A Calorimetric Study of the Mononuclear Fluoride Complexes of Zirconium(IV), Hafnium(IV), Thorium(IV) and Uranium(IV)

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By combining earlier stability studies with the calorimetric measurements of the present investigation, the thermodynamics of the fluoride complex formation of the tetravalent ions Zr^{4+}, Hf^{4+}, Th^{4+} and U^{4+} have been determined. The high stabilities of the complexes formed according to the reaction $MF_{n-1}^{4-n+1} + F^- \rightleftharpoons MF_n^{4-n}$ are for the steps (1)–(3) due to very positive entropy changes, while the enthalpy changes are small, exothermic or endothermic. These steps are evidently characterized by an extensive dehydration which on the whole provides the large decrease of Gibbs energy observed. For the fourth step the entropy gain is much smaller; on the other hand, the reactions are fairly exothermic. Most of the dehydration has evidently taken place before this complex is formed. Because metal ions are more strongly hydrated the smaller they are, the entropy gains due to dehydration should be larger, the smaller the ionic radius. In most cases this is indeed observed; the possible reason for an exception found for the second step of U^{4+} is discussed. Finally, entropy gains for the formation of neutral fluoride complexes have been compiled for a few representative acceptors, and the dependence of these gains upon the charges and radii of the acceptors is discussed.

In a previous paper,[1] one of the present authors has compared the stabilities of fluoride complexes of tetravalent metal ions belonging to two different classes of transition elements, viz. Zr^{4+}, Hf^{4+} and Th^{4+}, U^{4+}, Np^{4+}. As these ions are very prone to hydrolysis in aqueous solution, a strongly acid medium was chosen, viz. 4 M perchloric acid. In this medium, the hydrolysis of the actinide ions is virtually suppressed.[2] Also, the hydrolysis of Hf^{4+} is almost negligible, while that of Zr^{4+} amounts to a few percent in solutions free from fluoride.[3,4] At this acidity, the equilibria actually existing are:

$$MF_{n-1}^{4-n+1} + HF \rightleftharpoons MF_n^{4-n} + H^+ \quad n = 1 \rightarrow N$$

where N is the highest number of F^- ions attached. The constants experimentally determined refer to these equilibria. For a comparison between the affinities of water and fluoride for the M^{4+} ions, it is more rational, however, to consider the equilibria:

$$MF_{n-1}^{4-n+1} + F^- \rightleftharpoons MF_n^{4-n}$$
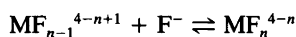
Their stability constants can evidently be calculated once the dissociation constant of hydrofluoric acid in the present medium is known.

It is generally found, however, that from stabilities alone, the factors of importance for the complex formation are difficult to discern. More, and safer, conclusions could

be drawn from a discussion of the enthalpy and entropy functions.[5–8] The present study therefore aims at the determination of these functions for four of the fluoride systems mentioned, viz. those of Zr^{4+}, Hf^{4+}, Th^{4+} and U^{4+}. On account of severe experimental difficulties, Np^{4+} was omitted.

The earlier measurements have generally been performed at 20 °C; for the present measurements the standard temperature 25 °C has been chosen. The stabilities previously determined have been recalculated accordingly.

Symbols[†]

C_M, C_{HF} = total concentrations of metal ion and hydrofluoric acid;

$\bar{n} = (C_{HF} - [HF])/C_M$ = ligand number;

$^*\beta_n = [MF_n][H]^n/[M][HF]^n$; $\beta_{nH} = {}^*\beta_n/[H]^n$;

$^*K_n = [MF_n][H]/[MF_{n-1}][HF]$; $^*K_1 = {}^*\beta_1$;
$K_n = [MF_n]/[MF_{n-1}][F]$;

Q_{exp} = heat change on addition of titrant (>0 if heat is evolved);

$Q_{corr} = Q_{exp} - Q_{dil}$ = heat change corrected for heat of dilution;

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† Charges omitted for simplicity.

V_0 = initial volume (ml) of the solution in the reaction vessel;

v = volume (ml) of titrant added; $V = V_0 + v$;

ε_V = heat equivalent (J Ω^{-1}) of the calorimeter system at the volume V;

$\Delta h_v = -\Sigma 1000\ Q_{corr}/C_M V$ = total molar heat change after addition of v;

$*\Delta G°_n$, $*\Delta H°_n$, $*\Delta S°_n$ = changes of Gibbs energy, enthalpy and entropy in the standard state for the reaction $MF_{n-1} + HF \rightleftharpoons MF_n + H$;

$\Delta G°_n$, $\Delta H°_n$, $\Delta S°_n$ = changes of Gibbs energy, enthalpy and entropy in the standard state for the reaction $MF_{n-1} + F \rightleftharpoons MF_n$.

