

The Fluoride Complexes of Hafnium(IV)

II. Determination of the Stability Constants by the Cation Exchange Method

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The fluoride complexes of hafnium(IV) have been studied by using the cation exchange method. The measurements have been performed in a 4 M perchloric acid medium and at a temperature of 20°C. From the data the stability constants K_1^* and K_2^* were determined. These results are compared with those obtained from the solvent extraction and emf measurements reported previously.

The fluoride complexes formed by hafnium(IV) have been investigated earlier by using both solvent extraction and emf measurements.¹ From the solvent extraction results the stability constants K_n^* ($1 \leq n \leq 5$) could be determined. From the emf measurements the stability constants starting with $n = 2$ were obtained. Since K_1^* is determined from solvent extraction measurements only, it was considered valuable to determine this constant by means of another method. The cation exchange method developed by Frønaes²⁻⁴ was therefore used in the present investigation.

CALCULATION

By applying the law of mass action on the various equilibria involved, cf. Refs. 5 and 6, the following expression is obtained for the distribution, φ , of Hf(IV) between the cation exchanger and the solution:

$$\varphi = \frac{C_{MR}}{C_M} = l_0 \frac{1 + \sum_{n=1}^3 l_n^* [\text{HF}]^n}{1 + \sum_{n=1}^N \beta_{nH} [\text{HF}]^n} \quad (1)$$

In the derivation of eqn. (1), cationic species only are presumed to be taken up by the resin. Unless otherwise stated, the symbols used are the same as in Ref. 6.

According to the method originally developed by Fronæus, the stability constants, β_{nH} , were evaluated from the functions f and g , derived from eqn. (1). To avoid these complicated functions, Fronæus has developed another method of calculation which has recently been applied to the neptunium(IV) fluoride system by Ahrland and Brandt.⁷ The new method utilizes the fact that the ligand concentration is much smaller in the resin phase than in the outer solution at not too high concentrations of supporting electrolyte. Thus it is probable that the dominating species in the resin phase are the free metal ion and the first complex. Furthermore, reliable values of φ can be obtained only at relatively low ligand concentrations, where C_{MR} is still appreciable. As a consequence of the low ligand concentration in the outer solution, only the formation of the first three complexes have to be considered. Eqn. (1) may therefore very likely be approximated to:

$$\varphi = l_0 \frac{1 + l_1^* [\text{HF}]}{1 + \sum_{n=1}^3 \beta_{nH} [\text{HF}]^n} \quad (2)$$

With this assumption, the following expression is obtained for $\varphi_1 = \left\{ \frac{l_0}{\varphi} - 1 \right\} \frac{1}{[\text{HF}]}$:

$$\varphi_1 = \beta_{1H} - l_1^* + \{\beta_{2H} - l_1^* (\beta_{1H} - l_1^*)\} [\text{HF}] + \frac{K[\text{HF}]^2}{1 + l_1^* [\text{HF}]} \quad (3)$$

where

$$K = \beta_{3H} - l_1^* [\beta_{2H} - l_1^* (\beta_{1H} - l_1^*)] \quad (4)$$

It follows from eqn. (3) that the difference, Δ , between the curve $\varphi_1([\text{HF}]$) and its tangent for $[\text{HF}] = 0$ is:

$$\Delta = \frac{K[\text{HF}]^2}{1 + l_1^* [\text{HF}]} \quad (5)$$

By plotting $[\text{HF}]^2/\Delta$ vs. $[\text{HF}]$, a straight line should be obtained, with the intercept = $1/K$ and the slope = l_1^*/K . Hence l_1^* can be found. From the relations:

$$\lim_{[\text{HF}] \rightarrow 0} \varphi_1 = \varphi_1^0 = \beta_{1H} - l_1^* \quad (6)$$

and

$$\lim_{[\text{HF}] \rightarrow 0} \left(\frac{d\varphi_1}{d[\text{HF}]} \right) = (\varphi_1')^0 = \beta_{2H} - l_1^* (\beta_{1H} - l_1^*) \quad (7)$$

β_{1H} and β_{2H} are obtained. Finally, β_{3H} is calculated from eqn. (4).

