

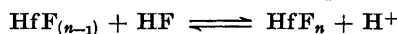
## The Fluoride Complexes of Hafnium(IV)

### I. A Solvent Extraction and Potentiometric Investigation

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The stability constants,  $K_n^*$ , for the complex equilibria



where  $1 \leq n \leq 6$ , have been determined by means of solvent extraction and potentiometric measurements (using the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  electrode). All measurements have been performed in 4 M  $\text{HClO}_4$ , and at a temperature of 20°C.

Hafnium(IV), like most four valent metal ions, is strongly hydrolysed in aqueous solution. The hydroxocomplexes are both mononuclear and polynuclear.<sup>2-8</sup> In order to avoid complications due to the formation of hydroxo or mixed hydroxo-fluoride complexes, the fluoride complexes of hafnium(IV) were therefore studied in only very acid solutions and at low metal ion concentrations. Previous measurements have been performed by some authors<sup>8-10</sup> using solvent extraction and electrometric methods under somewhat different conditions than those chosen for the present investigation.

Because of the complicated solution chemistry of hafnium(IV) it seems desirable to try methods other than those used by the aforementioned authors. Recently the fluoride complexes formed by neptunium(IV)<sup>11</sup> were studied by emf measurements using the "ferric" method of Brosset and Orring.<sup>12</sup> This method seems to be well suited for a corresponding investigation of the fluoride complexes of hafnium(IV) also. In order to suppress the hydrolysis of Hf(IV) the measurements were performed in 4.00 M perchloric acid solution.

Since the first fluoride complex of  $\text{Hf}^{4+}$  is much stronger than the corresponding  $\text{Fe}^{3+}$ -complex, the first stability constant could not be obtained. This was determined by making solvent extraction measurements, using thenoyltrifluoroacetone as an auxiliary ligand. The higher stability constants also could be calculated from the solvent extraction data, giving an independent check of the emf measurements.

## SYMBOLS

HTTA	= thenoyltrifluoroacetone
TOPO	= tri-octylphosphine oxide
[ ]	= equilibrium concentration in the aqueous phase
[ ] <sub>org</sub>	= equilibrium concentration in the xylene phase
$C_{HTTA}$	= initial total concentration of HTTA in the xylene phase
$C_{HF}$	= initial total concentration of HF in the aqueous phase
$C_M$	= initial total concentration of Hf(IV) in the aqueous phase
$C_{HF}$	= total equilibrium concentration of HF in the aqueous phase
$C_M$	= total equilibrium concentration of Hf(IV) in the aqueous phase
$C_{MO}$	= total equilibrium concentration of Hf(IV) in the xylene phase
$C_{II}$	= total concentration of Fe(II)
$C_{III}$	= total concentration of Fe(III)
$v$	= volume of aqueous phase
$v_{org}$	= volume of xylene phase
$q$	= $C_{MO}/C_M$
$q^0$	= $q$ when $[HF] = 0$
$K_d$	= $[HTTA]_{org}/[HTTA]$ the distribution constant of HTTA
$K_a$	= $[H^+][TTA^-]/[HTTA]$ the acid dissociation constant of HTTA
$\beta_n^*$	= $[HfF_n][H^+]^n/[Hf][HF]^n$
$\beta_{nH}$	= $\beta_n^*/[H^+]^n$
$\beta_{nH}^{II}$	= $\beta_{nH}$ for the Fe(II)-fluoride system
$\beta_{nH}^{III}$	= $\beta_{nH}$ for the Fe(III)-fluoride system
$K_n^*$	= $[HfF_n][H^+]/[HfF_{n-1}][HF]$ ; $K_1^* = \beta_1^*$
$X_H$	= $1 + \sum_{n=1}^N \beta_{nH}[HF]^n$
$X_H^{II}$	= $X_H$ for the Fe(II)-fluoride system
$X_H^{III}$	= $X_H$ for the Fe(III)-fluoride system
$X_{H0}$	= the value of $X_H$ for $[HF] = [HF]_0$ , the lower limit of integration of eqn. (14)
$X_I$	= $(X_H/X_{H0} - 1/X_{H0})[HF]^{-1} = (\beta_{1H} + \sum_{n=2}^N \beta_{nH}[HF]^{n-1})X_{H0}^{-1}$
$X_{II}$	= $(X_I - \beta_{1H}/X_{H0})[HF]^{-1} = (\beta_{2H} + \sum_{n=3}^N \beta_{nH}[HF]^{n-2})X_{H0}^{-1}$

## DERIVATION OF STABILITY CONSTANTS FROM THE SOLVENT EXTRACTION MEASUREMENTS

The calculation of the stability constants is based upon the assumption that the distribution equilibrium can be represented by the following reaction



The application of the law of mass action to this equilibrium gives

$$K = \frac{[Hf(TTA)_4]_{org}[H^+]^4}{[Hf^{4+}][HTTA]_{org}^4} \quad (2)$$

If  $\text{Hf}(\text{TTA})_4(\text{org})$  is the only hafnium containing species in the organic phase and the hydrogen ion concentration in the aqueous phase is constant, eqn. (2) may be transformed to

$$K' = q X_{\text{H}}[\text{HTTA}]_{\text{org}}^{-4} \quad (3)$$

provided that no complexes between  $\text{Hf}^{4+}$  and  $\text{TTA}^-$  are formed in the aqueous phase. Thus if the distribution ratio  $q^0$  is determined in a separate experiment with  $[\text{HF}] = 0$ , keeping both  $[\text{H}^+]$  and  $[\text{HTTA}]_{\text{org}}$  constant,  $X_{\text{H}}$  could be calculated from

$$X_{\text{H}} = q^0 q^{-1} \quad (4)$$

These derivations require that the activity factors are not altered in the two phases. This condition can be considered to be fulfilled concerning the aqueous phase, as this is mainly 4.00 M  $\text{HClO}_4$ . However, in the organic phase it was necessary to vary the concentration of HTTA, in order to extend the measurements to high ligand concentrations. As HTTA is the dominating species in this phase, the activity factors are altered. This has been corrected for. Assuming that  $f_{\text{Hf}(\text{TTA})_4} = f_{\text{HTTA}}$  the following expression is obtained

$$X_{\text{H}} = \frac{q^0}{q} \left( \frac{[\text{HTTA}]_{\text{org}}}{[\text{HTTA}]_{\text{org}}^0} \right)^4 \left( \frac{f_{\text{HTTA}}}{f_{\text{HTTA}}^0} \right)^3 \quad (5)$$

When  $[\text{HTTA}]_{\text{org}}$  was changed,  $q$  was always determined at some suitably chosen ligand concentrations, common to both of the used  $[\text{HTTA}]_{\text{org}}$  values. From these results  $f_{\text{HTTA}}/f_{\text{HTTA}}^0$  was calculated. Using this value of  $f_{\text{HTTA}}/f_{\text{HTTA}}^0$   $X_{\text{H}}$  could be calculated from the following determinations of  $q$  at the higher ligand concentrations corresponding to the new  $[\text{HTTA}]_{\text{org}}$  value etc.  $f_{\text{HTTA}}$  could also be calculated from  $f_{\text{HTTA}} = 1 - 0.24 [\text{HTTA}]_{\text{org}}^{0.48}$  (valid in benzene) given in Ref. 13. To within the experimental error, the value of  $f_{\text{HTTA}}/f_{\text{HTTA}}^0$  obtained equalled that calculated from Ref. 13, thus confirming the assumptions made.