Derivation of the enthalpy changes from the measurements

For the present measurements the conditions have been such that the concentration of the species F^- and HF_2^- could be neglected in comparison with the concentration of fluoride bonded in metal complexes and undissociated hydrofluoric acid.[9] Disregarding the formation of hydroxo and polynuclear metal complexes, the following mass balance equations are obtained:

$$C_{HF} = [HF] + [M] \sum_{n=1}^{N} n\ \beta_{nH} [HF]^n \qquad (1)$$

$$C_M = [M] (1 + \sum_{n=1}^{N} \beta_{nH} [HF]^n) = [M] X_H \qquad (2)$$

The stepwise enthalpy changes are related to the experimentally determined heat changes according to eqn. (3):[13]

$$\Delta h_v = \sum_{n=1}^{N} \sum_{k=1}^{n} \alpha_n *\Delta H°_k \qquad (3)$$

where

$$\alpha_n = \beta_{nH}[HF]^n / X_H \qquad (4)$$

The least-squares computer program, KALORI,[10] founded on these relationships, has been used for the evaluation of the values of $*\Delta H°_n$.

Experimental

Chemicals. Stock solutions of Hf(IV) were prepared from spectrographically pure $HfOCl_2 \cdot 8H_2O$ supplied by Johnson Matthey & Co., London. The stated zirconium content of this salt was <0.5 mass %, which did not warrant any

correction of the measured value of Δh_v. Other impurities were reported to be present only in ppm amounts. All other chemicals used were of analytical grade. The preparation and analysis of the stock solutions were performed as described previously,[1,11,12] except that the concentrations of free acid, C_H, in the primary stock solutions of Zr(IV) and Hf(IV) were determined in the same manner as for Th(IV).[1] Titration solutions having different values of C_M were prepared by dilution with perchloric acid so that the free acid concentration was 4.00 M. The values of C_H for these solutions were occasionally cross-checked by analysis[1] and were invariably found to be correct within the limits of experimental error.

Apparatus. A titration calorimeter of the isothermal jacket type previously used by Ahrland and Kullberg[13] and based on the design of Grenthe *et al.*[14] was used in the present work. Ref. 13 should be consulted for details of the construction and accuracy of the calorimeter.

Procedure. By means of a plastic pipette, V_0 ml of a hydrofluoric acid solution (in the following referred to as solution S), containing 4.00 M perchloric acid, was introduced into the inner gold vessel. Then the calorimeter was assembled and placed in a thermostat bath, kept at 25.000 ± 0.002 °C. An external piston burette filled with a metal perchlorate solution (T), also containing 4.00 M perchloric acid, was connected, and the calorimeter was left, usually overnight, to attain thermal equilibrium. The stirring of S was then initiated, causing a slow increase in its temperature. When the temperature (i.e. the thermistor reading in the reaction vessel) had reached a certain value, 3.000 ml of T was added over a period of 2 min. When the temperature change had been recorded, the solution was cooled (or heated) to its original temperature and a further aliquot of T added, etc. The thermistor value was selected so that no heat effects were obtained when S and T were both just 4.00 M $HClO_4$. With this procedure, fluoride solutions were never in contact with glass. In the thorium measurements, the volume in the gold vessel was kept constant at $V_0 = 102.38$ ml, by removal of 3.000 ml before the addition of a further aliquot. In all other measurements the volume V increased in a titration series from approximately 100 to 115 ml. The heat equivalent of the calorimetric system was determined by electrical calibration. It was found to depend linearly on V according to $\varepsilon_V = 2.053 + 0.0209\ (V - 99.98)$ J Ω^{-1}. Individual calibrations departed by at most 0.1 % from this relationship.

The heats of dilution were determined in separate titrations with only one of the reactants present. For all solutions S they were found to be zero within experimental error. The metal ion solutions (T) gave appreciable heats of dilution, however. Thus, when 3 ml solutions of 30 mM Zr(IV), Hf(IV), Th(IV) or U(IV) in 4.00 M $HClO_4$ were diluted to 100 ml, Q_{dil} = 0.5, 0.5, 0.1 and 0.01 J were found. Corresponding values of Q_{exp} and Q_{dil} were always determined by analogous titration series.

For the zirconium(IV) and hafnium(IV) systems, the initial concentrations C_{HF} of the solutions S were varied between 28.6 and 1.4 mM. This implies that the highest ligand numbers reached were ca. 3.4; as aliquots of T were added this number decreased, finally to ca. 0.3. Within this range, the first four mononuclear complexes are formed in both systems. Their stability constants are all fairly precisely known,[11,12] a factor which has determined our choice of the present range of measurements. Within this range no precipitation occurs. This had been ascertained during the stability measurements, and has been confirmed by the regular performance of the systems during calorimetric titration.