EXPERIMENTAL

Chemicals. Unless otherwise stated, the stock solutions used were prepared in the same manner and from the same chemicals as described in Ref. 1.

The ion exchanger, Dowex 50 W \times 8, 50–100 mesh, was converted to the hydrogen form by repeated shaking with 5 M HCl. It was washed with demineralized water, until no chloride ions could be detected in the eluate, and was finally dried in air. The amount of exchangeable hydrogen ions was found to be 4.10 mequiv. g^{-1} and did not change during the course of the investigation.

Procedure. Equilibrium between the aqueous phase and the cation exchanger was attained by mechanical shaking in a water thermostat at a temperature of $20.00 \pm 0.05^\circ C$. All solutions containing fluoride were shaken in plastic vessels. The distribution ϕ was determined in solutions prepared by mixing 0.600 ml of active hafnium(IV) solution (containing various amounts of inactive Hf(IV)) with 10.00 ml of ligand solution. To these solutions, m g of ion exchanger was added ($0.500 \text{ g} \leq m \leq 2.000 \text{ g}$; 2.000 g was used for the highest ligand concentrations, *i.e.* the lowest values of ϕ). The swelling factor, δ , determined at various values of $v \cdot m^{-1}$, is given in Table 1. After shaking for 20 h, equilibrium had been attained, *cf.* Table 2. The activity of a 5.00 ml sample of the solution phase was then measured. Simultaneously 0.600 ml of the active hafnium(IV) solution used, made up to a total volume of 5.00 ml, was counted. Thus corrections, due to the decay and to the altering of the relative amounts of the two hafnium nuclides present (*cf.* Ref. 1) during the shaking time, were unnecessary. ϕ was calculated according to eqn. (18) in Ref. 6.

Table 1. The swelling factor, δ , in 4 M $HClO_4$ for air dried Dowex 50 W \times 8, 50–100 mesh at various values of $v \cdot m^{-1}$.
 $T = 20^\circ C$.

$v \cdot m^{-1} \times 10^3$ $l \cdot g^{-1}$	δ
24	0.991
12	0.983
6	0.967
2.4	0.925

Table 2. l_0 at different equilibration times. $C_{HClO_4} = 4.00 \text{ M}$, $C_M' = 2.0 \times 10^{-5} \text{ M}$,
 $T = 20^\circ C$, $v \cdot m^{-1} = 20 \times 10^{-3} \text{ l } g^{-1}$.

Hours	$l_0 \times 10^3$ $l \cdot g^{-1}$
20	54.3
47	53.4
70	53.8

Determination of l_0 at different hafnium(IV) concentrations.

For various reasons, the distribution l_0 of the free central ion may vary with C_M (*cf.* Ref. 6). To check this, l_0 has been determined for varying C_M up to $1.3 \times 10^{-3} \text{ M}$. The results, shown in Fig. 1, are consistent with those found for Zr(IV).⁵ Within the range $1.5 \times 10^{-6} \text{ M} \leq C_M \leq 4.0 \times 10^{-5} \text{ M}$, l_0 is independent of C_M . Evidently the resin is monofunctional at these low Hf(IV) concentrations. As C_M exceeds 10^{-4} M , l_0 starts to increase, but at a rate which is slower than that for Zr(IV). Clearly, the polynuclear hydroxo complexes of Hf(IV) are not formed as easily as those of Zr(IV).

RESULTS

The ϕ values, determined at various total hydrofluoric acid concentrations, are given in Table 3 for the three different C_M' investigated. Some of these data are also shown in Fig. 2. The course of the ϕ (C_{HF}) function is very similar to that found for the zirconium(IV) fluoride system, Ref. 6. The value of ϕ for $C_{HF} = 0$ is independent of C_M' . As fluoride is added, the ϕ -functions first diverge. As C_{HF} is increased further, they start to converge again,

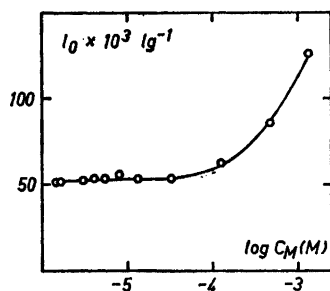


Fig. 1. l_0 as a function of $\log C_M$ for Dowex 50 W \times 8, 50–100 mesh. Exchange capacity: 4.10 mequiv. \times g^{-1} .

