CHAPTER TWENTY THREE

ACTINIDES IN SOLUTION: COMPLEXATION AND KINETICS

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23.1 INTRODUCTION

The solution chemistry of the actinide elements has been explored in aqueous and organic solutions. While the relative stabilities of the actinide oxidation states and the types of complexes formed with the actinide cations in these states vary between solvents, the fundamental principles governing their redox reactions and their complexation strengths are the same regardless of the solvent. This chapter focuses on aqueous actinide chemistry, reflecting the wide variety of studies on actinide reactions in aqueous solutions. However, three factors that are important for actinides in non-aqueous solvents should be noted. First, in non-aqueous solvents, the formation of neutral cation–anion ion pairs is often dominant due to the lower (as compared to water) dielectric constants of the solvents. Second, non-aqueous conditions also allow the formation of complexes between actinide cations and ligands containing soft Lewis base groups, such as sulfur. Third, non-aqueous solvents are often useful for stabilizing redox-sensitive actinide complexes, as oxidation states that are unstable in aqueous solution may be stable in non-aqueous solutions (Mikheev *et al.*, 1977; Hulet *et al.*, 1979).

Actinide cations can exist in a variety of oxidation states (2+ to 7+) in aqueous solution, with trivalent, tetravalent, pentavalent, and hexavalent actinides being the most common. However, there is wide variability in the stability of a particular oxidation state across the actinide series and for some actinides several oxidation states can coexist in the same solution. This is most evident for plutonium as there are small differences in the redox potentials of Pu(III), Pu(IV), Pu(V), and Pu(VI) over a range of pH values (Fig. 23.1).

The divalent oxidation state is the most stable form of nobelium in acidic aqueous solution. It is strongly stabilized, relative to the trivalent state, by the formation of a closed, $5f^{14}$ shell, as reflected in the large reduction potential of the No^{3+} aquo ion [$E°$(No(III)/No(II)) = +1.45 V vs NHE] (see Chapter 19).

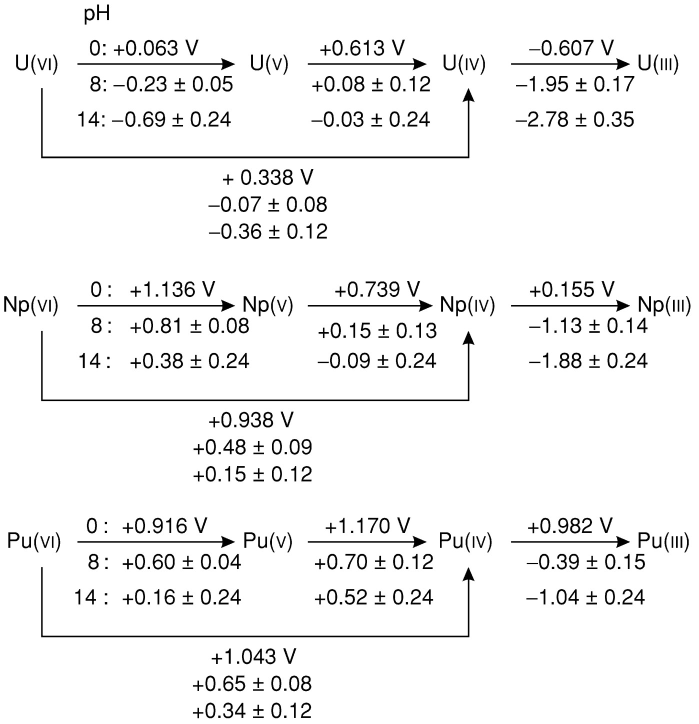


Fig. 23.1 *Reduction potential diagrams for uranium, neptunium, and plutonium for* 1 M $HClO_4$, *pH* 8, *and* 1 M *NaOH* (*Choppin* et al., 2002). *Values for* 1 M $HClO_4$ *are formal potentials for that medium.*

This is in direct contrast to nobelium's lanthanide homolog, ytterbium, which is significantly more stable as $E°(\mathrm{Yb(III)/Yb(II)}) = -1.05$ V vs NHE (Morss, 1985). The stability of No(II) suggests that isoelectronic Md(I) might be expected in aqueous solution. However, while Md(I) has been reported (Mikheev *et al.*, 1980), its existence has not been confirmed (Hulet *et al.*, 1979; Samhoun *et al.*, 1979). Md(II) is moderately stable in acidic solution [$E°(\mathrm{Md(III)/Md(II)}) = -0.15$ V vs NHE], and can be produced through the reduction of Md(III) by Cr(II), Eu(II), or metallic zinc. Nobelium and mendelevium are the only actinides stable as divalent cations in aqueous solution but Am(II), Cm(II), and Cf(II) can be produced transiently in aqueous acidic solutions by pulse radiolysis (Gordon *et al.*, 1978). Trivalent californium, einsteinium, and fermium also can be reduced to the divalent oxidation state by Sm(II) or Yb(II) in 85% ethanol/water.

The trivalent oxidation state is the most stable form of actinium and the transplutonium actinide ions, americium to mendelevium and lawrencium, in aqueous solution. Pu(III) is readily produced by reduction, but it is slowly oxidized to Pu(IV) by the radiolysis products from the α-decay if more than tracer amounts of ^{238}Pu or ^{239}Pu are present. Solutions of the long-lived plutonium isotopes ^{242}Pu and ^{244}Pu in 1 M perchloric acid show little oxidation of Pu(III) after storage for weeks. Np(III) is less stable than Pu(III) but its oxidation to Np(IV) is very slow in the absence of oxygen. U(III) is a strong reducing agent, oxidizing in water. Trivalent thorium and protactinium are not stable in solution.

All the actinides from thorium to californium form tetravalent species in aqueous solution. Th(IV) is the only oxidation state of thorium that is stable in solution. Pa(IV), U(IV), and Np(IV) are stable in the absence of oxygen. Low concentrations of Pu(IV) are stable in acidic aqueous solutions even in the presence of oxygen, but the similarity of the potentials of the Pu(IV)/Pu(V), Pu(V)/Pu(IV), and Pu(IV)/Pu(III) redox couples can make it difficult to prepare and maintain high concentrations of plutonium in a single oxidation state because of the resulting tendency of plutonium to undergo disproportionation reactions (see Section 23.10). Tetravalent americium, curium, berkelium, and californium are much less stable than the other An(IV) species, but they can be prepared in aqueous solution with strong oxidants in the presence of fluoride, phosphate, or polyoxometallate ligands, which form strong complexes with the tetravalent actinides. Bk(IV) is the most stable of the tetravalent transplutonium species with a Bk(IV)/Bk(III) reduction potential similar to that of Ce(IV) [$E°(\mathrm{Ce(IV)/Ce(III)}) = +1.6$ V vs NHE] (Antonio *et al.*, 2002).

The actinides from protactinium to americium can be prepared in the pentavalent oxidation state. Pa(V) and Np(V) are the most stable oxidation states of these elements in aqueous solution, though $\mathrm{NpO_2^+}$ disproportionates to Np(IV) and Np(VI) at high neptunium concentrations and acidities (>8 M $\mathrm{HNO_3}$). $\mathrm{UO_2^+}$ and $\mathrm{PuO_2{}^+}$ are very susceptible to disproportionation, but become more stable as the uranium or plutonium concentration is decreased or the pH is increased.

PuO_2^+ becomes the predominant dissolved form of plutonium in natural waters (Nelson and Lovett, 1978). AmO_2^+ is a strong oxidant and is reduced to Am(III) by alpha radiolysis.

The hexavalent oxidation state of the actinides, which is present as AnO_2^{2+} ions in aqueous solution, is known for the actinides from uranium to americium. UO_2^{2+} is the most stable form of uranium in solution and is the most stable of the actinyl(VI) cations. The stability of the actinyl(VI) cations decreases in the order $UO_2^{2+} >> PuO_2^{2+} > NpO_2^{2+} > AmO_2^{2+}$. Np(VI) can be reduced by cation exchange resin to Np(V) (Sullivan *et al.*, 1955).

The heptavalent actinides, Np(VII) and Pu(VII), are unstable in acidic solution. The reduction of Np(VII) and Pu(VII) to the hexavalent oxidation state is very slow in alkaline solutions (Spitsyn *et al.*, 1968; Sullivan and Zielen, 1969), and is reversible in 1 M NaOH (Zielen and Cohen, 1970). The structure of the Np(VII) anion, $NpO_4(OH)_2^{3-}$, is the same in the solid state (Burns *et al.*, 1973; Tomilin *et al.*, 1981; Grigor'ev *et al.*, 1986) and in solution (Appelman *et al.*, 1988; Williams *et al.*, 2001). The existence of Am(VII) (Krot *et al.*, 1974; Shilov, 1976) is still a matter of controversy.

Given the stabilities of the various oxidation states, as well as the limited availability and high specific activity of many of the actinide nuclides, there are comparatively few solution studies of the complexes of actinium, protactinium, and the transplutonium elements from berkelium to lawrencium. Quantitative information about the complexation of actinide ions in the less common oxidation states, An(II) and An(VII), also is very scarce. The lack of data on these species can often be filled by extrapolation from the behavior of other, better studied actinide cations.

Stability constants provide a measure of the resistance of a metal–ligand complex to dissociation in solution, and are directly related to the Gibbs energy of complexation. It is often difficult to measure the chemical activities of actinide ions, ligands, and complexes, so concentrations are used commonly in place of activities for calculations of stability constants. Such concentration stability constants are valid for only a limited range of conditions due to their dependence on the ionic strength of the solution. The concentration stability constant, β_{nq}, for the reaction of an actinide cation, An, with a ligand, L, according to the equation,

$$n\mathrm{An} + q\mathrm{L} \rightleftarrows \mathrm{An}_n\mathrm{L}_q$$

is

$$\beta_{nq} = [\mathrm{An}_n\mathrm{L}_q]/[\mathrm{An}]^n[\mathrm{L}]^q \tag{23.1}$$

This notation is used throughout this chapter to identify stability constants, Gibbs energies (ΔG_{nq}), enthalpies (ΔH_{nq}), and entropies (ΔS_{nq}) of complexation of n actinide cations by q ligands.

23.2 HYDRATION OF ACTINIDE CATIONS

The hydration of an actinide cation is a critical factor in the structural and chemical behavior of the complexes. Although f-element salts generally have large lattice energies, many are fairly soluble in water, reflecting the strength of the interactions between the metal cations and water molecules. Once an actinide cation is dissolved in an aqueous solution, the formation of inner sphere complexes involves displacement of one or more water molecules by each ligand. In the reaction with simple ligands to form inner sphere complexes, the release of water molecules from the hydration spheres of the ligand and actinide ion to the bulk solvent contributes to the thermodynamic strength of the complexes formed by increasing the entropy, but some of this gain is offset by a positive enthalpy contribution.

The size and structure of the hydration sphere of a metal ion have been probed by direct and indirect methods. Direct methods include X-ray and neutron diffraction, X-ray absorption fine structure (XAFS) measurements, luminescence decay, and nuclear magnetic resonance (NMR) relaxation measurements, while the indirect methods involve compressibility, NMR exchange, and optical absorption spectroscopy. Theoretical and computational studies are also becoming important in understanding the coordination geometry and coordination number (CN) of actinide ion hydrates (e.g. Spencer *et al.*, 1999; Hay *et al.*, 2000; Tsushima and Suzuki, 2000; Antonio *et al.*, 2001).

23.2.1 Trivalent actinides

Much of the initial hydration data reported for trivalent actinide cations were derived by analogy to the experimental data for the trivalent lanthanide ions. In the lanthanide studies, the data is consistent with formation of an isostructural series with nine water molecules coordinated to the early members of the lanthanide series that transitions to an isostructural series containing eight water molecules over the middle members of the lanthanide series. This reflects the decrease in radius with increasing atomic number; i.e. the lanthanide (and actinide) contraction. The transition between CN = 9 and 8 occurs between Pm(III) and Dy(III) for the Ln(III) series. The trivalent cations of both the An(III) and Ln(III) series have similar cationic radii, and a similar decrease in hydration number from nine to eight is observed for the trivalent actinide elements between Am(III) and Es(III) (Table 23.1), which span the same range of cationic radii as Pm(III)–Dy(III).

Initial measurements of the hydration of the trivalent actinides involved electrophoretic and diffusion methods in which it is difficult to differentiate between the total hydration (all of the water molecules that feel the effect of a cation over several concentric hydration spheres) and first sphere or primary hydration (i.e. the water molecules directly coordinated to the cation).

Table 23.1 *Hydration radii, R_b, hydration numbers, h, and primary sphere hydration, N_{H_2O}, of trivalent actinide ions obtained by electrophoresis and diffusion measurements* (*Lundqvist* et al., 1981; *Fourest* et al., 1984; *David*, 1986).

An^{3+}	R_b (Å)	h	N_{H_2O}
Am	4.60	13.6	9.0
Cm	4.69	14.4	8.9
	4.55	13.0	–
Cf	4.9	16.4	8.2
	4.64	13.8[a]	–
Es	4.92	16.6	8.0
Fm	4.95	16.9	–
Md	4.88	16.2	–

[a] Data obtained from diffusion measurements.

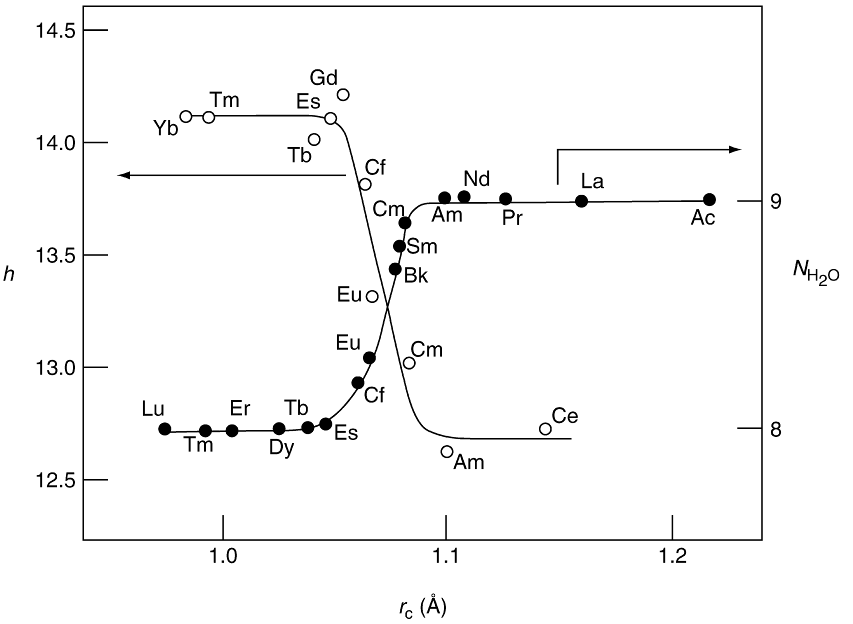


Fig. 23.2 *Total hydration* (*h*) *and number of water molecules in the primary coordination sphere*(N_{H_2O}) *of Ln^{3+} and An^{3+} cations* (*Rizkalla and Choppin,* 1994).

Fourest *et al.* (1984) estimated the primary, inner sphere coordination numbers, N_{H_2O} of the trivalent actinides by interpolation using the values of the lanthanide elements (Habenschuss and Spedding, 1979a, 1979b, 1980). The two sets of hydration numbers for Ln(III) and An(III) cations are presented in Fig. 23.2.

These values show that the primary hydration number, N_{H_2O}, of the trivalent metal ions as a function of cationic radius for coordination number 8 is, in both cases, sigmoidal with smaller primary hydration for the smaller, heavier cations. By contrast the opposite trend is seen for the total hydration number, *h*, which is smaller for the lighter cations. This was attributed by Fourest's group to the increase in the cationic charge density as the atomic number increases. It should be noted that the break in the properties of the two series also is observed in other physical data such as apparent molal volume, relative viscosity, heat of dilution, and electrical conductivity.

The coordination geometry in the first hydration sphere has been obtained primarily from neutron diffraction measurements and is consistent with formation of nona-coordinate lanthanides with a tricapped trigonal prismatic (TCTP) structure. X-ray crystal structures of nona-coordinate Ln(III) and Pu(III) triflates also show this geometry in the solid state (Chatterjee *et al.*, 1988; Matonic *et al.*, 2001). Similarly, the data for the heavier members of the series, with coordination number 8, are consistent with a square prismatic structure. The ions that are intermediate between these two extremes (Pm–Dy or Am–Es) show an equilibrium mixture of the structures for $N_{H_2O} = 8$ and $N_{H_2O} = 9$. Optical spectroscopy indirectly confirms that the solid state structures of the hydrated An(III) ions persist in solution as well (Carnall, 1989; Matonic *et al.*, 2001), and fluorescence lifetime measurements of Cm(III) solutions give a direct primary hydration number of (9.2 ± 0.5) (Kimura and Choppin, 1994).

While it cannot give the coordination geometry, XAFS measurements are useful for determining the average actinide–oxygen bond distances of the first hydration sphere and N_{H_2O} in liquid samples at concentrations much lower than those accessible by X-ray or neutron diffraction. An–OH_2 bond distances and coordination numbers have been determined by XAFS for all of the An(III) from U(III) to Cf(III) at concentrations of $0.5-20 \times 10^{-3}$ M. The An–O bond distances are all consistent with octa- or nona-coordination, and the average coordination number reported across the actinide series is (9 ± 1). As is the case with the other oxidation states, some investigators report hydration numbers 10–20% higher than this, but this is within the generally accepted absolute uncertainty of XAFS-based coordination number determinations and there are a number of factors that could explain systematic deviations from the true coordination number, as discussed by Allen *et al.* (2000).

23.2.2 Tetravalent actinides

Information relating to the hydration numbers of tetravalent actinide ions is somewhat limited. From NMR peak areas, an estimate of the primary hydration number of Th(IV) in an aqueous acetone solution of $Th(ClO_4)_4$ at −100°C indicated a hydration number of 9 (Butler and Symons, 1969; Fratiello *et al.*, 1970a) whereas an indirect, NMR line width method gave $N_{H_2O} = 10$ (Swift and Sayre, 1966). However, the direct and accurate method of solution X-ray diffraction gave $N_{H_2O} = (8.0 \pm 0.5)$ for acidic, 1–2 M $Th(ClO_4)_4$ and $ThCl_4$ solutions (Johansson *et al.*, 1991). Other reported values are: Th(IV) (10.8 ± 0.5) and U(IV) (10 ± 1) (Moll *et al.*, 1999), Np(IV) (11.2 ± 0.4) (Allen *et al.*, 1997), Th(IV) 11.0, U(IV) 10.65, Np(IV) 10.2, and Pu(IV) 10.0 (David and Vokhmin, 2003).

An entirely different method for the estimation of total hydration numbers from conductivity measurements has been proposed and developed by Gusev (1971, 1972, 1973). This method gave a value of $h = 20$ for the total hydration number of Th(IV), which can be compared to the values of 22 obtained from compressibility measurements (Bockris and Saluja, 1972a,b) that are based on the lower compressibility of a solvate's solvent molecules as a result of electroconstriction (Passynskii, 1938).

Reviews of the available evidence pertaining to hydration numbers of U(IV) and Np(IV) have suggested that two forms of each of these aquo ions may exist, differing in geometry and possibly coordination number (Rykov *et al.*, 1971; Sullivan *et al.*, 1976). Radial distribution functions from X-ray measurements on 2 M uranium(IV) perchlorate solutions indicate a primary hydration number of $N_{H_2O} = (7.8 \pm 0.3)$ with no perchlorate in the primary coordination sphere (Pocev and Johansson, 1973). XAFS measurements of Np(IV) and Bk(IV) aquo cations gave $N_{H_2O} = (9 \pm 1)$ and (7.9 ± 0.5), respectively (Antonio *et al.*, 2001, 2002). The An–O bond distances derived from XAFS for the An(IV) hydrates, which are more accurate than the coordination numbers, also are most consistent with a primary hydration number of 8. Changes in the optical absorption spectra of U(IV), Np(IV), and Pu(IV) also have been interpreted as consistent with $N_{H_2O} = 8$ (Rykov *et al.*, 1973).

23.2.3 Pentavalent and hexavalent actinides

The hydration of pentavalent actinyl cations has been studied less than any of the other common oxidation states, but the findings are quite consistent from study to study. In the solid state, neptunyl(V) perchlorate has a total equatorial coordination number of 5. Four oxygens come from inner sphere water molecules and a fifth oxygen comes from the '-yl' oxygen of a neighboring NpO_2^+ ion (Grigor'ev *et al.*, 1995), as discussed in Section 23.9. In solutions, where the AnO_2^+ concentration is usually quite small, cation–cation complexes (Section 23.9) of AnO_2^+ are not important, and fully hydrated AnO_2^+ cations are expected. Optical absorption spectra of AnO_2^+ in solution are consistent with a primary hydration number of 5, based on symmetry considerations and comparison with the spectra of solid state complexes of known structures (Garnov *et al.*, 1996). XAFS measurements on solutions containing 1×10^{-3} to 2×10^{-2} M NpO_2^+ agree well with this, consistently giving a hydration number of 5 and Np–O equatorial bond distances that suggest the coordination of 5 water molecules (Combes *et al.*, 1992; Allen *et al.*, 1997; Antonio *et al.*, 2001).

Hydration numbers of the hexavalent actinyl cations have received more attention, particularly for UO_2^{2+}. The Raman spectra of aqueous uranyl solutions were interpreted to show the presence of six inner sphere water molecules in the plane perpendicular to the O=U=O axis (Sutton, 1952). However, similar hydration numbers have been obtained by methods that are influenced by the second hydration shell. For example, activity coefficient measurements suggest a hydration number of 7.4 relative to an assumed hydration number of zero for Cs(I) (Hinton and Amis, 1971). Similarly, a hydration number of 7 has been derived from conductivity measurements (Gusev, 1971, 1972, 1973).

In the solid state, $UO_2(ClO_4)_2 \cdot 7H_2O$ contains discrete pentagonal bipyramidal $UO_2(H_2O)_5^{2+}$ cations and ClO_4^- anions (Alcock and Esperås, 1977), an indication that, like the actinyl(V) cations, penta hydration may be preferred by actinyl(VI) cations in solution. Garnov *et al.* (1996) also deduced a hydration number of 5 for AnO_2^{2+} from absorption spectra of PuO_2^{2+}. It seems likely that this is correct since XAFS measurements of AnO_2^{2+} solutions also give average hydration numbers of ranging from 4.5 to 5.3 and An–O equatorial bond distances that are close matches for those of pentacoordinate $UO_2(H_2O)_5^{2+}$ in $UO_2(ClO_4)_2 \cdot 7H_2O$ (Allen *et al.*, 1997; Wahlgren *et al.*, 1999; Antonio *et al.*, 2001). In agreement with this, a study of uranyl(VI) perchlorate solutions by X-ray diffraction concluded that the hydration number of UO_2^{2+} could be either 4 or 5 (Åberg *et al.*, 1983a).

