

## A Solvent Extraction and Potentiometric Study of Fluoride Complexes of Thorium(IV) and Uranium(IV)

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The properties of a fluoride membrane electrode have been studied. The electrode was employed for an investigation of the fluoride complexes formed by Th(IV) and U(IV) in 4.00 M perchloric acid solution and at a temperature of 20.00°C. The Th(IV) complexes were also studied in the same medium by means of solvent extraction measurements. The results obtained by the two methods have been compared.

The stability constants determined in the present work for Th(IV) and U(IV) have also been compared with those previously obtained for Zr(IV), Hf(IV), and Np(IV).

The stability constants of fluoride complexes of Zr(IV) and Hf(IV) in 4 M perchloric acid have been reported in a number of publications<sup>1-5</sup> by the present author. These studies form part of a general investigation of the complex formation between tetravalent cations and ligands of various donor properties in progress at this laboratory. Recently Ahrlund and Brandt<sup>6</sup> have determined the stability constants for the Np(IV) fluoride system in the above mentioned medium. The fluoride complexes of U(IV)<sup>7</sup> have also been studied but in a medium containing 0.6 M HClO<sub>4</sub> and 3.4 M NaClO<sub>4</sub> as the inert salt. The corresponding complexes of Th(IV) were investigated in 0.5 M NaClO<sub>4</sub> by Dodgen and Rollefson<sup>8</sup> using the "ferric" method of Brosset and Orring.<sup>9</sup> Concordant results were found in Refs. 10 and 11, where solvent extraction measurements were performed at the same ionic strength as in Ref. 8.

It was of interest to compare the stability of the fluoride complexes formed by zirconium and hafnium with those of four valent actinoid ions. A strict comparison of stability constants is only valid when the information is obtained from determinations in exactly the same medium. The aim of the present investigation was therefore to extend the study of the fluoride complexes formed in 4 M perchloric acid medium to include Th(IV). Since there might be a certain difference between the results obtained in 0.6 M HClO<sub>4</sub> + 3.4 M

$\text{NaClO}_4$  and 4 M  $\text{HClO}_4$ , respectively, the U(IV) fluoride system was also investigated.

Different experimental methods have been used in the study of the fluoride complexes of Zr(IV) and Hf(IV). Two of these (cation exchange<sup>1,5</sup> and solvent extraction<sup>3,4</sup>) made use of the fact that the distribution of the metal ion between an aqueous phase and a cation exchanger or a xylene solution of thenoyltrifluoroacetone varies with the ligand concentration of the aqueous solution. The composition and the concentrations of the various fluoride complexes formed can be determined from corresponding values of the distribution ratio and the free ligand concentration as described before.<sup>4,5</sup> For the reasons given on p. 2446 in Ref. 4 and on p. 2456 in Ref. 5 it was desirable to verify the previous experimental results by the use of an independent method, preferably a potentiometric one. To suppress the hydrolysis of the metal ions the method selected must work in strongly acid solution. It is therefore not possible to investigate these systems by measurements of  $[\text{H}^+]$  in fluoride buffers. The "ferric" method of Brosset and Orring was the only one available. This method has also been used for the investigations of Zr(IV),<sup>2</sup> Hf(IV),<sup>4</sup> and Np(IV).<sup>6</sup> A disadvantage of the method is the fact that the fluoride systems investigated form such strong complexes that the first stability constant can not be determined. The "ferric" method can not be used in the study of U(IV) because of reduction of Fe(III).

A new method for investigations of fluoride complexes is offered by the use of the recently invented fluoride membrane electrode. Since the potential across the membrane depends on the fluoride ion activity of the solution in which the electrode is immersed the free ligand concentration in solutions of fluoride complexes can easily be obtained. The fluoride membrane electrode has been successfully applied by Lingane<sup>12</sup> to analytical determinations of fluoride using a titration technique with thorium or lanthanum nitrate as a titrator. The results of Ref. 12 also seem promising for determinations of the stability constants for fluoride complexes of metal ions. The membrane electrode was therefore used for the present measurements. Since this electrode has never been employed for the purpose just mentioned the results obtained for Th(IV) were checked by solvent extraction measurements.

## EXPERIMENTAL

*Chemicals.* A stock solution of thorium(IV) perchlorate was prepared from  $\text{Th}(\text{NO}_3)_4 \cdot 5 \text{H}_2\text{O}$ , Merck *p.a.* The thorium(IV) nitrate was dissolved in  $\text{H}_2\text{O}$  and this solution was evaporated to nearly dryness several times with concentrated  $\text{HClO}_4$  *p.a.* to remove the nitrate. The residue was then dissolved in 4 M  $\text{HClO}_4$ . The stock solution was analysed for thorium according to Hecht and Ehrmann.<sup>13</sup> The oxinate precipitate was heated to  $\text{ThO}_2$  and weighed. The thorium(IV) concentration,  $C_{\text{Th}}$ , was found to be 179.3 mM. The total amount of perchlorate ions,  $C_{\text{ClO}_4^-}$ , was determined by passing 0.500 ml of the stock solution slowly through a cation exchanger in the hydrogen form. The concentration of free acid,  $C_{\text{H}}$ , was then calculated as the difference between  $C_{\text{ClO}_4^-}$  and 4  $C_{\text{Th}}$ . The value 3.74 M was obtained for  $C_{\text{H}}$ . From this primary stock solution the solutions used in the titrations having different values of  $C_{\text{Th}}$  were prepared by dilution with  $\text{HClO}_4$ . In all of these the free acid concentration was adjusted to 4.00 M.