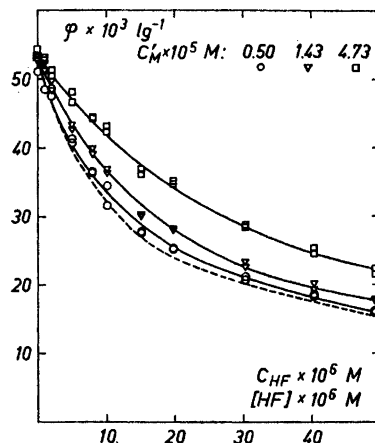


Fig. 2. ϕ as a function of C_{HF} at various values of C_M' . The signs refer to the following concentrations (in M) of C_M' : 0.50×10^{-5} \circ ; 1.43×10^{-5} ∇ ; 4.73×10^{-5} \square . Extrapolation to $C_M = 0$ gives ϕ as a function of $[HF]$, dashed curve.

finally to coincide for high ligand concentrations. Only within this range where $[HF] = C_{HF}$, the function ϕ ($[HF]$) is known *a priori*. For other values of C_{HF} it is obtained as follows. The family of ϕ (C_{HF}) curves are intersected

Table 3. Experimental values of $C_{HF} \times 10^6$ M and $\phi \times 10^3$ l \cdot g^{-1} for the ion exchange measurements determined at different C_M' values. Up to $C_{HF} = 80.7 \times 10^{-6}$ M, two determinations of ϕ were made. Ion exchanger: Dowex 50 W \times 8, 50–100 mesh; aqueous solution: 4.00 M $HClO_4$; $T = 20.0^\circ C$.

$C_M' = 0.50 \times 10^{-5}$ M:			
0.00,51.1,53.1;	0.99,48.5,51.4;	2.02,47.5,48.7;	5.05,40.7,41.3;
7.91,36.4,36.5;	10.1,31.6,34.5;	15.1,27.5,27.7;	19.8,25.3,25.4;
30.3,20.7,21.2;	40.4,18.3,18.5;	49.4,15.9,16.1;	80.7,12.7,13.0;
102,11.4;	200,7.97;	510,5.01;	1040,3.48;
2030,2.31;			
$C_M' = 1.43 \times 10^{-5}$ M:			
0.00,53.6,52.7;	0.99,51.3,52.3;	2.02,48.4,49.8;	5.05,43.3,42.6;
7.91,39.1,39.9;	10.1,36.3,36.9;	15.1,30.3,30.0;	19.8,28.3,28.1;
30.3,22.6,23.3;	40.4,20.1,19.2;	49.4,17.9,17.7;	80.7,13.4,13.7;
102,11.8	200,8.38;	510,5.08;	1040,3.58;
2030,2.43;			
$C_M' = 4.73 \times 10^{-5}$ M:			
0.00,53.3,54.3;	0.99,52.8,53.0;	2.02,50.5,51.3;	5.05,46.6,48.1;
7.91,44.5,44.5;	10.1,42.4,43.3;	15.1,36.2,36.9;	19.8,34.7,35.1;
30.3,28.7,28.5;	40.4,24.5,24.3;	49.4,22.4,21.6;	80.7,16.3,16.5;
102,13.4;	200,9.08;	510,5.31;	1040,3.52;
2030,2.42;			

Table 4. Corresponding values of φ and [HF]. The function φ_1 thus calculated. The deviations $100[(\varphi/\varphi_{\text{calc}}) - 1]$ calculated using the constants: $\beta_{1\text{H}} = 0.81 \times 10^5 \text{ M}^{-1}$; $\beta_{2\text{H}} = 1.0 \times 10^8 \text{ M}^{-2}$; $l_0 = 53.4 \times 10^{-3} \text{ l g}^{-1}$ and $l_1^* = 1.1 \times 10^4 \text{ M}^{-1}$.

