

The Sulphate Complexes of Neptunyl(VI), and a Comparison of the Strength of Corresponding Uranium and Neptunium Complexes in Aqueous Solution

STEN AHRLAND and LARS BRANDT

Division of Inorganic Chemistry, Chemical Center, University of Lund, Lund, Sweden

The sulphate complexes of the neptunyl(VI) ion have been studied at 21°C in a 1 M perchlorate medium, the acidity of which has been 0.20 or 1.00 M. A solvent extraction method has been used, the quantity measured being the distribution of neptunium between the aqueous solution and a solution of dibutyl phosphate in carbon tetrachloride. Within the range of ligand concentration measured ($[\text{SO}_4^{2-}] \leq 65 \text{ mM}$), only the two complexes NpO_2SO_4 and $\text{NpO}_2(\text{SO}_4)_2^{2-}$ are formed in the aqueous phase; there is no trace of hydrogen sulphate complexes.

Stability constants, valid under comparable conditions, have been collected in Table 5 for the fluoride and sulphate complexes of uranium(IV), neptunium(IV), uranyl(VI), and neptunyl(VI), and also for the hydroxide complexes of the first two acceptors mentioned. On the whole, the stabilities follow the trend to be expected if the bond between the ligand and the central ion is of an essentially electrostatic character, but very striking exceptions to this rule also occur. These have been interpreted as presumably connected with differences in the hydration shell between uranium and neptunium ions.

The fluoride complexes of neptunyl(VI) are considerably less stable than those of uranyl(VI) which is contrary to what should be expected as a result of the actinoid contraction taking place between uranium and neptunium.¹ It is of interest to find out whether complexes of other ligands behave in the same unexpected manner. Therefore, the neptunyl(VI) sulphate system has now been studied under conditions comparable to those prevailing in a previous investigation of the uranyl(VI) sulphate.² The comparison has also been extended to other systems of uranium and neptunium complexes in so far as reliable measurements have been available.

The method of measurement for neptunyl(VI) sulphate has been the same as used before for the fluoride complexes, *viz.* extraction of the neptunyl(VI) with a solution of dibutyl phosphate (DBP) in carbon tetrachloride.¹ An acid perchlorate medium of ionic strength 1 M has been used, and the

temperature has been 21°C. To prevent reduction of neptunium(VI), a trace of permanganate has been added to the aqueous phase.

In order to investigate if complexes containing the hydrogen sulphate ion as a ligand are possibly formed, measurements have been performed at the hydrogen ion concentrations $h=1.0$ and 0.2 M. These were kept virtually constant during a series of measurements by adding the sulphate as pure 0.940 M sulphuric acid in the case of $h=1.0$ M and as a buffer of suitable composition in the case of $h=0.2$ M.

For the calculation of this composition, the acidity constant K_s of HSO_4^- has to be known for the medium used; it has been measured separately. This constant is also necessary for the calculation of the variable $[\text{HA}]/h$, as set forth below.

For $h=1$ M, the ionic medium thus contained only acids, as in the fluoride measurements,¹ for $h=0.2$ M also sodium ions, added as perchlorate and sulphate, to the prescribed ionic strength of 1 M.

For the low $h=0.2$ M, it was necessary to use a lower DBP-concentration, C_B' , than before, in order to obtain well measurable distribution ratios. Consequently, the validity of the extraction formula



has to be investigated for these lower values of C_B' and h . If the extraction still occurs according to the same formula, the same value as before should of course be found for the equilibrium constant, K .