Since the hafnium(IV) concentration used was very small in comparison with  $C_{\text{HTTA}}'$ , the mass balance equation for HTTA will be given by

$$C_{\text{HTTA}}' = [\text{HTTA}]_{\text{org}} + \frac{v}{v_{\text{org}}} ([\text{HTTA}] + [\text{TTA}^-]) \quad (6)$$

Introducing the distribution constant,  $K_d$ , and the acid dissociation constant for HTTA,  $K_a$ , into eqn. (6), we obtain

$$C_{\text{HTTA}}' = \left\{ 1 + \frac{v}{v_{\text{org}}} \frac{1}{K_d} \left( 1 + \frac{K_a}{[\text{H}^+]} \right) \right\} [\text{HTTA}]_{\text{org}} \quad (7)$$

As  $\frac{v}{v_{\text{org}}} \frac{1}{K_d} \left( 1 + \frac{K_a}{[\text{H}^+]} \right) \ll 1$ <sup>13, 14</sup> and  $\frac{v}{v_{\text{org}}}$  is varied only by 10 %

$$C_{\text{HTTA}}' = \text{const.} [\text{HTTA}]_{\text{org}} \quad (8)$$

Therefore  $X_{\text{H}}$  can be calculated using  $C_{\text{HTTA}}'$  instead of  $[\text{HTTA}]_{\text{org}}$  in eqn. (5).

From  $X_{\text{H}}$ , the constants,  $\beta_{\text{nH}}$  may be obtained by the extrapolation method of Fronæus,<sup>15</sup> if corresponding values of  $X_{\text{H}}$  and  $[\text{HF}]$  are known. By using a

value of  $C_M$  small in comparison with the total concentration of ligand, the part of  $C_{HF}$  bound in the complexes could be neglected. Since the distribution constant for HF is of the magnitude  $10^{-4}$ , cf. Ref. 9, no correction is necessary for the amount of hydrofluoric acid dissolved in the xylene phase. Thus  $C_{HF}' \approx [HF]$ .

#### SOLVENT EXTRACTION MEASUREMENTS, EXPERIMENTAL

*Chemicals.* The hafnium concentrations, at the very low concentrations used in the distribution experiments, were determined by radiometrical analysis. A mixture of approximately equal amounts of the nuclides  $^{175}\text{Hf}$  (EC;  $t_{1/2} = 70$  d) and  $^{181}\text{Hf}$  ( $\beta^-$ ;  $t_{1/2} = 42.5$  d) in hydrochloric acid were obtained from A.E.R.E. Harwell. The hydrochloric acid was removed by repeated evaporation of the mixture to dryness with concentrated perchloric acid. A radioactive stock solution was then prepared by dissolving the residue in a known volume of 4.00 M perchloric acid. The concentration of hafnium(IV) was calculated from the data given by the supplier. Many different stock solutions were made having hafnium concentrations ranging from  $4 \times 10^{-6}$  M to  $1.2 \times 10^{-5}$  M.

4.00 M solutions of HF and  $\text{HClO}_4$  were prepared from *pro analysi* concentrated acids. The concentration was determined by titrations against sodium hydroxide. When mixing hydrofluoric acid solutions with perchloric acid, only plastic pipettes and plastic vessels were used.

Thenoyltrifluoroacetone (Columbia Organic Chemicals Co., Inc.) was used without any further purification. Stock solutions were prepared by dissolving a known amount of HTTA in a known volume of xylene.

The xylene was of analytical grade having a boiling range of 138–139.2°C.

*Procedure.* In all the distribution experiments, equilibrium between the two phases was attained by mechanical shaking in a water thermostat at a temperature of  $20.00 \pm 0.05^\circ\text{C}$ . Since xylene penetrated the wall of ordinary plastic vessels, the measurements were performed using teflon tubes and teflon stoppers. Various volumes (0.100–0.500 ml) of an active hafnium(IV) stock solution was mixed with 5.00 ml of the ligand solutions and then 5.00 ml of a xylene solution, containing a known concentration of HTTA, was added. After shaking to equilibrium, the two liquid phases were separated by centrifugation and equal volumes (usually 3.00 ml) were taken for  $\gamma$ -counting.  $q$  was obtained from the ratio of the two counting rates. The  $\gamma$ -radiation accompanying the disintegration of the hafnium nuclides was measured with a scintillation detector (Landis & Gyr; EQP 3.1). More than 10 000 counts were recorded to keep the standard deviation of the counting rate less than 1%. In some experiments the mass balance relationship was checked and found to be satisfied. No variation in the  $\gamma$ -ray absorption with the composition of the phases was found. Equilibrium was attained in less than half an hour irregardless of whether the hafnium nuclides originally were in the aqueous or in the organic phase. Nevertheless a shaking time of 2 h was used in most of the experiments.

Table 1.  $q^0$  at different  $C_M'$ -values used in the solvent extraction measurements.  $C_{\text{HTTA}}' = 50.0$  mM,  $C_{\text{HClO}_4} = 4.00$  M,  $T = 20.0^\circ\text{C}$ .

$C_M' \times 10^6$ M	$q^0$
0.24	1.09
0.46	1.06
1.1	1.09

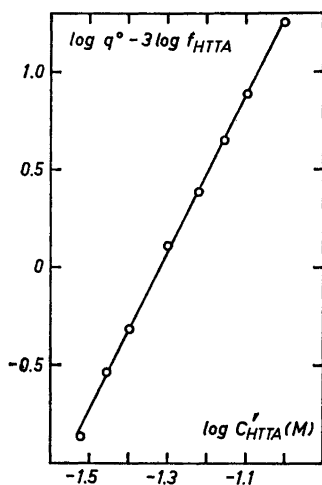


Fig. 1.  $\log q^0 - 3 \log f_{HTTA}$  as a function of  $\log C_{HTTA}'$ .  $C_M' = 1.6 \times 10^{-7}$  M. Aqueous phase: 4.00 M  $HClO_4$ .  $T = 20.0^\circ C$ .