For the thorium(IV) and uranium(IV) systems, on the other hand, precipitation of the tetrafluorides already occurs at fairly low fluoride concentrations.[1] To avoid this, the initial values of C_{HF} in solution S were chosen to be ≤ 6.7 mM for thorium(IV) and ≤ 12.9 mM for uranium(IV), implying ligand numbers of at most ca. 1.5 for thorium(IV) and ca. 2.0 for uranium(IV).

Results and calculations

The zirconium(IV) fluoride system. Titrations were carried out with $C_M = 50.38, 30.23$ and 20.15 mM in solution T. In the measurements of Q_{dil} for the highest value of C_M (50.38 mM), heat was evolved for an appreciable time following addition, particularly for the last additions. A slow reaction, presumably involving polynuclear hydroxo complexes, evidently takes place. Hence results from titrations at $C_M = 50.38$ mM were excluded from the values reported in Fig. 1.

According to previous investigations[3,12,15] of the zirconium fluoride system, the first four complexes must be considered in the present calculations. The values selected for the stability constants were $\beta_{1H} = 2.20 \times 10^5$ M^{-1}, $\beta_{2H} = 1.15 \times 10^9$ M^{-2}, $\beta_{3H} = 2.63 \times 10^{11}$ M^{-3} and $\beta_{4H} = 1.07 \times 10^{13}$ M^{-4}. Of these, only β_{1H} and β_{2H} had been experimentally determined at 25°C.[3] The values of β_{3H} and β_{4H} were calculated by means of eqn. (5).

$$d\ln {}^*K_n / dT = {}^*\Delta H^\circ_n / RT^2 \tag{5}$$

From the values of ${}^*K_3 = 1.0 \times 10^3$ and ${}^*K_4 = 1.9 \times 10^2$ determined at 20°C,[12] provisional values of β_{3H} and β_{4H} were calculated which, inserted in eqns. (3) and (4), yielded preliminary values of ${}^*\Delta H^\circ_3$ and ${}^*\Delta H^\circ_4$. With these, preliminary values of ${}^*K_3$ and ${}^*K_4$ at 25°C were calculated from eqn. (5). The cycle was iterated until consistent results were achieved (Table 1), which in fact occurred in the third cycle.

The hydrolysis of zirconium(IV) is very pronounced and, on the basis of existing information,[3,4,16] both mono- and polynuclear hydroxo species might be expected to form even in 4 M perchloric acid. Strictly speaking, the heat changes observed should therefore be corrected for the occurrence of these complexes. Fig. 1 shows Δh_v as a func-
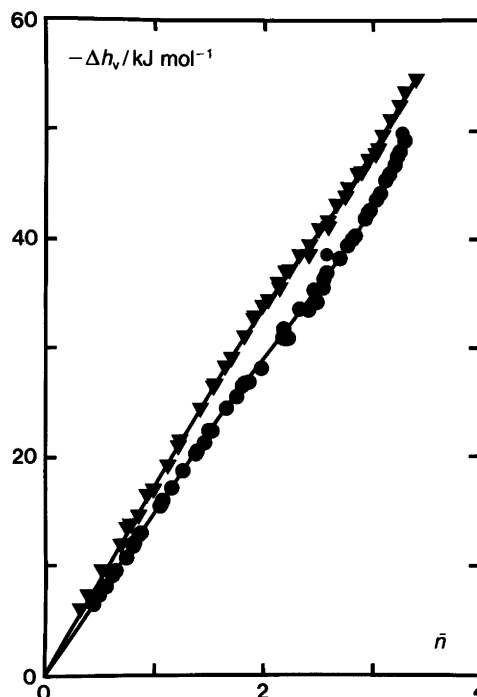

Fig. 1. The total molar heat change Δh_v plotted as a function of the ligand number $\bar{n}$ for the formation of fluoride complexes of Zr^{4+} (▼) and Hf^{4+} (●). The full curves have been calculated from the values of stability constants and enthalpy changes listed in Table 1.

tion of $\bar{n}$ [calculated from eqns. (1) and (2)] at various values of C_M. Evidently all points fall along the same curve, irrespective of the value of C_M used. This means either that the enthalpy changes for the break-up of the polynuclear hydroxo complexes presumed to be present are small or that the hydrolysis is less extensive than was previously thought. Whatever the case, the observed heat changes can be referred to the formation of the mononuclear fluoro complexes. This is confirmed by a comparison between the values of ${}^*\Delta H^\circ_1$ calculated from all measurements and from those performed at [HF] > 0.03 mM, where the formation of polynuclear hydroxo complexes is negligible. The values were 17.46 ± 0.19 and 17.26 ± 0.21 kJ mol^{-1}, respectively, i.e. they agree within the limits of error (one standard deviation). It may thus be concluded that the enthalpy values quoted in Table 1 really represent the formation of the mononuclear fluoride complexes.

