difference in interionic distance of closest approach, 0.1 Å, reported in X-ray studies.[10] Unfortunately, there is no way of judging the reliability of the lattice energy values. Since the triiodides have much more covalent character than the simple iodides and, in general, lattice energy calculations are most exact for simple ionic salts, the errors in the triiodide values may be appreciable. Due to the uncertainty in the value of $\Delta H_f{}^\circ$ for $NH_4{}^+(g)$ and lack of data for the other iodides, no calculations were made for the other salts studied.

With the calculated lattice energies, $\Delta H_1{}^\circ$ values[2] of -3.1 and -3.7 kcal for the rubidium and cesium systems, and eq 13, a value of $\Delta H_{1,3} = -9.{}_1$ kcal is obtained for the monoiodide–triiodide reaction, eq 15. The heat of the reaction

$$I^-(g) + I_2(g) = I_3{}^-(g) \qquad (19)$$

with all three components in the gaseous state can be obtained by subtracting from $-9.{}_1$ kcal the heat of sublimation of iodide and is $-24.{}_0$ kcal (see Table IV).

In addition to the above, a $\Delta H_f{}^\circ$ of $-56.{}_4$ kcal is found for $I_3{}^-(g)$ from eq 17; for the reaction

$$I_3{}^-(g) \longrightarrow I_3{}^-(aq) \qquad (20)$$

the heat of hydration $\Delta H_h = \Delta H_{soln}(MI_3) - L - \Delta H_h(M^+)^{14} = 44.{}_0$ kcal. This last value is about 10 kcal larger than ΔH_h for $I^-(aq)$, 33.8 kcal.[4b] From the Born equation[15]

$$\Delta G = \frac{Ne^2}{2r}(1 - 1/D) \simeq \Delta H \qquad (21)$$

where D is the dielectric constant of the medium and the difference in the heats of hydration is 10 kcal, the difference between the radii of the hydrated ions $I^-(aq)$ and $I_3{}^-(aq)$ is evaluated as about 0.3 Å or only 0.1 Å more than the calculated effective radii.

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[15] M. Born, *Z. Phys.*, **1**, 45 (1920).

CONTRIBUTION FROM BROOKHAVEN NATIONAL LABORATORY,
UPTON, NEW YORK 11973

Thorium Fluoride Complexes. Determination of the Stability Constants Using the Fluoride Ion Activity Electrode[1]

BY PAUL KLOTZ, ANIL MUKHERJI, STEPHEN FELDBERG, AND LEONARD NEWMAN*[2]

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Thorium(IV) in acidic media undergoes stepwise complexation with fluoride ion forming three soluble complexes, $ThF_3{}^+$, $ThF_2{}^{2+}$, $ThF_3{}^+$, and a precipitate, ThF_4. Using a titration technique and measuring the fluoride ion activity directly with a fluoride ion activity electrode, it was possible to evaluate the formation constants $*\beta_n = [ThF_n{}^{4-n}][H^+]^n[Th^{4+}]^{-1}[HF]^{-n}$ for the complexes and the solubility product constant for the precipitate $*K_{SO} = [Th^{4+}][HF]^4[H^+]^{-4}$ as log $*\beta_1 = 4.52 \pm 0.05$, log $*\beta_2 = 7.26 \pm 0.14$, log $*\beta_3 = 8.9 \pm 0.3$, and log $*K_{SO} = -15.17 \pm 0.15$. A calculation of the fraction of species present as a function of fluoride ion concentration using the value for $*\beta_3$ indicates that the fraction of $ThF_3{}^+$ never exceeds 0.1 under the conditions investigated. Accordingly, the value for $*\beta_3$ is at best approximate, and its elimination from the least-squares analysis of the data has almost no effect on the values of the other constants or on the standard deviations. Variation of the thorium ion concentration from 0.003 to 0.03 M indicates that polynuclear species do not play an important role. Experiments carried out at acid concentrations of 0.1 and 1.0 M show no evidence for acid–base equilibria of the thorium complexes.