23.2.4 Solvation and hydration in non-aqueous media

Solvation numbers of actinide cations in non-aqueous media have been measured for only a few systems. FTIR investigations of the homologous lanthanide solvates $[Ln(NO_3)_3(DMSO)_n]$ in anhydrous acetonitrile (Bünzli *et al.*, 1990) indicated a change in coordination number in the middle of the series near Eu(III) from nine to eight with increasing atomic number. NMR spectroscopy, stoichiometric, and XAFS measurements gave a solvation number of 2 for uranyl nitrate salts in tri(*n*-butyl)phosphate (TBP) solutions. The total coordination number would include two for TBP coordination and four for the bidentate nitrate coordination (Siddall and Stewart, 1967; Den Auwer *et al.*, 1997).

A commonly used extractant ligand in actinide separation science is thenoyltrifluoroacetone, TTA. The luminescent lifetimes of the Cm(III) complex with TTA in various organic solvents was 130–140 μs which gives $N_{H_2O} = (3.8 \pm 0.5)$. This indicates the formation of a Cm–TTA complex with a total CN = 10 (Dem'yanova *et al.*, 1986).

Solvation of UO_2^{2+} ions in water–acetone and water–dioxane mixtures were studied by ultrasound (Ernst and Jezowska-Trzebiatowska, 1975a,b). The resulting hydration numbers are listed in Table 23.2. The data show a decrease in the hydration numbers with increasing dioxane concentration. This can be attributed to a partial replacement of waters of hydration by the organic

Table 23.2 *Hydration numbers of* AnO_2^{2+} *ions in aqueous and mixed solvents.*

Salt	*Medium*	*Method*	*h*	*References*
UO_2SO_4	water	ultrasound	10.3	Ernst and Jezowska-Trzebiatowska (1975a,b)
$UO_2\,(NO_3)_2$	water	ultrasound	11.9	Ernst and Jezowska-Trzebiatowska (1975a,b)
UO_2SO_4	dioxane–water (20%)	ultrasound	6.3	Ernst and Jezowska-Trzebiatowska (1975a,b)
$UO_2\,(NO_3)_2$	dioxane–water (20%)	ultrasound	6.3	Ernst and Jezowska-Trzebiatowska (1975a,b)
UO_2SO_4	dioxane–water (45%)	ultrasound	4.8	Ernst and Jezowska-Trzebiatowska (1975a,b)
$UO_2\,(NO_3)_2$	dioxane–water (45%)	ultrasound	5.8	Ernst and Jezowska-Trzebiatowska (1975a,b)
$UO_2\,(ClO_4)_2$	acetone–water	PMR	4.0	Fratiello *et al.* (1970b)
$UO_2\,(NO_3)_2$	acetone–water	PMR	2.0	Fratiello *et al.* (1970b)
$UO_2\,(ClO_4)_2$	acetone–water	PMR	6.0	Shcherbakov and Shcherbakova (1976)
$UO_2\,(NO_3)_2$	acetone–water	PMR	6.0	Shcherbakov and Shcherbakova (1976)
UO_2Cl_2	acetone–water	PMR	6.0	Shcherbakov and Shcherbakova (1976)
$UO_2\,(ClO_4)_2$	acetone–water	PMR	4.7–4.9	Bardin *et al.* (1998)
$UO_2\,(ClO_4)_2$	acetone–water	PMR	4.5–4.9	Åberg *et al.* (1983a)
$NpO_2\,(ClO_4)_2$	acetone–water	PMR	6.0	Shcherbakov *et al.* (1974)
$NpO_2\,(ClO_4)_2$	acetone–water	PMR	4.8	Bardin *et al.* (1998)

solvent although inner sphere complexation by the anion would also reduce the hydration number.

This result is in agreement with low-temperature ^{1}H-NMR measurements for both UO_2X_2 (X is ClO_4^-, Cl^-, or NO_3^-) (Fratiello *et al.*, 1970b; Shcherbakov and Shcherbakova, 1976) and NpO_2^{2+} (Shcherbakov *et al.*, 1974) compounds (Table 23.2). For uranyl, the average number of bound waters was shown to increase with increasing molar ratio, $[H_2O]/[UO_2^{2+}]$, to a limiting value of six for ratios from 40 to 70 depending on the anion (Shcherbakov and Shcherbakova, 1976). The stronger the complexing ability of the anion, the higher the ratio required to reach maximum hydration. More recent high-field NMR measurements of UO_2^{2+} and NpO_2^{2+} hydration report $N_{H_2O} = 4.7–4.9$ for a range of $[H_2O]/[AnO_2^{2+}]$ ratios (Åberg *et al.*, 1983a; Bardin *et al.*, 1998).

23.2.5 Measurements of N_{H_2O} by TRLF technique

Beitz and Hessler (1980) reported the first study of aqueous Cm(III) photophysics, including measurement of the emission spectrum and lifetimes of aqueous of Cm^{3+} in H_2O and D_2O. Beitz (1994) reported a value of $N_{H_2O} = 9$ for the hydrated Cm^{3+} cation and smaller residual inner sphere hydration numbers for a number of Cm(III) complexes in a review of the theoretical and experimental aspects of such studies to 1994. Studies by time-resolved laser fluorescence (TRLF) with Cm(III) have proven very valuable for understanding the hydration of trivalent actinides. Measurement of the Cm fluorescence decay constant, k(Cm), as a function of residual hydration in crystals of lanthanide complexes of known structure and hydration doped with Cm(III) resulted in equation (23.2) for calculation of the residual hydration numbers (Kimura and Choppin, 1994):

$$N_{H_2O} = 0.65k(\mathrm{Cm}) - 0.88 \tag{23.2}$$

where k(Cm) is expressed in ms^{-1}. This equation assumes no contribution from the ligand to the deexcitation of the luminescence excited state and that quenching of the excitation results only from interaction with the OH vibrators of the water in the first coordination sphere. The absolute uncertainty in the hydration numbers calculated from equation (23.2) is ±0.5. Use of equation (23.2) gives a value for N_{H_2O} of Cm^{3+} in water of (9.2 ± 0.5).

The residual hydration in the primary coordination sphere of Cm(III) in a number of aminopolycarboxylate complexes (Kimura and Choppin, 1994) is plotted in Fig. 23.3 and shows the variation of the measured hydration number, N_{H_2O}, as a function of pH. These data indicate that the complexation is initiated around pH 2–4 and the hydration number remains constant until pH values of 10 and higher are reached. This constancy over the medium pH range is consistent with the formation of very strong 1:1 complexes. The two plateaus in the data for the NTA complex reflects the successive formation of 1:1 and 1:2 complexes for this smaller ligand. In Table 23.3, the calculated hydration numbers reported for the different complexes are listed for Am(III) and Nd(III) (Kimura and Kato, 1998) and Cm(III) and Eu(III) (Kimura *et al.*, 1996). In these systems, the total coordination number (i.e. the sum of the average number of ligand donor groups and primary water molecules) was (9.3 ± 0.4) for Cm(III), (10.7 ± 0.5) for Am(III), (8.8 ± 0.5) for Eu(III) and (9.9 ± 0.5) for Nd(III) complexation.

The TRLF technique has been used to characterize Cm(III) complexation in natural waters by ligands such as OH^-, CO_3^{2-}, NO_3^- and humic acids (Table 23.4). While the aqueous Cm^{3+} ion has nine water molecules in the primary coordination sphere, $N_{H_2O} = 8.5$, 8.0, 7.0, 5.0, and 3.0 are expected for monohydroxide, dihydroxide, monocarbonate, dicarbonate, and tricarbonate complexes, respectively, from the assumptions that OH vibrators of coordinated water molecules act independently in the de-excitation process and a carbonate ion coordinates with Cm(III) as a bidentate ligand. The N_{H_2O} for each

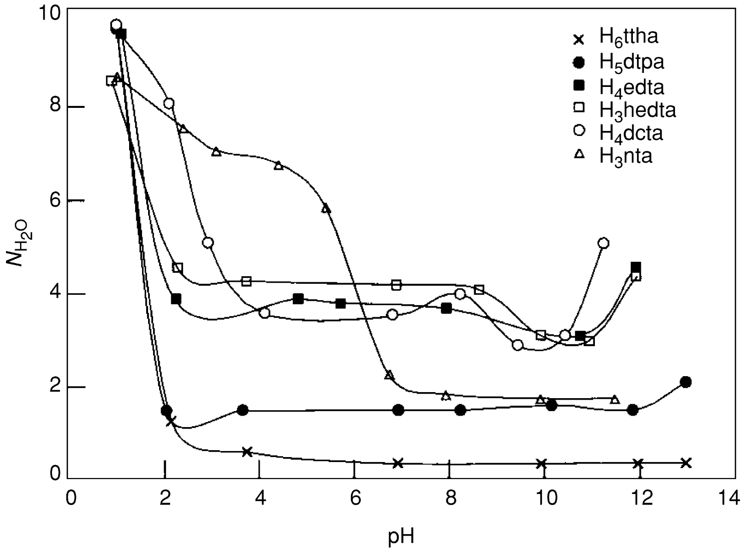


Fig. 23.3 *Dependence of the hydration number of Cm(III) complexes with polyaminopolycarboxylate ligands on pH.* $I = 0.1$ M $NaClO_4$, $[Cm] = 7.3 \times 10^{-6}$ M, $[ligand] = 8 \times 10^{-6}$ M. *H_6ttha = triethylenetetraaminehexaacetic acid, H_5dtpa = diethylenetriaminepentaacetic acid, H_4edta = ethylenediaminetetraacetic acid, H_3hedta = N-(2-hydroxyethyl) ethylenediaminetriacetic acid, H_4dcta = trans-1,2-diaminocyclohexane-tetraacetic acid, H_3nta = nitriliotriacetic acid.*

Table 23.3 *Inner sphere hydration numbers of Am(III), Cm(III), Nd(III) and Eu(III) complexes with aminopolycarboxylate ligands.*

	$N^{a}_{H_2O}$			
Ligand	*Am(III)*	*Cm(III)*	*Nd(III)*	*Eu(III)*
nta^{3-} (1:1)	6.5	6.3	5.6	4.5
nta^{3-} (1:2)	–	1.7	–	–
$hedta^{3-}$	5.1	4.2	4.5	3.2
$edta^{4-}$	4.8	3.7	4.0	2.7
$dcta^{4-}$	–	3.8	4.5	2.5
$dtpa^{5-}$	3.1	1.7	2.6	1.0
$ttha^{6-}$	1.6	0.6	0.7	1.2

[a] Uncertainties are ±0.5.

species calculated from the lifetime in Table 23.4 agrees with each expected value within the experimental uncertainty. The lifetimes measured for Cm(III) humate and fulvate complexes involves two components, which indicates the presence of two types of complexes. The first component gives an N_{H_2O} of 8.2–8.4 and the second, 3.6–3.7.

Table 23.4 *Inner sphere hydration number of Cm(*III*) complexes from fluorescence lifetimes.*

Medium	*Excitation* (nm)	*Emission* (nm)	*Lifetime* (μs)	N_{H_2O} (±0.5)	*References*
0.1 M $HClO_4$	396.7	593	68	8.7	Beitz *et al.* (1988)
1.0 M $HClO_4$	375.4	593.8	63	9.4	Klenze *et al.* (1991)
	381.3	–	–	–	
	396.5	–	–	–	
16 M HNO_3	383	603–607	107 ± 3	5.2	Beitz (1991)
0.1 M $HClO_4$	375.4	593.8	72.5 ± 1.3	8.1	Kim *et al.* (1991)
3 M K_2CO_3	337	608	240	1.8	Decambox *et al.* (1989)
1 M $NaCO_3$	383	590(sh)	160 ± 5	3.2	Beitz (1991)
	–	599(sh)	–	–	
0.1 M Na_2CO_3	377.5–399.4	607.4	141	3.7	Klenze *et al.* (1991)
$Cm(OH)^{2+}$	397.2	598.8	72 ± 2	8.2	Wimmer *et al.* (1992)
$Cm(OH)_2{}^+$	399.2	603.5	80 ± 10	7.3	Wimmer *et al.* (1992)
$Cm(CO_3)^+$	397.5	598.0	85 ± 4	6.8	Wimmer *et al.* (1992)
$Cm(CO_3)_2^-$	398.9	605.9	105 ± 5	5.3	Wimmer *et al.* (1992)
$Cm(CO_3)_3^{3-}$	399.9	607.6	215 ± 6	2.1	Wimmer *et al.* (1992)
Cm humate	398	601.0	72 ± 5 (80%)	8.2	Wimmer *et al.* (1992)
	–	–	145 (20%)	–	
Cm fulvate	374–398.5	600.3	70 ± 5 (80%)	3.6	Wimmer *et al.* (1992)
	–	–	142 (20%)	–	

All of the N_{H_2O} values calculated using equation (23.2) from the fluorescence lifetimes in the literature are chemically reasonable. The determination of the hydration number from fluorescence lifetimes makes it possible to characterize Cm(III) species in aqueous solution at high sensitivity, providing valuable insight into the primary structure of ions in solution.

23.2.6 Hydration in concentrated solutions

Data from luminescence studies in more concentrated media must be evaluated carefully. An example of this is shown in Fig. 23.4 in which the measured hydration number for the trivalent europium ion increases as the perchloric acid concentration increases. This presumably reflects the fact that as the electrolyte concentration increases, the number of water molecules in the

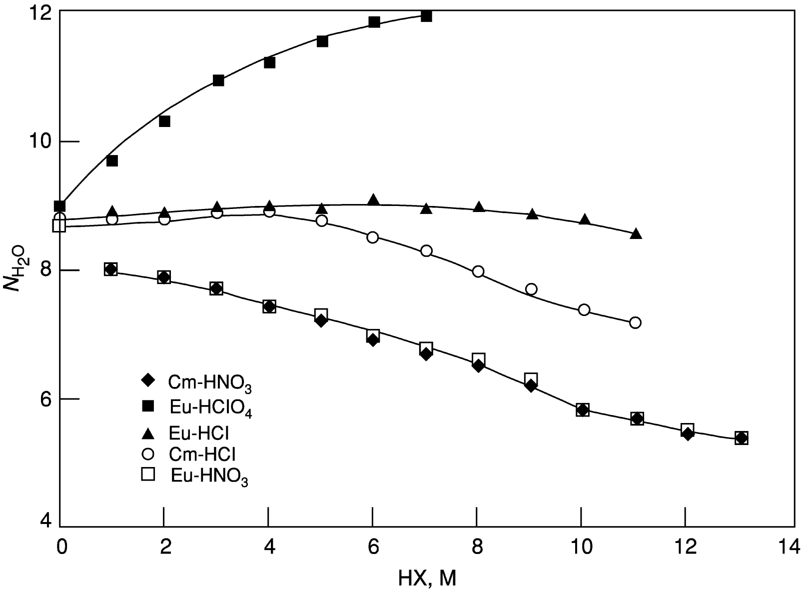


Fig. 23.4 *Variation of the number of water molecules in the primary hydration sphere of trivalent europium and curium ions as determined by TRLF.*

secondary hydration sphere decreases and, consequently, there is a tightening of the bond between the trivalent europium and the hydrate waters in the inner sphere. This tightening allows for more efficient quenching of the fluorescence by the hydroxyl groups of the H_2O. NMR studies (Choppin, 1997) have shown that inner sphere complexation by perchlorate ions does not occur below approximately 8–10 M. Obviously, this calculated increase in hydration number does not represent greater hydration nor does it represent an effect of complexation by perchlorate; rather, it is due to the tighter bonding.

The data in Fig. 23.4 show that the hydration number of the Eu(III) remains relatively constant in hydrochloric acid up to approximately 6–8 M, after which it decreases. The same is true for the Cm(III) hydration number in HCl, which begins a decline at about 5 M HCl. This difference presumably reflects greater complexation of the actinide trivalent ion by the relatively soft anion Cl^-. In fact, this difference in complexation has been used for over 40 years to provide efficient separation of trivalent actinides from trivalent actinides in concentrated HCl solutions by passage through columns of cation exchange resin. Independent studies (Rizkalla and Choppin, 1994) have shown that complexation does occur with the chloride anions for both trivalent actinides and lanthanides in 1.0 M HCl. The constancy of the hydration number in Fig. 23.4 for both cations to concentrations of ca. 4 M HCl indicates that up to this concentration, only outer sphere complexes are formed and, therefore, the primary hydration sphere is not affected. At higher concentrations, however, there is greater complexation by the soft donor Cl^- with the actinide, which has been interpreted as reflecting an enhanced covalent interaction of trivalent actinide ions relative to that of lanthanide ions of the same ionic radius (Diamond *et al.*, 1954, see Section 23.4). By contrast, in Fig. 23.4 it is seen that the Cm(III) and Eu(III) behavior as a function of nitric acid concentration is very similar from dilute acid to ≥ 12 M. Nitrate ions begin to form inner sphere complexes at lower concentrations than chloride anions do, as reflected in the decreased hydration number even at relatively lower concentrations. However, the oxygens of the nitrate are hard donors and, therefore, there is no evidence of any covalent enhancement in its bonding as is seen with the chloride anions for the trivalent actinide cations relative to the lanthanide cations.

23.2.7 Thermodynamic properties

As Chapter 19 of this work is devoted to the thermodynamic properties of the actinides, their ions and compounds, this section focuses only on the hydration behavior of the actinides to minimize overlap. The values used for the calculations of the thermodynamic properties in this section are taken from literature references, which are sometimes different from those accepted in recent critical assessments of the thermodynamic properties of the actinides (Grenthe *et al.*, 1992; Silva *et al.*, 1995; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003) or those in Chapter 19.

The thermodynamic properties of the actinide ions in the oxidation states III–VI have been reviewed by Morss (1976), Fuger and Oetting (1976), Fuger (1982), and David (1986). Calorimetric measurements of the heats of formation of the trivalent cations are limited to the actinides up to californium that are available in macroscopic quantities and with isotopes of sufficiently low specific radioactivity. Entropies of Pu(III) (Hinchey and Cobble, 1970; Fuger and Oetting, 1976), Th(IV) (Morss and McCue, 1976), and the actinyl ions UO_2^{2+} (Coulter *et al.*, 1940), NpO_2^+ and NpO_2^{2+} (Brand and Cobble, 1970) also have been reported. Data on other actinide species have been estimated across the entire actinide series using various models.

David *et al.* (1985) proposed a general expression for the calculation of the absolute enthalpy of hydration, $\Delta H^{\circ}_{\mathrm{hyd}}$, based on the semiempirical model of Bockris and Reddy (1970). The hydration enthalpy of a cation can be related to the crystallographic radius, R, the hydration number, $N_{\mathrm{H_2O}}$, and the ionic charge, $+Z$, by the equation:

$$\begin{aligned}\Delta H^{\circ}_{\mathrm{hyd}} = {} & \alpha Z^2(R+2R_{\mathrm{W}})^{-1} + \beta Z N_{\mathrm{H_2O}}(R+R_{\mathrm{W}})^{-2}\gamma Z N_{\mathrm{H_2O}}(R+R_{\mathrm{W}})^{-3} \\ & + \sigma Z^2 N_{\mathrm{H_2O}}(R+R_{\mathrm{W}})^{-4} + N_{\mathrm{H_2O}}W + P(-1)^Z \end{aligned} \tag{23.3}$$

where W is the hydration energy of one water molecule and R_w is the radius of a water molecule, 1.38 Å. The numerical values of the coefficients (α, β, etc.) of equation (23.3) were computed using hydration enthalpies (which included contributions from the hydration of halide anions) of 35 monovalent, divalent, trivalent, and tetravalent ions (David *et al.*, 1985) assuming $N_{\mathrm{H_2O}} = 4$ for monovalent, 6 for divalent, and 8 for trivalent and tetravalent cations. The estimated uncertainty between the experimental and calculated enthalpies is 0.4–0.5%.

Bratsch and Lagowski (1985a,b, 1986) proposed an ionic model to calculate the thermodynamics of hydration $\Delta G^{\mathrm{o}}_{\mathrm{hyd}}$, $\Delta H^{\mathrm{o}}_{\mathrm{hyd}}$, and $\Delta S^{\mathrm{o}}_{\mathrm{hyd}}$ using standard thermochemical cycles. The model uses the values of the enthalpy of formation of the monoatomic gas $[\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{M_g})]$, the ionization potential for the oxidation state under consideration, and the crystal ionic radius of the metal ion. Since the ionization potentials for the actinide ions are not all available, the authors 'back-calculated' an internally consistent set of ionization potentials from selected thermodynamic data (Bratsch and Lagowski, 1986). The general set of equations used are:

$$\Delta H^{\mathrm{o}}_{\mathrm{hyd}}(\mathrm{M}^{Z+}) = \Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{M}^{Z+}_{\mathrm{aq}}) - \Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{M}^{z+}_{\mathrm{g}}) + \mathrm{Z}[\Delta H^{\mathrm{o}}_{\mathrm{f}}(\mathrm{H}^{+}_{\mathrm{g}}) + \Delta H^{\mathrm{o}}_{\mathrm{hyd}}(\mathrm{H}^{+}_{\mathrm{aq}})] \tag{23.4a}$$

$$\Delta S^{\mathrm{o}}_{\mathrm{hyd}}(\mathrm{M}^{Z+}) = S^{\mathrm{o}}(\mathrm{M}^{Z+}_{\mathrm{aq}}) - S^{\mathrm{o}}(\mathrm{M}^{Z+}_{\mathrm{g}}) + Z[S^{\mathrm{o}}(\mathrm{H}^{+}_{\mathrm{g}}) + \Delta S^{\mathrm{o}}_{\mathrm{hyd}}(\mathrm{H}^{+}_{\mathrm{aq}})] \tag{23.4b}$$

$$\Delta G^{\mathrm{o}}_{\mathrm{hyd}}(\mathrm{M}^{Z+}) = \Delta G^{\mathrm{o}}_{\mathrm{f}}(\mathrm{M}^{Z+}_{\mathrm{aq}}) - \Delta G^{\mathrm{o}}_{\mathrm{f}}(\mathrm{M}^{Z+}_{\mathrm{g}}) + Z[\Delta G^{\mathrm{o}}_{\mathrm{f}}(\mathrm{H}^{+}_{\mathrm{g}}) + \Delta G^{\mathrm{o}}_{\mathrm{hyd}}(\mathrm{H}^{+}_{\mathrm{aq}})] \tag{23.4c}$$

The calculated Gibbs energies and enthalpies of hydration for the actinide ions are listed in Tables 23.5 and 23.6.