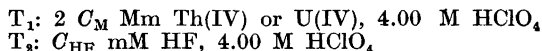
In the distribution experiments the nuclide  $^{234}\text{Th}$  ( $\beta^-$ ,  $t_{1/2} = 24.1$  d) was used.  $^{234}\text{Th}$  was prepared from  $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ , *p.a.* by the ion exchange procedure of Murase

*et al.*<sup>14</sup> The eluate from the last purification step was collected in a teflon evaporating dish. Concentrated HNO<sub>3</sub> and HClO<sub>4</sub> were added and the solution was evaporated to a small volume (<0.1 ml). The residue was dissolved in 5 ml 4.00 M HClO<sub>4</sub>. 0.2 ml of this solution was used in the distribution experiments. The decay of the radioactivity of the solution was followed and a half-life  $t_{1/2}$ =24.2 d was calculated from these measurements. This value is in close agreement with the literature value  $t_{1/2}$ =24.1 d.

Uranium(IV) stock solution was prepared from uranium(IV) perchlorate solution by cathodic reduction in the way described in Ref. 15. In the cathodic solution hydrogen ions are consumed according to the reaction  $\text{UO}_2^{2+} + 4 \text{H}^+ + 2 \text{e}^- \longrightarrow \text{U}^{4+} + 2 \text{H}_2\text{O}$ . Perchloric acid was therefore added to keep the concentration of hydrogen ions 3–4 M. The resulting cathode solution was diluted to the desired strength and stored under hydrogen in a closed system. The analyses of this solution were performed as in Ref. 7. The concentration of uranium(IV) was 235.8 mM and the content of uranium(VI) was found to be negligible. During the course of the investigation the concentration of U(IV) was checked. No measurable oxidation to U(VI) could be detected. The value of  $C_{\text{H}}=3.23$  M was obtained for the concentration of free acid.

Hydrofluoric acid solutions were mixed from acids *p.a.* keeping the hydrogen ion concentration constant at 4.00 M.

*Emf measurements.* For the emf measurements performed at  $20.00 \pm 0.02^\circ\text{C}$  using the fluoride membrane electrode (Orion Research Inc.), the same cell as written on p. 934 was set up. At the beginning of the titration the right half-cell contained 10.00 ml of a solution having a concentration of hydrofluoric acid of  $C_{\text{HF}}$  mM and 4.00 M of perchloric acid. From the measured emf value  $E_c$  was calculated. By adding 10.00 ml of solution T<sub>1</sub> the first  $E$  value corresponding to a certain  $C_{\text{M}}$  was obtained. The titration was then continued by adding equal volumes of the two solutions T<sub>1</sub> and T<sub>2</sub> having the compositions



The value of  $E_c$  was remeasured at the end of each titration series. In most cases  $E_c$  was 0.3 mV below the starting value. No correction was applied for this rather small drift. The stability of the obtained  $E$  values was usually better than  $0.1 \text{ mV h}^{-1}$ . In some series T<sub>2</sub> was replaced with 4.00 M HClO<sub>4</sub>. By starting these titrations with solutions having high values of  $C_{\text{HF}}$  the  $\bar{n}$  curve was obtained in the reversed order. Exactly the same results were found proving that the change of  $E_c$  during a titration had no influence on the values obtained for  $\bar{n}$  and [HF]. Between two titration series the FME-electrode was first rinsed with water and then stored dry. When the electrode was not used  $E_c$  was found to decrease by about  $0.5 \text{ mV d}^{-1}$ . This may depend upon that a very small amount of acid may have collected by capillary attraction at the interface around the crystal electrode body joint. The hydrogen ions then migrating slowly into the internal solution will cause this effect.

Even if the values of  $E_c$  varied, the values of  $E - E_c$  for different titration series were in very good agreement. For [HF] < 0.5 mM,  $E$  was unstable when measured in solutions containing no metal ions. Nevertheless stable  $E$  values could be determined in metal ion solutions having a free hydrofluoric acid concentration as low as  $10^{-6}$  M, provided that the total ligand concentration,  $C_{\text{HF}}$ , was higher than 0.5 mM. Evidently this is due to the greater "buffer" capacity of these solutions.