The hafnium(IV) fluoride system. In this case no slow heat evolution on dilution was observed for any of the solutions used. This is in keeping with the fact that hafnium is less extensively hydrolysed than zirconium.[3,4] Four fluoride complexes are formed within the investigated concentration range, cf. Ref. 11. The values of the stability constants $\beta_{1H} = 7.78 \times 10^4$ M^{-1} and $\beta_{2H} = 2.06 \times 10^8$ M^{-2} have been determined at 25°C.[3] Values of $\beta_{3H} = 5.28 \times 10^{10}$ M^{-3} and $\beta_{4H} = 1.76 \times 10^{12}$ M^{-4} were calculated, as described above

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Table 1. The stability constants used and the values of Gibbs energy, enthalpy and entropy changes for the stepwise complex formation $MF_{n-1}^{4-n+1} + HF \rightleftharpoons MF_n^{4-n} + H^+$ of the four systems investigated. The limits of error refer to one standard deviation, as obtained by computer. Medium 4.00 M perchloric acid; 25 °C.

	n	Acceptor			
		Zr^{4+}	Hf^{4+}	Th^{4+}	U^{4+}
$^*K_n$	1	$8.80(8) \times 10^5$	$3.11(1) \times 10^5$	$4.24(2) \times 10^4$	$3.02(1) \times 10^5$
	2	$2.09(4) \times 10^4$	$1.06(2) \times 10^4$	$0.73(2) \times 10^3$	$1.43(3) \times 10^3$
	3	$0.91(3) \times 10^3$	$1.03(7) \times 10^3$		$0.84(9) \times 10^2$
	4	$1.63(8) \times 10^2$	$1.33(8) \times 10^2$		
$-^*\Delta G^\circ_n / kJ\ mol^{-1}$	1	33.93(2)	31.35(1)	26.41(1)	31.28(1)
	2	24.66(5)	22.98(5)	16.34(7)	18.01(5)
	3	16.89(8)	17.2(2)		11.0(3)
	4	12.6(1)	12.1(1)		
$-^*\Delta H^\circ_n / kJ\ mol^{-1}$	1	17.5(2)	15.2(1)	14.3(1)	17.52(6)
	2	16.8(3)	15.0(2)	12.8(4)	9.8(2)
	3	11.2(6)	8.8(3)		8(2)
	4	22(1)	27.4(7)		
$^*\Delta S^\circ_n / J\ K^{-1}\ mol^{-1}$	1	55.1(6)	54.2(3)	40.6(4)	46.2(2)
	2	26(1)	26.8(6)	12(1)	27.5(6)
	3	19(2)	28(1)		11(5)
	4	−32(4)	−51(3)		

for zirconium, from values of $^*K_3$ and $^*K_4$ determined at 20 °C.[11]

Titrations were carried out with $C_M = 55.85$, 31.23 and 15.64 mM in the solution T. As for zirconium(IV), the function $\Delta h_v(\bar{n})$ is independent of the total metal ion concentration (Fig. 1), indicating that polynuclear complexes are not involved in these measurements. This agrees with the result arrived at previously.[3] Also, the monohydroxo complexes should be negligible in 4 M perchloric acid, amounting to ca. 2 % of C_M. Again, the enthalpy changes determined therefore refer to the formation of the mononuclear fluoride complexes.

The thorium(IV) fluoride system. The stability constants for the formation of the fluoride complexes of thorium(IV) in 4.00 M perchloric acid medium have been determined at 25 °C by means of a fluoride membrane electrode (Ref. 3, p. 1372). With these values ($\beta_{1H} = 1.043 \times 10^4\ M^{-1}$ and $\beta_{2H} = 1.67 \times 10^6\ M^{-2}$), the present measurements of Δh_v (Fig. 2) result in $^*\Delta H^\circ_1 = -14.13\ kJ\ mol^{-1}$ and $^*\Delta H^\circ_2 = -14.49\ kJ\ mol^{-1}$, respectively.