CALCULATION OF THE STABILITY CONSTANTS FROM THE MEASURED DISTRIBUTION DATA

The notation and the method of calculation are the same as for the fluoride measurements,¹ with the obvious modification that $\text{A}=\text{SO}_4^{2-}$. Further, as h is not the same in all measurements, the constants $\beta_{n\text{H}}$ are not convenient to use. Instead the concentrations $[\text{MA}_n]$ are expressed as

$$[\text{MA}_n] = \beta_n^* [\text{M}] [\text{HA}]^n h^{-n} \quad (2)$$

Hence, provided that no complexes containing hydrogen sulphate exist:

$$C_M = [\text{M}] + \sum_{n=1}^N [\text{MA}_n] = [\text{M}] X^* \quad (3)$$

where

$$X^* = 1 + \sum_{n=1}^N \beta_n^* ([\text{HA}]/h)^n \quad (4)$$

On the condition mentioned, $C_M/[\text{M}]$ will thus be a function of the variable $[\text{HA}]/h$ only. If, on the other hand, protonized complexes do exist, then this function will depend also on h . For the experimentally determined distribution ratio $q=C_{\text{MO}}/C_M$ we have (cf. Ref. 1):

$$q = K \cdot \frac{[\text{H}_2\text{B}_2]_0^2}{h^2} \cdot \frac{1}{X^*} \quad (5)$$

Here K is known from measurements of q_0 in sulphate-free solutions and $[\text{H}_2\text{B}_2\text{O}_6]$ is calculated as described before.¹ The values of h can be calculated from the amounts of perchloric acid and sulphate buffer added, if the acidity constant K_s of HSO_4^- is known, as the contribution to h from the reaction (1) is always negligible, because of the low values of C_M' . The found values of h have been entered in Table 3 for the lower acidity used; for the higher one they do not differ significantly from 1 M.

Thus all data are known for the calculation of X^* according to eqn. (5), and from corresponding values of X^* and $[\text{HA}]/h$, connected according to eqn. (4), the constants β_n^* can be calculated by means of a conventional graphical extrapolation procedure (cf. Ref. 1). The value of $[\text{HA}]/h$ corresponding to a certain X^* (or q) has been found from the dissociation equilibrium of HSO_4^- , remembering that the amount of sulphate bound as neptunium complexes is negligible:

$$[\text{HA}]/h = C_A/(h + K_s) \quad (6)$$

The experimental error in K_s is admittedly fairly large ($\approx 12\%$, Table 1) but as h is rather much larger than K_s even for $h=0.2$ M, this error will nevertheless be of minor influence on $[\text{HA}]/h$, and consequently on β_n^* . For $h=1.0$ M, $[\text{HA}]$ is in fact close to C_A .

In practice, the value of K determined in sulphate-free solutions has not been directly utilized for the computation of β_n^* . Instead, X^*/K has been calculated from (5). By extrapolation to $[\text{HA}]/h=0$, this function evidently yields (cf. eqn. (4)) an intercept $=1/K$. This value of K will be a check of that found by direct measurement. Then the function $(X^*/K - 1/K)/([\text{HA}]/h) = X_1^*/K$ is formed, with an intercept $=\beta_1^*/K$ for $[\text{HA}]/h=0$. For the present system, this function is in fact linear which means that only two complexes are formed within the range of $[\text{HA}]/h$ measured; the slope of the line will be β_2^*/K .

Table 1. The acidity constant of HSO_4^- (= HA) at $I = 1.0$ M and 20°C .

h mM	$[\text{A}]$ mM	$[\text{HA}]$ mM	K_s M
51.0	9.2	5.9	0.080
52.9	33.4	21.1	0.084
54.1	69.9	45.9	0.082
53.7	95.6	65.4	0.079
101.4	7.7	10.1	0.077
102.7	28.2	36.9	0.079
103.9	67.4	90.6	0.077
104.4	93.7	127.5	0.077
203.7	11.4	29.9	0.078
204.5	29.6	80.6	0.075
202.1	66.4	198.0	0.068
201.3	90.2	270.3	0.068

EXPERIMENTAL

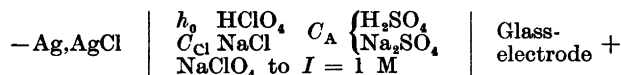
Chemicals. The preparation of stock solutions of neptunyl(VI) perchlorate and DBP has been described before.¹ All other chemicals were of analytical grade.