The absolute entropies for the gaseous ions are calculated with the equation (Johnson, 1982):

$$S^{\mathrm{o}}(\mathrm{M}^{Z+}_{\mathrm{g}}) = 1.5R\ \ln(\mathrm{at\,wt.}) + R\ \ln(2J + 1) + 108.75 \tag{23.5}$$

The values of the entropies of the trivalent aquo actinide ions were obtained by interpolation from the dependence of the corrected (structural) entropy term, $S^{\mathrm{o}}_{\mathrm{c}}$ (see Chapter 19, equation (19.6)), of the lanthanides on ionic radii (Fig. 23.5) These corrected entropy values are only dependent on the structure of the aquo ion (David *et al.*, 1985). Justification of this approach is provided by the agreement of the calculated value of $S^{\mathrm{o}}_{\mathrm{c}}$ of Pu(III) with that from experimental data (Fuger and Oetting, 1976). The entropies are listed in Table 23.7. Similarly, the entropies of the tetravalent actinides were obtained from pertinent data on Th(IV) (Morss and McCue, 1976) and Ce(IV) (Morss, 1976).

Table 23.5 *Gibbs energies of formation and hydration of the gaseous and hydrated actinide ions. Data from Bratsch and Lagowski* (1986) *and Marcus and Loewenschuss* (1986).

	Gas phase ΔG_f° (kJ mol^{-1})			*Aquo ion* ΔG_f° (kJ mol^{-1})				ΔG_{hyd}° (kJ mol^{-1})		
Element	+3	+4	+6	+3	+4	+5	+6	+3	+4	+6
Ac	3832	–	–	−614	–	–	–	−3093	–	–
Th	4182	6960	–	−314	−704	–	–	−3143	−5860	–
Pa	4136	7128	–	−411	−606	−1050	–	−3194	−5930	–
U	4114	7259	1177	−477	−539	−969	−953	−3238	−5994	−1228
Np	4115	7357	–	−516	−497	−915	−796	−3278	−6050	–
Pu	4095	7432	–	−571	−475	−850	−757	−3313	−6105	–
Am	4110	7598	–	−590	−356	−741	−587	−3347	−6150	–
Cm	4144	7700	–	−586	−298	–	–	−3377	−6194	–
Bk	4186	7622	–	−574	−416	–	–	−3407	−6234	–
Cf	4222	7822	–	−563	−250	–	–	−3432	−6268	–
Es	4256	7990	–	−554	−116	–	–	−3457	−6302	–
Fm	4285	8076	–	−547	−61	–	–	−3479	−6333	–
Md	4379	8219	–	−476	51	–	–	−3502	−6364	–
No	4523	8477	–	−351	282	–	–	−3521	−6391	–
Lr	4347	8452	–	−546	233	–	–	−3540	−6415	–

Table 23.6 *Standard enthalpies of formation of the gaseous and hydrated actinide ions. Data from Bratsch and Lagowski* (1986) *and Marcus and Loewenschuss* (1986). *Number in brackets denote experimental data.*

	Gas phase ΔH_f° (kJ mol^{-1})			*Aquo ion* ΔH_f° (kJ mol^{-1})				ΔH_{hyd}° (kJ mol^{-1})		
Element	+3	+4	+6	+3	+4	+5	+6	+3	+4	+6
Ac	3885	–	–	−633	–	–	–	−3224	–	–
Th	4242	7022	–	−327	−766	–	–	−3275	−6063	–
Pa	4197	7194	–	−411	−664	−677	–	−3326	−6133	–
U	4176	7327	1210	−423	−595	−1032	(−1019)	−3371	−6197	−1345
Np	4177	7425	–	−528	−553	−978	−861	−3411	−6253	–
Pu	4154	7498	–	−587	−534	−915	−822	−3447	−6307	–
	–	–	–	(−592)	–	–	–	–	–	–
Am	4165	7664	–	−608	−414	−805	−652	−3479	−6353	–
	–	–	–	(−617)	–	–	–	–	–	–
Cm	4199	7756	–	−608	−364	–	–	−3513	−6395	–
	–	–	–	(−615)	–	–	–	–	–	–
Bk	4241	7682	–	−597	−480	–	–	−3544	−6437	–
	–	–	–	(−601)	–	–	–	–	–	–
Cf	4277	7882	–	−587	−314	–	–	−3570	−6471	–
	–	–	–	(−577)	–	–	–	–	–	–
Es	4308	8048	–	−584	−182	–	–	−3598	−6505	–
Fm	4337	8135	–	−580	−127	–	–	−3623	−6437	–
Md	4432	8279	–	−510	−13	–	–	−3648	−6567	–
No	4580	8542	–	−382	223	–	–	−3668	−6594	–
Lr	4402	8518	–	−581	175	–	–	−3689	−6618	–

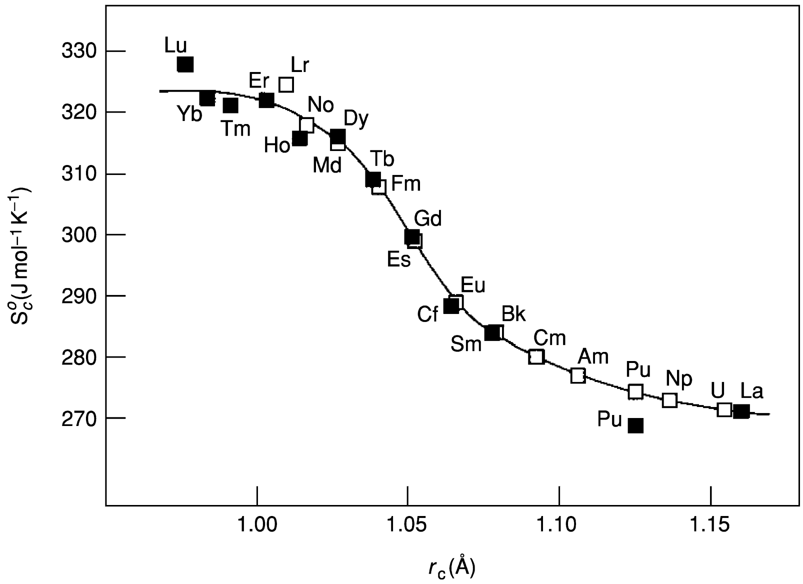


Fig. 23.5 *Variation of the corrected entropy,* S^o_c*, with the crystallographic radius of the trivalent lanthanides and actinides with CN* = 8. (■) *experimental data* (□) *extrapolated data.*

Differences in lanthanide and actinide hydration thermodynamics have been attributed by Bratsch and Lagowski (1986) to relativistic effects in the actinides which perturb the energies of the s, p, d, and f orbitals. The first and second ionization potentials of the 7s electrons of the actinides are higher than those of the 6s electrons of the lanthanides whereas the third ionization potentials are similar for both groups and the fourth ionization potential is lower for the actinides than the lanthanides. A small decrease in IP_3 and IP_4 for the f^7 configuration in the actinides results in smoother variations in the relative stabilities of the adjacent oxidation states across the actinide series while the greater spatial extension of the 5f orbitals increases the actinides' susceptibility to environmental effects (Johnson, 1982).

Nugent *et al.* (1973a,b) proposed equation (23.6) as a basis for comparison of the actinide and lanthanide thermodynamics:

$$P(\mathrm{M}) = \Delta H^o_f(\mathrm{M_g}) + \Delta E(\mathrm{M}) - \Delta H^o_f(\mathrm{M^{3+}_{aq}}) \qquad (23.6)$$

where ΔE(M) is the promotion energy from the ground state electron configuration to the $f^q d^1 s^2$ configuration where q varies from 0 (La and Ac) to 14 (Lu and Lr). ΔE(M) is approximately zero or near zero for La, Ce, Gd,

Table 23.7 *Standard entropies of the gaseous and hydrated actinide ions and standard entropies of hydration. Data from Bratsch and Lagowski* (1986), *Marcus and Loewenschuss* (1986), *David* (1986). *Number in brackets denote experimental data.*

	Gas phase S° ($\mathrm{JK^{-1}mol^{-1}}$)				*Aquo ion* S° ($\mathrm{JK^{-1}mol^{-1}}$)				$\Delta S^\circ_{\mathrm{hyd}}$ ($\mathrm{JK^{-1}mol^{-1}}$)			
Element	+3	+4	+5	+6	+3	+4	+5	+6	+3	+4	+5	+6
Ac	176	–	–	–	−199	–	–	–	−441	–	–	–
Th	192	177	–	–	−186	−417	–	–	−444	−682	–	–
Pa	195	192	–	–	−183	−402	−21	–	−444	−682	–	–
U	196	195	296	280	−183	−399	−26	−98	−445	−682	−323	−400
Np	195	196	280	273	−185	−398	−21	−94	−446	−682	−323	−411
Pu	192	196	281	277	−190	−399	−21	−92	−448	−683	−324	−413
Am	177	192	>271	278	−199	−402	−21	−88	−442	−682	<−314	−410
Cm	195	178	–	–	−194	−408	−25	−88	−455	−674	–	–
Bk	199	195	–	–	−194	−399	−30	–	−459	−682	–	–
Cf	201	199	–	–	−197	−395	−22	–	−464	−682	–	–
Es	201	201	–	–	−206	−393	–	–	−473	−682	–	–
Fm	201	202	–	–	−215	−393	–	–	−482	−683	–	–
Md	199	201	–	–	−224	−393	–	–	−489	−682	–	–
No	195	199	–	–	−231	−395	–	–	−492	−682	–	–
Lr	178	195	–	–	−255	−399	–	–	−499	−682	–	–

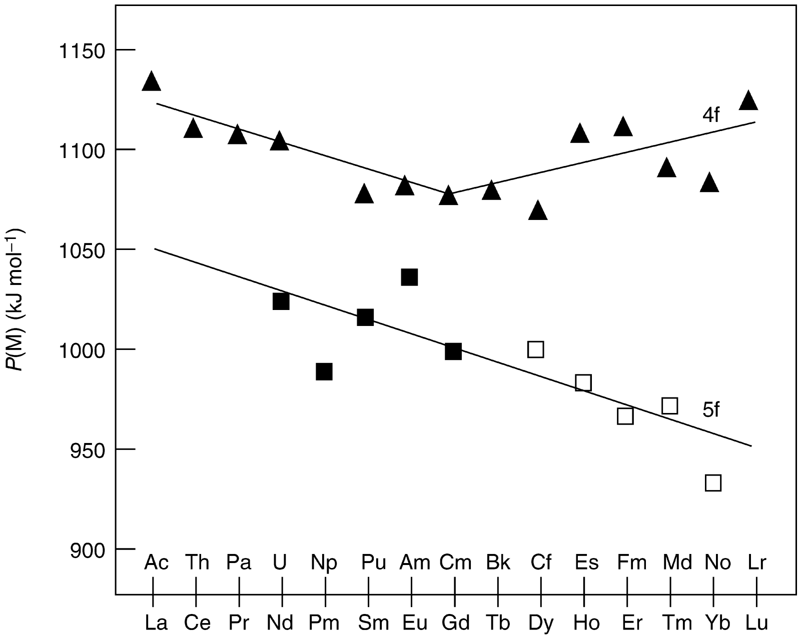


Fig. 23.6 *Plot of* P(*M*) *against atomic number for the lanthanide and actinide series.* (▲) *lanthanide experimental data,* (■) *actinide experimental data, and* (□) *extrapolated actinide data.*

and Lu, and for Ac, Pa, U, Np, Cm, and Lr. For the other f-elements, Δ*E*(M) is positive with accurately known values from spectroscopic measurements (Bratsch, 1983). Fig. 23.6 shows a graph of *P*(M) for lanthanide (4f) and actinide (5f) ions.

Only for UO_2^{2+} is there extensive data for the actinyl cations. Comparison of ΔH^o_{hyd} and ΔS^o_{hyd} with other 2+ and 3+ cations indicate that the enthalpy of hydration of actinyl(VI) cations is comparable to those of dipositive ions whereas the entropy of hydration is somewhat between that of dipositive and tripositive ions (Marcus and Loewenschuss, 1986). These authors assigned the increase in entropy to the large effective charge on the uranium center, +3.3. The non-spherical symmetry of the uranium atom caused by the shielding effect of the axial uranyl oxygens results in a lower hydration entropy than those of the typical trivalent cations. However, the strong primary sphere interactions from the charge–dipole effects causes more extensive but weaker secondary hydration. As a result, the net enthalpy of hydration is more similar to that of divalent than to trivalent cations.

23.3 HYDROLYSIS OF ACTINIDE CATIONS

Hydrolysis reactions occur for the f-elements in weakly acidic to alkaline solutions in the 3+, 4+, and 6+ oxidation states and often predominate over other complexation reactions in neutral and basic solutions. Hydrolysis of the pentavalent actinides occurs for pH ≥ 8. The hydrolysis reactions can be expressed by the general reaction

$$n\mathrm{An}^{z+} + q\mathrm{H_2O} \rightleftarrows \mathrm{An}_n(\mathrm{OH})_q^{nz-q} + q\mathrm{H}^+ \quad (\mathrm{An} = \mathrm{An(III)},\ \mathrm{An(IV)},\ \mathrm{AnO_2^+},\ \mathrm{AnO_2^{2+}}) \tag{23.7}$$

$$^*\beta_{nq} = [\mathrm{An}_n(\mathrm{OH})_q^{nz-q}][\mathrm{H}^+]^q/[\mathrm{An}^{z+}]^n$$

where $^*\beta_{nq}$ increases with increasing cationic charge density. Such hydrolysis reactions can be described as due to the positive charge of the metal ion polarizing the water molecule(s) sufficiently to release the proton(s). They are related to hydroxide complexation reactions:

$$n\ \mathrm{An}^{z+} + q\ \mathrm{OH}^- \rightleftarrows \mathrm{An}_n(\mathrm{OH})_q^{nz-q} \tag{23.8}$$

$$\beta_{nq} = [\mathrm{An}_n(\mathrm{OH})_q^{nz-q}]/[\mathrm{An}^{z+}]^n[\mathrm{OH}^-]^q$$

by $K_\mathrm{W} = [\mathrm{H}^+][\mathrm{OH}^-]$, making $\beta_{nq} = {}^*\beta_{nq}/K_\mathrm{w}^q$. The strength of hydrolysis follows the order:

$$\mathrm{An}^{4+} > \mathrm{AnO_2^{2+}} > \mathrm{An}^{3+} > \mathrm{AnO_2^+}$$

This is consistent with most thermodynamic data and reflects the effective charges on the actinide atoms in the actinyl(V) and actinyl(VI) ions (Section 23.4). Hydroxide-bridged polynuclear complexes have been observed for actinide cations and the tendency toward polymer formation (Fig. 23.7) is a function of the charge density of the actinide cation. In the case of Th^{4+} and U^{4+}, X-ray measurements indicate the formation of clusters built of units with an An–An distance in range 3.95–4.00 Å. The kinetics of polymerization–depolymerization becomes more complicated for Pu^{4+}. The slower rate of

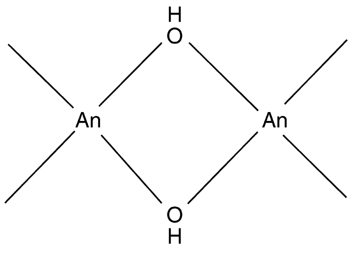


Fig. 23.7 *Structure of hydroxyl bridged actinide hydroxide polymers.*

depolymerization compared with the rate of polymer formation is due to an equilibrium between hydroxo and oxo bridge formation with aging.

23.3.1 Trivalent actinides

With a few exceptions, quantitative hydrolysis measurements of the actinide ions are complicated since the actinide hydroxides are quite insoluble and sorb to surfaces. The increasing pH required for hydrolysis also can result in significant changes in the oxidation state equilibria (e.g. for plutonium). Of the common oxidation states, the trivalent actinides have been the most intensively studied species. Solubility experiments (Rai *et al.*, 1983), solvent extraction (Caceci and Choppin, 1983a), spectroscopy (Stadler and Kim, 1988), and other techniques (Shalinets and Stepanov, 1972) have been used. The low solubility of $An(OH)_3$ in neutral/basic solutions prevents use of conventional absorption spectroscopy. However, time-resolved laser fluorescence spectroscopy allows measurements at the very low concentrations present in neutral/alkaline solutions (Stadler and Kim, 1988).

This laser spectroscopy technique was used to study the hydrolysis of Cm(III) at concentrations as low as 3×10^{-9} M. Values obtained for formation of the 1:1 and 1:2 species at 25°C in 0.10 M ($NaClO_4$) solutions are:

$$\log \beta_{11} = (6.67 \pm 0.18)$$

$$\log \beta_{12} = (12.6 \pm 0.28)$$

The laser fluorescence method has been used by Fanghänel and Kim (1994) to measure the values of log β_{11} and log β_{12} for Cm(III) over a range of ionic strengths from 0.011 to 6.15 M in NaCl solution at pH 8.6.

An evaluation of An(III) hydrolysis has been made by Rai *et al.* (1983). Table 23.8 lists the log $^*\beta_{nq}$ and log K_{sp} values for the hydrolytic reactions of Am(III) from this reference. In carbonate-free environments, $Am(OH)^{2+}$ and $Am(OH)_2^+$ are the major species at pH 8.2, while, in carbonate-rich waters, $Am(CO_3)^+$ and $Am(CO_3)_2^-$ may also be significant components (Fig. 23.8). Because of the strong sorption characteristics of the hydroxide species, Am(III) is frequently removed from solution onto colloids, sediments, and humic substances. Stadler and Kim (1988) and the OECD-NEA (Silva *et al.*, 1995, Guillaumont *et al.*, 2003) have reviewed americium hydrolysis, while the hydrolysis of trivalent actinides has been reviewed by Fuger *et al.* (1992) and Rizkalla and Choppin (1994).

Polynuclear hydroxides of the formula $An_2(OH)_2{}^{4+}$ have been reported for Np(III) (Allard *et al.*, 1980) and Pu(III) (Allard and Rydberg, 1983) with values for log$^*\beta_{22}$ of ca. −15 (Np) and −16 (Pu). Values for the $AnOH^{2+}$ hydrolysis formation constants for the trivalent actinide ions are listed in Table 23.9.

Table 23.8 *Hydrolysis constants for Am*(III), $I = 0$ M; $T = 22°C$ (*Rai* et al., 1983; *Felmy* et al., 1990).

I. $\log {}^*\beta_{nq}$ values for formation of $Am(OH)_q^{3\text{-}q}$	
$Am^{3+} + H_2O \rightleftarrows Am(OH)^{2+} + H^+$	$\log {}^*\beta_{11} \leq -8.2$
$Am^{3+} + 2\ H_2O \rightleftarrows Am(OH)_2^+ + 2H^+$	$\log {}^*\beta_{12} = -17.1$
$Am^{3+} + 3\ H_2O \rightleftarrows Am(OH)_3 + 3H^+$	$\log {}^*\beta_{13} = -28.6$
II. $\log K_{sp}$ values for solid $Am(OH)_3$	
$Am(OH)_{3(am)} \rightleftarrows Am^{3+} + 3OH^-$	$\log K_{sp} = -24.5$
$Am(OH)_{3(cr)} \rightleftarrows Am^{3+} + 3OH^-$	$\log K_{sp} = -27.0$

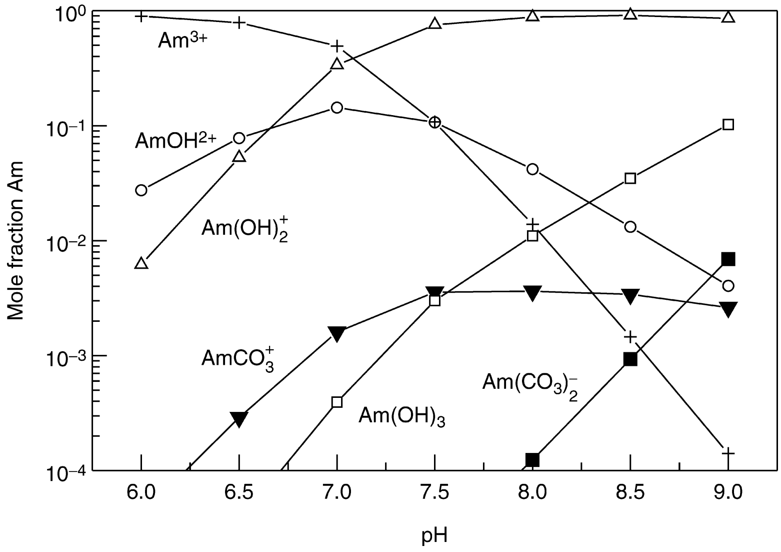


Fig. 23.8 *Fraction of Am*(III) *species in water in equilibrium with atmospheric carbon dioxide as a function of pH* (*Choppin* et al., 2002).

23.3.2 Tetravalent actinides

Study of the aqueous chemistry of tetravalent actinides can be difficult due to the very strong tendency of the cations to hydrolyze even in acidic solutions (pH $\leq$ ca. 2). Moreover, An(IV) cations of elements from protactinium through americium can undergo redox reactions relatively easily if the pH is not very low or in the absence of a strong complexant, making it difficult to ensure that only the tetravalent oxidation state is present.

Thorium is found in aqueous solution only in the 4+ oxidation state and is often used as a model for Np(IV) and Pu(IV) behavior. However, it has a smaller ionic charge density than these cations, due to its larger ionic radius, that results

Table 23.9 *Hydrolysis constants of trivalent actinide ions;* $T = 25°\mathrm{C}$ (*Rizkalla and Choppin,* 1994).