Introduction

Thorium fluoride complexation has been previously investigated by several workers[3-6] using various indirect methods. Dodgen and Rollefson[3] employed the ferrous–ferric couple to determine the fluoride ion activity; Day and Stoughton[4] and Zebroski, Alter, and Heumann[5] made use of thenoyltrifluoroacetone extraction methods in their studies; and Tananaev[6] utilized both solubility and light-absorption methods to determine the stability of $ThF_2{}^{2+}$ and $ThF_3{}^+$ complexes.

The development of the fluoride ion activity electrode has made possible the direct measurement of the fluoride ion activity (or concentration).[7,8] Recent studies by Mesmer and Baes[9] on beryllium fluoride complexes, by Bond and Hefter[10] on lead fluoride complexes, and by Bond and O'Donnell[11] on various 1+ and 2+ metal ions have shown the usefulness of the electrode in this type of investigation. Most recently the electrode membrane method has been employed for the study of thorium.[12]

In the present study we use the fluoride ion electrode to measure the fluoride ion activity during a titration

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[2] To whom correspondence should be addressed.

[3] H. W. Dodgen and G. K. Rollefson, *J. Amer. Chem. Soc.*, **71**, 2600 (1949).

[4] R. A. Day, Jr., and R. W. Stoughton, *ibid.*, **72**, 5662 (1950).

[5] E. L. Zebroski, H. W. Alter, and F. K. Heumann, *ibid.*, **73**, 5646 (1951).

[6] I. V. Tananaev and L. Chzhao-Da, *J. Inorg. Chem.* (*USSR*), **4**, 961 (1959).

[7] M. S. Frant and J. W. Ross, Jr., *Science*, **154**, 1553 (1966).

[8] K. Srinivasan and G. A. Rechnitz, *Anal. Chem.*, **40**, 509 (1968).

[9] R. E. Mesmer and C. F. Baes, Jr., *Inorg. Chem.*, **8**, 618 (1969).

[10] A. M. Bond and G. Hefter, *ibid.*, **9**, 1021 (1970).

[11] A. M. Bond and T. A. O'Donnell, *J. Electroanal. Chem.*, **26**, 137 (1970).

[12] B. Noren, Thesis, University of Lund, Sweden, 1969; *Nucl. Sci. Abstr.*, **24**, 2051 (1970).

TABLE I

EXPERIMENTAL SOLUTIONS

Run no.	Starting soln C_{Th}, M	C_{HClO_4}, M	C_{NaClO_4}, M	Titrant 1 C_{HF}, M	C_{HClO_4}, M	C_{NaClO_4}, M	Titrant 2 C_{Th}, M	C_{HClO_4}, M	C_{NaClO_4}, M
1	0.003	1.0	1.99	0.25	1.0	2.0	0.006	1.0	1.98
2	0.01	1.0	1.96	0.5	1.0	2.0	0.02	1.0	1.92
3	0.03	1.0	1.88	1.0	0.64	2.36	0.06	1.0	1.76
4	0.01	0.1	2.86	0.5	...	3.0	0.02	0.1	2.82
5	0.01	1.0	...	0.5	1.0	...	0.02	1.0	...

of thorium ion (Th^{4+}) with hydrofluoric acid. Perchloric acid and sodium perchlorate comprise the supporting electrolyte ($\mu = 3.0$ M except where noted).

Experimental Section

Reagents.—Reagent grade hydrated thorium(IV) perchlorate (K & K Laboratories) was used in preparing a thorium stock solution. The solution was standardized by EDTA titration.[13]

Stock hydrofluoric and perchloric acid solutions (both Mallinckrodt, AR grade) were standardized by titrating with standard 1.00 M sodium hydroxide. All HF solutions were stored in polyethylene bottles.

A 6.0 M stock solution of $NaClO_4$ was prepared with reagent quality anhydrous sodium perchlorate (G. F. Smith Chemical Co.). This was filtered before use.

The quinhydrone was reagent grade (Fisher Scientific Co.). Doubly distilled water (Barnstead still) was used for all solutions.