Distribution measurements. The technique was the same as before.¹ In the present measurements, the aqueous solutions of $h=0.2$ M contained so much non-volatile salt that their α -activity could not be measured directly. Instead the solutions had to be equilibrated once more with the organic phase. The expression $q=(a-c)/c$ used in Ref. 1 for the calculation of q according to this procedure will, however, not be valid with sufficiently good approximation in the present measurements, for two reasons. First, the lower values chosen for C_B' and h will make the DBP-species in the aqueous phase, *i.e.* [HB] and [B], relatively much more important than before, as the monomer, and its anion, will then be favoured on the cost of the dimer (*cf.* the expressions for K_a , K_d and K_2 quoted in Ref. 1). Therefore, the total DBP-concentration, and hence also $[H_2B_2]_o$, will be sensibly higher in the second equilibration, *i.e.* $[H_2B_2]_{oc} > [H_2B_2]_{oa}$. As a consequence, the wanted distribution ratio for the first extraction, $q=a/y$, will not be the same as that for the second extraction, $q'=c/z$. A relation between q' and q is found from eqn. (5), however, yielding the following corrected formula for q :

$$q = \frac{a - c([H_2B_2]_{oa}/[H_2B_2]_{oc})^2}{c} \quad (7)$$

For the present values of C_B' and h , $[H_2B_2]_{oa}/[H_2B_2]_{oc}$ differs appreciably from 1. Still, that would not matter very much if $c \ll a$. This condition has been fulfilled in the previous measurements performed with this technique which only involved solutions with merely DBP as a complex forming ligand.¹ In the present case, where the double extraction also has to be applied to solutions containing even large amounts of the main ligand, sulphate, c tends to be relatively large for many solutions, which is the second reason why the use of the corrected formula (7) becomes imperative here.

Emf measurements for the determination of K_s . The determination of K_s has to be performed in fairly acid solutions. It is thus especially important to avoid liquid junctions which would be the sites of large potentials, notoriously difficult to determine, or even reproduce. Diffusion-free cells of the following type have therefore been used:



The cell solution was prepared by adding to a solution S, containing the perchloric acid, a solution T, containing the sulphuric acid and sodium sulphate. Both solutions had the same C_{Cl} , around 10 mM, and about the same acidity. If E' denotes the emf measured for the solution S of known acidity = h_0 , and E that measured for a solution containing sulphate, than h of this solution is given by

$$E' - E = RTF^{-1} \ln h_0/h \quad (8)$$

provided that the activity coefficients stay constant. From this equation, and known stoichiometric relations, K_s is found. — The reproducibility of the emf's (measured by a Radiometer PHM 4) were within ± 0.2 mV.

RESULTS

Determination of K_s for HSO_4^- . Three series have been performed, with values of h around 50, 100, and 200 mM. Within each series, C_A has been varied widely. No significant variation of K_s has been found with h or C_A , Table 1, which strongly indicates that the activity coefficients are really constant, as postulated. The mean value is found to be $K_s = 0.077 \pm 0.009$ M which agrees very well with a value found before in a similar medium.³

Validity of the DBP-extraction formula. In the previous investigation,¹ the validity of eqn. (1) has been tested for values of h between 1000 and 422 mM and for values of C_B' between 100 and 24 mM. In the present measurements, the lowest values of h and C_B' are ≈ 200 and 12 mM, respectively, and it is thus necessary to check whether the extraction can be described by the same equilibrium also for these concentrations. In fact no significant difference of K is obtained, neither between the values determined now for $C_B'=12$ and 24 mM, Table 2, nor between these and the value of K determined for higher values of C_B' and h . The mean value of K from Table 2 is

Table 2. The validity of the extraction formula at $h=203$ mM; $C_B'=12$ and 24 mM. $C_M'=0.24$ mM; $I = 1.0$ M.