The constants have also been determined by the same method at 20 °C. Graphically values of $\beta_{1H} = (1.19 \pm 0.01) \times 10^4\ M^{-1}$ and $\beta_{2H} = (2.8 \pm 0.1) \times 10^6\ M^{-2}$ were obtained.[1] By applying the least-squares computer program developed by Sandell[17] to these measurements, values of $\beta_{1H} = (1.193 \pm 0.004) \times 10^4\ M^{-1}$ and $\beta_{2H} = (2.69 \pm 0.04) \times 10^6\ M^{-2}$ are obtained. These were recalculated to 25 °C by means of the values of $^*\Delta H^\circ_1$ and $^*\Delta H^\circ_2$ presently determined, yielding $\beta_{1H} = 1.082 \times 10^4\ M^{-1}$ and $\beta_{2H} = 2.21 \times 10^6\ M^{-2}$. The value of β_{1H} agree quite well with the experimental value at 25 °C quoted above, while the value of β_{2H}

differs somewhat. There is no obvious explanation for this difference, as both determinations were carried out by much the same method. The enthalpy changes presented in
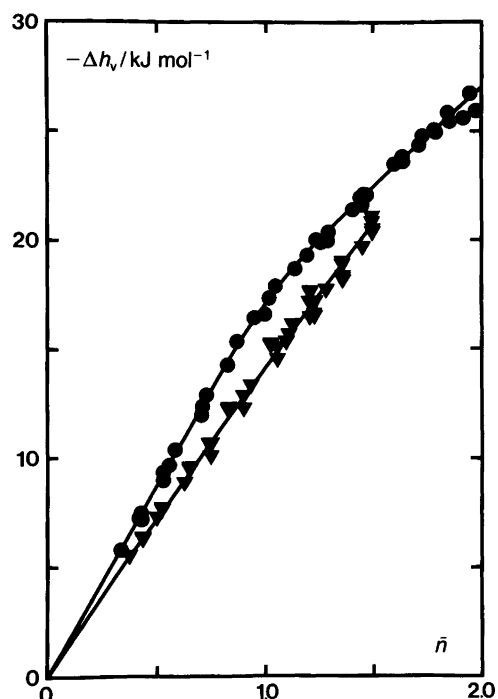

Fig. 2. The total molar heat change Δh_v plotted as a function of the ligand number $\bar{n}$ for the formation of fluoride complexes of Th^{4+} (▼) and U^{4+} (●). The full curves have been calculated from the values of stability constants and enthalpy changes listed in Table 1.

Table 2. Values of Gibbs energy, enthalpy and entropy changes for the stepwise complex formation $MF_{n-1}^{4-n+1} + F^- \rightleftharpoons MF_n^{4-n}$ calculated from the data of Table 1, by means of the values for H^+ quoted below. The radii r of the ions M^{4+} are also given.[a]

	n	Acceptor				
		H^+	Zr^{4+}	Hf^{4+}	Th^{4+}	U^{4+}
			$r/\text{Å}$			
			0.72	0.71	0.98	0.93
$-\Delta G°_n/\text{kJ mol}^{-1}$	1	20.2	54.1	51.6	46.6	51.5
	2		44.9	43.2	36.5	38.2
	3		37.1	37.4		31.2
	4		32.8	32.3		
$-\Delta H°_n/\text{kJ mol}^{-1}$	1	-11.9	5.6	3.3	2.4	5.6
	2		4.9	3.1	0.9	-2.1
	3		-0.7	-3.1		-4
	4		10	15.5		
$\Delta S°_n/\text{J K}^{-1} \text{mol}^{-1}$	1	108	163	162	149	154
	2		134	135	120	136
	3		127	136		119
	4		76	57		

[a] All values referred to the same coordination number 6; from Ref. 25 (Zr^{4+}, Hf^{4+}) and Ref. 26 (Th^{4+}, U^{4+}).

Table 1 were calculated using the mean values $\beta_{1H} = 1.06 \times 10^4 \text{ M}^{-1}$ and $\beta_{2H} = 1.94 \times 10^6 \text{ M}^{-2}$.

Titrations were carried out with $C_M = 105.9$, 52.94 and 39.70 mM in solution T. The function $\Delta h_v(\bar{n})$ does not vary significantly with C_M (Fig. 2), implying that no polynuclear hydroxo or fluoro complexes are present. This agrees with the results found in Refs. 1 and 3.

The uranium(IV) fluoride system. Stability constants for the fluoride complexes of uranium(IV) in 4.00 M $HClO_4$ have been determined only at 20 °C.[1] The results reported were obtained graphically. To obtain a better estimation of the limits of error, least-squares calculations[17] were applied to the primary data of Ref. 1, which resulted in $\beta_{1H} = (8.52 \pm 0.07) \times 10^4 \text{ M}^{-1}$, $\beta_{2H} = (3.26 \pm 0.06) \times 10^7 \text{ M}^{-2}$ and $\beta_{3H} = (7.3 \pm 0.7) \times 10^8 \text{ M}^{-3}$, in close agreement with the values originally obtained. These constants were used as starting values in the iterative procedure described above, which resulted in the following values for 25 °C: $\beta_{1H} = 7.55 \times 10^4 \text{ M}^{-1}$, $\beta_{2H} = 2.70 \times 10^7 \text{ M}^{-2}$, $\beta_{3H} = 5.7 \times 10^8 \text{ M}^{-3}$.

