})_P \qquad (44)$$

Combining equations (42) and (25), we obtain:

$$(Ce^{+3})_A = \frac{V_P}{V_A} \; (Ce^{+3})_P \; \frac{1 + K_3 \; (HF/H^+)_P}{1 + K_3 \; (HF/H^+)_A} \qquad (45)$$

From equations (43) and (25) we obtain:

$$(\Sigma F^-)_P = 3 \; (Ce^{+3})_P \; \left\{ 1 + K_3 \; (HF/H^+)_P \right\} \qquad (46)$$

From equations (44) and (25) and equilibrium (34) it follows that:

$$(\Sigma F^-)_P = K_{HF} \; (HF/H^+)_P + \frac{(\Sigma H^+)_P \; (HF/H^+)_P}{1 + (HF/H^+)_P} + (Ce^{+3})_P \; K_3 \; (HF/H^+)_P \qquad (47)$$

Subtracting $(V_A/V_P)(CeF^{+2})_A$ from both sides of (41) and rearranging with the help of equation (25), we obtain:

$$(Ce^{+3})_A = \frac{(V_P/V_A)\ (\Sigma F^-)_P - \left\{(\Sigma F^-)_A - (CeF^{+2})_A\right\}}{K_3\ (HF/H^+)_A} \quad (48)$$

Combining equations (48), (46) and (45) gives:

$$(Ce^{+3})_P = \frac{V_A/V_P\ \left\{(\Sigma F^-)_A - (CeF^{+2})_A\right\}}{\dfrac{1 + K_3\ (HF/H^+)_P}{1 + K_3(HF/H^+)_A}\left\{3 + 2K_3(HF/H^+)_A\right\}} \quad (49)$$

Combining equations (46), (47) and (49) yields:

$$(HF/H^+)_P = \frac{V_A/V_P\ \left\{(\Sigma F^-)_A - (CeF^{+2})_A\right\}}{\dfrac{1 + K_3(HF/H^+)_P}{1 + K_3(HF/H^+)_A} \cdot \dfrac{3 + 2K_3(HF/H^+)_A}{3 + 2K_3(HF/H^+)_P}\left\{K_{HF} + \dfrac{(\Sigma H^+)_P}{1 + (HF/H^+)_P}\right\}} \quad (50)$$

We now have the necessary equations to calculate K_s and K_s'. Knowing $(HF/H^+)_A$, $(\Sigma H^+)_A$, K_{HF}, K_1, K_2, K_H, $(\Sigma Fe^{+3})_A$ and E°_{A-C}, we can calculate the quantity $\left\{(\Sigma F^-)_A - (CeF^{+2})_A\right\}$ from equation (40). Then after solving equation (50) by successive approximations for $(HF/H^+)_P$, we can solve equation (49) for $(Ce^{+3})_P$. K_s and K_s' are then obtained from equations (38) and (39). The final results are found in Table 12.

<u>Method II.</u> K_s and K_s' can be calculated from the experimental results of Method II in the following manner:

The quantities $(HF/H^+)_A$ and $\left\{(\Sigma F^-)_A - (CeF^{+2})_A\right\}$ are calculated as in Method I (equations (16) and (40)). Equations (41), (45), (47) and (48) are also applicable here, along with:

$$(\Sigma F_i^-)_P = 3(CeF_3 \cdot 1/2\ H_2O)_P + (\Sigma F^-)_P \quad (51)$$

$$(\Sigma Ce_i^{+3})_P = (CeF_3 \cdot 1/2\ H_2O)_P + (Ce^{+3})_P + (CeF^{+2})_P \quad (52)$$

Combining equations (51) and (52), we obtain:

$$(\Sigma F^-)_P = 3(Ce^{+3})_P \left\{1 + K_3(HF/H^+)_P\right\} + (\Sigma F_i^-)_P - 3(\Sigma Ce_i^{+3})_P \tag{53}$$

Combination of equations (45) and (48) yields:

$$(\Sigma F^-)_P = K_3 \, (HF/H^+)_A \, (Ce^{+3})_P \cdot \frac{1 + K_3(HF/H^+)_P}{1 + K_3(HF/H^+)_A} + V_A/V_P \left\{(\Sigma F^-)_A - (CeF^{+2})_A\right\} \tag{54}$$

Equations (53) and (54) may now be solved for $(Ce^{+3})_P$:

$$(Ce^{+3})_P = \frac{V_A/V_P \left\{(\Sigma F^-)_A - (CeF^{+2})_A\right\} - (\Sigma F_i^-)_P + 3(\Sigma Ce_i^{+3})_P}{\dfrac{1 + K_3 \, (HF/H^+)_P}{1 + K_3 \, (HF/H^+)_A} \left\{3 + 2K_3(HF/H^+)_A\right\}} \tag{55}$$