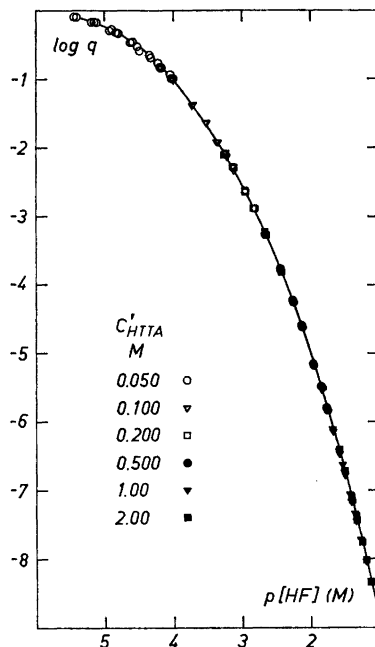


Fig. 2.  $\log q$ , normalized to  $C_{HTTA}' = 50.0$  mM, as a function of  $p[HF]$  (M). The curve was calculated using the stability constants obtained in the solvent extraction measurements.

No variation of  $q^0$  with  $C_M'$  was found, Table 1. Thus polynuclear hydroxocomplexes are not formed in the hafnium(IV) concentration range used.

To investigate the variation of  $q^0$  with  $[HTTA]_{org}$ , determinations of the distribution ratio were made; the aqueous phase was 4.00 M  $HClO_4$  and the concentration of HTTA in the xylene phase was varied. The result is given in Fig. 1, where  $\log q^0 - 3 \log f_{HTTA}$  is plotted against  $\log C_{HTTA}'$ . A straight line of slope  $4.00 \pm 0.08$  was obtained. This agrees with the assumptions made in the derivations.

#### SOLVENT EXTRACTION, RESULTS

The distribution ratios were determined with the total hafnium(IV) concentration within the range  $2.4 \times 10^{-7} M \leq C_M' \leq 1.1 \times 10^{-6} M$ . No variation of the  $q$  values with  $C_M'$  was observed. The experimental data of  $C_{HF}'$  and  $q$  at a selection of different values of  $C_{HTTA}'$  are given in Table 2.  $q^0$  was determined from separate experiments having  $C_{HTTA}' = 50.0$  mM. The mean value of nine determinations gave  $q^0 = 1.08 \pm 0.03$ . From these data,  $X_H$  was calculated according to eqn. (5).

At the largest hydrofluoric acid concentrations used,  $[H^+]$  was slightly lower than 4.00 M ( $[H^+] = 4.00 - C_{HF}'$  M). The effect on  $q$ , caused by this

Table 2. Corresponding values of  $C_{\text{HF}}' \times 10^4 \text{ M}$ ,  $q$ ,  $X_{\text{H}}$  and  $100(q \cdot q_{\text{calc}}^{-1} - 1)$  obtained in the solvent extraction measurements.  $2.4 \times 10^{-7} \leq C_{\text{M}}' \leq 1.1 \times 10^{-6} \text{ M}$ .  $C_{\text{HClO}_4} = 4.00 \text{ M}$ .  
 $T = 20.0^\circ\text{C}$ .

$C_{\text{HTTA}}' = 0.050 \text{ M}$

0.0364, 0.812, 1.33, -2; 0.0385, 0.812, 1.33, 0; 0.0392, 0.788, 1.37, -3; 0.0641, 0.676, 1.60, -3; 0.0654, 0.587, 1.84, -16; 0.0727, 0.681, 1.59, 2; 0.0769, 0.672, 1.61, 3; 0.0784, 0.639, 1.69, -2; 0.1212, 0.509, 2.12, -4; 0.1282, 0.530, 2.04, 3; 0.1307, 0.497, 2.17, -2; 0.1515, 0.477, 2.26, 2; 0.1602, 0.460, 2.35, 2; 0.1633, 0.438, 2.47, -2; 0.2424, 0.340, 3.18, -1; 0.2563, 0.349, 3.09, 6; 0.2614, 0.346, 3.12, 7; 0.3030, 0.295, 3.66, 2; 0.3202, 0.255, 4.24, -8; 0.3260, 0.268, 4.03, -2; 0.455, 0.219, 4.93, 7; 0.481, 0.204, 5.29, 5; 0.490, 0.193, 5.60, 0; 0.606, 0.169, 6.39, 8; 0.641, 0.147, 7.35, -1; 0.654, 0.143, 7.55, -1; 0.909, 0.114, 9.47, 11; 0.961, 0.101, 10.7, 4; 0.980, 0.100, 10.8, 6;

$C_{\text{HTTA}}' = 0.100 \text{ M}$ ,  $X_{\text{H}} \times 10^{-1}$

0.641, 2.09, 0.771, -5; 0.654, 2.14, 0.753, -1; 0.961, 1.46, 1.10, 1; 0.980, 1.42, 1.14, 1; 1.904, 0.613, 2.63, -3; 1.941, 0.627, 2.57, 2; 2.930, 0.349, 4.62, 1; 2.990, 0.347, 4.65, 4; 4.39, 0.177, 9.11, -5; 4.48, 0.177, 9.11, -2; 5.85, 0.114, 14.1, -1; 5.96, 0.111, 14.5, -1; 7.32, 0.0761, 21.2, -2; 7.47, 0.0695, 23.2, 0;

$C_{\text{HTTA}}' = 0.200 \text{ M}$ ,  $X_{\text{H}} \times 10^{-3}$

5.85, 1.70, 0.136, 2; 5.96, 1.72, 0.135, 7; 7.32, 1.12, 0.207, 0; 7.47, 1.09, 0.213, 1; 10.99, 0.517, 0.449, -1; 11.21, 0.493, 0.471, -2; 14.64, 0.286, 0.811, -2; 14.93, 0.285, 0.814, 2; 21.97, 0.124, 1.87, 2; 22.40, 0.117, 1.93, 1; 36.6, 0.0353, 6.48, 0; 37.3, 0.0343, 6.76, 0;