Apparatus.—The titrations were carried out in water-jacketed polyethylene beakers thermostated at 25 ± 0.1°. A nylon cap contained inlets for the fluoride ion electrode, reference electrode, platinum foil (quinhydrone electrode), and reagent additions. A magnetic stirrer and Teflon-coated magnetic stirring bar were used for mixing.

The Orion Model 94-09 fluoride electrode was used in conjunction with an Orion Model 90-01 single-junction reference electrode where the filling solution was 0.01 M NaCl–3.0 M $NaClO_4$, saturated with AgCl.

Potential measurements were made either with an Orion Model 801 digital pH meter or by employing a highly regulated variable-voltage source (Dial-A-Volt, General Resistance, Inc.) in conjunction with a solid-state electrometer (Keithley Instruments).

Methods.—A solution containing the desired concentrations of Th^{4+}, $HClO_4$, and $NaClO_4$ was titrated by the addition of equal volumes of two titrants: titrant 1 containing HF, $HClO_4$, and $NaClO_4$ and titrant 2 containing Th^{4+}, $HClO_4$, and $NaClO_4$. The compositions of the titrants were designed to maintain constant metal ion and acid concentrations and constant ionic strength. The exact compositions of solutions used for our experimental runs are shown in Table I. After addition and mixing of solution and titrants and after attainment of equilibrium, the potential of the fluoride ion electrode was noted. Once precipitation began, it was necessary to wait as long as 12 hr before steady-potential readings were obtained.

An effort was made to minimize variation of the hydrogen ion concentration during the titration (caused by release of protons from HF as the fluoride is complexed). At high acid and low thorium concentrations the problem could be ignored (runs 1, 2, and 5). In runs 3 and 4, however, the production of acid was partially compensated for by having a reduced concentration of $HClO_4$ in the titrant. In run 4, the hydrogen ion activity was also monitored with the quinhydrone electrode, and small amounts of 4 M NaOH were added to keep the pH constant. In the first two approaches the small errors that were introduced were corrected during the computer evaluation of the data.

The fluoride electrode was calibrated before and after titration by measuring its potential in several solutions having different known HF concentrations. Thorium was absent from these solutions and the concentrations of $HClO_4$ and $NaClO_4$ were the same as those used in the solution titrated.

Theory

The pertinent equations for fluoride complexation of thorium are

$$Th^{4+} + HF \xrightleftharpoons{*\beta_1} ThF^{3+} + H^+ \qquad (1)$$

$$Th^{4+} + 2HF \xrightleftharpoons{*\beta_2} ThF_2{}^{2+} + 2H^+ \qquad (2)$$

$$Th^{4+} + 3HF \xrightleftharpoons{*\beta_3} ThF_3{}^+ + 3H^+ \qquad (3)$$

$$4H^+ + ThF_4(s) \xrightleftharpoons{*K_{s0}} 4HF + Th^{4+} \qquad (4)$$

$$HF \xrightleftharpoons{K_a} F^- + H^+ \qquad (5)$$

The value for K_a has been determined and is 5.25×10^{-4} in 3 M $NaClO_4$.[14,15] The data in ref 14 and 15 indicate that formation of HF_2^- is negligible under the conditions used in this investigation.

Since the fluoride ion electrode is calibrated using solutions of known hydrogen ion and HF concentrations, one can relate the electrode potential directly to the concentration of HF. Since $K_a/[H^+] \ll 1$ in all our experiments

$$C_{HF_{ref}} \approx [HF] \qquad (6)$$

where $C_{HF_{ref}}$ is the analytical concentration in the calibrating solution.

The potential of the fluoride ion electrode can be expressed as

$$E = E° - \frac{RT}{\mathfrak{F}} \ln \frac{K_a}{[H^+]} - \frac{RT}{\mathfrak{F}} \ln [HF] \qquad (7)$$

Collecting terms and rearranging

$$C_{HF_{ref}} = [HF] = \exp\left[-\frac{\mathfrak{F}}{RT}(E - E°_{HF})\right] \qquad (8)$$