C_B' mM	a	c	$[H_2B_2]_{oa}$ mM	$[H_2B_2]_{oc}$ mM	q	K $\times 10^{-4}$
12.0	2248	196	4.7	5.7	10.79	2.01
12.0	2285	197	4.7	5.7	10.92	2.04
24.0	2400	50.6	10.2	11.7	46.7	1.85
24.0	2334	47.1	10.2	11.7	48.8	1.93
24.0	2370	50.7	10.2	11.7	46.0	1.83

$(1.93 \pm 0.11) \times 10^4$ which should be compared with the value $(2.0 \pm 0.1) \times 10^4$ finally arrived at before.¹ Eqn. (1) thus describes the extraction also for the present values of C_B' and h .

Table 3. Corresponding values of q and $[HA]/h$, and the functions X^*/K and X_1^*/K , for $h=0.2$ M. $C_M'=0.24$ mM; $C_B'=12$ or 24 mM.

a	c	$[H_2B_2]_{oa}$ mM	$[H_2B_2]_{oc}$ mM	q	C_A mM	h mM	$[HA]/h$	X^*/K $\times 10^4$	X_1^*/K $\times 10^4$
$C_B' = 12.0$ mM									
2021	288	4.8	5.7	6.31	30	203	0.107	0.886	3.61
2036	271	4.8	5.7	6.80	30	203	0.107	0.882	3.01
1960	391	4.8	5.6	4.28	60	204	0.214	1.294	3.71
1735	500	4.8	5.6	2.73	120	205	0.426	2.007	3.54
1294	628	4.9	5.6	1.295	241	207	0.849	4.327	4.51
1305	602	4.9	5.6	1.402	241	207	0.849	3.996	4.12
$C_B' = 24.0$ mM									
2285	109	10.2	11.7	20.20	60	204	0.214	1.237	3.44
2145	174	10.2	11.7	11.57	120	205	0.426	2.138	3.85
2085	311	10.2	11.6	5.93	241	207	0.849	4.093	4.23

Formation of sulphate complexes. The results of the extraction measurements with sulphate present are collected in Table 3, for $h=0.2$ M and in Table 4, for $h=1$ M. In Fig. 1, X^*/K has been plotted as a function of $[HA]/h$.

Table 4. Corresponding values of q and $[HA]/h$, and the functions X^*/K and X_1^*/K for $h=1.00$ M. $C_M'=0.24$ mM, $C_B'=24, 50$ and 100 mM.

$[H_2B_2]_0$ mM	q	C_A mM	$[HA]/h$	X^*/K $\times 10^4$	X_1^*/K $\times 10^4$
$C_B' = 24.0$ mM					
10.7	0.909	248.1	0.230	1.260	3.30
$C_B' = 50.0$ mM					
23.0	6.62	101.5	0.094	0.799	3.18
23.0	6.17	124.0	0.115	0.857	3.10
23.0	5.47	146.6	0.136	0.967	3.43
23.1	4.56	203.0	0.188	1.170	3.56
23.0	4.06	248.1	0.230	1.303	3.49
23.1	3.43	293.2	0.272	1.556	3.88
23.1	2.72	406	0.377	1.962	3.88
23.1	2.25	496	0.461	2.372	4.06
23.1	1.838	586	0.544	2.903	4.42
23.1	1.301	812	0.754	4.101	4.78
$C_B' = 100.0$ mM					
47.4	17.63	248.1	0.230	1.275	3.37
47.4	17.46	248.1	0.230	1.287	3.42
47.4	16.20	293.2	0.272	1.387	3.26
47.4	12.05	406	0.377	1.865	3.62
47.4	10.06	496	0.461	2.234	3.76

The function is independent of h as well as of C_B' . The former fact means that no hydrogen sulphate complexes are formed (*cf.* p. 1580), the latter that neither do sulphate complexes exist in the organic phase, nor DBP-complexes in the aqueous one (Ref. 1, p. 113). The complex formation thus occurs as postulated above (eqns. (3)–(5)).