By substituting equation (55) into (54) and then combining the result with equations (47) and (55), we obtain:

$$\left(\frac{HF}{H^+}\right)_P =$$

$$\frac{3\,\dfrac{V_A}{V_P}\left\{(\Sigma F^-)_A - (CeF^{+2})_A\right\}\left\{1 + K_3\left(\dfrac{HF}{H^+}\right)_A\right\} + K_3\left(\dfrac{HF}{H^+}\right)_A \left\{3(\Sigma Ce_i^{+3})_P - (\Sigma F_i^-)_P\right\}}{\left\{3 + 2K_3\left(\dfrac{HF}{H^+}\right)_A\right\}\left\{\dfrac{(\Sigma H^+)_P}{1+\left(\dfrac{HF}{H^+}\right)_P} + K_{HF} + K_3\left[\dfrac{\dfrac{V_A}{V_P}\left\{(\Sigma F^-)_A - (CeF^{+2})_A\right\} - (\Sigma F_i^-)_P + 3(\Sigma Ce_i^{+3})_P}{\dfrac{1 + K_3\left(\dfrac{HF}{H^+}\right)_P}{1 + K_3\left(\dfrac{HF}{H^+}\right)_A}\left\{3 + 2K_3\,(HF/H^+)_A\right\}}\right]\right\}} \tag{56}$$

Equation (56) can be solved for $(HF/H^+)_P$ by successive approximations. This value is then used to solve equation (55) for $(Ce^{+3})_P$.

The values obtained for K_s and K'_s using equations (38) and (39) are found in Table 12.

Method III. The ultra-violet absorption spectra of cerium(III) in perchlorate solutions has been determined by Stewart.[16] In analyzing the equilibrated mixtures for cerium(III), we used the 252 micron and the 238 micron adsorption bands. The cerium(III) concentrations presented in Table 11 are the averages of those calculated from the optical densities at these two wave lengths. The molar extinction coefficients were given by Stewart as 755 l/mole cm at 252 microns and 650 l/mole cm at 238 microns.

Even after centrifuging the equilibrated mixture, there was a small amount of colloid present in the supernatant. Since the intensity of the light scattered by colloidal particles is inversely proportional to the fourth power of the wave length,[17] it was possible to correct approximately for this scattering by measuring the optical density of the solution at 320 microns. At this wave length the molar extinction coefficient is relatively small and the optical density was taken as a measure of the colloidal scattering at 320 microns.

$(Ce^{+3})_P$ was calculated at each wave length from the following equations:

$$(Ce^{+3})_P = D/\varepsilon l \qquad (57)$$

$$D = D_P - D_B - D_C \qquad (58)$$

where ε is the molar extinction coefficient of cerium(III), l is the cell length in cm, D_P is the measured optical density of the equilibrated solution after centrifuging, D_B is the measured optical density of the perchloric acid-sodium perchlorate stock solution and D_C is the calculated correction for colloidal scattering.

We can now calculate K_s and K_s'. Stoichiometric considerations yield:

$$(\Sigma F^-)_P = 3\ (Ce^{+3})_P \tag{59}$$

$$(\Sigma F^-)_P = (F^-)_P + (HF)_P \tag{60}$$

$$(\Sigma H^+)_P = (H^+)_P + (HF)_P \tag{61}$$

Combination of equations (59), (60) and (61) yields:

$$(HF/H^+)_P = \frac{3(Ce^{+3})_P}{K_{HF} + \dfrac{(\Sigma H^+)_P}{1 + (HF/H^+)_P}} \tag{62}$$

Knowing $(Ce^{+3})_P$ and having solved equation (62) for $(HF/H^+)_P$, we can calculated K_s and K_s' from equations (38) and (39). These values are presented in Table 12. The results are only approximate since CeF^{+2} was neglected. (About 1% of the total cerium(III) is present as CeF^{+2}.) For this reason the results of Method III were not averaged with those of Methods I and II.

Table 12

Temperature = 25.0 ± 0.1° C μ = 0.50

	Run	$K_s \times 10^{10}$	$K_s' \times 10^{18}$
Method I	1	8.1	1.5
	2	7.0	1.3
	3	9.1	1.7
	4	6.4	1.2
	5	8.1	1.5
	6	5.9	1.1
	7	9.1	1.7
	8	9.1	1.7
Method II	9	7.0	1.3
	10	5.9	1.1
	11	8.1	1.5
	12	5.9	1.1
	13	7.5	1.4
	14	7.5	1.4
	Average	7.5 ± 1.0	1.4 ± .2
Method III	15	9.7	1.8
	16	7.0	1.3
	17	5.9	1.1
	Average	7.5	1.4

Discussion. In Methods I and II the following assumptions were made:

(a) The zero potential, $E_{o_{A-C}}$, can be neglected. One is not able to measure $E_{o_{A-C}}$ directly in these experiments, but measurements on similar solutions (Chapter III-A, also see Tsao[8] and Hepler[9]) show that $E_{o_{A-C}}$ is less than 0.2 mv.

(b) The complex fluorides FeF^{+2}, FeF_2^+ and CeF^{+2} are formed rapidly. The experiments discussed in Chapters II and III-A show this to be the case.

(c) No $CeF_3 \cdot 1/2\ H_2O_{(s)}$ dissolves upon adding one ml of iron

stock solution to half-cell A. Since it was found experimentally that $CeF_3 \cdot 1/2\ H_2O_{(s)}$ dissolves slowly and that E_{A-C} increased only slightly during the time required for a run, any error due to this approximation is negligible, especially since E_{A-C} was extrapolated back to zero time. This difficulty could be eliminated by separating solid $CeF_3 \cdot 1/2\ H_2O$ from the supernatant solution. The colloidal nature of $CeF_3 \cdot 1/2\ H_2O$, however, made a complete separation extremely difficult.