$C_{\text{HTTA}}' = 0.50 \text{ M}$ ,  $X_{\text{H}} \times 10^{-4}$

21.97, 3.91, 0.187, 2; 22.40, 3.70, 0.178, 1; 36.6, 1.13, 0.647, 0; 37.3, 1.09, 0.671, 1; 54.9, 0.404, 1.81, 4; 56.0, 0.378, 1.93, 2; 73.2, 0.172, 4.25, -1; 74.7, 0.162, 4.51, -1; 110.1, 0.0478, 15.3, -4; 112.3, 0.0451, 16.2, -3; 140.3, 0.0221, 33.1, -1; 143.0, 0.0215, 34.0, 2; 171.8, 0.0107, 68.3, -4; 175.2, 0.0101, 72.4, -4;

$C_{\text{HTTA}}' = 1.00 \text{ M}$ ,  $X_{\text{H}} \times 10^{-6}$

140.3, 0.267, 0.339, -4; 143.0, 0.256, 0.354, -2; 171.8, 0.133, 0.630, -4; 175.2, 0.121, 0.743, -6; 209.4, 0.0650, 1.39, -5; 213.5, 0.0598, 1.51, -6; 258.9, 0.0311, 2.91, 0; 264.0, 0.0234, 3.19, -2; 294.6, 0.0194, 4.66, 2; 312, 0.0153, 5.92, 0; 318, 0.0140, 6.46, -1; 370, 0.00717, 12.6, -8; 391, 0.00570, 15.9, -9; 437, 0.00370, 24.3, -7; 462, 0.00298, 30.5, -6; 533, 0.00155, 58.2, -11; 644, 0.000775, 116, -1; 756, 0.000383, 236, -2;

$C_{\text{HTTA}}' = 2.00 \text{ M}$ ,  $X_{\text{H}} \times 10^{-7}$

264.0, 0.358, 0.270, 15; 318, 0.169, 0.573, 11; 391, 0.0709, 1.36, 6; 399, 0.0636, 1.52, 3; 462, 0.0369, 2.63, 9; 471, 0.0322, 3.02, 3; 564, 0.0154, 6.29, 5; 644, 0.00855, 11.4, 2; 756, 0.00412, 23.6, -1; 986, 0.00124, 78.1, -3;

deviation, was estimated to be well within the experimental error. Therefore, no correction for this varying hydrogen ion concentration was made.

From corresponding values of  $X_{\text{H}}$  and  $C_{\text{HF}}'$  ( $= [\text{HF}]$ ), the stability constants were calculated according to the extrapolation method developed by Fronæus.<sup>15</sup> The following constants were obtained:

$$\beta_{1\text{H}} = (0.83 \pm 0.05) \times 10^5 \text{ M}^{-1}$$

$$\beta_{2\text{H}} = (2.3 \pm 0.2) \times 10^8 \text{ M}^{-2}$$

$$\beta_{3\text{H}} = (0.5 \pm 0.1) \times 10^{11} \text{ M}^{-3}$$

$$\beta_{4\text{H}} = (3 \pm 1) \times 10^{12} \text{ M}^{-4}$$

$$\beta_{5\text{H}} = (5 \pm 3) \times 10^{13} \text{ M}^{-5}$$

The limits of error were estimated graphically. The distribution ratios were recalculated, using this set of constants, and the deviations from the experimental values are given in Table 2. In Fig. 2,  $\log q$  (normalized to  $C_{\text{HTTA}}' = 50.0$  mM) is shown as a function of  $p[\text{HF}]$ .

#### DERIVATION OF STABILITY CONSTANTS FROM THE EMF MEASUREMENTS

The emf  $E$  of the cell used may be written

$$E = E_c + RTF^{-1} \ln [\text{Fe}^{3+}] [\text{Fe}^{2+}]^{-1} \quad (9)$$

assuming constant activity coefficients.  $E_c$  denotes the sum of all constant terms in the exact thermodynamic expression for  $E$  including the diffusion potential of the cell. Introducing  $X_{\text{H}}^{\text{II}}$  and  $X_{\text{H}}^{\text{III}}$  eqn. (9) can be transformed to

$$E = E_c + RTF^{-1} \ln C_{\text{III}} C_{\text{II}}^{-1} X_{\text{H}}^{\text{II}} (X_{\text{H}}^{\text{III}})^{-1} \quad (10)$$

For the initial solution, before any ligand has been added, the emf  $E_0$  is

$$E_0 = E_c + RTF^{-1} \ln C_{\text{III}} \cdot C_{\text{II}}^{-1} \quad (11)$$

Thus, for the difference  $E_A = E_0 - E$ , we obtain from eqn. (10) and (11)

$$E_A = RTF^{-1} \ln X_{\text{H}}^{\text{III}} (X_{\text{H}}^{\text{II}})^{-1} \quad (12)$$

if  $E_c$  and also  $C_{\text{III}} C_{\text{II}}^{-1}$  are constant throughout a titration series. From eqn. (12) it follows that  $E_A$  is a function only of  $[\text{HF}]$ .

From the titration series, the function  $E_A(C_{\text{HF}})$  was obtained. This was found to be independent of the total iron concentrations used. Thus  $[\text{HF}] = C_{\text{HF}}$  in the measurements that have only Fe(III) and Fe(II) in the cell. In the titration series for Hf(IV) the same low iron concentrations were used. In this case the total ligand concentration could therefore be written

$$C_{\text{HF}} = [\text{HF}] + \bar{n} C_{\text{M}} \quad (13)$$

By intersecting the family of  $E_A(C_{\text{HF}})$  curves, with  $C_{\text{M}}$  as parameter, at some suitably chosen values of  $E_A$ , values of  $C_{\text{HF}}$  and  $C_{\text{M}}$  corresponding to the same  $[\text{HF}]$  are obtained.  $C_{\text{HF}}$  is then plotted as a function of  $C_{\text{M}}$ . A straight line, giving  $\bar{n}$  from the slope and  $[\text{HF}]$  from the intercept, ought to be obtained, provided that Hf(IV) does not form any polynuclear hydroxo or fluoride complexes. It must be assumed too, that no mixed complexes are formed between Hf(IV) and Fe(III) or Fe(II). The  $E_A(C_{\text{HF}})$  curve with  $C_{\text{M}} = 0$  (the "iron curve") will also give us the free ligand concentration.