Total fluoride (C_{HF}) can be expressed as

$$C_{HF} = F^- + HF + ThF^{3+} + 2ThF_2{}^{2+} + 3ThF_3{}^+ + 4ThF_4(s) \qquad (9)$$

or, since $[F^-] \approx 0$

$$C_{HF} = [HF] + [Th^{4+}]\left[\sum_{n=1}^{3} n{*\beta_n}[HF]^n[H^+]^{-n}\right] + 4[ThF_4(s)] \qquad (10)$$

The "concentration" of $ThF_4(s)$ is the concentration it would have if it were in solution. The equation for total thorium is

$$C_{Th} = [Th^{4+}] + [ThF^{3+}] + [ThF_2{}^{2+}] + [ThF_3{}^+] + [ThF_4(s)] \qquad (11)$$

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(13) F. J. Welcher, "The Analytical Uses of Ethylenediaminetetraacetic Acid," Van Nostrand, Princeton, N. J., 1958, p 197.

(14) L. Ciavatta, *Ark. Kemi*, **21**, 129 (1963).

(15) H. N. Farrer and F. J. C. Rossotti, *J. Inorg. Nucl. Chem.*, **26**, 1959 (1964).

TABLE II

COMPILATION OF MEASURED CONSTANTS

Run no.	C_{Th}, M	C_H, M	μ, M	Log (constant) $*\beta_1$	$*\beta_2$	$*\beta_3$	$*K_{SO}$	σ
1	0.003	1.0	3.0	4.53	7.30	9.03	−15.13	0.0067
				4.53	7.37	. . .	−15.15	0.0079
2	0.01	1.0	3.0	4.50	7.13	8.99	−15.18	0.0181
				4.50	7.17	. . .	−15.19	0.0182
3	0.03	1.0	3.0	4.59	7.37	9.15	−15.36	0.0145
				4.59	7.39	. . .	−15.36	0.0145
4	0.01	0.10	3.0	4.46	7.08	8.58	−14.98	0.0157
				4.46	7.11	. . .	−14.99	0.0157
5	0.01	1.0	1.0	4.58	7.33	8.75	−15.33	0.0169
				4.58	7.34	. . .	−15.34	0.0169

or

$$C_{Th} = [Th^{4+}]\left[1 + \sum_{n=1}^{3} *\beta_n[HF]^n[H^+]^{-n}\right] + [ThF_4(s)] \quad (12)$$

There are two conditions to be considered: condition 1, when the solubility product for precipitation of ThF_4 is not exceeded, and condition 2, when it is exceeded. When condition 1 prevails

$$[ThF_4(s)] = 0 \quad (13)$$

Combining eq 10, 12, and 13 gives

$$C_{HF} = [HF] + \frac{C_{Th}\left[\sum_{n=1}^{3} n*\beta_n[HF]^n[H^+]^{-n}\right]}{1 + \sum_{n=1}^{3} *\beta_n[HF]^n[H^+]^{-n}} \quad (14)$$

When condition 2 prevails

$$[Th^{4+}] = *K_{SO}[H^+]^n[HF]^{-n} \quad (15)$$

Combining eq 10, 12, and 15 gives

$$C_{HF} = [HF] + *K_{SO}[H^+]^n[HF]^{-n} \times \left[\sum_{n=1}^{3}(n - 4)*\beta_n[HF]^n[H^+]^{-n} - 4\right] + 4C_{Th} \quad (16)$$

The least-squares computer evaluation of $*\beta_1$, $*\beta_2$, $*\beta_3$, and $*K_{SO}$ from data for each titration was carried out by systematic variation of these constants until the sum of errors, $\Sigma[(\log C_{HF})_{calcd} - (\log C_{HF})_{exptl}]^2$, was minimized. A theoretical uncertainty for each constant was estimated by noting the variation in a given constant required to double the standard deviation obtained for the best fit. The Control Data 6600 was used for these computations. All graphs were generated by the Calcomp CRT system.

Results and Discussion

A typical titration curve is shown in Figure 1. The upper curve is the best least-squares computer fit to the experimental points. Calculations were based only on those points having an experimental $\bar{n}$ (average number of bound ligands) less than 3.8. The lower curve (straight line) is the calibration curve for the fluoride electrode obtained as previously described; its slope was always very close to 0.059 V/decade change in HF concentration. The results of various calibrations suggested that the drift in the $E°$ of the fluoride electrode was small over the time period of an experiment.