The uncertainties introduced by the above assumptions, as well as changes in ionic strength and specific ion effects, could account for the rather large spread in K_s and K_s'. This spread could also be attributed in part to a change in solubility with particle size.

Method III served as a check on the concentration cell technique used in Methods I and II. In Methods I and II the fluoride concentration was determined experimentally and $(Ce^{+3})_P$ calculated. In Method III $(Ce^{+3})_P$ was measured directly and the fluoride concentration calculated. The values of K_s and K_s' obtained from these two different methods agreed very well.

C. The Heat of Precipitation of Cerium(III) Fluoride

It is the purpose of this investigation to measure calorimetrically the heat of precipitation of $CeF_3 \cdot 1/2\ H_2O_{(s)}$.

Experimental

The calorimeter used in this investigation has been previously described.[18,19] All heats were measured at 25.0 ± 0.5° C and are reported in terms of the defined calorie (1 cal = 4.1840 abs. joules). The uncertainty in the measured heats is ± 0.3 cal. Samples of con-

concentrated hydrofluoric acid solutions were contained in paraffin-coated, small glass bulbs and were introduced into standard cerous perchlorate-perchloric acid solutions by shattering the bulbs with a paraffin-coated glass rod. The glass surfaces of the calorimeter were coated with a thin layer of tygon paint (Series K, White, U. S. Stoneware).

Experimental Results

The experimental results are presented in Table 13. (a = moles HF in sample bulb, b = moles water in sample bulb, c = moles cerous perchlorate in calorimeter, d = moles perchloric acid in calorimeter, e = moles water in calorimeter and Q = measured heat evolved in calories.)

Table 13

Run	a	b	c x 10^3	d	e	Q
1	0.0509	0.509	9.12	0.01250	55.2	92.7
2	0.0500	0.500	9.12	0.01250	55.2	93.5
3	0.0510	0.509	9.12	0.01250	55.2	92.7

Analysis of Results

A schematic representation of the calorimetric reaction is:

$$\left\{\begin{array}{l} a\ HF \\ b\ H_2O \end{array}\right\} +$$

bulb

$$\left\{\begin{array}{l} c\ Ce^{+3} \text{ and } 3c\ ClO_4^- \\ d\ H^+ \text{ and } d\ ClO_4^- \\ e\ H_2O \\ \mu_1 \end{array}\right\} \longrightarrow \left\{\begin{array}{l} c\ CeF_3 \cdot 1/2\ H_2O_{(s)} \\ (d + 3c)\ H^+ \text{ and } (d + 3c)\ ClO_4^- \\ (a - 3c - y)\ HF \\ y\ H^+ \text{ and } y\ F^- \\ (b + e - c/2)\ H_2O \\ \mu_2 \end{array}\right\} \quad Q$$

calorimeter

Final solution in calorimeter

where μ_1 and μ_2 are the total ionic strengths of the respective solutions, and the coefficients indicate the number of moles of the particular substance present.

The amount of ionized hydrofluoric acid in the final solution was calculated by successive approximations from the following equations:

$$(\Sigma H^+) = (H^+) + (HF) \qquad (63)$$

$$(\Sigma F^-) = (F^-) + (HF) \qquad (64)$$

$$(H^+)(F^-)/(HF) = K_{HF} = 6.7 \times 10^{-4} \qquad (65)$$

where ( ) signifies moles/l. The total hydrogen ion concentration, (ΣH^+), and the total fluoride concentration, (ΣF^-), were calculated from the data of Table 13. The density of the final solution was taken as 1.00 gms/ml. (HF) was first taken as approximately equal to (ΣF^-) and (H^+) was calculated from equation (63). Equation (65) was then solved for (F^-) and a better value of (HF) was obtained from equation (64). This procedure was repeated until a consistent value for (F^-) was obtained. Knowing the total weight of solution and its density one can then calculate y, the moles of ionized hydrofluoric acid. The

concentrations of CeF^{+2} and HF_2^- were small and were neglected in all the calculations.

To obtain ΔH^o_{298} for the reaction

$$Ce^{+3} + 3HF + 1/2\ H_2O = CeF_3 \cdot 1/2\ H_2O_{(s)} + 3H^+ \qquad (66)$$

the experimentally observed heats were first corrected to infinite dilution for all species. Utilizing the principle of ionic strength we assume, for example, the heat of dilution of $HClO_4$ at $\mu = 0.1$ equals the heat of dilution of 0.1 M $HClO_4$. Then neglecting the heat of dilution of unionized HF, approximating that of $Ce(ClO_4)_3$ as equal to $LaCl_3$, and that of ionized HF as equal to HCl, we define:

Q_1 = heat evolved on diluting a moles of HF in b moles of water to infinite dilution plus the heat evolved on association of a moles of H^+ and a moles of F^- at infinite dilution.