$\varphi \times 10^3$ l g^{-1}	[HF] $\times 10^4$ M	$\varphi_1 \times 10^{-5}$ M^{-1}	$100[(\varphi/\varphi_{\text{calc}}) - 1]$
53.4	0	0.700	
50.0	0.0106	0.642	1
45.0	0.0274	0.681	0
40.0	0.0500	0.670	0
35.0	0.0790	0.665	-1
30.0	0.119	0.655	-2
25.0	0.182	0.624	-2
22.0	0.256	0.558	1
20.0	0.314	0.532	1
18.0	0.385	0.511	1
16.0	0.465	0.503	-1
14.0	0.580	0.485	-3
12.0	0.884	0.390	2
10.0	1.30	0.334	2
8.00	1.98	0.287	-1
6.00	3.33	0.237	-6
5.00	5.40	0.179	0
4.00	8.10	0.152	0
3.00	14.5	0.116	9

at constant values of φ , *i.e.* constant values of [HF], and C_{HF} then plotted as a function of C_{M} with φ as parameter. These straight lines are extrapolated to $C_{\text{M}} = 0$ giving, as intercept, the free ligand concentration, [HF], for the corresponding value of φ . The result is given in Table 4 and, as a dashed line, in Fig. 2.

l_0 was determined separately and was found to be $(53.4 \pm 0.9) \times 10^{-3} \text{ l g}^{-1}$. The same value of l_0 is obtained also from the extrapolation of φ to [HF] = 0. Using this value of l_0 , φ_1 is calculated. The results are given in Table 4 and partly shown in Fig. 3. By drawing the tangent to the φ_1 curve at [HF] = 0, it is now possible to obtain the differences, Δ . In Fig. 4 $[\text{HF}]^2/\Delta$ is plotted against [HF], giving $K^{-1} = (1.8 \pm 0.2) \times 10^{-13} \text{ M}^3$ and $l_1^*K^{-1} = (1.7 \pm 0.2) \times 10^{-9} \text{ M}^2$. From these values, $l_1^* = (1.0 \pm 0.2) \times 10^4 \text{ M}^{-1}$ is obtained, which, together with $\varphi_1^0 = (0.70 \pm 0.02) \times 10^5 \text{ M}^{-1}$, gives $\beta_{1\text{H}} = (0.80 \pm 0.04) \times 10^5 \text{ M}^{-1}$. The slope of the tangent in Fig. 3 yields a value of $\beta_{2\text{H}} - l_1^*(\beta_{1\text{H}} - l_1^*) = -(0.6 \pm 0.2) \times 10^9 \text{ M}^{-2}$. Then $\beta_{2\text{H}}$ is calculated and $\beta_{3\text{H}}$ according to eqn. (4). Unfortunately, both emerge as differences between almost equal quantities. Only for $\beta_{2\text{H}}$ a value is found, giving the order of magnitude for this constant as $\beta_{2\text{H}} \approx 10^8 \text{ M}^{-2}$.

As is evident from the course of the φ_1 function, the slope of the tangent, $(\varphi_1')^0$, is difficult to determine, *cf.* Fig. 3. The differences Δ are therefore uncertain and, consequently, the constants obtained from eqns. (5), (7), and (4) may be unreliable.

Another method of calculation has been proposed by Ahrlund and Brandt⁷ which presupposes that the third complex, HfF_3^+ , is not formed in appreci-

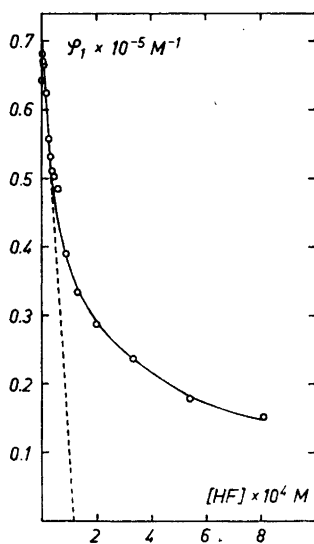


Fig. 3. φ_1 as a function of $[\text{HF}]$. The dashed line showing the tangent to the φ_1 curve at $[\text{HF}] = 0$.