It can be shown<sup>15,16</sup> that

$$\ln \frac{X_{\text{H}}}{X_{\text{H}0}} = \int_{[\text{HF}]_0}^{[\text{HF}]} \frac{\bar{n}}{[\text{HF}]} d[\text{HF}] \quad (14)$$

From the corresponding values of  $\bar{n}$  and  $[\text{HF}]$ , the integral is evaluated graphically to give corresponding values of  $X_{\text{H}} X_{\text{H}0}^{-1}$  and  $[\text{HF}]$ . Since

$$X_{\text{H}} X_{\text{H}0}^{-1} = \left( 1 + \sum_{n=1}^N \beta_{n\text{H}} [\text{HF}]^n \right) X_{\text{H}0}^{-1} \quad (15)$$

the constants,  $\beta_{nH}$ , can in principle be calculated by the well known extrapolation methods. However, the first complex,  $HfF^{3+}$ , is so easily formed that  $\bar{n}$  is  $> 1$  before measurable values of  $E_A$  are obtained. Hence  $X_{H0}^{-1}$  could not be determined from the extrapolation of  $X_{HI}X_{H0}^{-1}$  to  $[HF] = 0$ . Instead the new functions  $X_I$ ,  $X_{II}$  etc. are computed (cf. Ref. 11, p. 342). By extrapolation of these functions to  $[HF] = 0$ ,  $\beta_{IH}X_{H0}^{-1}$  and  $\beta_{2H}X_{H0}^{-1}$  etc. are obtained. From the constants,  $\beta_{nH}X_{H0}^{-1}$ , the consecutive constants,  $K_n^*$ , may finally be calculated.

### EMF MEASUREMENTS, EXPERIMENTAL

*Chemicals.* Stock solutions of hafnium(IV), 4.00 M in  $HClO_4$  were prepared from  $HfOCl_2 \cdot 8H_2O$  in a manner similar to that used for the radioactive stock solution. To avoid transforming the salt into a form which was difficult to dissolve, the last evaporation was not completely to dryness. The solutions were analysed by EDTA titrations using  $Bi^{3+}$  as a back titrating agent according to the method of Fritz and Johnsson.<sup>17</sup> The stock solutions gave no  $AgCl$  precipitate with 0.5 M  $AgNO_3$ . The  $HfOCl_2 \cdot 8H_2O$  used was supplied by Johnsson, Matthey & Co., London, and was reported to be spectrographically pure. An X-ray spectrographic analysis done by the supplier gave a zirconium content of 0.6%. Other impurities found were Si, Al, Mg, Cu, and Mn present in amounts less than 10 ppm. More than 40 different elements were specifically sought but not detected. No corrections to the calculations were made for the zirconium impurity.

A solution of  $Fe^{2+}$  was prepared by dissolving a known amount of iron, *pro analysi*, in 4.00 M  $HClO_4$ . A portion of this solution was taken and oxidized to  $Fe^{3+}$  using hydrogen peroxide. The excess of hydrogen peroxide was carefully destroyed by boiling the solution. The concentration of  $HClO_4$  was then adjusted to 4.00 M.

*Procedure.* Cells having the following composition were used

-Ag,AgCl	0.0100 M HCl 3.99 M $HClO_4$	4.00 M $HClO_4$	$C_{III}$ mM Fe(III) $C_{II}$ mM Fe(II) $C_M$ mM Hf(IV) $C_{HF}$ mM HF 4.00 M $HClO_4$	Au,Pt +
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The emf of these cells was measured with a Norma precision compensation bridge type 54 connected to a Kipp lightspot galvanometer type AL 2. With freshly plated gold electrodes the sensitivity was better than 0.01 mV. The right-hand electrode vessel as well as the salt bridge and gas inlet tube were made from plastic material. The cell was placed in a water thermostat at  $20.00 \pm 0.02^\circ C$ . A stream of oxygen free nitrogen was passed through the solution in the right-hand halfcell during the course of a titration. During 20 h the emf of the cell did not change by more than 0.10 mV. The oxidation of  $Fe^{2+}$  to  $Fe^{3+}$ , during a titration, could therefore be neglected. At low values of  $C_{HF}$  and  $C_M$ ,  $E_A$  could be reproduced within  $\pm 0.01$  mV. Over  $E_A = 10$  mV  $|dE_A|E_A^{-1}$  was 0.003–0.01.

The initial solution in the right-hand half cell was prepared by adding 10.00 ml of  $T_1$  to 10.00 ml 4.00 M  $HClO_4$ . The emf,  $E_0$ , was measured. The titration was then started by adding equal volumes of the two solutions  $T_1$  and  $T_2$  having the compositions

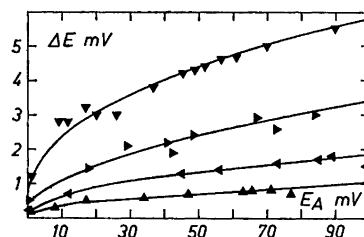
$$T_1: 2 C_{III} \text{ mM Fe(III)}, 2 C_{II} \text{ mM Fe(II)}, 2 C_M \text{ mM Hf(IV)}, 4.00 \text{ M } HClO_4,$$

$$T_2: C_{HF} \text{ mM HF}, 4.00 \text{ M } HClO_4,$$

and the emf,  $E'$ , was measured. The additions were made from plastic pipettes with an accuracy better than 0.2%.  $T_1$  was prepared from the stock solutions mentioned above. In the titration series performed without Hf(IV) in solution  $T_1$ ,  $C_{III}C_{II}^{-1}$  was 0.77. The  $E_A(C_{HF})$  curves obtained were independent of  $C_{III}$  in the concentration range, 0.364 mM  $\leq C_{III} \leq 1.45$  mM.



Fig. 3.  $\Delta E$  as a function of  $E_A$  with  $C_M$  as parameter.  $C_{\text{III}} = 0.379$  mM,  $C_{\text{II}} = 0.474$  mM. The signs refer to the following concentrations (in mM) of Hf(IV): 11.18  $\blacktriangle$ ; 23.3  $\blacktriangleleft$ ; 46.6  $\blacktriangleright$ ; 93.2  $\blacktriangledown$ .