Q_2 = heat evolved on diluting c moles of $LaCl_3$ in ionic strength μ_1 to infinite dilution.

Q_3 = heat evolved on diluting d moles of $HClO_4$ in ionic strength μ_1 to infinite dilution.

Q_4 = heat evolved on diluting d + 3c moles of $HClO_4$ in ionic strength μ_2 to infinite dilution.

Q_5 = heat evolved on diluting y moles of HCl in ionic strength μ_2 to infinite dilution plus the heat evolved on association of y moles of H^+ and y moles of F^- at infinite dilution.

$$Q^o = Q - Q_1 - Q_2 - Q_3 + Q_4 + Q_5$$

The heats of dilution of HF, $LaCl_3$, $HClO_4$ and HCl were obtained from Bureau of Standards data.[20] The heat of dissociation of HF was taken as -3.18 kcal/mole.[21]

ΔH^o_{298} for reaction (66) can be calculated from the following equation:

$$\Delta H^o_{298} = -Q^o/c \qquad (67)$$

The results of these calculations are found in Table 14. Taking into account uncertainties in heats of dilution, we find $\Delta H^o_{298} = -10.0 \pm 0.7$ kcal.

Table 14

	Run I	Run II	Run III
Q_1 (cal)	-6.4	-6.3	-6.4
Q_2 (cal)	6.1	6.1	6.1
Q_3 (cal)	-0.4	-0.4	-0.4
Q_4 (cal)	-0.8	-0.8	-0.8
Q_5 (cal)	-1.2	-1.2	-1.2
$y \times 10^4$ (moles)	3.85	3.71	3.87
ΔH^o_{298} (kcal/mole)	-10.0	-10.1	-10.0

IV. LANTHANUM(III) FLUORIDE

The purpose of this investigation is to determine both the extent of complexing of lanthanum(III) by fluoride ion and the solubility of lanthanum(III) fluoride in aqueous solutions. The experimental techniques employed are exactly the same as those used with cerium(III). Both the apparatus and procedure have been described in detail in Chapter III, Sections A and B. The freshly precipitated lanthanum(III) fluoride used in solubility method I was prepared by adding aqueous sodium fluoride to a lanthanum chloride-hydrochloric acid stock solution. After centrifuging and washing well, the moist precipitate was transferred to a perchloric acid-sodium perchlorate solution to be equilibrated.

Experimental Results

Complexing. The experimental results used to determine the extent of complexing of lanthanum(III) by fluoride ion at 25° C are presented in Table 15. (V_A = volume of solution in half-cell A, $(La_i^{+3})_A$ = initial lanthanum(III) concentration in half-cell A, $(H_i^+)_A$ = initial hydrogen ion concentration in half-cell A, $(\Sigma F^-)_{A,B}$ = total fluoride concentrations in half-cells A and B, and E_{A-C} and E_{B-C} = potentials of concentration cells A-C and B-C.)

Table 15

Temperature = 25.00 ± 0.01° C μ = 0.50

	$(\Sigma F^-)_{A,B} \times 10^4$ (moles/l)	V_A (ml)	E_{A-C} (mv)	E_{B-C} (mv)
Run I				
$(La_i^{+3})_A$ = 0.00888 M	3.19	110.0	10.06	10.58
	6.38	110.1	19.72	20.73
$(H_i^+)_A$ = 0.05451 M	9.57	110.2	28.22	29.70
	12.75	110.2	35.49	37.45
$(V_A)_i$ = 109.9 ml	15.92	110.3	41.34	44.19
Run II				
$(La_i^{+3})_A$ = 0.00888 M	3.19	110.0	7.52	7.74
	6.36	110.1	14.54	14.98
$(H_i^+)_A$ = 0.0996 M	9.54	110.2	20.83	21.48
	12.71	110.2	26.42	27.25
$(V_A)_i$ = 109.9 ml	15.88	110.3	31.32	32.40
	19.04	110.4	35.73	37.00
	22.20	110.5	39.64	41.17
Run III				
$(La_i^{+3})_A$ = 0.01277 M	3.05	115.0	9.54	10.10
	6.10	115.1	18.62	19.82
$(H_i^+)_A$ = 0.05615 M	9.14	115.2	26.63	28.42
	12.17	115.3	33.10	35.87
$(V_A)_i$ = 115.0 ml	15.21	115.3	38.3	42.37
Run IV				
$(La_i^{+3})_A$ = 0.004649 M	3.35	105.0	10.72	10.84
	6.69	105.1	21.01	21.41
$(H_i^+)_A$ = 0.05273 M	10.02	105.2	30.08	30.74
	13.35	105.2	37.87	38.79
$(V_A)_i$ = 104.9 ml	16.68	105.3	44.58	45.75
	20.00	105.4	50.26	51.86

Solubility

Method I. The experimental conditions and the results obtained by using Method I (Chapter III-B) to determine the solubility of lanthanum(III) fluoride are presented in Table 16. Sodium perchlorate

was used in all the runs to keep μ, the total ionic strength, constant. (V_P is the volume of equilibrated solution added to half-cell A. V_A is the final volume of solution in half-cell A. $(\Sigma Fe^{+3})_A$, $(\Sigma Fe^{+2})_A$ and $(\Sigma H^+)_A$ are respectively the total iron(III), iron(II) and hydrogen ion concentrations in half-cell A. $(\Sigma H^+)_P$ is the total hydrogen ion concentration in the equilibrated solution.)