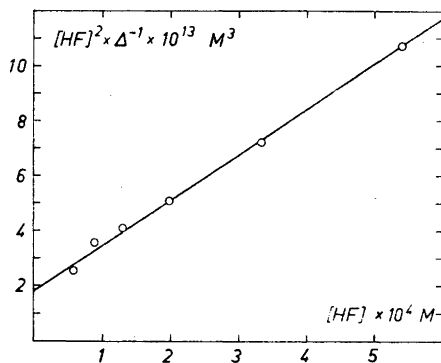


Fig. 4. $[\text{HF}]^2/\Delta$ as a function of $[\text{HF}]$, giving the constants l_1^* and K of eqn. (5).

able amounts within the ligand concentration range investigated. Since the results obtained so far confirm this assumption, the term $\beta_{3\text{H}}[\text{HF}]^3$ is neglected in eqn. (2), resulting in the following expression for φ :

$$\varphi = l_0 \frac{1 + l_1^* [\text{HF}]}{1 + \beta_{1\text{H}} [\text{HF}] + \beta_{2\text{H}} [\text{HF}]^2} \quad (8)$$

According to Ahrland and Brandt⁷ the constants, l_1^* , $\beta_{1\text{H}}$ and $\beta_{2\text{H}}$, can be determined from eqn. (8) via the function φ_2 :

$$\varphi_2 = \frac{l_0 - \varphi}{[\text{HF}]} - \beta_{1\text{H}} \varphi = -l_1^* l_0 + \beta_{2\text{H}} [\text{HF}] \quad (9)$$

The reiteration procedure, outlined in Ref. 7 for obtaining the constants, may be avoided, if $\beta_{1\text{H}}$ in eqn. (9) is substituted with $\varphi_1^0/l_0 + l_1^*$ (eqn. (6)). Eqn. (9) may then be transformed to:

$$\varphi_3 = \frac{1}{[\text{HF}]} - \frac{\varphi_1^0 \varphi}{l_0 - \varphi} = -l_1^* + \beta_{2\text{H}} \frac{\varphi[\text{HF}]}{l_0 - \varphi} \quad (10)$$

From the experimental data φ_3 can be calculated. Thus a straight line should be obtained from a plot of φ_3 against $\varphi[\text{HF}]/l_0 - \varphi$. The intercept and the slope of this line, shown in Fig. 5, yield $l_1^* = (1.1 \pm 0.2) \times 10^4 \text{ M}^{-1}$ and $\beta_{2\text{H}} = (1.0 \pm 0.3) \times 10^8 \text{ M}^{-2}$, respectively. Finally, $l_1^* = (1.1 \pm 0.2) \times 10^4 \text{ M}^{-1}$ is combined with $\varphi_1^0 = (0.70 \pm 0.02) \times 10^5 \text{ M}^{-1}$, giving $\beta_{1\text{H}} =$

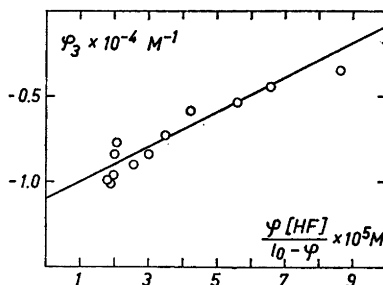


Fig. 5. φ_3 as a function of φ [HF] $(l_0 - \varphi)^{-1}$.

$= (0.81 \pm 0.04) \times 10^5 \text{ M}^{-1}$. It is obvious that the two graphical methods employed for the calculation of the constants give essentially the same results.

The deviations, $100[(\varphi/\varphi_{\text{calc}}) - 1]$, from the φ values found, are given in Table 4. φ_{calc} is calculated using the constants $\beta_{1\text{H}} = 0.81 \times 10^5 \text{ M}^{-1}$, $\beta_{2\text{H}} = 1.0 \times 10^8 \text{ M}^{-2}$, $l_0 = 53.4 \times 10^{-3} \text{ l g}^{-1}$ and $l_1^* = 1.1 \times 10^4 \text{ M}^{-1}$. Within the experimental limits of error, these constants give a quite satisfactory fit to the data.