In the uranium(IV) measurements no precautions were undertaken to exclude air from the titration vessel. Since the drift of the  $E$  values usually was less than  $0.1 \text{ mV h}^{-1}$  no noticeable oxidation of U(IV) to U(VI) took place in the cell. The secondary U(IV) stock solutions were prepared immediately before a titration series. Their concentration of U(IV) did not change during the measurements.

According to  $\text{M}^{4+} + n\text{HF} \rightleftharpoons \text{MF}_n^{4-n} + n\text{H}^+$  hydrogen ions are formed when the complex formation proceeds. Since  $\bar{n} C_{\text{M}} < 25$  mM this increase of the hydrogen ion concentration was neglected.

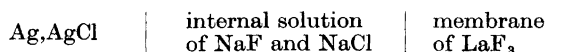
The titration vessel was made of plastic material and all hydrofluoric acid containing solutions were stored in plastic bottles and handled using plastic pipettes. Good mixing in the titration vessel was achieved by a magnetic stirrer.

*Distribution measurements.* Thenoyltrifluoroacetone (HTTA) was dissolved in xylene. These solutions were then equilibrated at  $20.00 \pm 0.05^\circ\text{C}$  with 4.00 M aqueous solutions

of perchloric acid containing various concentrations of hydrofluoric acid. To each one of these solutions 0.200 ml of the  $^{234}\text{Th}$  stock solution and inactive Th(IV) were added.  $q$  was obtained by measuring the  $\gamma$ -activity of the two phases. A more detailed description of the distribution experiments is given in Ref. 4.

#### THE BEHAVIOUR OF THE FLUORIDE MEMBRANE ELECTRODE

The electrode consists of a fluoride sensitive membrane of a single crystal of  $\text{LaF}_3$ , doped with  $\text{Eu}^{2+}$ . The membrane is in contact with an internal solution of  $\text{NaF}$  and  $\text{NaCl}$ . A silver-silverchloride electrode is immersed in the internal solution and connected with the external lead. The electrode can be written



and in the text it is represented by FME (fluoride membrane electrode). Fluoride ions are the only species capable of transporting electrical charge through the  $\text{LaF}_3$  crystal. When the electrode is in contact with an external solution containing fluoride ions an electrical potential difference,  $e$ , is set up between the two solutions. Theoretically  $e$  is related to the fluoride ion activity of the two solutions by the following relationship

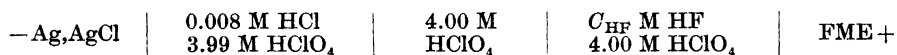
$$e = \text{constant} + \frac{RT}{F} \ln \frac{\{\text{F}^-\}_{\text{internal}}}{\{\text{F}^-\}_{\text{external}}} \quad (1)$$

Eqn. (1) was experimentally verified by Frant and Ross.<sup>16</sup> Since the activity of the fluoride ions in the internal solution is constant, eqn. (1) is equal to

$$e = e_c - RT \cdot F^{-1} \ln \{\text{F}^-\}_{\text{external}} \quad (2)$$

where  $e_c$  is a constant.

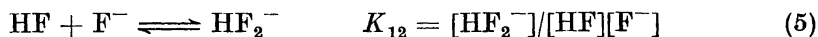
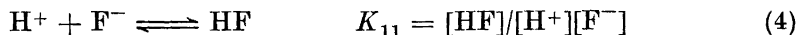
To verify that the FME-electrode functions properly for the present measurements the following cell was set up



The expression for the emf,  $E$ , of this cell becomes

$$E = e_c - e_{\text{Ref.}} - RT \cdot F^{-1} \ln \{\text{F}^-\}_{\text{external}} \quad (3)$$

According to Farrer and Rossotti<sup>17</sup> the following equilibria have to be considered for the proton-fluoride association



For the total concentration of hydrofluoric acid one obtains

$$C_{\text{HF}} = [\text{HF}] + [\text{F}^-] + 2 [\text{HF}_2^-] \quad (6)$$

By combination of eqns. (4), (5), and (6)  $C_{\text{HF}}$  can also be written

$$C_{\text{HF}} = [\text{F}^-](K_{11}[\text{H}^+] + 1) + 2 K_{12}[\text{HF}] \quad (7)$$

By using the values of  $K_{11}$  and  $K_{12}$  given in Ref. 17 (valid in  $\text{NaClO}_4$  medium of ionic strength 3 M and a temperature of  $25^\circ\text{C}$ ) it can be shown that for the conditions chosen in the present measurements a good approximation of eqn. (7) is

$$C_{\text{HF}} = [\text{HF}] = K_{11} [\text{H}^+][\text{F}^-] \quad (8)$$

Since in the measurements the ionic strength is constant ( $I=4.00$  M) activities can be replaced by concentrations. Finally eqns. (3) and (8) give a rather simple relationship between the measured emf and the total concentration of hydrofluoric acid

$$E = E_c - RT \cdot F^{-1} \ln C_{\text{HF}} \quad (9)$$

or

$$E = E_c - RT \cdot F^{-1} \ln [\text{HF}] \quad (9a)$$

In these eqns.  $E_c$  stands for all the terms that can be treated as constants in the thermodynamic expression for  $E$ , including the liquid junction potential of the cell.