Table 16

Temperature = 25.0 ± 0.1° C V_A = 100.95 ml

μ = 0.5 V_P = 99.95 ml

Run	$(\Sigma Fe^{+3})_A \times 10^4$ (moles/l)	$(\Sigma Fe^{+2})_A \times 10^4$ (moles/l)	$(\Sigma H^+)_A$ (moles/l)	$(\Sigma H^+)_P$ (moles/l)	E_{A-C} (mv)
1	5.111	3.902	0.0726	0.0721	25.3
2	5.111	3.902	0.0488	0.0480	22.8
3	3.709	3.873	0.0998	0.0992	27.2
4	3.709	3.873	0.0998	0.0992	26.8
5	3.709	3.873	0.0752	0.0744	26.9
6	3.709	3.873	0.0506	0.0496	27.9

Method II. The experimental conditions and the results obtained by using Method II (Chapter III-B) to determine the solubility of lanthanum(III) fluoride are presented in Table 17. Sodium perchlorate was used in all the runs to keep the total ionic strength constant. (V_P, V_A, $(\Sigma Fe^{+3})_A$ $(\Sigma Fe^{+2})_A$, $(\Sigma H^+)_A$ and $(\Sigma H^+)_P$ have the same significance as in Table 16. $(\Sigma F_i^-)_P$ and $(\Sigma La_i^{+3})_P$ are respectively the initial total fluoride concentration and the initial total lanthanum(III) concentration in the equilibrated solution.)

Table 17

Temperature = 25.0 ± 0.1° C V_A = 100.95 ml

μ = 0.5 V_P = 99.95 ml

$(\Sigma Fe^{+3})_A$ = 3.709 x 10^{-4} M

$(\Sigma Fe^{+2})_A$ = 3.873 x 10^{-4} M

Run	$(\Sigma H^+)_A$ (moles/l)	$(\Sigma H^+)_P$ (moles/l)	$(\Sigma F_i^-)_P$ x 10^3 (moles/l)	$(\Sigma La_i^{+3})_P$ x 10^3 (moles/l)	E_{A-C} (mv)
7	0.1020	0.1015	10.20	4.781	19.1
8	0.1020	0.1015	10.20	4.781	18.8
9	0.0631	0.0622	7.685	3.841	16.7
10	0.0440	0.0429	3.881	3.873	12.1

Analysis of Results

Complexing. As in the case of cerium(III), E_{A-C} and E_{B-C} plotted as a function of the total fluoride concentration do not give identical curves. The absence of a Tyndall beam in half-cell A over this range indicates the presence of complex fluorides of lanthanum(III).

The experimental results could be satisfactorily interpreted assuming the equilibrium:

$$La^{+3} + HF = LaF^{+2} + H^+ \qquad K_3 \qquad (68)$$

The equilibrium quotient

$$K_3 = \frac{(LaF^{+2})_A \, (H^+)_A}{(La^{+3})_A \, (HF)_A} \qquad (69)$$

was calculated by the method described in Chapter III-A. $(\ )_A$ represents concentration in moles/l in half-cell A.

The values obtained for K_3 are presented in Table 18. The uncertainty in K_3 is estimated to be 10%.

Table 18

Temperature = 25.00 ± 0.01° C

Run	K_3
I	0.62
II	0.60
III	0.55
IV	0.57
Average	0.59

Solubility. The composition of hydrated lanthanum(III) fluoride is reported in the literature as $LaF_3 \cdot 1/2\ H_2O$.[2,12] As was the case with cerium(III) fluoride, the $LaF_3 \cdot 1/2\ H_2O_{(s)}$ in contact with the equilibrated solution was colloidal in nature.

The equilibria to be considered in analyzing the data are the same as in Chapter III-B. Those involving lanthanum(III) are:

$$La^{+3} + HF = LaF^{+2} + H^+ \qquad K_3 \qquad (70)$$

$$LaF_3 \cdot 1/2\ H_2O_{(s)} + 3H^+ = La^{+3} + 3HF + 1/2\ H_2O \qquad K_s \qquad (71)$$

$$LaF_3 \cdot 1/2\ H_2O_{(s)} = La^{+3} + 3F^- + 1/2\ H_2O \qquad K_s' \qquad (72)$$

The K's are equilibrium quotients, for example:

$$K_s = \frac{(La^{+3})_P\ (HF)_P^3}{(H^+)_P} \qquad (73)$$

$$K_s' = (La^{+3})_P\ (F^-)_P^3 = K_s K_{HF}^3 \qquad (74)$$

where $(\ \ )_P$ designates concentration in moles/l in the equilibrated solution.

K_s and K_s' were calculated from the data in Tables 16 and 17 by the methods described in Chapter III-B. The results are presented in Table 19.