DISCUSSION

In the present work, the constants $K_1^* = (3.2 \pm 0.2) \times 10^5$ and $K_2^* = (5 \pm 2) \times 10^3$ are obtained, *cf.* eqns. (4) and (9) of Ref. 6. The value of K_1^* , determined from the solvent extraction measurements reported in Ref. 1, is $K_1^* = (3.3 \pm 0.2) \times 10^5$. Thus, within the limits of error, both methods give consistent values for this constant. For the second stability constant K_2^* , a considerably smaller value is obtained from the present investigation than from both the solvent extraction ($K_2^* = (1.1 \pm 0.2) \times 10^4$) and the emf ($K_2^* = (1.2 \pm 0.4) \times 10^4$) measurements of Ref. 1. This certainly depends upon the rather high value of l_1^* . Since $(\varphi_1')^0$ is negative the largest term in eqn. (7) is $l_1^*(\beta_{1\text{H}} - l_1^*)$. A more accurate value for $\beta_{2\text{H}}$ (and K_2^*) should be obtained, if the conditions were chosen so that:

$$l_1^*(\beta_{1\text{H}} - l_1^*) < \beta_{2\text{H}} \quad (11)$$

or, approximately,

$$l_1^* < \beta_{2\text{H}}/\beta_{1\text{H}} \quad (12)$$

According to Fronæus,⁴ eqn. (12) can also be written as:

$$K' \frac{[\text{H}^+]}{[\text{H}^+]_{\text{R}}} < \frac{\beta_2}{\beta_1 \beta_{1\text{R}}} \quad (13)$$

where the symbols are defined by:

$$\begin{aligned} \beta_n &= [\text{HfF}_n]/[\text{Hf}^{4+}] [\text{F}^-]^n \\ \beta_{1\text{R}} &= [\text{HfF}]_{\text{R}}/[\text{Hf}^{4+}]_{\text{R}} [\text{F}^-]_{\text{R}} \\ K' &= [\text{H}^+]_{\text{R}} [\text{F}^-]_{\text{R}}/[\text{H}^+] [\text{F}^-] \quad (\text{the Donnan equation}) \end{aligned}$$

If the stability constants, for the two phases, are influenced only slightly by the composition of the phases, the right-hand side of eqn. (13) is a constant, which is defined for each system investigated. According to eqn. (13), we have to choose the experimental conditions so as to make $K'[\text{H}^+]/[\text{H}^+]_{\text{R}}$, if possibly, smaller than this constant. The quantity $K'[\text{H}^+]_{\text{R}}$ is connected with the properties of the cation exchanger, and should preferably be as small as possible. For the cation exchanger Dowex 50 W, it was found in Ref. 8, Table 9 that $K'[\text{H}^+]_{\text{R}} (= \lambda_1' \beta_{1\text{R}}/[\text{H}^+]; [\text{H}^+] = \text{constant} = 1.89 \text{ M})$ decreased with an increasing degree of cross-linking in the resin (if $\beta_{1\text{R}}$, for $\text{Bi}^{3+} \dots \text{Cl}^-$, is assumed to be independent of the degree of cross-linking). For the determination of stability constants it is thus advantageous to use a resin with a high degree of cross-linking. Dowex 50 W \times 16 would have been better than the present Dowex 50 W \times 8.

It follows from eqn. (13) that, for a given cation exchanger, it must be favourable to measure at a low concentration of supporting electrolyte, *i.e.* to keep $[\text{H}^+]$ low. For the present investigation the acidity had to be rather high (4 M HClO_4) in order to suppress the hydrolysis of Hf^{4+} . Moreover, fluoride systems are known⁹ to have unusually low values of the ratios β_2/β_1^2 . Presumably the same is true for the ratios $\beta_2/\beta_1\beta_{1\text{R}}$. Also for this reason, it is difficult to fulfill eqn. (13).

All these factors, acting together, will make the determination of $\beta_{2\text{H}}$ for the present system unfavourable.

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