Species	*Medium*	*Method*[a]	*log* $^*\beta_{nq}$
$Np(OH)^{2+}$	0.3 M $NaClO_4$	pH	−7.43 ± 0.12
$Pu(OH)^{2+}$	1.0 M $NaClO_4$	pH	−5.53
	0.2 M $LiClO_4$, 23°C	ex	−3.80 ± 0.2
$Am(OH)^{2+}$	1.0 M $NaClO_4$	sol	−7.03 ± 0.05
	1.0 M $NaClO_4$	ex	−7.50 ± 0.3
	0.7 M NaCl, 21°C	ex	−7.54 ± 0.2
	0.5 M$(H,NH_4)ClO_4$	ex	−6.80 ± 0.3
	0.1 M $LiClO_4$, 23°C	ex	−5.92
	0.1 M $LiClO_4$, 23°C	ex	−5.30 ± 0.1
	0.1 M $NaClO_4$	sol	−7.68
	0.1 M $NaClO_4$	sol	−7.93
	0.1 M $NaClO_4$	sol	−6.34 ± 0.83
$Am(OH)_2^+$	0.2 M $NaClO_4$	ex	−14.76
	0.1 M $NaClO_4$	sol	−16.56
	0.1 M $NaClO_4$	sol	−14.77
	0.1 M $NaClO_4$	sol	−13.64 ± 0.63
$Am(OH)_3$	0.1 M $NaClO_4$	sol	−24.84
	0.1 M $NaClO_4$	sol	−24.71
$Cm(OH)^{2+}$	0.1 M $LiClO_4$, 23°C	ex	−5.92 ± 0.13
	0.1 M $LiClO_4$, 23°C	ex	−5.40 ± 0.1
	0.1 M $LiClO_4$	ex	−5.93
$Bk(OH)^{2+}$	0.1 M $LiClO_4$, 23°C	ex	−5.66
$Cf(OH)^{2+}$	0.1 M $LiClO_4$, 23°C	ex	−5.62
	0.1 M $LiClO_4$, 23°C	ex	−5.05
$Es(OH)^{2+}$	0.1 M $LiClO_4$, 23°C	ex	−5.14
$Fm(OH)^{2+}$	0.1 M $LiClO_4$, 23°C	ex	−3.8 ± 0.2

[a] pH, potentiometric titration; sol, solubility; ex, solvent extraction.

in significant differences in the extent of the hydrolytic reactions. The hydrolysis of Th^{4+} involves extensive formation of polynuclear complexes. In the earlier stages of the hydrolysis in perchlorate media, when the number of hydroxide ions per thorium atom in the complexes is ≤ 2, the hydrolytic reactions are fully reversible and equilibrium is quickly reached (Hietanen, 1954; Kraus and Holmberg, 1954; Baes *et al.*, 1965). The first extensive measurements of the hydrolysis behavior were interpreted (Hietanen, 1954) as indicating the formation of an infinite series of 'core + links' complexes, $Th((OH)_3Th)_n^{4+n}$. However, other measurements over large pH and Th(IV) concentration ranges could be satisfactorily fitted with three polymers, $Th_2(OH)_2^{6+}$, $Th_4(OH)_8^{8+}$, and $Th_6(OH)_{15}^{9+}$, and two monomers, $ThOH^{3+}$ and $Th(OH)_2^{+}$ (Kraus and Holmberg, 1954; Baes *et al.*, 1965). In Table 23.10, the constants $^*\beta_{nq}$ are listed for the reactions:

$$n\mathrm{Th}^{4+} + q\mathrm{H_2O} \rightleftarrows \mathrm{Th}_n(\mathrm{OH})_q^{4n-q} + q\mathrm{H}^+$$

Of the complexes mentioned, $\mathrm{Th_2(OH)_2^{6+}}$ is significant in chloride media (Hietanen and Sillen, 1968; Baes and Mesmer, 1976; Milic, 1981) as well as $\mathrm{Th_2(OH)_3^{5+}}$ and $\mathrm{Th_6(OH)_{14}^{10+}}$. In nitrate media, the complexes $\mathrm{Th_2(OH)_2^{6+}}$, $\mathrm{Th_6(OH)_{15}^{9+}}$ and $\mathrm{Th_3(OH)_5^{7+}}$ predominate (Milic and Suranji, 1982). Constants for the hydroxo complexes are somewhat smaller in chloride and nitrate than in perchlorate media (Table 23.10).

For values $n \geq 2$ (equation (23.7)), equilibrium is more slowly attained than for mononuclear complex formation, resulting in formation of larger polymers before precipitation takes place. Direct structural determinations by X-ray diffraction on hydrolyzed thorium nitrate solutions confirmed the existence of the dimer $\mathrm{Th_2(OH)_2^{6+}}$ (Johansson, 1968). The Th–Th distance is 3.99 Å, i.e. exactly the same as in the solid $\mathrm{Th_2(OH)_2(NO_3)_6(H_2O)_8}$ that contains dimers joined by double hydroxo bridges. As the hydrolysis reaction proceeds, complexes of higher nuclearity become prominent although the Th–Th distance stays almost the same, approximately 3.94 Å. The hydrolytic complexes formed in concentrated nitrate solutions also contain nitrate ions coordinated as bidentate ligands. As expected, the number of nitrate ions coordinated per thorium decreases as hydrolysis becomes more extensive. Diffraction measurements by Johansson (1968) on hydrolyzed solutions of thorium perchlorate and chloride give the same Th–Th distance 3.94 Å, implying that the same type of hydroxo-bridged complexes are formed in these media.

Rai *et al.* (1997) have reported a value of $\log K_{\mathrm{sp}}^0 = -45.5$ for amorphous $\mathrm{Th(OH)_4}$ while Neck and Kim (2001) have proposed for a value of $\log K_{\mathrm{sp}}^0$ of –(47.0 ± 0.8) (Table 23.11). The values of $\log K_{\mathrm{sp}}^0$ of Th(IV) are larger than for

Table 23.10 *Hydrolysis constants, log* $^*\beta_{\mathrm{nq}}$, *for Th*(IV) *in different media.*

	T				
n, q	0°C 1 M *NaClO₄*[a]	25°C 1 M *NaClO₄*[b]	95°C 1 M *NaClO₄*[a]	25°C 3 M *NaCl*[c]	25°C 3 M *NaNO₃*[d]
1, 1	−4.31	−4.23	−2.25	–	–
1, 2	−8.46	−7.69	−4.51	–	–
2, 2	−5.59	−4.61	−2.59	−4.69	−5.19
2, 3	–	–	–	−8.73	–
4, 8	−22.80	−19.16	−10.44	–	–
6, 14	–	–	–	−36.37	–
6, 15	−43.81	−37.02	−20.61	–	−42.3

[a] Molality scale, Baes *et al.* (1965).

[b] Kraus and Holmberg (1954).

[c] Data recalculated from Hietanen and Silen (1968).

[d] $\mathrm{Th_3(OH)_5{}^{7+}}$ also suggested with $\log {}^*\beta_{35} = -14.23$, by Milic and Suranji (1982).

Table 23.11 *Hydroxide complexation constants for An*(IV) *cations*, $I = 0$ M (*Neck and Kim*, 2001).

	Th(IV)	*U*(IV)	*Np*(IV)	*Pu*(IV)
$\log K^{\circ}_{\mathrm{sp(cr)}}$	-54.2 ± 1.3	-60.86 ± 0.36	-63.7 ± 1.8	-64.0 ± 1.2
$\log K^{\circ}_{\mathrm{sp(am)}}$	-47.0 ± 0.8	-54.5 ± 1.0	-56.7 ± 0.4	-58.5 ± 0.7
$\log \beta^{\circ}_{11}$	11.8 ± 0.2	13.6 ± 0.2	14.5 ± 0.2	14.6 ± 0.2
$\log \beta^{\circ}_{12}$	22.0 ± 0.6	26.9 ± 1	28.3 ± 0.3	28.6 ± 0.3
$\log \beta^{\circ}_{13}$	31.0 ± 1.0	37.3 ± 1	39.2 ± 1	39.7 ± 0.4
$\log \beta^{\circ}_{14}$	38.5 ± 1.0	46.0 ± 1.4	47.7 ± 1.1	48.1 ± 0.9
$\log \beta^{\circ}_{24}$	59.1[a]	–	–	–
$\log \beta^{\circ}_{4,12}$	141.3	–	–	–
$\log \beta^{\circ}_{6,15}$	176.0	196[b]	–	–

[a] Calculated for $I = 0$ from data in Moon (1989).

[b] $\log \beta_{6,15}$ for $I = 3$ M $NaClO_4$ (Baes and Mesmer, 1976).

the other An(IV) ions, presumably due to inclusion of polynuclear species of Th(IV) in the concentration of the soluble fraction (Neck and Kim, 2001).

Evidence is scarce and conflicting on the hydrolysis of Pa^{4+}. Values of $\log {}^*\beta_{11} = -0.14$ and $\log {}^*\beta_{12} = -0.52$ have been measured for the first two mononuclear complexes in a 3 M $(Li,H)ClO_4$ medium, by means of a solvent extraction method (Guillaumont, 1968). This would lead to about 50% of the protactinium present as unhydrolyzed Pa^{4+} in 1 M perchloric acid; however, other extraction measurements indicate that $Pa(OH)_2^{2+}$ is the predominant species in 1 M acid (Lundqvist, 1974). The mononuclear complexes are predominant only in extremely dilute solutions. Polymers become significant at protactinium concentrations as low as 10^{-5} M.

Hydrolysis of U(IV) is of concern only in reducing solutions as UO_2^{2+} is the form present in oxic waters. The hydrolysis of U(IV) increases with increasing ionic strength and increasing temperature. Polynuclear hydrolytic species form readily and are likely to be present except in strongly acidic solutions or at very low concentrations of U(IV). Hydrolysis constant values were reported for a series of polynuclear $U_{(n+1)}(OH)_{3n}^{(4+n)+}$complexes in 3 M $(H,Na)ClO_4$ by Hietanen (1956) using a 'core+links' model of thread-like chains of $U(OH)_2U$ links. However, this model has fallen out of favor and reevaluation of these experiments showed that only $U(OH)^{3+}$ and one polynuclear species, $U_6(OH)_{15}^{9+}$, were required to reproduce the data with $\log {}^*\beta_{11} = -2.1$ and $\log {}^*\beta_{6,15} = -16.9$ (Baes and Mesmer, 1976) except at the highest $q{:}n$ ratios. This suggests that dinuclear or tetranuclear hydroxide complexes are less important for U(IV) than for Th(IV), but that hexanuclear $U_6(OH)_{15}^{9+}$ and higher oligomers of U(IV) with $n > 6$ and $q/n > 2.5$ do form in millimolar solutions of U(IV) when the pH exceeds 1.5.

As can be seen in the data in Table 23.11, the hydrolysis of Np(IV) is quite similar to that of Pu(IV) but greater than that of Th(IV) and U(IV). The ease of oxidation of Np(IV) to NpO_2^+ in non-reducing solutions results in Np(V) being the dominant neptunium species in oxic waters. Although there has been little research on hydrolytic polymers of Np(IV), it is very probable that the same polymers observed for Th(IV), U(IV), and Pu(IV) are formed by Np(IV).

Similar to the situation for Np(IV), the hydrolysis of Pu(IV) is difficult to investigate. At $pH \geq 1.0$, tetravalent plutonium experiences hydrolysis and also oxidizes to PuO_2^+. Disproportionation reactions also occur in these acid solutions to form Pu(III) and PuO_2^{2+}. Preparation and maintenance of a solution with only Pu(IV) present is a challenge in any investigation of Pu(IV) behavior. This is reflected in the inconsistent data in a number of publications on Pu(IV) hydrolysis. The tendency of hydrolyzed plutonium(IV) to form intrinsic colloids or to sorb on other colloids is also a complicating factor. It has been demonstrated that colloidal Pu(IV) can be present at pH = 0 to 1 and total Pu(IV) concentrations smaller than 10^{-3} M (Kim and Kanellakopulos, 1989). Ultrafiltration removes such colloids if a sufficiently small filter size is used. However, without filtration, the solubility data used to calculate solubility product constants may be more than an order of magnitude too large due to the presence of colloids. Hydrolyzed plutonium species also have a strong tendency to sorb to surfaces. The surfaces of equipment used for plutonium experimentation must be treated to minimize sorption in solubility and extraction measurements (Caceci and Choppin, 1983b).

Freshly precipitated $Pu(OH)_4 \cdot xH_2O$, dehydrates over time with the hydroxo bridges between neighboring plutonium ions converting to an oxo bridged structure (Fig. 23.9). The resulting crystalline PuO_2 has a value of $\log K^{o}_{sp(cr)} = -64$ (Table 23.11), compared to the value of the amorphous hydrate of $\log K^{o}_{sp(am)} = -58.5$. The measured value of $\log K^{o}_{sp(cr)}$ (−64.0) reflects the reduced solubility of the aged precipitate; but measured solubilities in solutions of $pH \geq 7$ are those of the amorphous solid, independent of whether $An(OH)_{4(am)}$ or $AnO_{2(cr)}$ were used for the initial solid phase. This can be attributed to the bulk crystalline solid being covered by a surface layer of the amorphous species. The amorphous form dissolves readily in strong acid but dissolution of the aged PuO_2 precipitate is very difficult due to the strength of

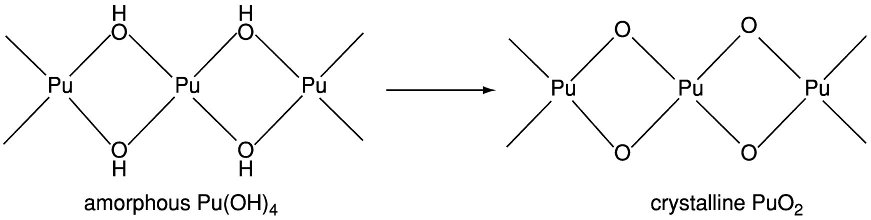


Fig. 23.9 *Conversion of amorphous* $Pu(OH)_4$ *into crystalline* PuO_2 *by loss of* H_2O.

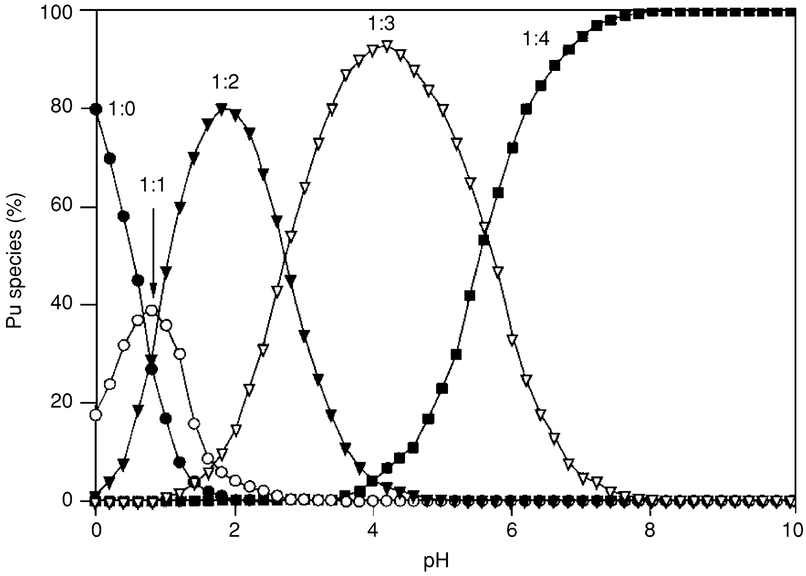


Fig. 23.10 *Fraction of mononuclear plutonium*(IV) *hydrolysis products as a function of pH in* 1 M *$NaClO_4$ solution* (*Choppin,* 2003).

the Pu–O bonding. Generally, aged $PuO_{2(cr)}$ must be contacted with an acidic oxidizing solution which converts the Pu(IV) to the much more soluble PuO_2^{2+} species.

The variation of mononuclear Pu(IV) hydrolytic species with pH is shown in Fig. 23.10. At pH 1.0, there are almost equal concentrations of Pu^{4+}, $Pu(OH)^{3+}$, and $Pu(OH)_2^{2+}$, demonstrating strong hydrolysis of Pu(IV). The fraction of polynuclear species present increases as the plutonium and/or the pH concentration increases. The hydrolysis constants of Pu(IV) indicate an extremely low value for soluble plutonium in neutral solutions. However, the net plutonium solubility is much larger than predicted ($\leq 10^{-6}$ M) by the constants in Table 23.11, as it is due to the relatively high concentration of PuO_2^+ ($\sim 10^{-6}$ to 10^{-7} M) in redox equilibrium with the ultratrace concentrations of soluble Pu(IV).

23.3.3 Pentavalent actinides

The protactinium(V) ion is a much stronger acid than other pentavalent actinides with $\log{}^*\beta_{11} = -4.5$ in 3.5 M (Li, H)ClO_4 (Guillaumont, 1968). In both the tetravalent and pentavalent states, protactinium hydrolyzes much more readily than do the other actinides. A structure different from the other actinyl(V) ions, e.g. $PaO(OH)_2^+$, with a strongly covalent protactinium–oxo bond has been proposed (Guillaumont *et al.*, 1968).

The tendency of UO_2^+ and PuO_2^+ to disproportionate and the strong oxidation properties of AmO_2^+ have led to few hydrolytic studies of these cations. NpO_2^+ is relatively stable, however, and is the most studied actinyl(v) species. Pentavalent neptunium does not hydrolyze in solutions with pH less than 8. Sullivan *et al.* (1991), Itagaki *et al.* (1992), and Neck *et al.* (1992) have discussed neptunium hydrolysis in some detail. A value of $\log{}^*\beta_{11}$ for NpO_2^+ (ca. −8.85 at $I = 0$) was reported by Baes and Mesmer (1976) and Schmidt *et al.* (1980). The stability of NpO_2^+ has led to its use as a chemical analog for pentavalent plutonium since PuO_2^+ is environmentally important at low concentrations of plutonium (Nelson and Lovett, 1978).

A study of the thermodynamics of NpO_2^+ hydrolysis (Sullivan *et al.*, 1991) in a solution of $I = 1.0$ M $(CH_3)_4NCl$ at $T = 25°C$ gave the following values for the reaction $NpO_2^+ + OH^- \rightleftarrows NpO_2OH$:

$$\log {}^*\beta_{11} = -(9.26 \pm 0.06)$$

$$\Delta H_{11} = -(22.10 \pm 0.04)\,\mathrm{kJ\,mol^{-1}}$$

$$\Delta S_{11} = (16 \pm 5)\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

This value for ${}^*\beta_{11}$ indicates that at pH 9.26, NpO_2^+ is 50% hydrolyzed.

Sullivan *et al.* (1991) estimated that $\log\beta_{11}$ for PuO_2^+ would be ca. 4.5, which indicates that PuO_2^+ does not form a significant fraction of hydroxide species until pH 9. Of all the plutonium oxidation states, the pentavalent state has the least tendency to hydrolyze (Choppin, 1991) and is most stable in basic solution (Peretrukhin *et al.*, 1994). Unlike the case of NpO_2^+, the redox potential of Pu(v)/Pu(iv) and the strong hydrolysis of Pu(iv) limit the concentration of $PuO_2{}^+$ in marine waters. Plutonium redox and sorption have been reviewed by Morse and Choppin (1991) and plutonium hydrolysis by Clark *et al.* (1995).

23.3.4 Hexavalent actinides

The hydrolysis of the uranyl cation, UO_2^{2+}, has been studied more intensely than that of any other actinide cation, partially because the lower level of radioactivity of natural uranium allows use of a wider variety of techniques than for shorter lived actinides. Also, the hydrolysis of U(vi) forms a wide variety of polynuclear hydrolytic species, resulting in a quite complex chemistry (Table 23.12 and Fig. 23.11).

The hydrolysis of the cations of the actinyl(vi) species decreases in the order $UO_2^{2+} > NpO_2^{2+} > PuO_2^{2+}$, with a larger difference between NpO_2^{2+} and PuO_2^{2+} (Table 23.13). The actinide radial contraction with atomic number would lead to the opposite trend. The pattern is different also from that for the actinide(iv) ions where the order of acidities is $U^{4+} > Np^{4+} < Pu^{4+}$. For these ions, the unexpected decrease between U^{4+} and Np^{4+} is followed by a marked reversal at Pu^{4+}.

In very dilute solutions, $\leq 10^{-6}$ M U(VI), the hydrolysis of UO_2^{2+} first forms mononuclear $UO_2(OH)_q^{2-q}$ species, but above this concentration UO_2^{2+} exists mainly in polynuclear species. Within wide ranges of pH and C_M (metal concentration), the predominant complex is the dimer ($(UO_2)_2(OH)_2^{2+}$). As the pH increases, the trimer $(UO_2)_3(OH)_5^+$ becomes prominent (Fig. 23.12). In chloride solutions $(UO_2)_3(OH)_4^{2+}$ is also formed. In concentrated solutions of low pH, $(UO_2)_2OH^{3+}$ may be present. Other complexes which have been proposed to form are $(UO_2)_3(OH)_7^-$, $(UO_2)_3(OH)_{10}^{4-}$, $(UO_2)_4(OH)_6^{2+}$, $(UO_2)_4(OH)_7^+$,

Table 23.12 *Hydrolysis constants at* I = 0 *and* 25°C *for formation of* $(UO_2)_n(OH)_q$ *species.*

n, q	$\log{}^*\beta^\circ_{nq}$ (*Palmer and Nguyen-Trung*, 1995)	$\log{}^*\beta^\circ_{nq}$ (*Guillaumont* et al., 2003)
1, 1	-5.42 ± 0.04[a]	-5.25 ± 0.24
2, 2	-5.51 ± 0.04	-5.62 ± 0.04
3, 5	-15.33 ± 0.12	-15.55 ± 0.12
3, 7	-27.77 ± 0.09	-32.2 ± 0.8
3, 8	-37.65 ± 0.14	–
3, 10	-62.4 ± 0.3	–

[a] For $I = 0.10$ M (KNO_3).

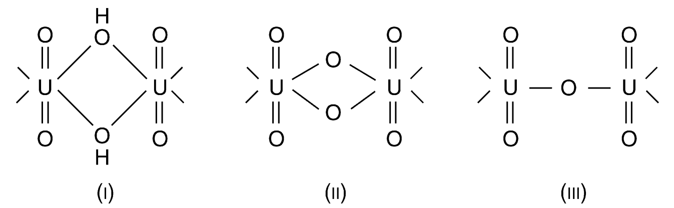


Fig. 23.11 *Structures of dinuclear uranyl hydroxide and oxide complexes.*

Table 23.13 *Hydrolysis constants,* $\log{}^*\beta_{nq}$, *of hexavalent actinides,* NpO_2^{2+} *and* PuO_2^{2+}, *in* $NaClO_4$ *solution;* $T = 25$°C.