To investigate the Hf(IV) complexes formed at high ligand concentrations, it was necessary to increase the hafnium(IV) concentration to about 100 mM. At these high values of  $C_M$ , the emf was slightly influenced by the hydrogen ions set free when the fluoride complexes were formed. However,  $\bar{n}$  could be calculated approximately from the titration curves obtained. By using this  $\bar{n}$ -value, additions of water to  $T_1$  and  $T_2$  were calculated to give solutions with  $[\text{H}]^+ = 4.00$  M and the emf,  $E$ , was measured. From measurements at the same  $C_M$  and  $C_{\text{HF}}$ , the correction  $\Delta E$ , was calculated according to the following relationships

$$E_A' = E_0 - E' \quad (16)$$

$$E_A = E_0 - E \quad (17)$$

$$\Delta E = E_A - E_A' \quad (18)$$

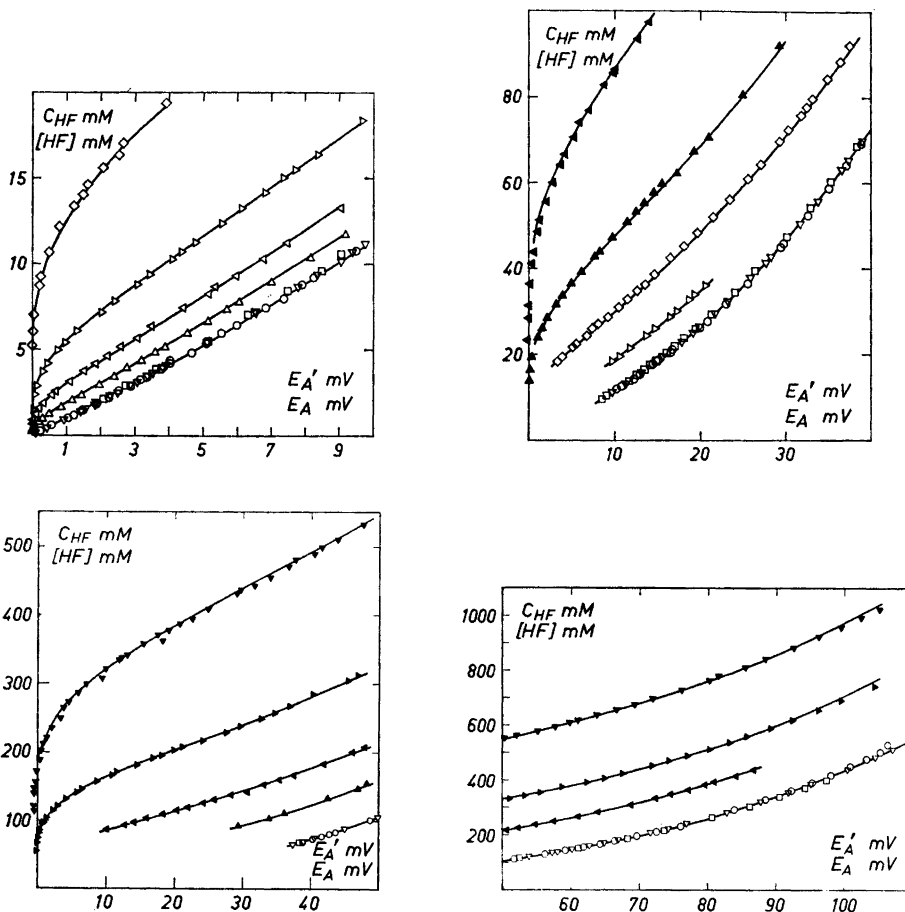
In Fig. 3,  $\Delta E$  is given as a function of  $E_A$  for the highest  $C_M$  values used.

#### EMF MEASUREMENTS, RESULTS

The measured  $E_A$  values, obtained from titration series of solutions containing no Hf(IV), are given in Figs. 4, 5, 6, and 7. Under the present conditions, the fluoride complexes formed by  $\text{Fe}^{2+}$  may be neglected,<sup>18</sup> *i.e.*  $X_{\text{H}}^{\text{II}} = 1$ . Thus  $X_{\text{H}}^{\text{III}}([\text{HF}])$  could be calculated from eqn. (12), giving the stability constants  $\beta_{\text{HF}}^{\text{III}} = 40.3 \pm 0.7$  M<sup>-1</sup> and  $\beta_{2\text{HF}}^{\text{III}} = 180 \pm 3$  M<sup>-2</sup> for the fluoride complexes of  $\text{Fe}^{3+}$ . The lowest curve in Figs. 4, 5, 6, and 7 is calculated using these values.

The experimental data of  $C_{\text{HF}}$  and  $E_A'$ , obtained at various  $C_M$  values, are shown in Figs. 4, 5, 6, and 7. Suitable  $E_A$  values were chosen and  $E_A'$  was calculated from  $\Delta E$  taken from Fig. 3. Values of  $C_{\text{HF}}$  and  $C_M$ , corresponding to the various  $E_A$ -values selected, were then obtained from Figs. 4, 5, 6, and 7. Using these,  $\bar{n}$  and  $[\text{HF}]$  were determined graphically according to eqn. (13). The correction,  $\Delta E$ , was large for high values of  $C_M$  and small ligand concentrations. Thus for  $[\text{HF}] < 1$  mM only results from titration series having  $C_M \leq 5.83$  mM were used. The corresponding  $[\text{HF}]$  and  $\bar{n}$ -values, so obtained, are given in Table 3. Since no systematic variation of  $\bar{n}$  with  $C_M$  is observed, it may be concluded that no polynuclear complexes are formed under the present conditions. The error limits were estimated to less than  $\pm 2\%$  in both  $[\text{HF}]$  and  $\bar{n}$  except for the last four points. The variation of  $\bar{n}$  here was about  $\pm 4\%$ .

The lower limit for the graphical evaluation of the integral in eqn. (14) was chosen to be  $[\text{HF}] = 0.092$  mM. No value of  $X_{\text{H}0}^{-1} \neq 0$  could be obtained from plotting  $X_{\text{H}} X_{\text{H}0}^{-1}$  against  $[\text{HF}]$ . Since  $X_{\text{H}0}^{-1}$  obviously is  $< 1$ , it was



Figs. 4, 5, 6, and 7. The connection between  $C_{\text{HF}}$  and  $E_A'(E_A)$ . For the lowest curve  $C_{\text{M}} = 0$ . For this curve, the signs refer to the following concentrations (in mM) of  $C_{\text{III}}$  and  $C_{\text{II}}$ : 0.364, 0.474,  $\circ$ ; 0.727, 0.947,  $\nabla$ ; 1.45, 1.89,  $\square$ . All the other curves were obtained in titration series having  $C_{\text{III}} = 0.379$  mM,  $C_{\text{II}} = 0.474$  mM and the following concentrations (in mM) of Hf(IV): 0.466,  $\triangle$ ; 1.044,  $\triangleleft$ ; 2.33,  $\triangleright$ ; 5.83,  $\diamond$ ; 11.18,  $\blacktriangle$ ; 23.3,  $\blacktriangleleft$ ; 46.6,  $\blacktriangleright$ ; 93.2,  $\blacktriangledown$ . The curves have been calculated using the constants obtained.