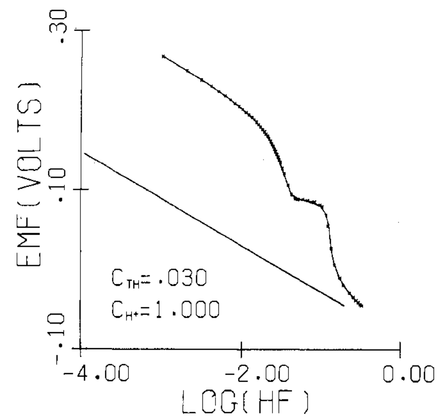

Figure 1.—A plot of the potential of the fluoride ion activity electrode *vs.* the log of the total fluoride concentration (C_{HF}). Upper curve: $C_{Th} = 0.03$ M, $C_{HClO_4} = 1.0$ M, $\mu = 3.0$ M. Symbols (× ×) are the experimental points and the line is the least-squares fit for log $*\beta_1 = 4.59$, log $*\beta_2 = 7.37$, log $*\beta_3 = 9.2$, and log $*K_{SO} = -15.36$. Lower curve: experimental reference curve for $C_{HClO_4} = 1.0$ M, $\mu = 3.0$ M.

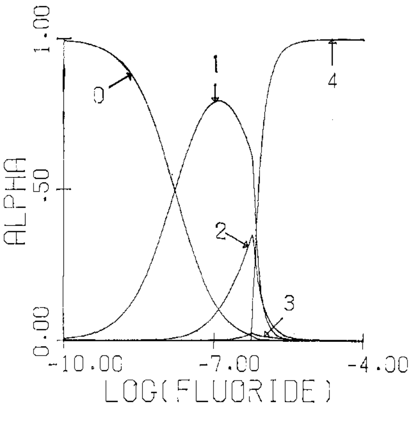

Figure 2.—The fractional distribution of thorium fluoride complexes as a function of the log of the free fluoride ion concentration. Numbers on curves correspond to n in the formula ThF_n^{4-n}. Curves are calculated for log $*\beta_1 = 4.52$, log $*\beta_2 = 7.26$, log $*\beta_3 = 8.9$, log $*K_{SO} = -15.17$, pK_a = 3.28, and $C_{Th} = 0.03$ M.

The evaluation of the constants for all experiments is shown in Table II. Two sets of constants were obtained: one set in which the computer was allowed to best fit the data using all four constants and the other set in which the value of $*\beta_3$ was forced to zero. A comparison of the values of the constants $*\beta_1$, $*\beta_2$, and $*K_{SO}$ and the standard deviations for the two sets indicates that the value for $*\beta_3$ is at best tenuous. A calcu-

TABLE III
COMPARISON WITH LITERATURE VALUES

C_{Th}, M	C_H, M	μ, M	Log (constant) $*\beta_1$	$*\beta_2$	$*\beta_3$	$*K_{SO}$	Ref
3×10^{-3}–3×10^{-2}	1.0 and 0.1	3.0	4.52 (±0.05)	7.26 (±0.14)	8.9 (±0.3)	−15.17 (±0.15)	This work
2×10^{-4}–5×10^{-3}	0.05	0.5	4.65	7.46	8.98	−14.69	3
1×10^{-6}	0.5	0.5	4.63	7.49			4
2×10^{-4}–5×10^{-3}	0.05	0.5	4.70	7.46			5

lation of the fraction of each of the complexes existing at a given fluoride ion activity (Figure 2) shows that the fraction of ThF_3^+ is very small, never exceeding 0.1 at the concentrations of thorium studied. It should be noted here that, unlike the similar diagrams for systems involving only soluble mononuclear complexes, the diagram for this system, because of precipitate formation and the associated solubility product, exhibits a dependence on the total thorium concentration.