Table 19

Temperature = 25.0 ± 0.1° C μ = 0.5

	Run	$K_s \times 10^{10}$	$K_s' \times 10^{18}$
Method I	1	8.1	1.5
	2	7.0	1.3
	3	7.5	1.4
	4	7.0	1.3
	5	7.5	1.4
	6	8.6	1.6
Method II	7	8.1	1.5
	8	7.5	1.4
	9	7.0	1.3
	10	7.5	1.4
	Average	7.6 ± 0.4	1.4 ± 0.1

V. TRENDS IN FLUORIDE COMPLEXING AND SOLUBILITY THROUGH THE LANTHANIDE SERIES

Some preliminary experiments on the extent of complexing of gadolinium(III) by fluoride ion and on the solubility of gadolinium(III) fluoride are reported in this chapter. The results are used in discussing the trends to be expected in the lanthanide series for both the extent of complxing by fluoride ion and the solubility of the trivalent fluorides.

Gadolinium(III) Fluoride

The apparatus, procedures and methods of calculation used to determine the extent of complexing of gadolinium(III) by fluoride ion and the solubility of gadolinium(III) fluoride are identical to those described in Chapter III. The freshly precipitated gadolinium(III) fluoride used in solubility Method I was prepared by adding aqueous sodium fluoride to a gadolinium perchlorate-perchloric acid stock solution. After centrifuging and washing well, the moist precipitate was transferred to a perchloric acid-sodium perchlorate solution to be equilibrated.

Popovici[3] has reported that gadolinium(III) fluoride precipitated from aqueous solution has the composition GdF_3. We will therefore write the expression for the solubility equilibrium in terms of GdF_3.

The experimental results are found in Tables 20 and 21.

Table 20

Temperature = 25.00 ± 0.01° C μ = 0.50

$(Gd_i^{+3})_A$ = 0.002765 M

$(H_i^+)_A$ = 0.04981 M

$(V_i)_A$ = 104.9 ml

$(\Sigma F^-)_{A,B} \times 10^4$ (moles/l)	V_A (ml)	E_{A-C} (mv)	E_{B-C} (mv)
3.35	105.0	12.31	13.34
6.69	105.1	23.18	25.18
10.02	105.2	32.31	35.00
13.35	105.2	40.01	43.22
16.68	105.3	46.67	50.20
20.00	105.4	52.52	56.32
23.31	105.5	57.74	61.78
45.32	106.0	83.40	88.3
67.12	106.5	101.40	107.3

(V_A = volume of solution in half-cell A, $(Gd_i^{+3})_A$ = initial gadolinium(III) concentration in half-cell A, $(H_i^+)_A$ = initial hydrogen ion concentration in half-cell A, $(\Sigma F^-)_{A,B}$ = total fluoride concentrations in half-cells A and B, and E_{A-C} and E_{B-C} = potentials of concentration cells A-C and B-C.)

Table 21

Temperature = 25.0 ± 0.1° C

μ = 0.5 $(\Sigma Fe^{+3})_A = 3.709 \times 10^{-4}$ M

V_A = 100.95 ml $(\Sigma Fe^{+2})_A = 3.873 \times 10^{-4}$ M

V_B = 99.95 ml

Run	$(\Sigma H^+)_A$ (moles/l)	$(\Sigma H^+)_P$ (moles/l)	E_{A-C} (mv)
1	0.0752	0.0744	52.7
2	0.0506	0.0496	53.7

(Sodium perchlorate was used to keep μ, the total ionic strength, constant. V_P is the volume of equilibrated solution added to half-cell A. V_A is

the final volume of solution in half-cell A. $(\Sigma Fe^{+3})_A$, $(\Sigma Fe^{+2})_A$ and $(\Sigma H^+)_A$ are respectively the total iron(III), iron(II) and hydrogen ion concentrations in half-cell A. $(\Sigma H^+)_P$ is the total hydrogen ion concentration in the equilibrated solution.)

The results calculated from the above data are summarized in Table 22.

Table 22

Temperature = 25.00° C $\mu = 0.50$

$Gd^{+3} + HF = GdF^{+2} + H^+$ $K_3 = 2.9$

$GdF_3 = Gd^{+3} + 3F^-$

Run	$K'_s \times 10^{17}$
1	6.5
2	6.9
Average	6.7 ± 0.2

The K's are equilibrium quotients, for example:

$$K_3 = \frac{(GdF^{+2})_A \ (H^+)_A}{(Gd^{+3})_A \ (HF)_A} \tag{75}$$

$$K'_s = (Gd^{+3})_P \ (F^-)^3_P \tag{76}$$

where $(\ )_A$ and $(\ )_P$ signify concentrations in moles/l in half-cell A and in the equilibrated solution respectively.

Complexing of Trivalent Rare Earths by Fluoride Ion.

It has been suggested that bonding in the fluoride complexing of tripositive metal ions is mostly ionic.[8,9] This seems reasonable because the fluoride ion is relatively unpolarizable and will therefore have little tendency to form covalent bonds with the cation. The relative stability of the complex fluorides will depend upon the radii of the respective cations.