neglected in the calculations of  $X_{\text{I}}$ . When the functions  $X_{\text{I}}$ ,  $X_{\text{II}}$  etc. were extrapolated to  $[\text{HF}] = 0$ , the following constants were obtained

$$\begin{aligned} \beta_{1\text{H}}X_{\text{H}0}^{-1} &= (0.8 \pm 0.1) \times 10^4 \text{ M}^{-1} \\ \beta_{2\text{H}}X_{\text{H}0}^{-1} &= (2.2 \pm 0.1) \times 10^7 \text{ M}^{-2} \\ \beta_{3\text{H}}X_{\text{H}0}^{-1} &= (0.60 \pm 0.04) \times 10^{10} \text{ M}^{-3} \\ \beta_{4\text{H}}X_{\text{H}0}^{-1} &= (2.5 \pm 0.2) \times 10^{11} \text{ M}^{-4} \\ \beta_{5\text{H}}X_{\text{H}0}^{-1} &= (3.0 \pm 0.4) \times 10^{12} \text{ M}^{-5} \\ \beta_{6\text{H}}X_{\text{H}0}^{-1} &= (2 \pm 1) \times 10^{12} \text{ M}^{-6} \end{aligned}$$

Table 3. Corresponding values of  $\bar{n}$  and [HF] found from the emf measurements and the functions  $X_I$ ,  $X_{II}$ ,  $X_{III}$ ,  $X_{IV}$ ,  $X_V$ , and  $X_{VI}$  hence calculated.

$E_A$ mV	[HF] mM	$\bar{n}$	$X_I \times 10^{-7}$ M <sup>-1</sup>	$X_{II} \times 10^{-9}$ M <sup>-2</sup>	$X_{III} \times 10^{-10}$ M <sup>-3</sup>	$X_{IV} \times 10^{-11}$ M <sup>-4</sup>	$X_V \times 10^{-12}$ M <sup>-5</sup>	$X_{VI} \times 10^{-12}$ M <sup>-6</sup>
	0.000		0.00076	0.0224	0.600	2.45	3.05	2.0
0.10	0.092	1.05	0.00109					
0.25	0.230	1.35	0.00136					
0.50	0.457	1.69	0.00191	0.0252				
0.75	0.694	1.84	0.00263	0.0269				
1.00	0.928	1.97	0.00341	0.0286				
1.50	1.461	2.09	0.00550	0.0324	0.684			
2.00	1.987	2.23	0.00790	0.0359	0.679			
2.50	2.516	2.35	0.01070	0.0395	0.680			
3.00	3.053	2.43	0.01400	0.0434	0.688			
3.50	3.585	2.51	0.01767	0.0472	0.691			
4.00	4.150	2.59	0.02216	0.0516	0.703			
5.00	5.32	2.70	0.03340	0.0614	0.732			
6.00	6.50	2.81	0.04746	0.0719	0.761			
7.00	7.72	2.91	0.06540	0.0837	0.794			
8.00	8.92	2.99	0.08673	0.0964	0.830			
9.00	10.19	3.06	0.1135	0.1106	0.866			
10.00	11.51	3.14	0.1467	0.1268	0.907			
12.00	14.18	3.26	0.2321	0.1632	0.993			
14.00	16.99	3.38	0.3530	0.2073	1.088	2.87		
16.00	20.01	3.49	0.5257	0.2623	1.199	2.99		
18.00	23.31	3.58	0.7752	0.3322	1.329	3.13		
20.00	26.49	3.66	1.085	0.4093	1.461	3.25		
22.00	30.24	3.74	1.553	0.5133	1.623	3.38		
24.00	34.15	3.80	2.177	0.6373	1.800	3.51	3.12	
26.00	38.23	3.87	3.000	0.7845	1.993	3.64	3.12	
28.00	42.40	3.92	4.052	0.9554	2.200	3.77	3.12	
30.00	46.91	3.99	5.464	1.165	2.436	3.91	3.12	
34.00	56.6	4.10	9.714	1.716	2.992	4.23	3.14	
38.00	67.3	4.20	16.76	2.490	3.667	4.56	3.13	
42.00	79.5	4.30	28.77	3.619	4.524	4.94	3.13	
46.00	91.3	4.40	45.74	5.010	5.463	5.33	3.15	
50.00	105.9	4.47	76.27	7.202	6.780	5.84	3.20	
54.00	121.2	4.56	122.7	10.12	8.333	6.38	3.24	
58.00	138.0	4.62	195.9	14.20	10.28	7.01	3.31	1.9
62.00	156.6	4.67	311.0	19.86	12.67	7.71	3.36	2.0
66.00	177.0	4.73	489.8	27.67	15.62	8.49	3.41	2.0
70.00	198.7	4.78	756.9	38.09	19.16	9.34	3.47	2.1
74.00	222.7	4.82	1169	52.49	23.56	10.31	3.53	2.2
78.00	249.3	4.85	1803	72.32	29.00	11.39	3.59	2.2
82.00	276.9	4.89	2709	97.83	35.32	12.54	3.64	2.1
86.00	306.7	4.94	4046	131.9	43.01	13.83	3.71	2.2
90.00	338.6	4.98	5992	177.0	52.27	15.26	3.78	2.2
94.00	373.3	4.99	8848	237.0	63.49	16.85	3.86	2.2
98.00	411.1	5.00	13010	316.5	76.99	18.58	3.92	2.1
102.0	453.6	4.97	19280	425.0	93.70	20.52	3.99	2.1
106.0	502	4.90	28760	572.9	114.1	22.61	4.02	1.9
110.0	558	4.96	43620	781.7	140.1	25.00	4.04	1.8

The curves in Figs. 4, 5, 6, and 7 were calculated using these values. For the lowest [HF] values, a small correction (< 10 %) was done for the [Hf<sup>4+</sup>] still present, by using the  $\beta_{1H}$ -value obtained in the solvent extraction measurements. This correction decreased rapidly and was < 1 % when [HF] > 0.5 mM.

## DISCUSSION

The constants,  $K_n^*$ , obtained in this investigation are given in Table 4 together with corresponding constants found by Varga and Hume<sup>9,10</sup> for 3.00 M HClO<sub>4</sub>. The distribution of hafnium(IV) between the different com-

Table 4. The stability constants  $K_n^*$  for the fluoride system of hafnium(IV) in 4 M perchloric acid at 20°C. The results of Varga and Hume,<sup>9,10</sup> also given, are valid in 3 M perchloric acid at 25°C.