Titrations were carried out with $C_M = 82.71$, 47.26 and 28.37 mM in solution T. As for the other systems studied, the function $\Delta h_v(\bar{n})$ is independent of total metal ion concentration (Fig. 2).

Discussion

The values of $*K_n$ and the enthalpy changes $*\Delta H°_n$ determined are collected in Table 1. From these, the values for $*\Delta G°_n$ and $*\Delta S°_n$, also listed in Table 1, have been calculated from eqns. (6) and (7).

$$*\Delta G°_n = -RT \ln *K_n \tag{6}$$

$$*\Delta G°_n = *\Delta H°_n - T*\Delta S°_n \tag{7}$$

The enthalpy and entropy terms generally contribute in a similar degree to the fairly large decreases of Gibbs energy characterizing the fluoride complex formation as formulated in Table 1. Marked exceptions are, however, the fourth step in the two cases Zr^{4+} and Hf^{4+}, where this step could be investigated. These reactions are much more exothermic than any of the previous steps; moreover, they are characterized by a decrease in entropy while all the other steps display a sizeable increase in entropy.

Obviously, these values depend on the dissociation of hydrofluoric acid as well as on the fluoride complex formation of the M^{4+} ions. To discuss the latter process, the influence of the former has to be subtracted. In this way one arrives at the processes considered in Table 2, i.e. the exchange of water in the hydration shells of the M^{4+} ions for fluoride ions.

In Table 2 the thermodynamic functions of the hydrogen fluoride system used in this calculation are also listed. To conform with the presentation of the other systems, these refer to the association equilibrium $H^+ + F^- \rightleftharpoons HF$. Values referring to the present conditions have been arrived at as follows. Kleboth[18] and Hefter[19] have determined $K_1(H^+)$ in a 4 M sodium perchlorate medium at 25 °C, arriving at the same value, $\log K_1(H^+) = 3.54$. This value should also be a fair approximation for the acid medium presently used: hence the value of $\Delta G°_1(H^+)$ listed in Table 2. For $\Delta H°_1(H^+)$, a reasonable estimate can be obtained from the measurements of Kozlov *et al.*[20] in perchlorate solutions of

varying ionic strength. From the values of $\Delta G^\circ_1(\text{H}^+)$ and $\Delta H^\circ_1(\text{H}^+)$ thus chosen, $\Delta S^\circ_1(\text{H}^+)$ is calculated.

For all the M^{4+} ions investigated, the exchange of water for fluoride is characterized by small heat effects as far as the first three steps are concerned. The values of ΔH°_n are either slightly exothermic or slightly endothermic (Table 2). The entropy changes of these reactions are all strongly positive, however, so in the end very stable complexes result. In the two cases where a fourth complex is formed within the range of ligand concentration available, viz. Zr^{4+} and Hf^{4+}, this step is much more exothermic than the previous ones; the entropy changes are, on the other hand, much less positive (Table 2).

Enthalpy and entropy changes accompanying the formation of fluoride complexes of tetravalent cations have previously been determined by Baumann,[21] by Choppin and Unrein[22] and by Grant et al.[23]

In the thorium(IV) system, at zero ionic strength and 25 °C, Baumann found the following values from the temperature coefficients of the stability constants: ΔH°_n $(n = 1 \rightarrow 4) = -5.0, -3.3, -3.3$ and -3.8 kJ mol^{-1}; ΔS°_n $(n = 1 \rightarrow 4) = 145, 115, 80$ and 52 J K^{-1} mol^{-1}. (The values of ΔS°_1 and ΔS°_2 have been slightly corrected by the present authors.) Calorimetrically, Choppin and Unrein found, in a perchlorate medium of $I = 1$ M and 25 °C, $\Delta H^\circ_1 = 3.0$ kJ mol^{-1}. From the temperature coefficients of the stability constant, determined by two different methods, values of $\Delta H^\circ_1 = 1.1$ and 2.3 kJ mol^{-1} were obtained, corresponding to $\Delta S^\circ_1 = 145$ and 150 J K^{-1} mol^{-1}, respectively. Quite recently, Grant et al.[23] have determined calorimetrically the enthalpy and entropy changes for the first three steps. In a perchlorate medium of $I = 0.5$ M and 25 °C they found ΔH°_n $(n = 1 \rightarrow 3) = 1.6, 2.7$ and 3.5 kJ mol^{-1} and ΔS°_n $(n = 1 \rightarrow 3) = 150, 120$ and 100 J K^{-1} mol^{-1}.