	NpO_2^{2+}	PuO_2^{2+}		
n, q	I = 1 M (*Cassol* et al., 1972*a*)	I = 1 M (*Kraus and Dam*, 1949)	I = 1 M (*Cassol* et al., 1972*b*)	I = 3 M (*Schedin*, 1975)
1, 1	−5.17	−5.71	−5.97	–
2, 2	−6.68	–	−8.51	−8.23
3, 5	−18.25	–	−22.16	–
4, 7	–	–	–	−29.13

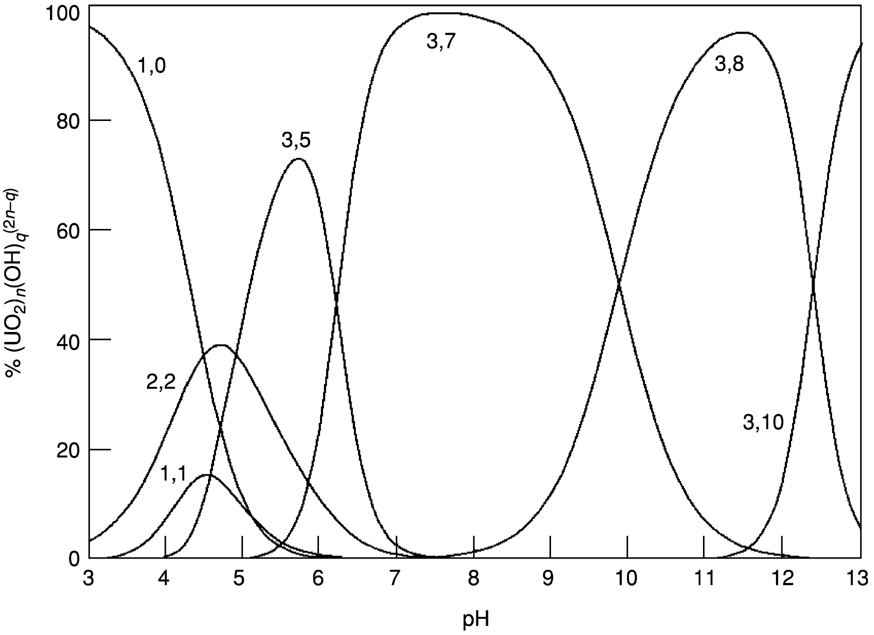


Fig 23.12 *Speciation diagram (n,q) for the formation of* $(UO_2)_n(OH)_q^{(2n-q)}$. $[UO_2^{2+}]_{total} = 4.75 \times 10^{-4} M$, $T = 25\,°C$, *from the data of Palmer and Nguyen-Trung* (1995) *extrapolated to* $I = 1.0$ M.

Table 23.14 *Hydrolysis constants for* UO_2^{2+} *at different ionic strengths;* $T = 25°C$.

I (M)	*log* $^*\beta_{11}$	*log* β_{11}
0[a]	−5.88	8.12
0.05	−6.02	7.00
0.1	−6.09	7.70
0.4	−6.20	7.56
0.7	−6.07	7.71
1.0	−6.20	7.82

[a] Extrapolated values.

and $(UO_2)_5(OH)_8^{2+}$. The variation of the hydrolysis constant of $UO_2(OH)^+$ as a function of ionic strength is shown in Table 23.14.

The existence of the dimer $(UO_2)_2(OH)_2^{2+}$ has been confirmed by direct determination of the species present in hydrolyzed uranyl(VI) chloride solutions (Åberg, 1970). Even in the concentrated solutions (C_M = 3 M) used in these diffraction studies, the dimer is an important species at the lower ligand numbers investigated.

The average U–U distance in this concentrated solution is 3.88 Å, which is close to the distance of 3.94 Å found in the solids $[(UO_2)_2(OH)_2Cl_2(H_2O)_4]$ and $[(UO_2)_2(OH)_2(NO_3)_2(H_2O)_3]H_2O$ (Åberg, 1969; Perrin, 1976).

23.4 BONDING IN ACTINIDE COMPLEXES

Actinide ions in all common solution oxidation states (2+ to 6+) are hard Lewis acids, and actinide–ligand bonds are predominantly ionic, as expected from the electropositive nature of the actinides. This is manifested in kinetically labile, non-directional bonds, and a marked preference for binding to ligands via hard Lewis base donor atoms like fluorine or oxygen. The thermodynamic bond strengths of actinide–ligand complexes are determined primarily by electrostatic attraction and steric constraints. The electrostatic attraction between an actinide cation and a ligand is proportional to the product of the effective charges of the metal and ligand divided by the actinide–ligand distance. The steric constraints may arise from the properties of the actinide cation (ion size and presence or absence of actinyl oxygen atoms) or of the ligand (number and spatial relationship of donor atoms, size of the chelate rings, and flexibility of ligand conformations).

23.4.1 Ionicity of f-element bonding

As a consequence of the predominantly ionic nature of the metal–ligand bonding in actinide complexes, the strength of the complexes and the associated chemistry are determined primarily by the effective charge of the actinide cation and of the coordinating ligands. Similar to the lanthanide 4f orbitals, the actinide 5f orbitals are well shielded from environmental influences and have little influence on bonding energies of the outer 6d orbitals, which dominate the radii values. The orbital energies and the radii of actinide ions in a given oxidation state vary slowly and smoothly across the actinide series. As a result, the types of actinide complexes formed and the strength of those complexes, as reflected by the stability constants, are relatively uniform within an oxidation state in comparison to transition metal complexes where covalence and ligand field stabilization energies can cause significant variations (Fig. 23.13). An important exception to the regularities of complex formation within an actinide oxidation state is Pa(v), which is the only pentavalent actinide that does not form the linear transdioxo actinyl(v) moiety, and whose chemistry is closer to that of pentavalent niobium and tantalum (Kirby, 1959) than that of AnO_2^+ cations.

23.4.2 Thermodynamics of bonding

The predominantly ionic nature of actinide–ligand bonding also accounts for the enthalpies and entropies of actinide complexation. The formation of inner sphere 1:1 actinide–ligand complexes in aqueous solution is characterized

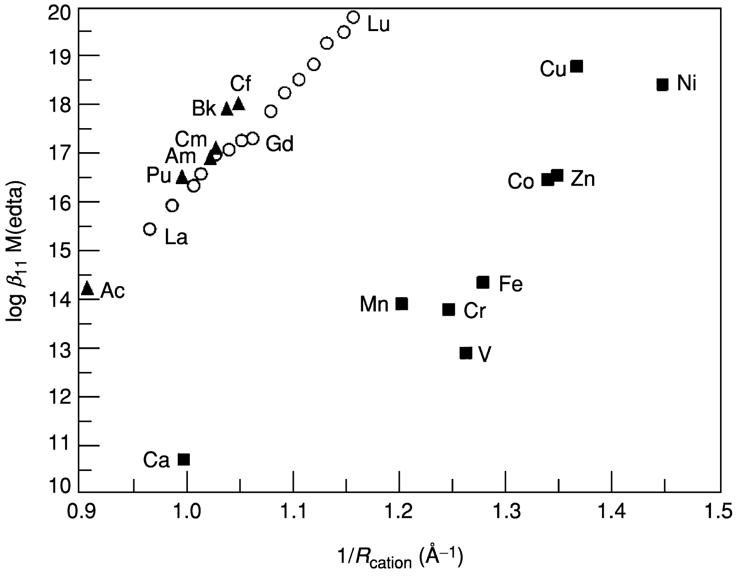


Fig. 23.13 *Variation of the stability constants of metal complexes with ethylenediaminetetraacetate (edta^{4-}) with ion size for the trivalent actinide* (▲), *trivalent lanthanide* (○), *and divalent fourth row metal cations* (■). *Stability constant data from Martell* et al. (1998) *and Makarova* et al. (1972) *for* I = 0.1 M, *and* $T = 25°\text{C}$. R_{cation} *from Shannon* (1976) *for* $CN = 6$.

by positive values of the formation entropies, ΔS_{11}, and of the values of the formation enthalpies, ΔH_{11}, that vary from moderately endothermic (positive and unfavorable) to moderately exothermic (negative and favorable) depending on the charge and coordination number of the ligand. For simple ligands, the entropic component of the Gibbs energy tends to be the more important in determining the magnitude of the Gibbs energy change (ΔG) upon complexation and, hence, of the equilibrium constant. In aqueous media, the entropy changes (ΔS) for formation of 1:1 lanthanide and actinide complexes arise primarily from the partial dehydration of the metal and ligand that is associated with the formation of an inner sphere complex. For a given ligand, the ΔS values tend to increase as the effective charge of the actinide ion increases, as expected for electrostatic bonding (Laidler, 1956). Also, since the complexation entropies are linked to dehydration of the metal and ligand, characteristic values of $\Delta S/n$ exist for a given actinide oxidation state and a particular class of ligands, as shown for actinide carboxylate complexation in Table 23.15 (n can be either the number of donor groups bound to the cation or the number water molecules displaced from the inner coordination sphere of the cation).

Table 23.15 *Average entropy change per coordinated carboxylate group, n, for carboxylate, polycarboxylate, and aminopolycarboxylate ligands* (*standard deviation* ±10%).

Cation	*Average* $\Delta S/n$ ($\mathrm{J\,K^{-1}mol^{-1}}$)	*References*
Th^{4+}	96	Martell *et al.* (1998)
UO_2^{2+}	73	Martell *et al.* (1998)
Am^{3+}	62	Rizkalla *et al.* (1989)
Sm^{3+}	59	Choppin (1993)
NpO_2^+	27	Jensen and Nash (2001)
Ca^{2+}	25	Choppin *et al.* (1992a)

23.4.3 Coordination numbers

Typical coordination numbers of transition metal ions, where d-orbitals participate in the formation of directional covalent bonds, range from four to six, with well-defined stereochemistry (tetrahedral, square planar, octahedral, etc.). In contrast, most actinide–ligand bonds are characterized by a very small degree of covalence, if any, and the coordination geometry of the complexes is not determined by the directionality of the bonding overlap of the actinide and ligand orbitals. Combined with the somewhat larger size of actinide cations relative to the 3d and 4d transition metal cations, this results, for actinide cations, in larger and variable coordination numbers, which are determined by the maximum number of ligands (including Lewis base solvent molecules) that can fit around the actinide. Increasing oxidation state decreases the ionic radii of the actinide ions (Shannon, 1976), thus favoring lower coordination numbers than are observed for actinides in the lower oxidation states. In water, or in other oxygenated solvents with similar steric demands, typical inner sphere coordination numbers of actinide ions range between seven and nine (including the -yl oxygen atoms of the actinyl cations) with coordinated solvent molecules filling space not occupied by other ligands.

The size and shape of the ligands are very important in determining the exact coordination number of actinide cations. Coordination numbers as low as four or five, for example in $U(NPh_2)_4$ (Reynolds *et al.*, 1977) or UO_2(*p-tert*-butylhexahomotrioxacalix[3]arene)$^-$ (Masci *et al.*, 2002), are observed for bulky ligands in low polarity media. In contrast, coordination numbers of 10 or 12 are not uncommon in solid state and solution-phase complexes containing small, bidentate ligands, such as CO_3^{2-} and NO_3^- [e.g. ten-coordinate $An(CO_3)_5^{6-}$ (Clark *et al.*, 1995) and 12-coordinate $An(NO_3)_6^{2-}$ (Ryan, 1960; Šcavnicar and Prodic, 1965)].

The constraints imposed by the presence of the two oxo groups in the linear, pentavalent AnO_2^+ and hexavalent AnO_2^{2+} cations provide an inherent, steric limitation on the number of ligand donor groups that can form bonds to the actinyl cations. The stability constants of the complexes of actinide cations in each of the common oxidation states with a series of carboxylate and aminocarboxylate ligands are presented as a function of the number of potential donor groups present in each ligand in Fig. 23.14. For the spherical An(III) and An(IV) cations, which lack the -yl oxygen atoms of the higher actinide oxidation states, the stability constants of the metal–ligand complexes increase regularly with the increased number of donor groups in the ligand. The size, spherical symmetry, and lack of strong, directional covalent bonding in these complexes allow An(III) and An(IV) cations to accommodate polydentate ligands that form multiple chelate rings. In contrast, the linear dioxo structure of AnO_2^+ and AnO_2^{2+} cations constrains the interactions with ligands to the

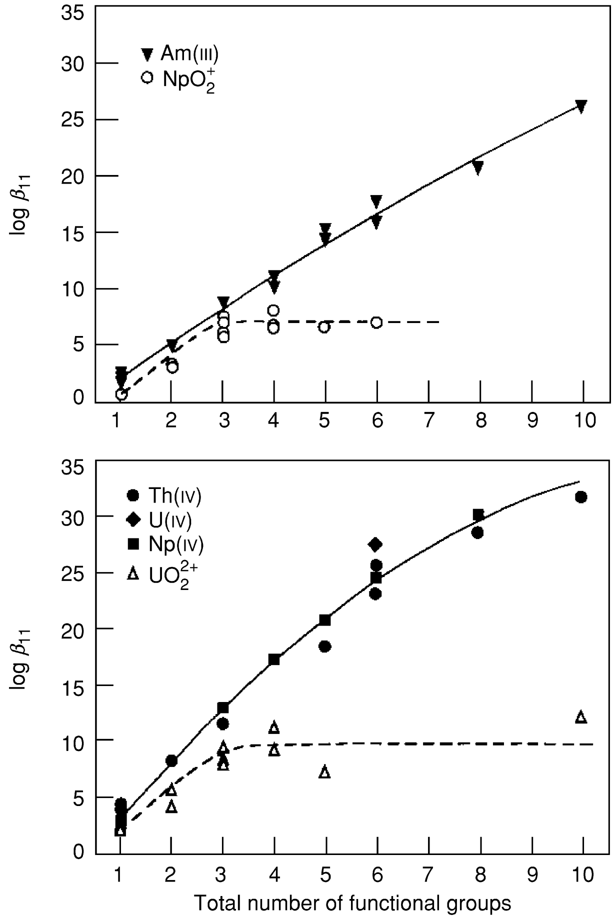


Fig. 23.14 *Effect of the steric constraints imposed by actinyl oxygen atoms of neptunyl(V) and uranyl(VI) on the stability constants of the carboxylate and aminocarboxylate ligands as compared to trivalent and tetravalent actinides. Data from Martell* et al. (1998), *Rizkalla* et al. (1990*a*), *and Tochiyama* et al. (1994).

plane perpendicular to the actinyl oxygens (referred to as the equatorial plane hereafter). Generally, this limits the number of bound donor groups in a single ligand to three or four for the actinyl ions. As shown in Fig. 23.14, the thermodynamic stability of the complexes of AnO_2^+ and AnO_2^{2+} cations increases regularly until three donor groups are present in a given ligand. The presence of additional (more than three) donor groups causes no significant increase in the stability constants of the actinyl complexes because the additional donors do not form bonds with the actinyl cation. Interesting exceptions to this general observation are the pentacoordinate calixarene-based ligands (Shinkai *et al.*, 1987; Guilbaud and Wipff, 1993a), which have the proper geometry to be strong and highly selective complexants for the actinyl(vi) ions.

23.4.4 Steric effects in actinyl bonding

The '-yl' oxygen atoms can interfere with the complexation of rigid ligands, even if the ligand contains three or fewer donor atoms, by restricting ligand donor atoms to bonding only in the equatorial plane of the actinyl ion. In rigid ligands this restriction can cause torsional strain within a bound ligand, or, if the ligand is too large to be contained in the equatorial plane, portions of the ligand and the actinyl oxygens may come into steric conflict. This was reported for the uranyl(vi) complexes of the relatively rigid ligand tetrahydrofuran-2,3,4,5-tetracarboxylic acid, for which the stability constant of the uranyl complex is two orders of magnitude smaller than expected from the stability constants of the complexes of the ligand with the sterically undemanding trivalent lanthanide cations or the uranyl complexes of similar, but more flexible, ligands (Morss *et al.*, 2000).

When steric constraints are not important, the strength of actinide–ligand interactions are primarily governed by electrostatic attraction. Increasing effective charge and decreasing ion size (i.e. increasing charge density) of either the actinide cation or the ligand favor stronger bonds, as discussed in Section 23.6. For a given oxidation state, the radii of actinide ions become progressively smaller with increasing atomic number, imparting a larger charge density to the actinide cation and, generally, making the complexes of the heavier actinides progressively more stable. Unfortunately, little data is available for elements heavier than curium, but the measured stability constants support such correlations.

23.4.5 Relative strength of complexation

For a given ligand, the strength of the actinide complexes usually increases in the order

$$AnO_2^+ < An^{3+} \lesssim AnO_2^{2+} < An^{4+}$$

when steric effects are not important. Obviously the order tracks neither the oxidation state nor the formal charge of the actinide cations. While the overall, formal charges of the actinyl(v) and actinyl(vi) cations are +1 and +2, respectively, the order of the stability constants implies that the effective charge (Z_{eff}) felt by a ligand bound to the actinyl cations in the equatorial plane is considerably larger. This suggests that the -yl oxygen atoms of the actinyl(v) and actinyl(vi) cations retain a partial negative charge. Assuming completely electrostatic bonding (except for the actinyl oxygens) and that the effective charges of Ca^{2+}, Nd^{3+}, Am^{3+}, and Th^{4+} are equal to their formal charges, the effective charge felt by ligands bound to pentavalent and hexavalent actinyl cations were estimated empirically. For NpO_2^+, Z_{eff} was estimated as $+(2.2 \pm 0.1)$ (Choppin and Rao, 1984). For AnO_2^{2+} (An = U, Np, Pu), cations this approach estimated Z_{eff} between $+3.0$ and $+3.3$, depending on the cation and the estimation procedure (Choppin and Unrein, 1976; Choppin, 1983; Choppin and Rao, 1984). In the series of AnO_2^{2+}–fluoride complexes, the derived value of Z_{eff} decreases with increasing atomic number. These experimental Z_{eff} values agree with those from theoretical calculations (Walch and Ellis, 1976; Matsika and Pitzer, 2000), providing theoretical foundations for the observed order of actinide complex stabilities.

The stability constants of a few carboxylate complexes of No^{2+} have been reported (McDowell *et al.*, 1976). They are smaller than those of the actinyl(v) cations, and are similar to those observed for Ca^{2+} or Sr^{2+}. This suggests that the divalent actinides have the lowest effective charge and form the weakest complexes of any actinide oxidation state.

23.4.6 Covalent contribution to bonding

Although an ionic model adequately describes most actinide complexes in solution, measurable covalent bonding is present in the actinide–ligand bonds of some compounds. The most prevalent example of covalence in actinide bonding comes from actinide–ligand multiple bonds (Kaltsoyannis, 2000; Denning *et al.*, 2002), particularly the short (ca. 1.7–1.8 Å) O=An=O bonds in the linear dioxo actinyl ions of the pentavalent and hexavalent light actinides, AnO_2^+ and AnO_2^{2+} (An = U, Np, Pu, Am). Other well-characterized examples of actinide–ligand bonds with some degree of covalence are found in actinide–organometallic complexes (Cramer *et al.*, 1983; Brennan *et al.*, 1987, 1989). More surprising examples come from computation (Pepper and Bursten, 1991) and experiments that suggest that a measurable covalent contribution is present even in An–F bonds, the actinide–ligand bonds expected to be the most strongly ionic. Bleaney *et al.* (1956) and Kolbe and Edelstein (1971) observed superhyperfine splitting, attributable to covalence, in the EPR of trivalent uranium and plutonium fluorides, which are present as cubic AnF_8^{5-} in a fluorite host. In contrast, superhyperfine splitting was not observed for the equivalent compounds of the trivalent lanthanides doped in fluorite, implying that the An–F bonds have measurably greater covalent character than Ln–F bonds. However, the presence of some covalence in the actinide–ligand bonds does not diminish the overarching importance of ionic interactions in the formation of these bonds.

In solution, the best evidence for some degree of covalence in actinide–ligand bonds comes from the thermodynamic differences in the complexes of the trivalent lanthanides and the trivalent actinides with soft donor ligands (i.e. ligands containing N, S, or halide donors other than F^-). The complexes formed by An^{3+} cations and Ln^{3+} cations with hard donor, oxygen-based, ligands (carboxylates, organophosphates) are nearly indistinguishable for Ln^{3+} and An^{3+} ions with similar ionic radii (e.g. Am^{3+} and Pm^{3+}). However, as first observed by Diamond *et al.* (1954), An^{3+} cations form thermodynamically more stable complexes with soft donor ligands than the equivalent Ln^{3+} cations do. This deviation from predictions based solely on electrostatic bonding has been interpreted as indicating slightly greater covalence in the actinide–soft donor ligand bond. The stability constants of aqueous complexes of trivalent lanthanide and actinide cations with some representative hard and soft donor ligands, as well as ligands containing both hard and soft donor groups, are summarized in Table 23.16.

23.4.7 Soft ligand bonding

A greater degree of covalence in the bonds between an actinide ion and soft donor ligand should also be reflected in more exothermic complexation enthalpies, relative to the equivalent lanthanide complexes. Significant differences in the enthalpies of metal–nitrogen bonds were not observed in the aminocarboxylate complexes of americium, curium, and europium (Rizkalla *et al.*, 1989). However, large differences in the complexation enthalpies of trivalent lanthanide and actinide cations consistent with enhanced covalence in actinide–soft donor bonds have been reported for ligands containing only soft donor atoms in both aqueous and organic solutions (Zhu *et al.*, 1996; Jensen *et al.*, 2000a; Miguirditchian, 2003).

The preference of actinide ions for softer donor ligands is the common basis for successful chemical separations of the trivalent actinides from the trivalent lanthanides (Nash, 1993a). Although actinide–soft donor bonds are thermodynamically stronger than the corresponding lanthanide–soft donor bonds, neither series of f-element cations forms particularly strong complexes with ligands containing only soft donors, as illustrated by the stability constants in Table 23.16. The likelihood of observing complexes between actinide ions and soft donor ligands is further reduced in aqueous solution by the high background concentration of the hard Lewis base H_2O, 55 mol L^{-1}. Thus, forming actinide complexes with soft donor ligands in aqueous solution requires either high concentrations of the soft ligand, multiple soft donor sites within a single ligand, or the presence of both hard and soft donors within the same ligand. Soft donor binding in aqueous solution is also encouraged when the soft donor groups are relatively acidic, which allows the soft donor ligand to compete with hydrolysis reactions. As a result, actinide soft donor reactions are most easily observed in non-aqueous solvents.

Table 23.16 *Stability constants of trivalent lanthanide and actinide cations of similar ionic radius with oxygen donor and nitrogen donor ligands in aqueous* $NaClO_4$, $T = 25°C$. (*Crystal radii according to Shannon* (1976) $Nd^{3+} = 1.249$ Å, $Pm^{3+} = 1.233$ Å, $Sm^{3+} = 1.219$ Å, $Am^{3+} = 1.230$ Å *for CN* = 8.)