The crystal radii of the tripositive rare-earth ions decrease going from lanthanum to lutecium. Zachariasen[22] has calculated the following values from crystal data on the rare-earth fluorides:

La^{+3}	r = 1.04 A°	Nd^{+3}	r = 0.99 A°
Ce^{+3}	r = 1.02 A°	Sm^{+3}	r = 0.97 A°
Pr^{+3}	r = 1.00 A°	Eu^{+3}	r = 0.97 A°

We have estimated that of Gd^{+3} to be 0.95 A° from the data of Templeton and Zalkin.[23]

From Table 23 we see that as the crystal radius of the tripositive ion becomes smaller MF^{+2} becomes more stable.

Table 23

	K_3	M^{+3} Crystal Radius (A°)
$La^{+3} + HF = LaF^{+2} + H^+$	0.59	1.04
$Ce^{+3} + HF = CeF^{+2} + H^+$	1.6	1.02
$Gd^{+3} + HF = GdF^{+2} + H^+$	2.9	0.95

When analyzing solubility data on the rare-earth fluorides, it becomes apparent from the values for K_3 in Table 23, that one must consider the species MF^{+2}. In the experiments described above with gadolinium(III) fluoride, for example, approximately 10% of the total gadolinium(III) was present as GdF^{+2}. If gadolinium(III) fluoride were equilibrated with pure water instead of the perchloric acid-sodium perchlorate stock solution used above, this amount would increase to 18%.

Solubility of Trivalent Rare Earth Fluorides

Moeller and Kremmers[24] have measured the solubility of the tri-positive rare-earth hydroxides. They found that the solubility product

$$K_p = (M^{+3})(OH^-)^3 \qquad (77)$$

decreased in going from lanthanum to lutectium. This does not appear to be the case with the fluorides.

$$K_s' = (M^{+3})(F^-)^3 \qquad (78)$$

was found to be approximately the same for lanthanum and cerium. Instead of having decreased, however, K_s' for gadolinium(III) fluoride was found to be 50 times as large.

A similar change in solubility is found for the alkaline-earth fluorides (Table 24).

Table 24[25]

	M^{+2} Crystal Radius[26] (A°)	Solubility (18° C) (g/100 g H_2O	Crystal Type
BaF_2	1.35	0.163	fluorite
SrF_2	1.13	0.012	fluorite
CaF_2	0.99	0.0016	fluorite
MgF_2	0.65	0.0076	rutile

In going from barium to calcium there is a decrease in solubility of the alkaline-earth fluorides with a fluorite type crystal structure. MgF_2, however, which has a rutile type structure is found to be more soluble than CaF_2.

Templeton and Zalkin[23] have found that lanthanum, cerium, praseodymium, neodymium, samarium and europium trifluorides prepared from solution have a hexagonal type crystal structure. Trifluorides of gadolinium, terbium and dysprosium, however, prepared from solution were found to be orthorombic. It is thus not surprising, in view of the change in crystal structure, to find gadolinium(III) fluoride more soluble than lanthanum(III) fluoride.

VI. SUMMARY OF THE CHEMICAL THERMODYNAMIC PROPERTIES DETERMINED IN THIS INVESTIGATION

In the preceding sections we have determined thermodynamic data for the trifluorides of lanthanum, cerium and gadolinium. These data are summarized in Table 25.

Table 25

		ΔF_{298} = 27.0 kcal/mole
(1)	$CeF_3 \cdot 1/2\ H_2O_{(s)} = Ce^{+3} + 3F^- + 1/2\ H_2O$	ΔH_{298} = 0.5 kcal/mole
		ΔS_{298} = -89 eu
(2)	$Ce^{+3} + F^- = CeF^{+2}$	ΔF_{298} = -4.3 kcal/mole
(3)	$LaF_3 \cdot 1/2\ H_2O_{(s)} = La^{+3} + 3F^- + 1/2\ H_2O$	ΔF_{298} = 26.9 kcal/mole
(4)	$La^{+3} + F^- = LaF^{+2}$	ΔF_{298} = -3.7 kcal/mole
(5)	$GdF_{3(s)} = Gd^{+3} + 3F^-$	ΔF_{298} = 24.6 kcal/mole
(6)	$Gd^{+3} + F^- = GdF^{+2}$	ΔF_{298} = -4.6 kcal/mole

The ΔF_{298}'s for reactions (1), (3) and (5) were obtained by estimating activity coefficients at $\mu = 0.5$ ($\gamma \pm CeF_3 = 0.33$, $\gamma \pm LaF_3 = 0.34$ and $\gamma \pm GdF_3 = 0.34$). For reactions (2), (4) and (6) ΔF_{298} was calculated from the measured K_3 using $K_{HF} = 1.23 \times 10^{-3}$ to correct for the ionization of hydrofluoric acid.

From the data in Table 25 one is able to calculate the following free energies of formation, heats of formation and entropies. The values tabulated for $CeF_3 \cdot 1/2\ H_2O_{(s)}$, $LaF_3 \cdot 1/2\ H_2O_{(s)}$ and $GdF_{3(s)}$ refer to the solid in an apparently reproducible colloidal state.

$Ce^{+3}_{(aq)}$ Latimer[27] gives $\Delta F^{\circ}_{298} = -171.75$ kcal/mole. The partial molal entropy is estimated to be -40 eu.[28] From these values we calculate $\Delta H^{\circ}_{298} = -173.8$ kcal/mole.