For the uranium(IV) system,[22] the temperature coefficient yielded $\Delta H^\circ_1 = 0.8$ kJ mol^{-1} and $\Delta S^\circ_1 = 151$ J K^{-1} mol^{-1} [and for neptunium(IV) $\Delta H^\circ_1 = 3.2$ kJ mol^{-1} and $\Delta S^\circ_1 = 155$ J K^{-1} mol^{-1}]. These results are, as far as they go, certainly consistent with ours. Considering the differences in the medium and in the methods of measurement, the values of ΔS°_n, in particular, found by the various investigators agree surprisingly well with ours in most cases (Table 2). It follows that the stability constants used here are also in broad agreement with those found by other authors.[21-24]

The results can be rationalized as follows. The coordination of a fluoride ion implies neutralization of charges on the metal ion as well as on the ligand. Consequently, a strong dehydration takes place, most extensively around the highly charged metal ion, but the contribution from F$^-$ is certainly also sizeable. The effect is also felt outside the inner hydration sphere, so the process involves a large decrease of order, reflected in the very large entropy gain. On the other hand, the energy spent on this extensive dehydration is seemingly almost compensated by the gain

from complex formation, so the net value of ΔH°_n becomes small.

As the charge on the complex decreases, the values of ΔS°_n should also decrease. This happens for all the ions between the first and second steps. For U^{4+} a similar decrease also takes place between the second and third steps. For Zr^{4+} and Hf^{4+}, however, the decrease at this step is small, or nonexistent (Table 2). One might speculate that for these small ions an extra-large dehydration, connected with some structural change, takes place at the third stage, a change which does not occur in the case of the considerably larger U^{4+}. The sharp decrease in ΔS°_n between the third and fourth steps would indicate that the dehydration has gone quite far with the formation of the third complex, so that the coordination of a further ligand involves only a modest gain of entropy. On the other hand, no large dehydration enthalpy has to be spent at this step, so the values of ΔH°_4 becomes rather exothermic (Table 2).

For M^{4+} ions, the hydration enthalpies are not very accurately known, but the hydration is certainly stronger, the smaller the ion.[27,28] The dehydration accompanying each step should therefore tend to be more extensive, and the entropy gain consequently larger, the smaller the ion. For the first step this result evidently holds, as seen from an inspection of the values of ΔS°_1 and r (Table 2). Moreover, as might be expected, practically the same values are found for Zr^{4+} and Hf^{4+}. The second step also fits into this picture, except that the value found for U^{4+} is unexpectedly large. The anomalous behaviour of U^{4+} at this step stands out more clearly if the reactions $M^{4+} + MF_2^{2+} \rightleftharpoons 2\ MF^{3+}$ are considered. In Table 3 the equilibrium constants, $^*K_1/^*K_2$, and the thermodynamic functions for these reactions are listed. In spite of the unexpectedly high value of ΔS°_2, the second complex is less stable relative to the first one for U^{4+} than for any of the other acceptors investigated. This depends upon the unfavourable value of ΔH°_2. This is reflected in the functions quoted in Table 3. The uranium(IV) reaction is considerably more exothermic than the other reactions, and this more than compensates the less favourable entropy change. As to the reason for the special behaviour of U^{4+}, one might guess, from the values of ΔH°_1 and ΔH°_2 reported in Table 2, that the first complex F$^-$ is more strongly bonded in UF^{3+} than in the other

Table 3. The equilibrium constant $^*K_1/^*K_2$ and the functions ΔG°, ΔH° and ΔS° for the reactions $M^{4+} + MF_2^{2+} \rightleftharpoons 2\ MF^{3+}$. Medium 4.00 M perchloric acid; 25 °C. Errors indicated refer to one standard deviation.

Acceptor	$^*K_1/^*K_2$	$-\Delta G^\circ$ kJ mol^{-1}	$-\Delta H^\circ$ kJ mol^{-1}	ΔS° J K^{-1} mol^{-1}
Zr^{4+}	42.1(9)	9.27(6)	0.7(4)	29(1)
Hf^{4+}	29.3(6)	8.38(5)	0.2(2)	27.4(7)
Th^{4+}	58(2)	10.07(7)	1.5(4)	29(1)
U^{4+}	211(4)	13.27(5)	7.8(2)	18.3(7)

Table 4. Entropy gains[a] for neutralization reactions $M^{n+} + nF^-$ $\rightleftharpoons MF_n$ in aqueous solutions for acceptors of different charges and radii.[b]

Acceptor	$\Delta S^\circ_{\beta n}$/J K^{-1} mol^{-1}	r/Å
Zr^{4+}	500	0.72
Hf^{4+}	490	0.71
Al^{3+}	336	0.53
Fe^{3+}	293	0.65
Be^{2+}	145	0.27
VO^{2+}	158	
UO$_2^{2+}$	160	

[a]For the tri- and divalent ions these have been taken from the compilation in Ref. 5. [b]From Ref. 25; they refer to six-cooordination, except for Be^{2+}, where four-coordination seems a natural choice.

complexes MF^{3+}, while the opposite occurs for the second complex.