It was found that the plastic body, of which the FME-electrode was manufactured, was attacked by the 4 M perchloric acid used. A teflon case covering the electrode was therefore made. At one end of the case a hole was cut for the crystal. The case was fastened on the original electrode body *via* a rubber packing in order to avoid leakage of solution.

The function of the electrode was checked by measuring the emf in solutions of different HF concentrations. The results of the measurements of  $E$  for hydrofluoric acid concentrations within the range  $4 \times 10^{-4} \text{ M} \leq C_{\text{HF}} \leq 2 \times 10^{-1} \text{ M}$  are given in Table 1. The values of  $E$  were obtained at a temperature of  $20.00 \pm 0.02^\circ\text{C}$ . For  $C_{\text{HF}} = 1 \text{ mM}$  the equilibrium potential was reached within 20 min, but for higher values it was attained after 5–10 min. When  $E$  changed

Table 1. Corresponding values of  $E$  and  $C_{\text{HF}}$  measured by the Fluoride Membrane Electrode for a constant hydrogen ion concentration of 4.00 M and at a temperature of  $20.00^\circ\text{C}$ . The two series given were obtained with different internal solutions.

$C_{\text{HF}} \times 10^3$ M	$E$ mV	$E_c = E + 58.0$ $\log C_{\text{HF}}$ mV	$C_{\text{HF}} \times 10^3$ M	$E$ mV	$E_c = E + 58.6$ $\log C_{\text{HF}}$ mV
1.524	78.1	-85.3	0.4066	296.0	97.3
5.17	47.7	-84.9	0.813	278.1	97.0
8.39	35.4	-85.0	1.585	261.0	96.9
13.74	23.0	-85.0	2.620	248.2	96.9
26.57	6.2	-85.2	4.351	235.5	97.1
54.7	-11.9	-85.1	6.68	224.7	97.2
92.7	-25.1	-85.0	12.01	209.7	97.2
150.3	-37.3	-85.0	21.39	194.9	97.0
224.9	-47.4	-85.0	29.38	186.9	97.1
			41.15	178.2	97.0
			68.3	165.3	97.0
			110.2	153.1	97.0

by less than  $0.1 \text{ mV h}^{-1}$  the value was taken as the equilibrium potential. The experimentally obtained values of  $E$  are in accordance with eqn. (9); cf. Table 1.

Measurements were also performed keeping  $C_{\text{HF}}$  within the range  $10^{-5}$  M up to  $10^{-4}$  M. However, stable  $E$  values could not be obtained.  $E$  drifted always towards lower values which could be explained either by an increase of  $[\text{F}^-]_{\text{external}}$  or by a decrease of  $[\text{F}^-]_{\text{internal}}$ . If hydrogen ions from the external solution migrated into the internal solution this would certainly cause a decrease of  $[\text{F}^-]_{\text{internal}}$ . But in that case an unstable potential should have been obtained also for higher values of  $C_{\text{HF}}$ . This was not observed. On the other hand dissolution of lanthanum fluoride from the membrane should increase the concentration of fluoride ions in the external solution; cf. Ref. 12, p. 886. For sufficiently high total hydrofluoric acid concentrations this contribution should have no influence on the stability of the measured emf. Evidently the observations favour the last explanation.

In the present measurements the slope ( $RT \cdot F^{-1} \ln 10$ ) was found to be  $58.0 \pm 0.2 \text{ mV}$  and  $58.6 \pm 0.2 \text{ mV}$  for the two series reported in Table 1, as compared with the theoretical value of  $58.2 \text{ mV}$ . From corresponding values of  $E$  and  $C_{\text{HF}}$ ,  $E_c$  was calculated according to eqn. (9). The results for the two series were  $E_c = -(85.1 \pm 0.2) \text{ mV}$ , respectively  $E_c = 97.1 \pm 0.2 \text{ mV}$ . Thus  $E_c$  is a constant for each series within the limits of the random experimental errors. Hence it may be concluded that the validity of eqn. (9) has been proved.

The two values of  $E_c$  were obtained for different compositions of the internal solution.  $E_c = 97.1 \text{ mV}$  corresponded to  $0.1 \text{ M NaCl}$  and  $0.1 \text{ M NaF}$  as internal solution. All of the measurements on the complex equilibria involving Th(IV) or U(IV) were performed with this solution.