Complex formed[a]	$\log\beta_{1q}$			*Ligand donor atoms*	I (M)	*References*
	Nd	*Sm*	*Am*			
Hard donors						
$M(ac)^{2+}$	1.92	2.03	1.96	1 or 2 O	2	Grenthe (1964); Choppin and Schneider (1970)
$M(ox)^{+}$	5.18 (Pm)	–	5.25	2 O	0.1	Stepanov (1971)
$M(ox)_2^{-}$	8.78 (Pm)	–	8.85	4 O	0.1	Stepanov (1971)
Both hard and soft donors						
$M(edta)^{-}$	15.75	16.20	16.77	4 O, 2 N	0.5	Gritmon *et al.* (1977); Rizkalla *et al.* (1989)
$M(dtpa)^{2-}$	20.09	20.72	21.12	5 O, 3 N	0.5	Gritmon *et al.* (1977); Rizkalla *et al.* (1989)
Soft donors						
MN_3^{2+}	0.4	–	1.3	1 N	–[b]	Musikas *et al.* (1983)
$M(N_3)_2^{+}$	0.6	–	1.6	2 N	–[b]	Musikas *et al.* (1983)
$M(N_3)_3$	0.7	–	1.4	3 N	–[b]	Musikas *et al.* (1983)
$M(tpen)^{3+}$		4.70	6.73	6 N	0.1	Jensen *et al.* (2000a)
$M(tptz)^{3+}$	2.8	3.4	4.2	3 N	1[c]	Musikas (1984)

[a] ac^{-}, acetate; ox^{2-}, oxalate; $edta^{4-}$, ethylenediaminetetraacetate; $dtpa^{5-}$, diethylenetriaminepentaacetate; tpen, *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine; tptz, 2,4,6-tri(2-pyridyl)-1,3,5-triazine.

[b] Ionic strength not given.

[c] 1 M KCl.

In summary, actinide–ligand bonding, though primarily ionic, should be considered as intermediate between the strongly ionic bonding observed in lanthanide complexes and the more covalent bonding found in transition metal complexes. The exact behavior of an actinide ion is determined by its oxidation state, the hard or soft characteristics of the ligand, and the position of an actinide element within the actinide series, with the actinides becoming more lanthanide-like with increasing atomic number.

23.5 INNER VERSUS OUTER SPHERE COMPLEXATION

Although the concept of outer sphere complexation was introduced by Werner (1913) and the theory first given a mathematical base by Bjerrum (1926) progress in understanding the factors involved in the competition between inner and outer sphere complexation was slow.

The term 'outer sphere complex' refers to species in which the ligand does not enter the primary coordination sphere of the cation but remains separated by at least one solvent molecule. Such species are known also as 'solvent separated' ion pairs to distinguish them from inner sphere complexes in which the bonding involves direct contact between the cation and the ligand. Some ligands cannot displace the water and complexation terminates with the formation of the outer sphere species. Actinide cations have been found to form both inner and outer sphere complexes and for some ligands, both types of complexes may be present simultaneously.

For labile complexes, it is often quite difficult to distinguish between inner and outer sphere complexes. Adding to this confusion is the fact that stability constants for such labile complexes determined by optical spectrometry are often lower than those of the same system determined by other means such as potentiometry, solvent extraction, etc. This has led some authors to identify the former as 'inner sphere' stability constants and the latter as 'total' stability constants. However, others have shown that this cannot be correct even if the optical spectra of the solvated cation and the outer sphere complex are the same (Beck, 1968; Johansson, 1971). Nevertheless, the characterization and knowledge of the formation constants of outer sphere complexes are important as such complexes play a significant role in the Eigen–Tamm mechanism for the formation of labile complexes (Eigen and Wilkins, 1965). The Eigen–Tamm mechanism assumes rapid formation of an outer sphere association complex (i.e. an ion pair) and the subsequent rate-determining step in which the ligand displaces one or more water molecules,

$$\mathrm{M(H_2O)}_q^{z+} + \mathrm{L}^{x-} \rightarrow \mathrm{M(H_2O)}_q^{z+}\text{- - -}\mathrm{L}^{x-} \rightarrow \mathrm{M(H_2O)}_{q-1}\mathrm{L}^{z-x} + \mathrm{H_2O}$$

The conversion of the outer sphere complex to the inner sphere complex is the rate-determining step and is dependent on the equilibrium concentration of the outer sphere complex. Consequently, calculations of rate constants by the Eigen model involve estimation of the stability constants of the outer sphere species. Actinide cations form labile, ionic complexes of both inner and outer sphere character and serve as useful probes to study the competition between inner and outer sphere complexation due to ligand properties.

It has been proposed (Choppin and Strazik, 1965; Choppin and Ensor, 1977; Khalili *et al.*, 1988) that the thermodynamic parameters of complexation can be used as a criterion for evaluation of inner versus outer sphere complexation. For outer sphere complexes, the primary hydration sphere is minimally perturbed. As a result, an exothermic enthalpy results from the cation–ligand interaction while the entropy change can be expected to be negative since the ordering of ionic charges is not accompanied by a compensatory disordering of the hydration sphere. By contrast, when inner sphere complexes are formed, the primary hydration sphere is sufficiently disrupted that this contribution to the entropy and enthalpy of complexation frequently exceeds that of the cation–ligand interaction and the result is an endothermic enthalpy and a positive entropy change. These considerations have led, for trivalent lanthanides and actinides in their 1:1 complexes (i.e., ML), to assignment of predominately outer sphere character to the Cl^-, Br^-, I^-, ClO_3^-, NO_3^- and sulfonate complexes and of inner sphere character to the F^-, IO_3^- and SO_4^{2-} complexes (Choppin, 1971).

The experimental, total, stability constant, β^{exp} is related to β_{os} and β_{is} by

$$\beta^{\text{exp}} = \beta_{\text{is}} + \beta_{\text{os}}$$

where β_{is} and β_{os} are the stability constants for inner and outer sphere formation, respectively. The effect of cationic charge on the equilibrium between inner and outer sphere complexation by the halate and chloroacetate anions has been investigated (Rizkalla *et al.*, 1990b; Choppin *et al.*, 1992b). In the case of halate systems, the entropy change for the complexation with monochlorate ($pK_a(HClO_3) = -2.7$) was considered to indicate 100% outer sphere character while that of the monoiodate ($pK_a(HIO_3) = 0.7$) led to the assignment of a predominately inner sphere character. The data for the 1:1 europium bromate ($pK_a\ (HBrO_3) = -2.3$) complex was interpreted to show a mixed nature with the outer sphere character more dominant. For thiocyanate complexes, stepwise stability constant patterns are reported for An(III) (Harmon *et al.*, 1972a) and AnO_2^{2+} (Ahrland and Kullberg, 1971a) to be $K_1 > K_2 < K_3$, indicating predominant outer sphere nature of the 1:1 and 1:2 complexes which changes to inner sphere for the 1:3 system. For An(IV), the pattern (Laubscher and Fouché, 1971) is $K_1 > K_2 > K_3 < K_4$, indicating that inner sphere complexation occurs only in the 1:4 species.

A series of related ligands, acetate and chloroacetates (Ensor and Choppin, 1980), was studied by solvent extraction and calorimetry to ascertain the relationship of ligand pK_a and inner versus outer sphere character. The relationship of experimental values of log β_{11} with the ligand pK_a as well as the relationships of the calculated values of log β_{is} and log β_{os} is shown in Fig. 23.15. Acetate (ac^-, $pK_a = 4.8$) formed inner sphere complexes and trichloroacetate (Cl_3ac^-, $pK_a = -0.5$), outer sphere complexes. The inner sphere nature increased with pK_a (Rinaldi *et al.*, 1979) with estimates for inner character of 100% $La(ac)^{2+}$, 50% $La(Clac)^{2+}$, 22% $La(Cl_2ac)^{2+}$, and 0% $La(Cl_3ac)^{2+}$. These values agreed satisfactorily with calculations using a modified Born equation (Choppin and Strazik, 1965). For the uranyl(VI) system, similar calculations (Khalili *et al.*, 1988) provided the following values for the percent inner sphere character: $UO_2(ac)^+$, 100%; $UO_2(Clac)^+$, 42%; $UO_2(Cl_2ac)^+$, 9%; $UO_2(Cl_3ac)^+$, 4%.

The data are consistent with an increased tendency to outer sphere complexation for the same cation as the ligand pK_a values decrease since the more acidic ligand is less competitive with hydration. Conversely, there is a stronger tendency to outer sphere complexation with increased charge on the metal cation, reflecting the increased hydration strength for higher cation charge. From acetate/haloacetate 1:1 complexation data with An^{3+} and AnO_2^{2+}, it

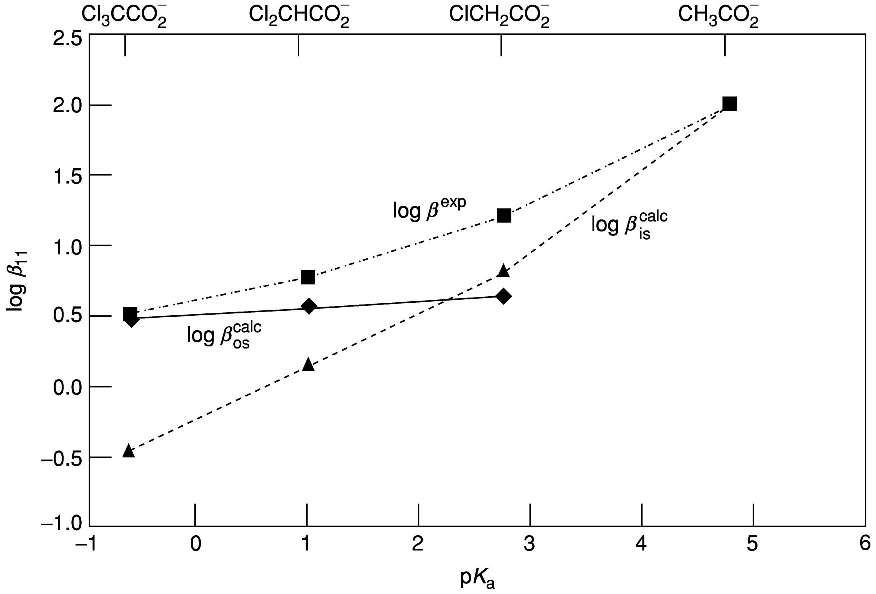


Fig 23.15 *Dependence of the experimentally measured total stability constant,* β^{exp}, *and the calculated inner* (β_{is}) *and outer* (β_{os}) *sphere stability constants for Am(III) complexes on the acidity of* $Cl_{3-n}H_nCCO_2H$ *ligands.*

was estimated that equal amounts of inner and outer sphere complexation would be observed for carboxylate ligands of pK_a ~ 2.8–3.0 (Khalili *et al.*, 1988). For NpO_2^+ and Th^{4+} cations, equal amounts of inner and outer sphere complexes would be present in 1:1 complexes with carboxylate ligands of pK_a ~ 1.1 and 4.2, respectively (Choppin and Rizkalla, 1994).

The thermodynamic data of Eu(halate)$^{2+}$ and Th(halate)$^{3+}$ complexation are listed in Table 23.17. The entropy for the monochlorate (pK_a $HClO_3 = -2.7$) was interpreted as indicating 100% outer sphere character with Eu(III) and a predominance of it with Th(IV). The values for the monoiodate (pK_a $HIO_3 = 0.7$) complexes led to assignment of a predominately inner sphere character for both Eu(III) and Th(IV) (Choppin and Ensor, 1977). The data for the 1:1 europium complex with bromate (pK_a $HBrO_3 = -2.3$) were interpreted as showing a mixed nature with more outer sphere character. Values of 70, 80, and 85% (±10%) were estimated as the percent of outer sphere nature in the $EuBrO_3^{2+}$, $UO_2BrO_3^+$, and $ThBrO_3^{3+}$ complexes (Rinaldi *et al.*, 1979; Ensor and Choppin, 1980; Khalili *et al.*, 1988). This is consistent with increased outer sphere nature with larger effective charge of U in UO_2^{2+}. This pattern is likely due to the increase in hydration strength as the cationic charge increases.

Table 23.17 *Thermodynamic parameters for halate complexation.*

Complex	*log* β_{11}	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J K^{-1}mol^{-1})	*% inner sphere*
$EuClO_3^{2+}$	0.04	−0.25	−6.3	−20	0
$EuBrO_3^{2+}$	0.59	−3.39	−2.5	3	ca. 30
$EuIO_3^{2+}$	1.14	−6.53	11.0	59	100
$ThClO_3^{3+}$	0.14	−0.78	2.4	11	≥0
$ThBrO_3^{3+}$	0.63	−3.61	2.5	20	ca. 15
$ThIO_3^{3+}$	2.49	−14.24	6.5	70	100

23.6 CORRELATIONS

Actinide cations interact with hard Lewis bases through strongly ionic bonds whose thermodynamic strength is dependent of the charges of the actinide cations and of the ligands and on any steric constraints imposed by the actinide ion or ligand (see Section 23.4). In the absence of steric effects, the predominance of ionic bonding in actinide complexes and the regular decrease in the size of actinide ions within an oxidation state as the atomic number increases are the basis for the systematics of actinide–ligand complexation, which can be exploited for important predictive capabilities. The stoichiometries, structures, and stability constants of actinide–ligand complexes in solution can often be predicted from the chemistry of related ligands or of other metal ions, including those in other oxidation states. Such empirical correlations can provide fairly accurate estimates of the properties of actinide–ligand complexes, although no correlation is universally applicable to all ligands, actinide ions, or actinide oxidation states because of electronic effects (e.g. covalency) or steric constraints. Given the large number of potential ligands, the ability to use such correlations to predict the strength of the interaction between a metal ion and a ligand accurately is very useful. The difficulties in working with radioactive materials further increase the value of these correlations.

The interactions of H^+ and An^{z+} with ligands are governed primarily by the same physical forces, electrostatics. Consequently, ligand basicity is often a good predictor of the relative thermodynamic strength of the interactions of ligands with actinide cations. In practice, ligand basicity may be expressed either in the Brønsted sense as the affinity of a ligand for protons or, more generally, as the affinity of a ligand for Lewis acids (i.e. other metal cations). Since both the pK_a and the logarithmic stability constant of a metal–ligand complex (M_nL_q), $\log \beta_{nq}$, are directly proportional to the Gibbs energy of reaction,

$$\Delta G_{\text{protonation}} = -2.303RT\,pK_a \tag{23.9}$$

$$\Delta G_{\text{complexation}} = -2.303RT\log\beta_{nq} \tag{23.10}$$

the correlation of stability constants with ligand basicity falls in the general category of linear Gibbs energy correlations.

The database of ligand pK_a values is the most extensive set of data available for correlating and interpreting actinide–ligand bonding. The logarithm of the stability constant for actinide–ligand complexation is expected to be directly proportional to the basicity of the ligand, expressed as the pK_a, within a series of ligands containing a single bonding functionality where variations in steric effects are negligible. Examples of this type of correlation for the formation of 1:1 UO_2^{2+}:monocarboxylate complexes and of both 1:1 and 1:2 NpO_2^+:β-diketonate complexes are shown in Fig. 23.16. The monocarboxylic acids could behave as monodentate or bidentate ligands (Howatson *et al.*, 1975; Denecke *et al.*, 1998; Rao *et al.*, 2002), while the β-diketonate ligands form bidentate six-membered chelate rings with the neptunyl(v) ion. The deviation of the $UO_2(O_2CCHCl_2)^+$ complex from the correlation likely arises from the formation of a mixture of inner and outer sphere dichloroacetate complexes (Section 23.5), while the other ligands form only inner sphere complexes with the uranyl(vi) cation.

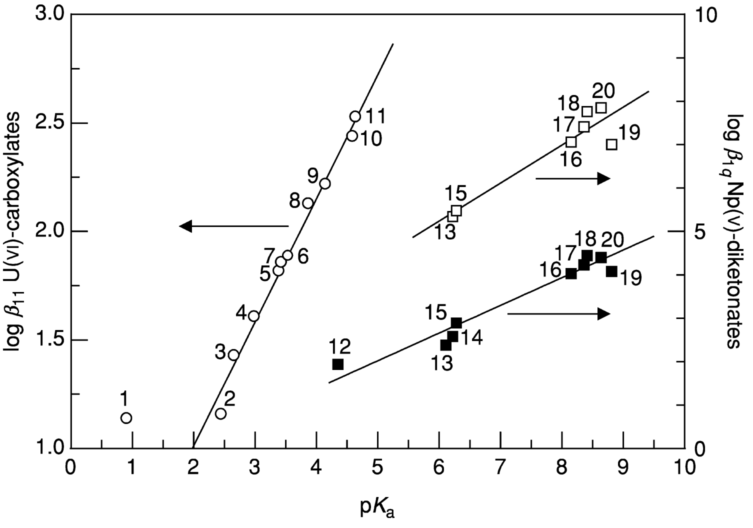


Fig. 23.16 *Linear Gibbs energy correlation of the stability constants of* 1:1 *uranyl*(*vi*)*: monocarboxylate* (○), *and* 1:1 (■) *and* 1:2 (□) *neptunyl*(*v*)*:β-diketonate complexes with the ligand basicity. Data from Martell* et al. (1998), *Gross and Keller* (1972), *and Sekine* et al. (1973). (1) *Dichloroacetate,* (2) *glycine,* (3) *chloroacetate,* (4) 2-*furoate,* (5) 2-*thenoate,* (6) *formate,* (7) *thioglycolate,* (8) 3,5-*dihydroxybenzenecarboxylate,* (9) *phenylacetate,* (10) *acetate,* (11) *propionate,* (12) *hexafluoroacetylacetone,* (13) 2-*furoyltrifluoroacetone,* (14) *trifluoroacetylacetone,* (15) 2-*thenoyltrifluoroacetone,* (16) *difuroylmethane,* (17) 2-*thenoylacetone,* (18) 2-*furoylacetone,* (19) *acetyacetone,* (20) *benzoylacetone.*

Using the pK_a to represent ligand basicity is straightforward for simple ligands, such as monocarboxylate and β-diketonate ligands (Fig. 23.16), where all of a ligand's donor atoms are available for coordination once the single ionizable proton is removed from the ligand. The correlation of actinide complexation constants to ligand basicity is more complicated when the ligand contains multiple basic sites or can form more than a single chelate ring. Summing the pK_a values for each of a ligand's donor groups yields a single parameter representing an effective, total basicity. These values, ΣpK_a, usually correlate fairly well with the stability constants, log β_{11}, of an actinide ion, as shown in Fig. 23.17. Such correlations between stability constants and ΣpK_a values is the strongest within groups of related ligands, as similarity of the structural features of the complex is more likely. In some cases, all of the

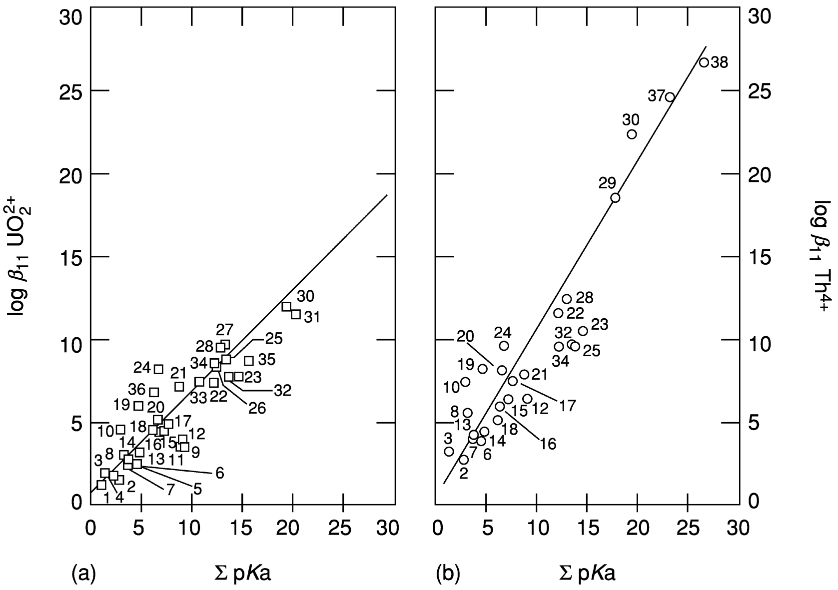
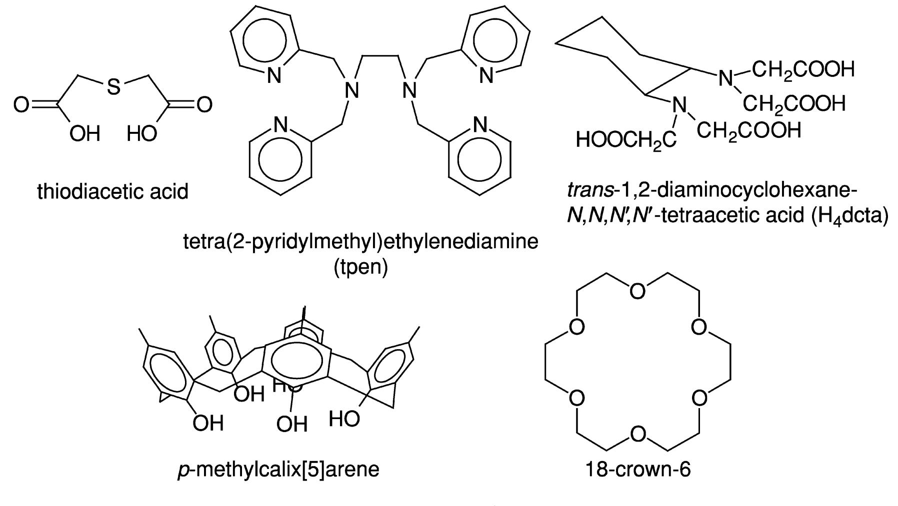


Fig. 23.17 *Linear Gibbs energy correlation between the stability constants and total ligand basicity for* (*a*) *uranyl*(VI) *and* (*b*) *thorium*(IV) *complexes.* (1) *Dichloroacetate,* (2) *chloroacetate,* (3) *sulfate,* (4) *nicotinate,* (5) *ascorbate,* (6) *acetate,* (7) *glycolate,* (8) *thiodiacetate,* (9) *adipate,* (10) *fluoride,* (11) *glutarate,* (12) *succinate,* (13) *lactate,* (14) *α-hydroxyisobutyrate,* (15) *maleate,* (16) *phthalate,* (17) *malonate,* (18) *picolinate,* (19) *oxalate,* (20) *oxydiacetate,* (21) *acetylacetonate,* (22) *citrate,* (23) *oxinate,* (24) *tropolonate,* (25) *iminodiacetate,* (26) *N-*(2-*hydroxyethyl*)*iminodiacetate,* (27) *N-methyliminodiacetate,* (28) *nitriliotriacetate,* (29) *N-*(2-*hydroxyethyl*)*ethylenediamine-N, N′,N′-triacetate–hedta*$^{3-}$, (30) *ethylenediaminetetraacetate–edta*$^{4-}$, (31) *ethylenediamine-N,N′-diacetate–edda*$^{2-}$, (32) *hydroxide,* (33) *monoprotonated ethylenediaminetetraacetate–H*(*edta*)$^{3-}$, (34) *sulfoxinate,* (35) *carbonate,* (36) *thenoyltrifluoroacetonate,* (37) *trans-*1, 2-*diaminocyclohexane-N,N,N′,N′-tetraacetate–dcta*$^{4-}$, (38) *diethylenetriaminepentaacetate–dtpa*$^{5-}$, (39) *tetra*(2-*pyridylmethyl*)*ethylenediamine–tpen.*

potential donor atoms represented by the individual pK_a values do not bind the metal ion, either because of actinide- or ligand-based steric considerations, or because the donor atoms are not well matched to actinide chemistry (e.g. sulfur donors in aqueous solution). For such complexes, the actual An–L stability constant is smaller than predicted. In other cases, the assumption of An–L bonds being primarily ionic may be invalid, or the presence of a ligand containing donor atoms that are Lewis bases without appreciable Brønsted basicity (e.g. ether oxygens), would result in an An–L stability constant that is greater than that predicted by the ΣpK_a correlation.