$CeF^{+2}_{(aq)}$ Neglecting activity coefficient corrections, we calculate $\Delta F^{\circ}_{298} = -242$ kcal/mole.

$CeF_3 \cdot 1/2\ H_2O_{(s)}$ $\Delta F^{\circ}_{298} = -425.3$ kcal/mole, $\Delta H^{\circ}_{298} = -444.4$ kcal/mole and $S^{\circ}_{298} = 50$ eu. The uncertainty in S°_{298} is approximately 7 eu. Using Latimer's method for estimating the entropy of solid compounds,[29] one obtains $S^{\circ}_{298} = 31$ eu. for macroscopic $CeF_3 \cdot 1/2\ H_2O_{(s)}$.

$LaF^{+2}_{(aq)}$ Neglecting activity coefficient corrections, we calculate $\Delta F^{\circ}_{298} = -244.3$ kcal/mole.

$LaF_3 \cdot 1/2\ H_2O_{(s)}$ $\Delta F^{\circ}_{298} = -428.1$ kcal/mole

$GdF^{+2}_{(aq)}$ Neglecting activity coefficient corrections, we calculate $\Delta F^{\circ}_{298} = -236.5$ kcal/mole.

$GdF_{3(s)}$ $\Delta F^{\circ}_{298} = -388.7$ kcal/mole.

VII. PREPARATION AND ANALYSIS OF REAGENTS

All solutions were prepared with water redistilled from alkaline permanganate.

HF. A stock solution of 5 molal hydrofluoric acid was prepared by diluting the Cp. 48% acid. This solution was stored in a polyethylene container and analyzed as follows: A five gram aliquot was weighed into a paraffin-coated glass bulb which was then immersed in an excess of standard sodium hydroxide. After breaking the bulb, the unreacted sodium hydroxide was titrated with standard perchloric acid to a phenolphthalein end point.

$Ce(ClO_4)_3 - HClO_4$ A stock solution of cerous perchlorate and perchloric acid was prepared in the following manner: Analytical reagent ammonium hexanitrato cerate was dissolved in distilled water. This solution was added slowly with vigorous stirring to 2 M ammonium hydroxide. The light yellow precipitate was filtered and rinsed until the wash water gave negative tests for NH_4^+ and NO_3^-. The hydrous ceric hydroxide was dissolved in perchloric acid and reduced with analytical grade 35% hydrogen peroxide. This solution was boiled and after several days was filtered through sintered glass.

The cerium(III) concentration was determined in a manner similar to that described by Smith.[30] Cerium(III) was oxidized by ammonium persulfate to cerium(IV). After the addition of an exess of standard sodium arsenite, the solution was back titrated with a standard ceric solution. Osmium tetroxide was used as a catalyst and "ferroin" as an indicator.

After adding an excess of sodium fluoride to precipitate all the cerium(III) the perchloric acid concentration was determined by

titrating with carbonate-free sodium hydroxide to a phenolphthalein end point.

$La(ClO_4)_3 - HClO_4$ A lanthanum perchlorate-perchloric acid stock solution was prepared by dissolving a known weight of pure La_2O_3 in standard perchloric acid. Spectrographic analysis showed that the La_2O_3 contained no other rare earths and less than 0.01% of Al, Ca, Fe and Si.

$Gd(ClO_4)_3 - HClO_4$ A gadolinium perchlorate-perchloric acid stock solution was prepared by dissolving a known weight of Gd_2O_3 (Research Chemicals, Inc. - .8% Sm and .1% Dy) in standard perchloric acid.

NaF Cp. sodium fluoride, ignited in platinum, was dissolved in conductivity water to make a standard fluoride solution.

$NaClO_4$ A stock solution of sodium perchlorate was prepared by adding an excess of double vacuum-distilled 72% perchloric acid to analytical reagent sodium carbonate. The solution was boiled to expel carbon dioxide and the pH adjusted to 5 with carbonate-free sodium hydroxide solution. After several days this solution was diluted and filtered through sintered glass. The solution was standardized by evaporating aliquots to dryness in the presence of an excess of sulfuric acid and weighing the residue as sodium sulfate.[31] Several aliquots were evaporated to dryness and weighed as $NaClO_4$ after drying at 160° C for two hours. The two methods of analysis gave results that agreed within 0.1%.

$HClO_4$ Double vacuum-distilled 72% perchloric acid was diluted with conductivity water to yield a stock solution which was standardized against mercuric oxide using methyl red as indicator.

$Fe(ClO_4)_3$ - $Fe(ClO_4)_2$ - $HClO_4$ A stock solution of ferrous perchlorate, ferric perchlorate and perchloric acid was prepared by reacting electrolytic iron with a standard perchloric acid solution. Hydrogen peroxide was added to the resulting solution to oxidize a portion of the ferrous perchlorate to ferric perchlorate. The ferrous ion concentration was determined by titrating to a "ferroin" end point with a standard ceric solution. Since the ferrous perchlorate, total iron and initial perchloric acid concentrations were known, we were able to calculate the final ferric perchlorate and perchloric acid concentrations. These agreed with those experimentally determined using the method of Schumb, Sherrill and Sweetser.[32]

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