#### CALCULATIONS AND RESULTS OF THE EMF MEASUREMENTS

A titration series was started with a known value of  $[\text{HF}]$  in the cell. From the  $E$  value thus obtained  $E_c$  was calculated using eqn. (9a). The titration was then continued keeping the total metal ion concentration,  $C_{\text{M}}$ , constant. According to eqn. (9a) the measured values of  $E$  give the free hydrofluoric acid concentrations corresponding to the various values of  $C_{\text{HF}}$  and  $C_{\text{M}}$  used. Since  $[\text{F}^-]$  and  $[\text{HF}_2^-]$  can be neglected (see p. 000)  $\bar{n}$  can be calculated from the expression

$$C_{\text{HF}} = [\text{HF}] + \bar{n} C_{\text{M}} \quad (10)$$

From corresponding values of  $\bar{n}$  and  $[\text{HF}]$   $X_{\text{H}}X_{\text{H}_0}^{-1}$  and then the various constants  $\beta_{\text{nH}}X_{\text{H}_0}^{-1}$  are obtained according to the calculation procedure outlined in Ref. 4 on pp. 2441 and 2442. In the present cases also  $X_{\text{H}_0}^{-1}$  can be computed with a high degree of accuracy. Finally the stability constants,  $\beta_{\text{nH}}$ , are easily calculated from the values of  $X_{\text{H}_0}^{-1}$  and  $\beta_{\text{nH}}X_{\text{H}_0}^{-1}$ .

*The Th(IV)–HF system.* The values obtained in the various titrations series are shown in Fig. 1, where  $\bar{n}$  is plotted versus  $-\log[\text{HF}]$ . The  $\bar{n}$  curve was determined for three different  $C_{\text{M}}$  values, 0.897, 1.793, and 4.483 mM. Within the investigated ligand concentration range,  $8 \times 10^{-6} \text{ M} < [\text{HF}] < 5 \times 10^{-3}$

M, the same  $\bar{n}$  curve is obtained for all the  $C_M$  values used. This fact proves that no polynuclear fluoride complexes are formed within this concentration range.  $\bar{n}$  values could not be determined for larger [HF] than 5 mM because  $\text{ThF}_4$  was precipitated. To avoid such precipitation a titration series having  $C_M=0.466$  mM was performed. However,  $\bar{n}$  could not be determined accurately enough for [HF] > 5 mM because only about 10 % of the fluoride was bound. To illustrate the close agreement between the results obtained for various titration series  $\bar{n}[\text{HF}]^{-1}$  is plotted *versus* [HF] for [HF] values around 0.4 mM in Fig. 2. As seen from this figure the various series deviate by less than  $\pm 0.6$  % from the curve calculated using the experimental stability constants.

Table 2. Thorium(IV). Corresponding values of [HF] and the functions  $X_{\text{H}}X_{\text{H}_0}^{-1}$ ,  $X_{\text{I}}$ , and  $X_{\text{II}}$  found by the graphical integration.

$[\text{HF}] \times 10^3$ M	$X_{\text{H}} \cdot X_{\text{H}_0}^{-1}$	$X_{\text{I}} \times 10^{-4}$ M <sup>-1</sup>	$X_{\text{II}} \times 10^{-6}$ M <sup>-2</sup>
0	0.893	1.062	2.50
0.02000	1.106	1.065	
0.03400	1.255	1.065	
0.0550	1.483	1.073	
0.0750	1.701	1.077	
0.1000	1.976	1.083	
0.1700	2.771	1.105	
0.2300	3.471	1.121	
0.3000	4.308	1.138	
0.3800	5.29	1.158	
0.4800	6.58	1.184	2.54
0.620	8.45	1.218	2.52
0.710	9.70	1.239	2.49
0.900	12.47	1.287	2.50
1.100	15.59	1.336	2.49
1.300	18.91	1.386	2.49
1.500	22.41	1.435	2.49
1.900	30.04	1.534	2.48
2.400	40.78	1.662	2.50
3.000	55.5	1.821	2.53
4.000	84.8	2.099	2.59
5.00	119.9	2.379	2.63

The corresponding values of  $X_{\text{H}}X_{\text{H}_0}^{-1}$  and [HF] obtained from eqn. (14) in Ref. 4 by the graphical integration are given in Table 2. From the extrapolations the following values for the constants were obtained:

$$X_{\text{H}_0}^{-1} = 0.893 \pm 0.004$$

$$\beta_{1\text{H}}X_{\text{H}_0}^{-1} = (1.06 \pm 0.01) \times 10^4 \text{ M}^{-1}; \quad \beta_{1\text{H}} = (1.19 \pm 0.01) \times 10^4 \text{ M}^{-1}$$

$$\beta_{2\text{H}}X_{\text{H}_0}^{-1} = (2.5 \pm 0.1) \times 10^6 \text{ M}^{-2}; \quad \beta_{2\text{H}} = (2.8 \pm 0.1) \times 10^6 \text{ M}^{-2}$$

*The U(IV)–HF system.* Also for this system titration series having three different  $C_M$  values were performed. The  $\bar{n}$  curve obtained is shown in Fig. 3.