Deviations from the expected correlation between a *measured* stability constant and ΣpK_a for a particular An–L pair can be a useful diagnostic for determining the denticity or coordination modes of ligands in actinide complexes (Jensen and Nash, 2001). The complexation of Np(v) by thiodiacetic acid (H_2tda) in 0.5 M $NaClO_4$ solution (Rizkalla *et al.*, 1990a) is a good example of this approach. Thiodiacetic acid (Fig. 23.18), is a potentially tridentate ligand, capable of forming two five-membered –S–C–C–O– chelate rings with metal ions of the proper size. However, the low affinity of actinide ions for ligands with sulfur donor atoms and the low effective charge of the neptunyl(v) cation, +2.2, combine to keep the ligand from forming such chelate rings. Based on the ΣpK_a (3.07 + 4.00 = 7.07), the correlation predicts a stability constant for $NpO_2(tda)^-$ of $\log\beta_{11} = 3.0$. A favorable Np–S interaction yielding a tridentate complex with two –S–C–C–O– chelate rings would make the stability constant still larger. However, the reported stability constant is much smaller ($\log\beta_{11} = 1.2$), indicating that the complex is not tridentate. The magnitude of the stability constant does match those of NpO_2^+ complexes with monofunctional carboxylic acid ligands ($\log\beta_{11} = 0.7–1.3$), and is only slightly larger than


thiodiacetic acid

tetra(2-pyridylmethyl)ethylenediamine (tpen)

trans-1,2-diaminocyclohexane-*N,N,N′,N′*-tetraacetic acid (H_4dcta)

p-methylcalix[5]arene

18-crown-6

Fig. 23.18 *Ligand structures.*

the value predicted, log $\beta_{11} = 0.8$, by considering NpO_2^+ complexation only at the most acidic site where pK_a = 3.07. The agreement of the experimental stability constant with that for a single ligand pK_a leads to the conclusion that there is no significant Np–S interaction and that tda^{2-} binds to NpO_2^+ only through a single carboxylate group. The lack of a Np–S bond also is consistent with the crystal structure of $NaNd(tda)_2$, in which only Nd–O bonds are observed (Kepert *et al.*, 1999).

The uncertainty in the nature of the interactions of certain actinide ions with particular ligands can make it difficult to understand or predict actinide complexation chemistry based solely on the basicity of a ligand, as the size and charge of the proton are very different from those of the actinide ions in solution. Using the Gibbs energies of complexation for other metal ions instead of pK_a values can overcome this limitation if the Lewis acids (metal ions) used for the correlations impose steric constraints, electrostatic fields, and degrees of covalency similar to those of the actinide ions under consideration. Since the lanthanide cations form metal–ligand bonds that are predominantly ionic and are of approximately the same size as actinide cations, they often are good models for actinide–ligand complexes. Hard transition metal cations, such as Fe^{3+} or Zn^{2+} (Hancock and Martell, 1989; Jarvis and Hancock, 1991), and alkaline earth cations, such as Ca^{2+} (Choppin *et al.*, 1992a), also can be used, with care, in some actinide–ligand bonding correlations. Figs. 23.18 and 23.19 compare the stability constants of actinide–ligand complexes of actinide cations in each of the common solution oxidation states (3+, 4+, 5+, and 6+) with the stability constants of the complexes formed by the same ligands with the trivalent lanthanide cations Nd^{3+} or Sm^{3+}. The correlations are considerably better than for the stability constants of the UO_2^{2+} –ligand or Th^{4+}–ligand complexes with the ΣpK_a values depicted in Fig. 23.17. However, as discussed in Section 23.4, the correlation fails when the assumption of similar steric constraints is incorrect for the complexes of actinyl ions with polydentate ligands containing more than three donor groups per ligand (Figs. 23.19a and 23.20a). In contrast, when the $Np(V)O_2^+$ complexes are compared to the complexes of An(VI)O_2^{2+} cations, which are subject to similar steric constraints, the stability constants of polydentate ligands track the correlation well (Fig. 23.19b).

The stability constants of An(IV) cations, represented by Th^{4+}, and of An(III) cations, represented by Am^{3+}, track the Gibbs energies of trivalent lanthanide (Nd^{3+} or Sm^{3+}) complexation well (Fig. 23.20), indicating that any steric constraints imposed on the ligands by the trivalent and tetravalent actinide cations are similar to those of the lanthanide cations. However, one complex obviously deviates from the correlation. The stability constant of the Am $(tpen)^{3+}$ complex (Ligand #39, tetra(2-pyridylmethyl)ethylendiamine, Fig. 23.18) is two orders of magnitude larger than expected based on the stability constant of the $Sm(tpen)^{3+}$ complex, even though the larger radius of Am^{3+} suggests that the stability constant should be smaller for $Am(tpen)^{3+}$.

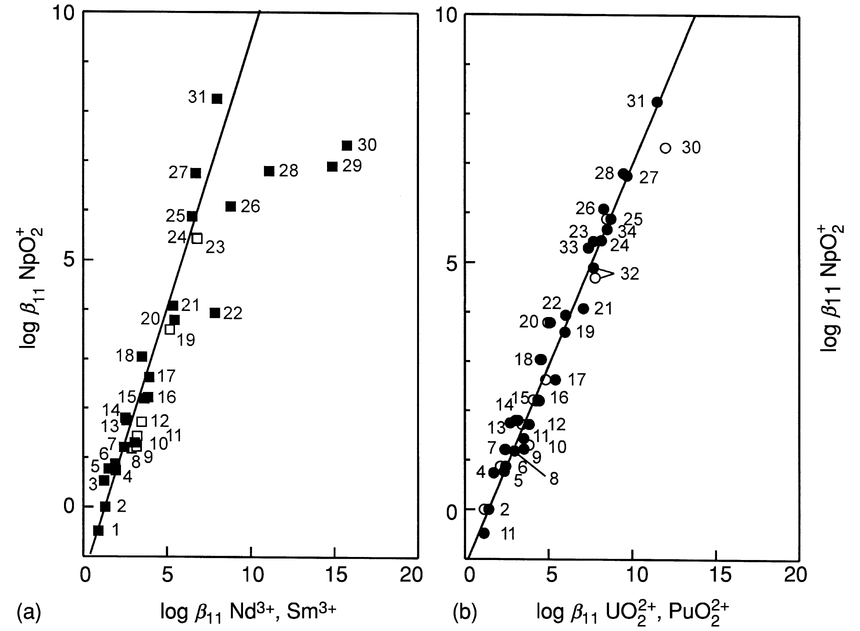


Fig. 23.19 *Correlation between the stability constants of neptunyl(*v*) complexes and the stability constants of the complexes of (a) the trivalent lanthanides Nd^{3+} (■) and Sm^{3+} (□), and (b) the hexavalent actinides UO_2^{2+} (●) and PuO_2^{2+} (○). See Fig.* 23.17 *for the ligands' numerical identities.*

(The crystal radius of Am^{3+} is 1.230 Å for coordination number 8, while for Sm^{3+} it is 1.219 Å under the same conditions [Shannon, 1976].) All six of the potential nitrogen donor atoms in the tpen ligand appear to be coordinated to both Ln^{3+} and An^{3+} cations, with some coordinated water molecules remaining in the inner coordination sphere of the metal ions in aqueous solution (Jensen *et al.*, 2000a). Based on the similar size and coordination environment of the two cations, steric constraints would be expected to play no role in this deviation of the Am^{3+}–Ln^{3+} correlation. The greater stability of the Am^{3+}–tpen complex most likely arises from an enhanced degree of covalence in the An–N bonds as compared to the Ln–N bonds (Choppin, 1983).

The size of the ligand chelate rings can also affect the stability of actinide–ligand complexes. Examining the Gibbs energy relationships for the complexes of two different ligands with numerous different metal ions can be instructive for understanding the interactions of actinide ions with ligands (Jensen and Nash, 2001). Five-membered chelate rings are the most stable ring size for complexes of actinide-sized cations (Hancock, 1992), and the strength of actinide–ligand interactions for chelating ligands usually decreases with ring size in the order $5 > 6 \gg 7 \sim 8$ for all actinide oxidation states (Stout *et al.*, 1989). If the

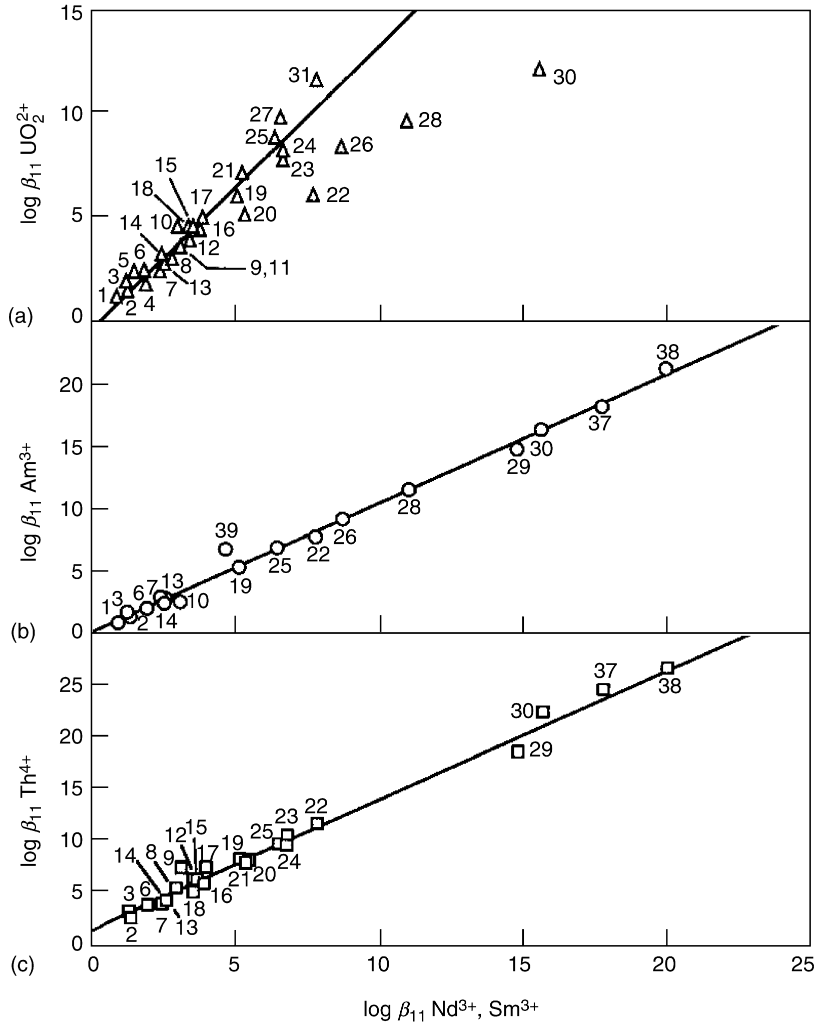


Fig. 23.20 *Correlation between the stability constants of trivalent lanthanide complexes and the stability constants of the complexes of* (*a*) *a hexavalent actinide,* (*b*) *a trivalent actinide, and* (*c*) *a tetravalent actinide. See Fig.* 23.17 *for the ligands' numerical identities.*

donor groups are strongly basic, ligands that form seven-membered rings can be quite stable. Presumably this is because the large size and non-directional electrostatic bonding of the actinide cations can accommodate the larger chelate ring (Rapko *et al.*, 1993). Complexes with eight-membered chelate rings formed by inter-ligand hydrogen bonding also are important species in non-aqueous media, most notably for phosphoric acid based extractants such as bis(2-ethylhexyl)phosphoric acid (Ferraro and Peppard, 1963).

The basis for the empirical correlations between the stability constants of the actinide ion complexes with the acid constants of ligands or the stability constants of other metal ions is the strongly ionic character of the bonding in these systems. Born (1920) calculated the solvation energy of an ion in solution (M^{Z+}) from a model of a sphere of charge $+Z$ and radius R in a system with a dielectric constant, D, by the equation

$$\Delta G_{\text{solvation}}(M^{Z+}) \propto Z^2/DR \tag{23.11}$$

Modifications to the Born equation (Münze, 1972) have formed a useful basis for estimating and comparing actinide–ligand complexation constants (Choppin, 1983; Rizkalla *et al.*, 1990b), and may be useful for describing the entropies of complexation as well (Manning, 1996). For cations of the same charge (Z), the modified Born equation predicts a linear relationship between the logarithmic stability constant and $1/R_{\text{cation}}$, the reciprocal of the cation radii. This relationship holds over a range of cationic radii for numerous metal–ligand complexes, as shown for trivalent lanthanides and for trivalent and tetravalent actinides in Fig. 23.21. In systems where an approximately linear relationship does not hold for f-element complexes, such as citrate complexes (Fig. 23.21), significant steric effects or specific interactions (metal–solvent, ligand–solvent, complex–solvent, or ligand–ligand) are likely. However, it is not known if the order of magnitude deviation of the Fm(dcta)$^-$ and Md(dcta)$^-$ (dcta^{4-} = *trans*-1,2-diaminocyclohexane-*N*,*N*,*N′*,N′-tetraacetate, Fig. 23.18) complexes from the correlation with $1/R_{\text{cation}}$ in Fig. 23.21 arises from such chemical factors or from the higher uncertainties associated with stability constant measurements of complexes involving high specific activity radionuclides.

The cationic charge used in the Born equation, Z, could be taken to be equal to the formal charge of An(III) and An(IV) cations, but it is less clear what the value of Z should be for AnO_2^+ and AnO_2^{2+} species since the oxo ligands appear to retain a partial negative charge. As discussed in Section 23.4, electrostatic correlations based on the Born equation for actinyl–fluoride complexes, suggest that the effective cationic charge experienced by a ligand bound to NpO_2^+ is +2.2, and for ligands bound to UO_2^{2+} is +3.3 (Choppin and Unrein, 1976; Choppin and Rao, 1984).

Defining the ligand charge in the cases of neutral ligands, polydentate ligands, or ligands containing both anionic functional groups (e.g., CO_2^- or PO_3^{2-}) and neutral donor sites (e.g. –N= or –O–) is also difficult. Effective anionic charges have been estimated for some organic ligands by assuming that the Born equation is valid for ligand protonation (Choppin, 1983), which results in a linear relationship between ΣpK_a and the effective anionic charge of a ligand, Z_{an},

$$Z_{\text{an}} = 0.208 \cdot \Sigma pK_a$$

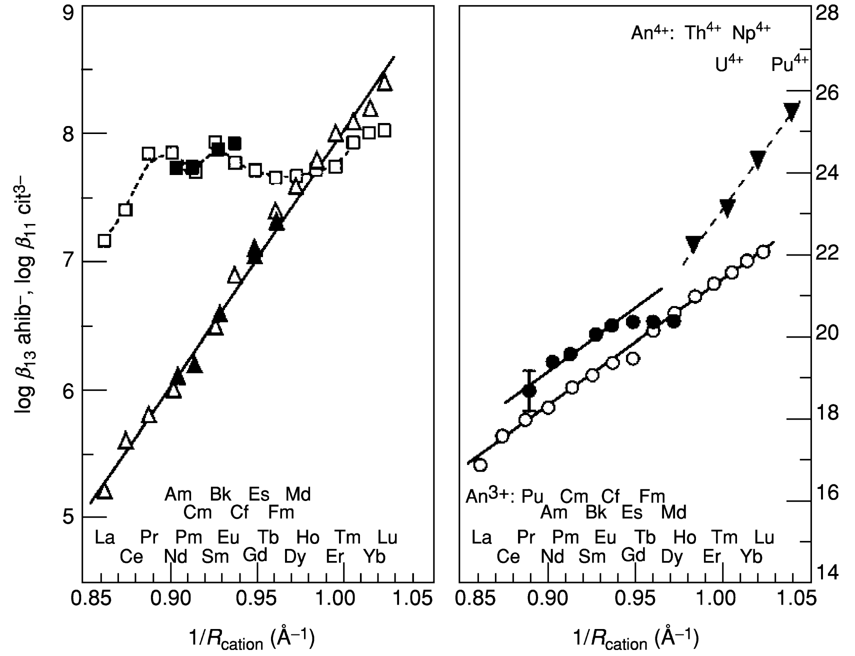


Fig. 23.21 *Dependence of the stability constants of actinide (solid symbols) and lanthanide (open symbols) complexes on cation size as dictated by a purely electrostatic bonding model:* (■, □) 1:1 *complexes of trivalent cations with citrate (cit*$^{3-}$*),* (▲, △) 1:3 *complexes of trivalent cations with α-hydroxyisobutyrate (ahib*$^{-}$*),* (●, ○) 1:1 *complexes of trivalent cations with trans-*1,2*-diaminocyclohexane-N,N,N′,N′-tetraacetate (dcta*$^{4-}$*),* (▼) 1:1 *complexes of tetravalent actinide cations with ethylenediaminetetraacetate (edta*$^{4-}$*). Stability constant data from* (▲) *Starý* (1966) *and Brüchle* et al. (1988) *at* $I = 0.5$ M; (△) *Martell* et al. (1998) *at* $I = 0.1$ M; (■, □) *Martell* et al. (1998) *at* I = 0.1 M (*ionic strength correction applied to Pu*$^{3+}$); (▼) *Martell* et al. (1998) *with Pu value average of Cauchetier and Guichard* (1973), *Krot* et al. (1962), *and Mikhailov* (1969) *at* I = 0.5 M (*ionic strength correction applied to Np*$^{4+}$*, and Pu*$^{4+}$*). Ionic radii from David* (1986) *for CN* = 8.

The Born approach has been useful in describing actinide–ligand complexation in solution, but there has been much discussion over the years about the proper form that an equation describing general electrostatic bonding interactions should take. This debate eventually waned due to the understanding that the general function, Z^n/r^m, is suitable (Huheey, 1976). The Brown–Sylva–Ellis equation, a semiempirical correlation using a complicated function of Z^2/r^2 coupled to a number of electronic corrections appears very successful for describing metal–ligand interactions for a wide range of metal ions, including the actinides (Brown *et al.*, 1985). Other electrostatic models that incorporate corrections for inter-ligand repulsion (Moriyama *et al.*, 1999, 2002; Neck and

Kim, 2000) into the general Born framework have been able to reproduce the stability complexes for higher mononuclear complexes of the actinides (i.e. β_{1q} with $q > 1$).

Inter-ligand interactions are not important for 1:1 An^{z+}:L^- complexes and the metal–ligand interactions can be represented by the simplest form of the coulombic attraction between a metal ion and a monovalent L^- ligand with $\log \beta_{11} \propto Z/d_{M\text{–}L}$ ($d_{M\text{–}L}$ = the distance between the center of the metal ion and the ligand donor atom). Fig. 23.22 depicts this correlation for the 1:1 complexes of hydroxide and fluoride anions with neptunium in the trivalent, tetravalent, pentavalent, and hexavalent oxidation states, using estimates of the actinide–ligand bond distances derived from extended X-ray absorption fine structure measurements of aqueous actinide complexes (Allen *et al.*, 1997, 2000; Moll *et al.*, 1999; Vallet *et al.*, 2001) and effective charges of +2.2 and +3.2 for NpO_2^+ and NpO_2^{2+} cations, respectively. The correlation also holds for more complicated inorganic and organic ligands.

Correlations based on electrostatic considerations are important for understanding actinide–ligand bonding, but other correlations could also be used. Drago and Wayland (1965) used an empirical, four-parameter equation,

$$-\Delta H_{11} = E_A E_B + C_A C_B \qquad (23.12)$$

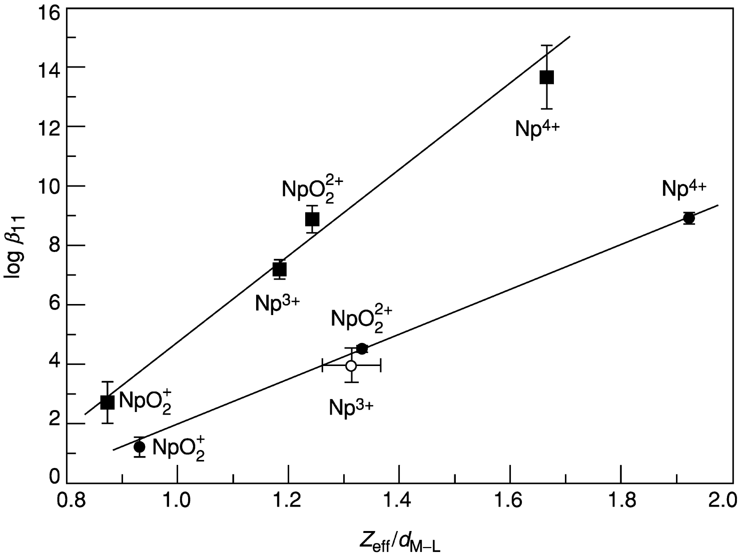


Fig. 23.22 *Dependence of the stability constants of neptunium fluoride* (●) *and neptunium hydroxide* (■) *on the effective ionic potential at* I = 0 M *and* 25°C. *Data from Lemire* et al. (2001) *with the value for* NpF^{2+} (○) *estimated from the* LnF^{2+} *stability constants of Martell* et al. (1998).

to describe the enthalpy of adduct formation between a Lewis acid (the E_A and C_A terms) and a Lewis base (the E_B and C_B terms). E_A and E_B are related to the tendency of an acid and base to form electrostatic bonds and C_A and C_B are related to their tendency to form covalent bonds. The equation was subsequently related to the molecular orbitals of the complexes formed (Marks and Drago, 1975). Hancock and Marsicano (1980) extended this approach to Gibbs energies of complexation using two additional parameters to include the steric constraints of the Lewis acid and base. Stability constants of aqueous Pu(IV) and U(VI) complexes with a number of ligands were estimated in this way (Hancock and Marsicano, 1980; Jarvis *et al.*, 1992; Jarvis and Hancock, 1994). This parameterization also has been used to understand bonding in lanthanide–ligand systems (Choppin and Yao, 1988; Carugo and Castellani, 1992). For a given lanthanide ion, the stability constants with oxygen donor ligands, which form strongly ionic bonds, were found to be well correlated to E_B, the ligand electrostatic parameter. In contrast, the stability constants of the complexes of the softer, nitrogen donor ligands were correlated with the ligand-based covalent parameter, C_B. Ionization potentials and electronegativities have also been used in correlations with the Gibbs energies of complexation of other families of metal ions (Hefter, 1974; Hancock and Martell, 1996).