Extrapolation of X^*/K to $[HA]/h=0$ yields a value of $K=(2.1\pm 0.2)\times 10^4$, in good agreement with all values of K determined before, in the present as well as in the previous measurements. The function X_1^*/K (p. 1581) can then be computed, and turns out to be a straight line, Fig. 2, with the intercept $\beta_1^*/K=(3.1\pm 0.3)\times 10^{-4}$ and the slope $\beta_2^*/K=(1.8\pm 0.6)\times 10^{-4}$.

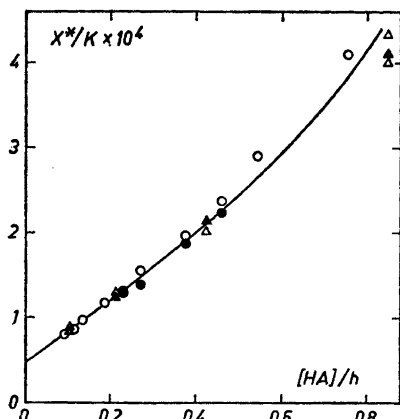


Fig. 1. X^*/K as a function of $[HA]/h$. The signs refer to the following concentrations (in M) of h and C_B' : Δ ; 0.20, 0.0240, \blacktriangle ; 1.00, 0.0240, \odot ; 1.00, 0.0500, \circ ; 1.00, 0.1000, \bullet .

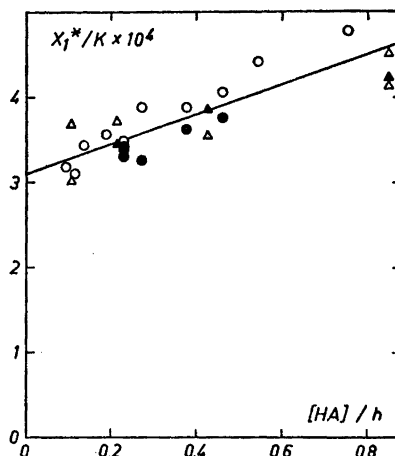


Fig. 2. X_1^*/K as a function of $[HA]/h$. The signs refer to the same series as in Fig. 1.

There is no indication of a third complex within the range investigated. With a mean of $K = (2.0 \pm 0.1) \times 10^4$ from all determinations performed, we obtain

$$\beta_1^* = 6.2 \pm 0.9 \quad \text{and} \quad \beta_2^* = 3.6 \pm 1.3.$$

The only previous investigation of the neptunyl(VI) sulphate system is the spectrophotometric study of Sykes and Taylor.⁴ Only the first complex was proved to exist, with a constant $K_1 = 44 \text{ M}^{-1}$ (for the equilibrium in the form of eqn. (9) below). This value refers to a 2 M sodium perchlorate medium, and 25°C. The corresponding value of β_1^* (cf. p. 1586) would be 3.7. Even with due consideration to the differences in medium, temperature, and experimental method, this value seems somewhat too low to be quite compatible with ours, especially as a *higher* value of β_1^* is found in 2 M than in 1 M perchlorate medium for the corresponding uranyl(VI) complex.^{2,5}

THE RELATIVE STABILITIES OF URANIUM AND NEPTUNIUM COMPLEXES IN AQUEOUS SOLUTION

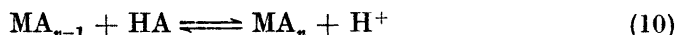
With the information now available, it seems worthwhile to examine the stabilities of corresponding complexes of uranium and neptunium, in order to discern, if possible, the factors of importance for their formation. The comparison should comprise both the tetravalent ions M^{4+} and the VI(VI) ions MO_2^{2+} , in combination with as many various ligands as possible.