The very strong hydration of tetravalent ions is impressively reflected in the very high total entropy gains found for the formation of the neutral complexes, i.e. for $\Delta S^\circ_{\beta n}$ (Table 4). Much higher values are found for Zr^{4+} and Hf^{4+} than for the trivalent Al^{3+} and Fe^{3+}, in spite of the smaller size of the latter ions. For divalent ions, the entropy gains are fairly small even for very small ions, as illustrated by Be^{2+}. Ions that do not possess spherical symmetry might display much larger entropy gains than would be warranted by their size and charge, as illustrated by VO^{2+} and UO$_2^{2+}$. In these cases the charge is of course a much more formal quantity than for ions of spherical symmetry. For the ions quoted, the actual charge on the central atom is certainly higher than 2. Applying an extended Born equation, Choppin and Rao[29] found an "effective" charge of +3.2 on the uranium atom of UO$_2^{2+}$.

References

1. Norén, B. *Acta Chem. Scand. 23* (1969) 931.
2. Ahrland, S. In: Katz, J. J., Seaborg, G. T. and Morss, L. R., Eds., *The Chemistry of the Actinide Elements,* Chapman and Hall, London, New York 1986, Vol. 2, Chap. 21.
3. Norén, B. *Acta Chem. Scand. 27* (1973) 1369.
4. Baes, C. F. and Mesmer, R. E. *The Hydrolysis of Cations,* John Wiley & Sons, New York 1976.
5. Ahrland, S. *Struct. Bonding 15* (1973) 167.
6. Ahrland, S. *Svensk Naturvetenskap* (1972) 215.
7. Ahrland, S., Ishiguro, S., Marton, A. and Persson, I. *Acta Chem. Scand., Ser. A 39* (1985) 227.
8. Johnsson, M., Persson, I. and Portanova, R. *Inorg. Chim. Acta 127* (1987) 35.
9. Farrer, H. N. and Rossotti, F. J. C. *J. Inorg. Nucl. Chem. 26* (1964) 1959.
10. Karlsson, R. and Kullberg, L. *Chem. Scr. 9* (1976) 54.
11. Norén, B. *Acta Chem. Scand. 21* (1967) 2435.
12. Norén, B. *Acta Chem. Scand. 21* (1967) 2457.
13. Ahrland, S. and Kullberg, L. *Acta Chem. Scand. 25* (1971) 3471.
14. Grenthe, I., Ots, H. and Ginstrup, O. *Acta Chem. Scand. 24* (1970) 1067.
15. Norén, B. *Acta Chem. Scand. 23* (1969) 379.
16. Fay, R. C. In: Wilkinson, G., Gillard, R. D. and McCleverty, J. A., Eds., *Comprehensive Coordination Chemistry,* Pergamon Press, Oxford 1987, Vol. 3, p. 384.
17. Sandell, A. *Acta Chem. Scand. 25* (1971) 2609.
18. Kleboth, K. *Monatsh. Chem. 101* (1970) 768.
19. Hefter, G. T. *J. Solution Chem. 11* (1982) 45.
20. Kozlov, Yu. A., Blokhin, V. V., Shurukhin, V. V. and Mironov, V. E. *Zhur. Fiz. Khim. 47* (1973) 2386.
21. Baumann, E. W. *J. Inorg. Nucl. Chem. 32* (1970) 3823.
22. Choppin, G. R. and Unrein, P. J. In: Müller, W. and Lindner, R., Eds., *Transplutonium Elements,* North Holland Publishing Co., Amsterdam 1976, p. 97.
23. Grant, P. M., Kinard, W. F. and Baisden, P. A. *J. Solution Chem. 18* (1989) 211.
24. Bond, A. M. and Hefter, G. T. *Critical Survey of Stability Constants and Related Thermodynamic Data of Fluoride Complexes in Aqueous Solution,* IUPAC Chemical Data Series, No. 27, Part A, Pergamon Press, Oxford 1980.
25. Shannon, R. D. and Prewitt, C. T. *Acta Crystallogr., Sect. B 25* (1969) 925.
26. Peterson, J. R. and Cunningham, B. B. *Inorg. Nucl. Chem. Lett. 3* (1967) 327.
27. Jones, A. D. and Chopping, G. R. *Actinides Rev. 1* (1969) 311.
28. Smith, D. W. *J. Chem. Educ. 54* (1977) 540.
29. Choppin, G. R. and Rao, L. F. *Radiochim. Acta 37* (1984) 143.