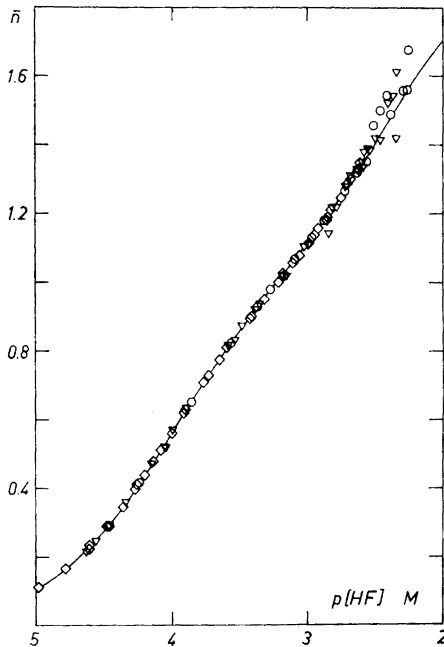


Fig. 1. Values of  $\bar{n}$  experimentally obtained for Th(IV) plotted versus  $-\log [\text{HF}]$ . The signs refer to the following concentrations (in mM) of  $C_{\text{Th}}$ : 0.897,  $\circ$ ; 1.793,  $\nabla$ ; 4.483,  $\diamond$ .

The curve was calculated using the constants obtained.

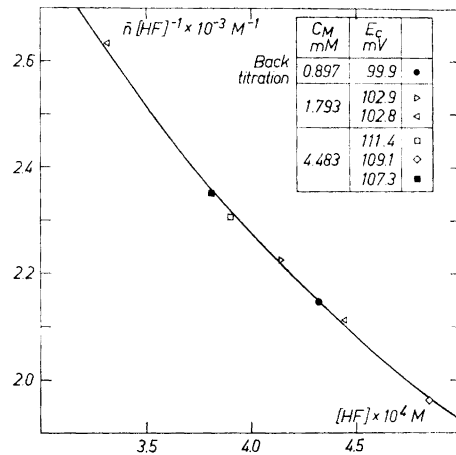
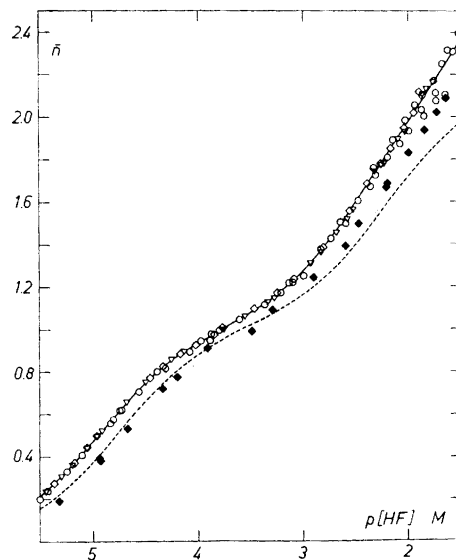


Fig. 2. A part of the function  $\bar{n}[\text{HF}]^{-1}$  for the Th(IV) fluoride system. The curve was calculated using the constants obtained.

Fig. 3. The complex formation curve (marked —) for the U(IV) fluoride system calculated from the stability constants obtained in the present work. The signs refer to the experimentally determined values of  $\bar{n}$  for titration series having the following concentrations (in mM) of  $C_U$ : 2.655,  $\circ$ ; 5.31,  $\nabla$ ; 10.62,  $\diamond$ . The dashed curve was calculated using the constants given in Ref. 7 valid in 0.6 M  $\text{HClO}_4$ , 3.4 M  $\text{NaClO}_4$ . The  $\bar{n}$  values obtained by means of the FME-electrode for  $C_U = 10.62$  mM in this medium are marked by  $\blacklozenge$ .





Independent of the  $C_M$  value used the same curve was found. Evidently no polynuclear complexes are formed within the concentration range investigated. Back titrations starting at high hydrofluoric acid concentrations were also made. The same results were obtained for these proving that no oxidation of U(IV) to U(VI) took place during a titration series. Since  $UF_4$  was precipitated the measurements could not be extended over  $[HF] \approx 30$  mM.

Table 3. Uranium(IV). Corresponding values of  $[HF]$  and the functions  $X_H X_{H_0}^{-1}$ ,  $X_I$ ,  $X_{II}$ , and  $X_{III}$  found by the graphical integration.