For a true appreciation of the coordinating ability of the various ligands, it is necessary to consider the constants referring to the direct stepwise reac-

tions between the central ion and the ligand, *i.e.* the constants K_n of the equilibria



The M^{4+} ions are very easily hydrolyzed⁶ and also the MO_2^{2+} ions are rather prone to hydrolysis.⁷⁻⁹ In order to suppress extensive hydrolysis of the central ions involved, and their complexes, it is therefore often necessary to measure in solutions so acid that the ligands exist more or less exclusively as the corresponding acids HA. The stepwise constants primarily obtained will then be $K_n^* = \beta_n^* / \beta_{n-1}^*$ ($K_1^* = \beta_1^*$), referring to the reactions



The wanted constants K_n are easily calculated, however, according to

$$K_n = K_n^* K_1(\text{H}^+) \quad (11)$$

provided only that the constant $K_1(\text{H}^+)$ of the equilibrium $\text{H}^+ + \text{A} \rightleftharpoons \text{HA}$ is known for the medium and temperature used.

Stability constants to be directly compared, *i.e.* those of corresponding uranium and neptunium complexes, must also refer to the same medium and temperature. It is even desirable that the same conditions, as far as possible, should prevail for all the systems compared.

As standard temperature, 20°C has been chosen, as the measurements of the present authors on the fluoride complexes of UO_2^{2+} , NpO_2^{2+} , and Np^{4+} (Refs. 10, 1, 11) and on the sulphate complexes of UO_2^{2+} and NpO_2^{2+} (Ref. 2 and this paper, respectively) have all been performed at this temperature (or very close to it). It also turns out that values of ΔH are available to recalculate most other constants of interest to this temperature. Only for the hydrolysis constants, values valid for 25°C have to be used.

The medium is perchloric acid, or sodium perchlorate, or a mixture of both, of the same ionic strength in all measurements that are directly compared. Due to lack of data, the same ionic strength cannot be adopted throughout the comparison, however. The survey, as presented in Table 5, in fact contains constants referring to three different values of I , *viz.* 1, 2, and 4 M.

For HF, the actinoid measurements demand the value of $K_1(\text{H}^+)$ at $I=1$ and 4 M. The former is available from Ref. 10; a value close to that ($\log K_1(\text{H}^+) = 2.92$) is found if the value given by Farrer and Rossotti¹² for 25°C is recalculated to 20°C with the association enthalpy $\Delta H_1 = 3$ kcal.¹³ A value for $I=4$ M and 25°C may fairly confidently be calculated from the formula found by Farrer and Rossotti to describe the variation of $K_1(\text{H}^+)$ with I up to $I=3$ M. The resulting $\log K_1(\text{H}^+) = 3.48$ has been recalculated to 20°C on the reasonable assumption that ΔH_1 is still = 3 kcal.

For HSO_4^- , $K_1(\text{H}^+)$ is demanded for $I=1$ and 2 M. The former value has been measured above ($=1/K_s$), the latter has been calculated from the value of $K_s = 0.084$ for 25°C given by Zebroski *et al.*¹⁴ and the value of $\Delta H_1 = 5.54$ kcal given by Zielen.¹⁵

For the sake of comparison, the concentration constant should be used also for H_2O . Taking the most probable value¹⁶ of $\text{p}K_w$ in 2 M NaClO_4 at

Table 5. Comparison of the stabilities of uranium and neptunium complexes in aqueous solution. Temperature 20°C, or, for the OH⁻-systems, 25°C.

Central ion →		H ⁺	U ⁴⁺	Np ⁴⁺	UO ₂ ²⁺	NpO ₂ ²⁺	
Ligand	<i>n</i>	log <i>K_n</i>					
	<i>I</i> →	1	4	4		1	
F ⁻	1	2.93	3.44	8.98	8.26	4.54	3.86
	2			6.62	6.13	3.35	
	3			5.40	5.78	2.57	
	4				4.7	1.35	
	<i>I</i> →	1	2	2		1	
SO ₄ ²⁻	1	1.11	1.01	3.57	3.46	1.73	1.90
	2			2.35	2.01	0.87	
	<i>I</i> →	2		2			
OH ⁻	1	15.68		14.00	13.38		

25°C as 13.97, and using for log [H₂O] in this medium (of *d*=1.155) the value 1.71, we arrive at log *K*₁(H⁺)=15.68.