It was found that the long-term aging required for stable potential readings during precipitation consistently produced data indicating $\bar{n} > 4.0$. An analysis of the aged precipitate showed that it was $NaThF_5$. This observation corroborates the previous findings of Tananaev and Chzhao-Da,[16] who noted that 10 hr was required to form this precipitate from ThF_4 and NaF. Since our data were not evaluated for $\bar{n}$ greater than 3.8, we feel that the values obtained for the constant $*K_{SO}$ represents the solubility product for ThF_4. Run 5 (Tables I and II) was carried out in the absence of $NaClO_4$ and gave a value for $*K_{SO}$ in substantial agreement with those obtained for runs 1–4. Long periods of time were still required to obtain stable potential readings in the region of precipitation. Ionic strength, of course, was different but the other constants are also in good agreement with those obtained for runs 1–4, suggesting that ionic strength effects cancel. The solid in this case was analyzed as ThF_4.

Within the range of thorium concentrations investigated there were no apparent indications of polynuclear species. Data obtained in 0.1 M $HClO_4$ (run 4) compared with the remaining data obtained in 1.0 M $HClO_4$ suggest that at least within this limited range of acidity, protonated complexes are not formed.

As Table III indicates, the average values we have obtained for the constants are in good agreement with those previously reported in the literature. Tananaev and Chzhao-Da[6] (not given in the table) reported much weaker constants than any other measurements. The acidities of their solutions are not reported, but from the design of the experiments they are probably low enough that the measured constants were influenced by the hydrolysis of thorium.

We can rewrite our constants as

$$\beta_n = \frac{[ThF_n^{4-n}]}{[Th^{4+}][F^-]^n} = *\beta_n K_a^{-n} \tag{17}$$

$$K_{SO} = [Th^{4+}][F^-]^4 = *K_{SO}K_a^4 \tag{18}$$

Employing the value for the dissociation constant for HF measured at an ionic strength of 3.0,[12,13] the values obtained are log β_1 = 7.80, log β_2 = 13.82, log β_3 = 18.78, and log K_{SO} = −28.29.

Utilizing the individual constants obtained for each run, plots of $\bar{n}$ *vs.* free fluoride concentration were made. A compilation is shown in Figure 3. The self-consistency of the data is excellent and this plot indicates the position of the concentration "walls" caused by the precipitate.

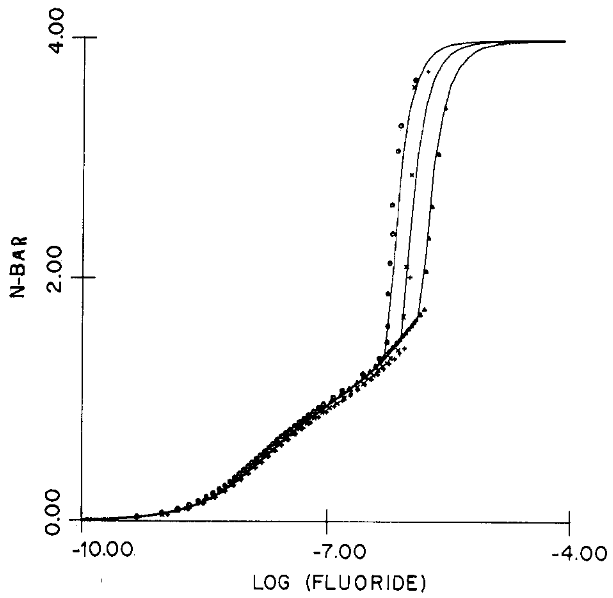

Figure 3.—Plot of average number of fluorides bound to each thorium (N-BAR or $\bar{n}$) as a function of the log of the free fluoride ion concentration. The symbols ▲, ×, O, and + represent the experimental points for runs 1, 2, 3, and 4 (Table I), respectively. The lines are the theoretical curves corresponding to log $*\beta_1$ = 4.52, log $*\beta_2$ = 7.26, log $*\beta_3$ = 8.9, log $*K_{SO}$ = −15.17, and pK_a = 3.28.

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[16] I. V. Tananaev and L. Chzhao-Da, *J. Inorg. Chem. (USSR)*, **4**, 959 (1959).