$[HF] \times 10^4$ M	$X_H X_{H_0}^{-1} \times 10^{-1}$	$X_I \times 10^{-4}$ M <sup>-1</sup>	$X_{II} \times 10^{-7}$ M <sup>-2</sup>	$X_{III} \times 10^{-8}$ M <sup>-3</sup>
0	0.0788	6.93	2.60	6.0
0.04000	0.1066	6.95		
0.0600	0.1202	6.90		
0.0800	0.1340	6.90		
0.1100	0.1551	6.94		
0.1500	0.1830	6.95		
0.2000	0.2175	6.94		
0.3600	0.3298	6.97		
0.560	0.4732	7.04		
0.850	0.685	7.13		
1.300	1.022	7.25	2.46	
1.800	1.413	7.41	2.67	
3.400	2.745	7.84	2.68	
4.600	3.838	8.17	2.70	
6.20	5.41	8.60	2.69	
8.00	7.36	9.10	2.71	
12.00	12.23	10.13	2.67	
18.00	21.33	11.80	2.71	
28.00	41.16	14.67	2.76	
40.00	73.1	18.25	2.83	
54.0	122.6	22.69	2.92	5.9
70.0	196.3	28.03	3.01	5.8
110.0	472.8	42.97	3.28	6.2
150.0	901	60.1	3.55	6.3
210.0	1862	88.7	3.89	6.1
300.0	4174	139.1	4.41	6.0

The results given in Table 3 were obtained by graphical integration of the function  $\bar{n}[HF]^{-1}$ . From the functions  $X_I$ ,  $X_{II}$  etc., the constants:

$$X_{H_0}^{-1} = 0.788 \pm 0.005$$

$$\beta_{1H} X_{H_0}^{-1} = (6.9 \pm 0.1) \times 10^4 \text{ M}^{-1}; \quad \beta_{1H} = (8.8 \pm 0.2) \times 10^4 \text{ M}^{-1}$$

$$\beta_{2H} X_{H_0}^{-1} = (2.6 \pm 0.1) \times 10^7 \text{ M}^{-2}; \quad \beta_{2H} = (3.3 \pm 0.2) \times 10^7 \text{ M}^{-2}$$

$$\beta_{3H} X_{H_0}^{-1} = (6.0 \pm 0.5) \times 10^8 \text{ M}^{-3}; \quad \beta_{3H} = (8 \pm 1) \times 10^8 \text{ M}^{-3}$$

were obtained by extrapolations to  $[HF]=0$ .

A representative part of the  $\bar{n}[HF]^{-1}$  curve for this system is shown in Fig. 4, where the titration results found within the range  $0.1 \text{ mM} < [HF] < 0.4 \text{ mM}$  are plotted as  $\bar{n}[HF]^{-1}$  versus  $[HF]$ . The curve is computed using the above

stability constants. None of the values deviate by more than 2 % from this curve which must be considered as fairly satisfying.

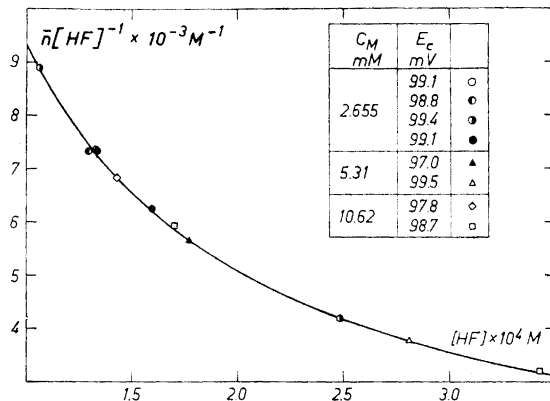


Fig. 4. A part of the function  $\bar{n}[\text{HF}]^{-1}$  for the U(IV) fluoride system. The curve was calculated using the constants obtained.

#### CALCULATIONS AND RESULTS OF THE SOLVENT EXTRACTION MEASUREMENTS

From the distribution ratios obtained in the solvent extraction measurements of Th(IV) the stability constants were calculated by the method described in Ref. 4. Corresponding values of  $C_{\text{HF}} = [\text{HF}]$  and  $q$  are given in Table 4. Using these,  $X_{\text{H}}$  and  $X_{\text{IH}} = (X_{\text{H}} - 1)[\text{HF}]^{-1}$  were calculated. Within the ligand range investigated the results could be explained by the formation of only one complex having the stability constant  $\beta_{\text{IH}} = (1.0 \pm 0.1) \times 10^4 \text{ M}^{-1}$  or  $K_1^* = (4.2 \pm 0.4) \times 10^4$ . The distribution experiments were performed having  $C_{\text{HTTA}}' = 1.98 \text{ M}$ . In spite of this high concentration of HTTA a rather small

Table 4. Distribution ratios obtained for Th(IV) at different values of  $C_{\text{HF}} \cdot C_{\text{HTTA}}' = 1.98 \text{ M}$ ;  $C_{\text{Th(IV)}} = 10^{-6} \text{ M}$ ;  $C_{\text{HClO}_4} = 4.00 \text{ M}$ ;  $T = 20.00^\circ\text{C}$ .