The fluoride system of U⁴⁺ has been investigated by Norén,¹⁷ using a fluoride membrane electrode. His values of *K_n*^{*} (*n*=1-3), valid in 4 M HClO₄ at 20°C, yields, with the relevant value of *K*₁(H⁺), the values of *K_n* entered in Table 5.

As to the sulphate system of U⁴⁺, the constants determined for 25°C by Day *et al.*¹⁹ have been recalculated to 20°C by means of the values of Δ*H*₁^{*} and Δ*H*₂^{*} determined by the same authors.* These measurements have been performed at *I*=2 M which excludes a direct comparison with our results¹¹ for the corresponding Np⁴⁺-complexes investigated at *I*=4 M. Sullivan and Hindman²⁰ have measured this system at *I*=2 M, however and moreover at 10.2, 25.2, and 35.3°C. From their values of *K_n*^{*} (at 25.2°C) and Δ*H_n*^{*}, combined with the value of *K*₁(H⁺) for *I*=2 and 20°C, the values of *K_n* entered in Table 5 have been calculated.

The values for the hydrolysis constants of U⁴⁺ and Np⁴⁺ are both founded on the measurements of Sullivan and Hindman.⁶ There is no basis for a recalculation to 20°C.

* It is then to be observed that, as far as sulphate is concerned, the Δ*H*-values of Table III of Ref. 19 in fact refer to the reactions U⁴⁺ + *n* HSO₄⁻ ⇌ U(SO₄)_{*n*}^{4-2*n*} + *n* H⁺.

Generally, the tetravalent ions form much stronger complexes with a given ligand than do the yl-ions. Also, for a given central ion, the fluoride complexes are always much stronger than the sulphate complexes. The fluoride complexes, especially of the tetravalent ions, are in fact extremely strong. This is all in accordance with the view that the complex formation of actinoid ions are essentially governed by the electrostatic interaction between the ligand and the central ion; the actinoid acceptors have a very strongly marked class (*a*), or hard, character.²¹⁻²³

On the other hand, the fluoride complexes of U^{4+} and UO_2^{2+} are stronger than those of Np^{4+} and NpO_2^{2+} . This is certainly not compatible with the very simplest electrostatic model which would demand an increase of the stability with the actinoid contraction, as has already been pointed out above. The reversal is strongest for the first complex. The constant K_1 is about five times lower for neptunium than for the corresponding uranium ions; for K_2 this factor is already considerably lower.

Also for the hydroxide systems of U^{4+} and Np^{4+} , the same condition prevails.

As to the sulphate systems, a mild reversal is observed for the tetravalent ions while the yl-ions show the trend expected from simple electrostatics, with at least the first NpO_2^{2+} -complex appreciably stronger than the corresponding UO_2^{2+} -complex.

The most probable interpretation of the reversed trend of complex stability between uranium and neptunium seems to be along the lines suggested by Grenthe²⁴ for a presumably analogous behaviour displayed by the lanthanoid(III) ions. With decreasing ionic radius of the acceptor, a change in the hydration shell is likely to occur along the series. This change will affect both the enthalpy and the entropy term which together make up the change of free energy of the complex formation reaction. *i.e.* determine the stability of the complex. The effect is bound to be especially large for ions of the present types, with high hydration energies^{25,26} and high hydration numbers.²⁷

At the formation of a complex, the exchange of the water molecules of the hydration shell for the ligand certainly takes place in various ways for various ligands, and for consecutive steps involving the same ligand. It is therefore rather to be expected that the reversal does not occur at the same acceptor for all ligands, or for all steps of a given ligand. Grenthe^{24,28} has in fact found a fairly wide variation in these respects, and the data discussed here indicate similar conditions within the actinoid series.