Ref.	Method	$K_1^* \times 10^{-5}$	$K_2^* \times 10^{-4}$	$K_3^* \times 10^{-3}$	$K_4^* \times 10^{-2}$	$K_5^* \times 10^{-2}$	$K_6^*$
This work	extr. HTTA	3.3 ± 0.2	1.1 ± 0.2	0.9 ± 0.3	2 ± 1	0.7 ± 0.5	
	emf		1.2 ± 0.4	1.1 ± 0.2	1.6 ± 0.3	0.5 ± 0.1	3 ± 2
Ref. 9	extr. HTTA	0.79 ± 0.09	0.40 ± 0.16	1.31 ± 0.78	3.0 ± 1.6		
Ref. 10	extr. TOPO	0.44 ± 0.08	1.28 ± 0.34	0.61 ± 0.21	2.6 ± 0.9		

plexes, HfF<sub>n</sub>, obtained from the solvent extraction and emf measurements is shown in Fig. 8.

The solvent extraction method gives uncertain results at high ligand concentrations, where extreme distribution ratios are obtained and large corrections have to be applied for the variation of the activity factors in the xylene phase. The emf measurements give no information about the first stability constant. Furthermore, the extrapolation of  $X_1$ , giving  $\beta_{1H}X_{H0}^{-1}$ , is determined mainly by the lowest  $E_A$ -values, making this intercept rather uncertain. On the other hand the values of  $\beta_{2H}X_{H0}^{-1}$ ,  $\beta_{3H}X_{H0}^{-1}$ , etc. may be determined having small limits of error. One should therefore expect the two methods both to give good results only in the ligand concentration range  $4 \times 10^{-4} \text{ M} < [\text{HF}] < 4 \times 10^{-3} \text{ M}$ . It is seen in Fig. 8, that the results do in fact coincide in this interval, proving that systematic errors can be excluded. The solvent extraction measurements have good accuracy at low ligand concentrations but poor at high ones, while the contrary is true of the emf measurements. Hence it is reasonable to select a common set of constants. The following are considered to be the best set:

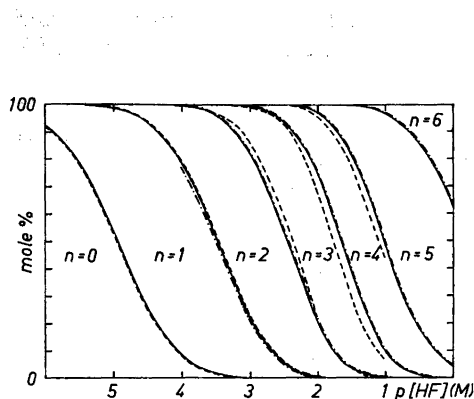


Fig. 8. The distribution of hafnium(IV) between different fluoride complexes,  $\text{HfF}_n$ . The full drawn curves were calculated using  $K_1^* = 3.3 \times 10^5$ ,  $K_2^* = 1.1 \times 10^4$ ,  $K_3^* = 1.1 \times 10^3$ ,  $K_4^* = 1.6 \times 10^2$ , and  $K_5^* = 0.5 \times 10^2$ , and  $K_6^* = 3$ . The curves marked ----- and -.-.- were calculated from the stability constants obtained in the solvent extraction and emf measurements, respectively.

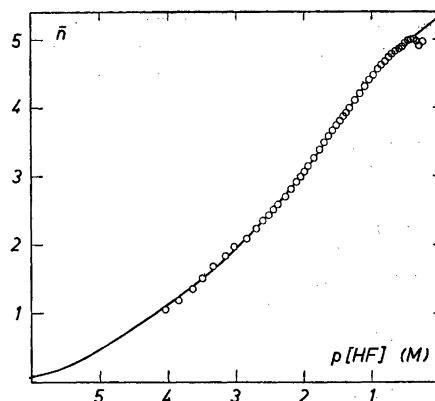


Fig. 9. The complex formation curve for the hafnium(IV) fluoride system valid at  $I = 4.00 \text{ M}$  and  $T = 20.0^\circ\text{C}$ . The curve was calculated from the constants:  $K_1^* = 3.3 \times 10^5$ ;  $K_2^* = 1.1 \times 10^4$ ;  $K_3^* = 1.1 \times 10^3$ ;  $K_4^* = 1.6 \times 10^2$ ;  $K_5^* = 0.5 \times 10^2$ , and  $K_6^* = 3$ . The circles represent corresponding values of  $\bar{n}$  and  $[\text{HF}]$  obtained in the emf measurements.

$$\begin{aligned} K_1^* &= (3.3 \pm 0.2) \times 10^5 \\ K_2^* &= (1.1 \pm 0.2) \times 10^4 \\ K_3^* &= (1.1 \pm 0.2) \times 10^3 \\ K_4^* &= (1.6 \pm 0.3) \times 10^2 \\ K_5^* &= (0.5 \pm 0.1) \times 10^2 \\ K_6^* &= 3 \pm 2 \end{aligned}$$

The full drawn curves in Figs. 8 and 9 are calculated using these.

The values found by Varga and Hume<sup>9,10</sup> in 3 M perchloric acid at  $25^\circ\text{C}$  are also included in Table 4. In Ref. 9 they used solvent extraction with HTTA and also emf measurements with quinhydrone electrode. In the latter measurements, the change in emf, caused by the change of hydrogen ion concentration due to the reaction between Hf(IV) and HF, was determined. Since the hafnium(IV) concentration was only 1 mM and the measurements were performed in 3 M  $\text{HClO}_4$ , the emf change was never more than 0.03 mV. This experimental approach is questionable and no confidence may be placed on the constants obtained. Therefore the stability constants determined are to be considered to be obtained only from the solvent extraction data. In the other solvent extraction investigation reported,<sup>10</sup> the partition reaction is more complicated than when HTTA is used. Several species are extracted into the organic phase, introducing new parameters in the calculations. No evidence for the formation of  $\text{HfF}_5^-$  was found. On the other hand  $\text{HfF}_6^{2-}$

was reported to be formed with  $\beta_6^* = (3.1 \pm 0.5) \times 10^{15}$ . From the emf results in the present work it may confidently be concluded that both a fifth and a sixth complex are formed.

The  $K_1^*$  value found in the present investigation is higher than those found by Varga and Hume. This may be attributed to the different media used. For the corresponding constants for the fluoride and sulphate complexes of Zr(IV) and the sulphate complexes of Np(IV) the same increase with the acidity is observed, cf. Refs. 1, 11, 19 and 20. The cation exchange investigation of the fluoride complexes of Zr(IV)<sup>1</sup> was performed using the same medium as was used here. Since only  $K_1^*$  and  $K_2^*$  were determined, a complementary investigation, using the "ferric" method, is planned for Zr(IV) also. A comparison of the stability constants for the fluoride complexes of Hf(IV) and Zr(IV) is postponed therefore, until the results of this investigation are available.

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