$C_{\text{HF}} \times 10^4$ M	$q$	$X_{\text{H}}$	$X_{\text{IH}} \times 10^{-4}$ $\text{M}^{-1}$
0	0.3842		
0.471	0.2554	1.50	1.06
0.678	0.2172	1.77	1.14
0.999	0.1858	2.07	1.07
1.355	0.1604	2.40	1.03
2.054	0.1234	3.11	1.03
3.808	0.0775	4.96	1.04
5.60	0.0608	6.32	0.95
9.61	0.0370	10.39	0.98

$q_0$  value (0.384) was obtained evidently depending on the high acidity (4.00 M) of the aqueous phase. For  $C_{\text{HF}}=0.961$  mM the xylene phase contained only about 4 % of the total amount of Th(IV). To extend the measurements to higher ligand concentrations,  $C_{\text{HTTA}}$  has to be increased over 1.98 M. This was not possible and thus only the first stability constant could be determined.

## DISCUSSION

From the results of the present investigation it can be concluded that the fluoride membrane electrode functions properly under the conditions chosen. By means of this electrode free hydrofluoric acid concentrations can be determined with a high degree of accuracy.

Almost the same value of  $K_1^*$  for the Th(IV)—HF system is obtained both from the solvent extraction ( $K_1^*=(4.2\pm 0.4)\times 10^4$ ) and the emf ( $K_1^*=(4.76\pm 0.04)\times 10^4$ ) measurements in the present work. The  $\bar{n}$  curve calculated from the values of the stability constants given in Ref. 7 for the U(IV)—HF system (assuming that the acid dissociation constant for HF is the same in both media) is shown in Fig. 3. This curve deviates from the result of the present investigation. Since this may depend on the different media used, measurements using the fluoride membrane electrode were performed under the same conditions as in Ref. 7. The  $\bar{n}$  values thus obtained for  $[\text{HF}] < 1$  mM agree closely with the results of Grenthe and Varfeldt; cf. Fig. 3. Hence we may conclude that the assumption on which the calculations of Ref. 7 is based (*e.g.* that only mononuclear complexes are formed) is correct. The deviations found for larger ligand concentrations may be caused by the precipitation of small amounts of  $\text{UF}_4$ ; cf. Ref. 7, p. 997. For the fluoride systems of Th(IV) and U(IV) we have thus shown that the same results are obtained both from the fluoride membrane electrode measurements and from the two other methods referred to. Accordingly no systematic errors are involved in the stability constants determined using the FME-electrode. The reproducibility of the measured  $\bar{n}[\text{HF}]^{-1}$  values was between  $\pm 1$  % and  $\pm 2$  % except for the higher ligand concentrations, where it was about  $\pm 5$  %. Hence the values of the stability constants are obtained with relatively small random errors.

Table 5. A collection of the stability constants  $K_n^*$  and the ratio  $K_1^*/K_2^*$  for various four valent metal ions determined in 4 M  $\text{HClO}_4$  and at a temperature of 20°C.

Ref.	Metal ion	$K_1^*$ $10^{-4}$	$K_2^*$ $10^{-3}$	$K_3^*$ $10^{-2}$	$K_4^*$ $10^{-2}$	$K_5^*$ $10^{-1}$	$K_6^*$	$K_1^*/K_2^*$
1, 2, 3	Zr(IV)	76	23	10	1.9	3.4	2	33
4, 5	Hf(IV)	33	11	11	1.6	5	3	30
This work	Th(IV)	4.8	0.94					51
This work	U(IV)	35	1.50	0.92				234
6	Np(IV)	6.6	0.49	2				135

In Table 5 the results are collected for the various metal ions investigated. The stability constants given refer to 4 M HClO<sub>4</sub> and a temperature of 20°C. Apparently all of the metal ions form very strong fluoride complexes. As seen from the values of  $K_n^*$  the metal ions can be divided into two groups. The first group containing Zr(IV) and Hf(IV) have markedly larger values of  $K_n^*$  than the second group, the actinoid ions. Since Zr(IV) and Hf(IV) both have distinctly smaller ionic radius than the actinoid ions this is in accordance with the assumption that mainly electrostatic forces govern the formation of the complexes.<sup>18</sup>  $K_1^*$  for U(IV) is the only exception to this rule.

From an inspection of the ratios  $K_1^*/K_2^*$  it is evident that the first fluoride complex is much more stable than the second one for all the metal ions. The actinoides have, however, considerably larger values of this ratio than zirconium and hafnium. As pointed out by Ahrlund and Brandt<sup>18</sup> irregularities are observed for  $K_1^*$  and also for  $K_1^*/K_2^*$  in the actinoid series. The value of  $K_1^*$  for uranium(IV) is higher than for the neighbouring actinoides, and so is also the value of  $K_2^*$ , though not in the same degree. A determination of the enthalpy changes for the various complex formation reactions may give some useful information about the possible reasons for these remarkable trends.<sup>19</sup>

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