For a final proof that the reversal found for the actinoid acceptors is of the same nature as that found for the lanthanoid(III) ions, the enthalpies of the complex formation reactions have to be determined, in addition to the free energies already known.

We gratefully acknowledge the valuable support given to this work by *Statens naturvetenskapliga forskningsråd* (The Swedish Natural Science Research Council) and by *AB Atomenergi* (The Swedish Atomic Energy Company).

REFERENCES

1. Ahrland, S. and Brandt, L. *Acta Chem. Scand.* **22** (1968) 106, and references quoted therein.
2. Ahrland, S. *Acta Chem. Scand.* **5** (1951) 1151.
3. Fronæus, S. *Acta Chem. Scand.* **4** (1950) 72.
4. Sykes, K. W. and Taylor, B. L. *Proc. 7 ICCO, Stockholm 1962*, p. 31.
5. Day, R. A., Jr. and Powers, R. M. *J. Am. Chem. Soc.* **76** (1954) 3895.
6. Sullivan, J. C. and Hindman, J. C. *J. Phys. Chem.* **63** (1959) 1332.
7. Ahrland, S. *Acta Chem. Scand.* **3** (1949) 374.
8. Rush, R. M., Johnson, J. S. and Kraus, K. A. *Inorg. Chem.* **1** (1962) 378, and references quoted therein.
9. Rush, R. M. and Johnson, J. S. *J. Phys. Chem.* **67** (1963) 821.
10. Ahrland, S., Larsson, R. and Rosengren, K. *Acta Chem. Scand.* **10** (1956) 705.
11. Ahrland, S. and Brandt, L. *Acta Chem. Scand.* **20** (1966) 328.
12. Farrer, H. N. and Rossotti, F. J. C. *J. Inorg. Nucl. Chem.* **26** (1964) 1959.
13. Ahrland, S. *Helv. Chim. Acta* **50** (1967) 306.
14. Zebroski, E. L., Alter, H. W. and Heumann, F. K. *J. Am. Chem. Soc.* **73** (1951) 5646.
15. Zielen, A. J. *J. Am. Chem. Soc.* **81** (1959) 5022.
16. Sillén, L. G. and Martell, A. E., (Eds.), *Stability Constants of Metal Ion Complexes*, 2nd Ed., The Chemical Society, London 1964.
17. Norén, B. *Acta Chem. Scand.* *In press*.
18. Leden, I. *Pure Appl. Chem.* **8** (1964) 171.
19. Day, R. A., Jr., Wilhite, R. N. and Hamilton, F. D. *J. Am. Chem. Soc.* **77** (1955) 3180.
20. Sullivan, J. C. and Hindman, J. C. *J. Am. Chem. Soc.* **76** (1954) 5931.
21. Ahrland, S., Chatt, J. and Davies, N. R. *Quart. Rev.* **12** (1958) 265.
22. Pearson, R. G. *J. Am. Chem. Soc.* **85** (1963) 3533.
23. Ahrland, S. *Structure and Bonding*, Springer, Berlin, Heidelberg, New York 1966, Vol. 1, p. 207.
24. Grenthe, I. *Acta Chem. Scand.* **18** (1964) 293.
25. Phillips, C. S. G. and Williams, R. J. P. *Inorganic Chemistry*, Clarendon Press, Oxford 1965, Vol. 1, p. 160.
26. Halliwell, H. F. and Nyburg, S. C. *Trans. Faraday Soc.* **59** (1963) 1126.
27. Monk, C. B. *Electrolytic Dissociation*, Academic, London and New York 1961, p. 267.
28. Grenthe, I. *Kompleksemiska studier av karboxylatkomplex hos trevärdade joner i lantan och actiniumserien*, (Diss.), Lund 1964.