The success of such correlations, whether based on linear Gibbs energy relationships of stability or protonation constants, on the Born solvation model, or on empirical parameterization is a reflection of the regularity of the solution chemistry of actinide cations and the strongly electrostatic nature of the bonding of their complexes.

23.7 ACTINIDE COMPLEXES

The complexes formed by actinide ions have been the focus of much research because of the importance of separating individual actinide elements from each other or from other elements in the nuclear fuel cycle, and of understanding the environmental chemistry of the actinide elements. A wide variety of experimental methods have been used to identify the stoichiometry or quantify the appropriate equilibrium constants of kinetically labile actinide complexes in solution. The accuracy of these studies depends strongly on the oxidation state purity of the actinide, which can be a problem for less stable oxidation states [e.g. U(III), U(V), Pu(V), Pu(VII), Am(IV), Am(V), or Am(VI)] and when multiple oxidation states can coexist in the same solution as is the case for neptunium and plutonium. The stoichiometry and strength of the actinide complexes with a given ligand are similar within a fairly narrow range for a particular oxidation state due to the predominantly ionic nature of the actinide–ligand bonds and the small differences in cationic radii. The consistent exception to this is Pa(V), which does not exist as an actinyl(V) cation.

23.7.1 Complexes with inorganic ligands

The reactions of actinide ions with halide and pseudohalide anions have been studied extensively. The complexes are, with the exception of the fluoro complexes, moderately weak in aqueous solution. As a consequence, measurements of the complexation constants often require high ligand concentrations (>1 M) and acidic media to allow sufficient amounts of the complexes to form and to avoid interference from hydrolysis reactions. This is most necessary for the tetravalent actinides which can undergo hydrolysis even when $\text{pH} \leq 1$. Many of the halide complexes are sufficiently weak that outer sphere complexes are formed, particularly for the 1:1 (M:L) complexes.

Aqueous fluoro complexes of the actinide ions are known for the trivalent through the hexavalent oxidation states. The fluoride ligand has a much higher affinity for actinide cations than the heavier halides and all actinide fluoro complexes are inner sphere complexes. The neutral fluoro complexes of trivalent and tetravalent actinides, AnF_3 and AnF_4, are insoluble in aqueous solution ($pK_{sp} = 16.4$ for PuF_3 and 26.7 for PuF_4 at $I = 0$ M [Lemire *et al.*, 2001]). In contrast, all of the aqueous actinyl(V) and actinyl(VI) fluoro complexes are soluble. Separation of actinyl species from actinides in the lower oxidation states by fluoride precipitation is an effective method for determining the oxidation state speciation of trace actinides (Kobashi and Choppin, 1988). Cationic complexes formed in the equilibria

$$\mathrm{An}^{z+} + q\mathrm{F}^- \rightleftarrows \mathrm{AnF}_q^{(z-q)+}$$

(An^{z+} = An(III), An(IV), An(V), and An(VI), and $q < z$) have been identified. Anionic complexes of AnO_2^+ and AnO_2^{2+} have also been studied (Ahrland and Kullberg, 1971b; Inoue and Tochiyama, 1985), and pentagonal bipyramidal $UO_2F_5^{3-}$ forms at high fluoride concentrations (Vallet *et al.*, 2002). Stability constants and thermodynamic parameters for the formation of the fluoro complexes of actinides in various oxidation states are summarized in Table 23.18. The stability constants of the 1:1 An:F complexes vary in the order $UO_2^{2+} > NpO_2^{2+} > PuO_2^{2+}$ for hexavalent actinides [see Section 23.4, and Choppin and Rao (1984)], $Th^{4+} < U^{4+} > Np^{4+} \geq Pu^{4+}$ for tetravalent actinides, and $Am^{3+} < Cm^{3+} < Bk^{3+} < Cf^{3+}$ for trivalent actinides (Chaudhuri *et al.*, 1999). Stability constants for the fluoro complexes of the pentavalent actinides have been reported only for protactinium (Guillaumont, 1966; Kolarich *et al.*, 1967) and neptunium (as assessed by Lemire *et al.*, 2001). The reversal in the sequence of the stability constants from the order expected based on the cationic radii of the tetravalent actinides is small, and the expected order is observed for AnF_2^{2+} and AnF_3^+. In each of these oxidation states, the stability of the actinide fluoro complexes is due to the highly favorable entropy contribution while the complexation enthalpies either oppose complex formation or are weakly favorable (Table 23.18). These ΔH and ΔS values reflect the importance of ion dehydration in the formation of inner sphere actinide complexes.

Table 23.18 *Stability constants, and Gibbs energies, enthalpies, and entropies of complexation for the reactions* $An^{z+} + qF^- \rightleftarrows AnF_q^{z-q}$ *and*$AnO_2^{z+} + qF^- \rightleftarrows AnO_2F_q^{z-q}$ *at* 25°C.

Number of F^-	*log* β_{1q}	ΔG (kJmol^{-1})	ΔH (kJmol^{-1})	ΔS (JK^{-1}mol^{-1})	*References*
Am^{3+}, $I = 0.1$ M					
1[a]	2.49	−14.2	28	140	Choppin and Unrein (1976)
1	2.59	−14.8	23	126	Nash and Cleveland (1984a)
2	4.75	−27.1	24	170	Nash and Cleveland (1984a)
Th^{4+}, $I = 4$ M					
1	8.17	−46.6	−2.4	149	Ahrland *et al.* (1990)
2	14.57	−83.1	−3.3	120	Ahrland *et al.* (1990)
U^{4+}, $I = 4$ M					
1	9.02	−51.5	−5.6	154	Ahrland *et al.* (1990)
2	15.72	−89.7	−3.5	136	Ahrland *et al.* (1990)
3	21.18	−120.9	0.5	119	Ahrland *et al.* (1990)
Pu^{4+}, $I = 2$ M					
1	7.59	−43.3	5.6	164	Nash and Cleveland (1984b)
NpO_2^+, $I = 1$ M					
1	1.3	−7.4	–	–	Martell *et al.* (1998)
UO_2^{2+}, $I = 1$ M					
1	4.54	−25.9	1.7	92.5	Ahrland and Kullberg (1971c)
2	7.98	−45.5	2.1	160	Ahrland and Kullberg (1971c)
3	10.41	−59.5	2.4	207	Ahrland and Kullberg (1971c)
4	11.89	−67.9	0.3	229	Ahrland and Kullberg (1971c)
5	0.60[b]	–	–	–	Vallet *et al.* (2002)

[a] $I = 1.0$ M.

[b] K_5 for the reaction $UO_2F_4^{2-} + F^- \rightleftarrows UO_2F_5^{3-}$, $I = 1.0$ M, $T = -5$°C.

The actinide complexes of the heavier halides are much weaker than those of the fluoro complexes. They also are quite soluble. To the extent that equilibrium constants are available, the strength of the monohalogeno complexes decreases in the order $Cl^- > Br^- > I^-$ (Grenthe *et al.*, 1992) and they appear to be outer sphere under most circumstances (Section 23.2.6). Data on aqueous bromide complexation is scarce and the reducing power of iodide as well as the weakness of the complexes formed have limited studies of the iodide complexes to U(IV), Np(IV), and Pu(III) species (Vdovenko *et al.*, 1963; Khopkar and Mathur, 1974; Patil *et al.*, 1978). Stability constants for actinide complexation with chloride anions in aqueous solution are available for 1:1 and usually 1:2 species for trivalent (Ac, Pu–Es), tetravalent (Th–Pu), pentavalent (Np), and hexavalent

(U–Pu) actinides (Fuger *et al.*, 1992). For actinyl(VI) cations the complexation enthalpies for formation of the monochloro and dichloro complexes are endothermic in 2 M $HClO_4$ at 25°C ($\Delta H_{11} = +[9.2 \pm 0.5]$ and $\Delta H_{12} = +[18 \pm 1]$ kJ mol^{-1} for UO_2^{2+} and $\Delta H_{11} = +[14 \pm 2]$ kJmol^{-1} for PuO_2^{2+} (Rabideau and Masters, 1961; Awasthi and Sundaresan, 1981)). The values of the corresponding complexation entropies range from +26 to +50 JK^{-1}mol^{-1}.

Anionic chloro complexes are often used for separations purposes. Reliable stability constants are not known for these species, but anion exchanging resins or solvent extraction reagents promote the formation of these inner sphere complexes. The trivalent actinides form anionic $AnCl_4^-$ complexes in the resin or organic phase when the concentration of hydrochloric acid exceeds 8 M. Tetravalent uranium, neptunium, and plutonium form anionic chloro complexes with increasing ease, though anionic Th(IV) chloro complexes were reported as being only minor species in 12 M LiCl/0.1 M HCl (Kraus *et al.*, 1956). The actinyl(VI) cations also form anionic chloro complexes that absorb on anion exchange resins. Both the tetravalent and hexavalent actinides absorb as the doubly charged anionic complexes, $AnCl_6^{2-}$ and $AnO_2Cl_4^{2-}$, in 12 M HCl, while $AnCl_5^-$ and $AnO_2Cl_3^-$ are the likely species at lower chloride concentrations (Ryan, 1961; Allen *et al.*, 1997). Although anionic complexes form in the resin phase, in non-aqueous solvents (Marcus and Bomse, 1970) and in the solid state (Brown, 1972), anionic actinide chloro, bromo, and iodo complexes are not present in appreciable amounts in the aqueous phase, except at the highest halide concentrations (Marcus, 1966; Allen *et al.*, 2000). The stability constants for formation of the 1:1 complexes at $I = 1.0$ M are listed in Table 23.19.

The pseudohalides azide (N_3^-)and nitrogen-coordinated thiocyanate (NCS^-) form complexes with actinide cations that are moderately stronger than the equivalent chloro complexes (Table 23.19). The greater stability of the An(III) complexes with these softer ligands (i.e. Cl^-, N_3^-, and NCS^-) relative to that of the Ln(III) complexes has been the basis for group separations of the trivalent 5f elements from the 4f elements (Diamond *et al.*, 1954; Sekine, 1965; Starý, 1966; Musikas *et al.*, 1983; Borkowski *et al.*, 1994). Despite the greater strength of the pseudohalide complexes, spectroscopic measurements indicate that the 1:1 and, probably, the 1:2 An(III):SCN^- complexes are outer sphere complexes (Harmon *et al.*, 1972b). Strong evidence for the aqueous anionic complexes, $An(SCN)_4^-$, $AnO_2(SCN)_3^-$, and $AnO_2(N_3)_3^-$ and $AnO_2(N_3)_4^{2-}$ also have been reported (Ahrland, 1949; Sherif and Awad, 1961; Sekine, 1965; Kinard and Choppin, 1974; Chierice and Neves, 1983).

23.7.2 Complexes with inorganic oxo ligands

Actinides in the common oxidation states form complexes with inorganic oxo ligands. The complexes of the most common of these ligands, H_2O and OH^- are discussed in Sections 23.2 and 23.3, while the complexes of the halate ligands are considered in Section 23.5.

Table 23.19 *Stability of* 1:1 *actinide chloride, azide, and thiocyanate complexes at* I = 1 M *and* 25°C (*Martell* et al., 1998).

An^{z+}	*log*β_{11} *chloride*	*log*β_{11} *azide*	*log*β_{11} *thiocyanate*
Ac^{3+}	−0.10	–	0.05
Pu^{3+}	−0.10	–	0.46
Am^{3+}	−0.1	0.67	0.43
Cm^{3+}	–	0.64	0.44
Bk^{3+}	−0.18[a]	–	0.49
Cf^{3+}	–	0.70	0.53
Es^{3+}	−0.18[a]	–	0.56
Th^{4+}	0.18	–	1.08
U^{4+}	0.40	–	1.49[c]
Pu^{4+}	0.14	–	–
NpO_2^+	−0.35[b]	–	0.32[b]
UO_2^{2+}	−0.10[c]	2.31[d]	0.74

[a] $I = 0.5$ M.
[b] $I = 2.0$ M.
[c] $T = 20$°C.
[d] $I = 0.1$ M.

The stabilities of the actinide complexes with inorganic oxo anions vary in the order $NO_3^- < SO_4^{2-} \ll CO_3^{2-} < PO_4^{3-}$, as expected from the increasing charge and basicity of the ligands. The actinide nitrato complexes are important in the processing of nuclear reactor fuel, especially in separations where the neutral actinide nitrates can be extracted into organic solvents and the anionic, hexanitrato actinide(IV) complexes are used in anion exchange separations. The reported stability constants of the 1:1 An:NO_3^- complexes are slightly larger than those of the analogous chloro complexes, and the anionic nitrato species form more readily than the corresponding chloro complexes. For the actinides, nitrate ions usually act as bidentate chelating ligands with two oxygen atoms from each nitrate coordinated to an actinide.

Sulfate, carbonate, and phosphate complexes can be important in actinide processing, and, along with silicates, are important ligands in determining the environmental behavior of actinide cations. Normally, the stability constants of the complexes with these ligands increase in the usual sequence of $AnO_2^+ < An^{3+} < AnO_2^{2+} < An^{4+}$.

The trivalent actinides have been shown to form 1:1 and 1:2 An:SO_4^{2-} complexes, while the trisulfato complexes also form for the tetravalent and hexavalent actinides. For the weakly complexing actinyl(V) cations, only $NpO_2SO_4^-$ has been reported (Halperin and Oliver, 1983). Stability constants for some actinide–sulfate complexes are summarized in Table 23.20. The thermodynamics of actinide–sulfate complexation are consistent with the formation of inner sphere

Table 23.20 *Stability constants of actinide sulfate complexes at* I = 2 M *and* 25°C (*De Carvalho and Choppin,* 1967*; Ahrland and Kullberg,* 1971*a; Halperin and Oliver,* 1983*; Nash and Cleveland,* 1983*; Martell* et al., 1998) *and carbonate complexes at* I = 0 M *and* 25°C (*Grenthe* et al., 1992; *Silva* et al., 1995; *Lemire* et al., 2001).

	Sulfate (I = 2 M)		*Carbonate* (I = 0 M)		
An^{z+}	*log*β_{11}	*log*β_{12}	*log*β_{11}	*log*β_{12}	*log*β_{13}
Ac^{3+}	1.36[a]	2.68[a]			
Pu^{3+}	1.55	2.12			
Am^{3+}	1.43	1.85	7.8	12.3	15.2
Th^{4+}	3.25	5.53			
U^{4+}	3.48	5.82			
Np^{4+}	3.49	6.06			
Pu^{4+}	3.80	6.6			
$UO_2{}^{+}$					7.4
$NpO_2{}^{+}$	0.19		4.96	6.53	5.50
$PuO_2{}^{+}$					5.1
$UO_2{}^{2+}$	1.81[a]	2.76[a]	9.68	16.94	21.60
$NpO_2{}^{2+}$			9.3	16.5	19.37
$PuO_2{}^{2+}$			11.6	14.5	17.7

[a] $I = 1$ M.

Table 23.21 *Thermodynamic parameters for actinide sulfate complexation in* 2 M *perchlorate media at* 25°C (*Sullivan and Hindman*, 1954; *Zielen*, 1959; *Jones and Choppin*, 1969; *Ahrland and Kullberg*, 1971*a*; *Halperin and Oliver*, 1983).

Actinide ion	ΔG_{11} ($kJ mol^{-1}$)	ΔH_{11} ($kJ mol^{-1}$)	ΔS_{11} ($J K^{-1} mol^{-1}$)	ΔG_{12} ($kJ mol^{-1}$)	ΔH_{12} ($kJ mol^{-1}$)	ΔS_{12} ($J K^{-1} mol^{-1}$)
Am^{3+}	−8.4	18.4	90	–	–	–
Cm^{3+}	−7.5	17.2	83	–	–	–
Cf^{3+}	−7.9	18.8	90	–	–	–
Th^{4+}	−18.8	20.9	133	−32.6	40.4	245
Np^{4+}	−20.0	18.3	128	–	–	–
NpO_2^{+}	−1.1	19	66	–	–	–
UO_2^{2+}[a]	−10.3	18.2	96	−15.7	35.1	171

[a] $I = 1$ M $NaClO_4$.

complexes. The endothermic enthalpies of complexation vary little between actinides in different oxidation states and the strength of a particular actinide–sulfate complex relative to that of other actinide–sulfate species is determined mainly by the complexation entropies (Table 23.21). Sulfate complexes of uranyl(VI) can form polynuclear, ternary hydroxo-sulfato complexes in weakly acidic solutions (Grenthe and Lagerman, 1993; Moll *et al.*, 2000).

Carbonate complexes of the actinides have been investigated often, as reviewed by Newton and Sullivan (1985) and Clark *et al.* (1995). Although the solubility of neutral $AnO_2(CO_3)$ is low, the triscarbonato uranyl(vi) complex, $UO_2(CO_3)_3^{4-}$, is responsible for the relatively high concentration of uranium in seawater (Spence, 1968). The complexes $NpO_2(CO_3)_3^{4-}$ and $PuO_2(CO_3)_3^{4-}$ are less important in the environment because the stability constants of the actinyl (vi) triscarbonato complexes decrease by four orders of magnitude from UO_2^{2+} to PuO_2^{2+} as the effective charge on the actinide decreases (Table 23.20). Similar to nitrate, the carbonate ligands are bidentate, binding in the equatorial plane of the actinyl cations, forming triscarbonato actinyl complexes with hexagonal bipyramidal geometry. Carbonate complexes also are among the few soluble complexes of uranyl(v), plutonyl(v), and americyl(v) that have been quantitatively studied (Bennet *et al.*, 1992; Giffaut and Vitorge, 1993; Docrat *et al.*, 1999). The stabilities of the triscarbonato actinyl(v) complexes are roughly 13 orders of magnitude smaller than the corresponding actinyl(vi) complexes (Lemire *et al.*, 2001). Nevertheless, carbonate ligands stabilize actinyl(v) ions, especially in the solid state (Keenan and Kruse, 1964; Madic *et al.*, 1983a). Few measured stability constants for $An(\text{IV})-CO_3^{2-}$ complexes have been reported, but those of the limiting solution species, $An(CO_3)_5^{6-}$ (Clark *et al.*, 1998), are large, exceeding 10^{35} M^{-5}. Well-characterized polynuclear complexes of the actinyl(vi) cations with bridging and terminal carbonate ligands have an $AnO_2^{2+} : CO_3^{2-}$ stoichiometry of 3:6 (Åberg *et al.*, 1983b; Allen *et al.*, 1995). Carbonate complexes of Np(vii) also have been proposed (Shilov *et al.*, 1976).

The actinide complexes of highly charged inorganic ligands, such as phosphates, arsenates, or silicates, can precipitate in a variety of different solid phases. Soluble, protonated complexes of these ligands, for example $AnO_2(HPO_4)_n^{2-2n}$, have lower stability constants than complexes of the fully deprotonated ligands because of the reduced charge of the protonated ligand. The actinyl(v) and actinyl(vi) cations form soluble 1:1 complexes with PO_4^{3-} that are strong enough to compete with carbonate complexation (Sandino and Bruno, 1992; Brendler *et al.*, 1996; Morgenstern and Kim, 1996).

Singly deprotonated orthosilicic acid, $H_3SiO_4^-$, forms complexes with trivalent and hexavalent actinides in solutions that are weakly acidic to neutral (Yusov and Fedoseev, 2003 and references therein), and the stability constants of the orthosilicate complexes are proportional to the hydrolysis constants of the metal cations (Jensen and Choppin, 1998).

Multicharged, complex inorganic oxides, such as polyphosphates, polymeric silicates, and polyoxometallates, with properties intermediate between those of simple ligands and of oxide or mineral surfaces also form complexes with actinide cations. Stability in acidic solution and the ability to create soluble, well-defined structures with extensive redox activity make the actinide polyoxometallates interesting complexes (Yusov and Shilov, 1999). The rich chemistry of polyoxometallates results in the complexation and stabilization of transplutonium actinides in oxidation states usually not stable in aqueous solutions, for example Am(IV), Cm(IV), and Cf(IV) (Kosyakov *et al.*, 1977). Many common polyoxometallate anions, such as $SiW_{12}O_{40}^{4-}$, $P_2W_{18}O_{62}^{6-}$, $Nb_6O_{19}^{8-}$, and $NaP_5W_{30}O_{110}^{14-}$, form complexes with actinide cations, and both 1:1 and 1:2 complexes have been identified. The stability constants for the Th^{4+} complexes of $SiW_{12}O_{40}^{4-}$ are $\log \beta_{11} = 11.3$ and $\log \beta_{12} = 17.8$, and are characterized by large positive complexation entropies, $\Delta S_{11} = 232\ \mathrm{J\,K^{-1}mol^{-1}}$ and $\Delta S_{12} = 356\ \mathrm{J\,K^{-1}mol^{-1}}$ (Choppin and Wall, 2003). The binding sites on the surfaces of some polyoxometallate ligands can accommodate the steric requirements of the actinyl cations as well as the simple actinide cations (Gaunt *et al.*, 2002). Certain polyoxometallates, like the Preyssler anion $P_5W_{30}O_{110}^{15-}$, also can encapsulate actinide cations internally, forming inert, but soluble, compounds (Creaser *et al.*, 1993; Antonio *et al.*, 1998).

23.7.3 Complexes with organic ligands

The variety and strength of organic ligands that form complexes with actinide ions in aqueous solution are limited by the preference of the actinides for hard donor ligands and by the tendency of actinide cations toward hydrolysis. Consequently, ligands that bind actinide cations in aqueous solution usually contain some hard base, oxygen donor sites because the strength and basicity of organic ligands containing only softer donor groups, generally, are insufficient to suppress the precipitation of actinide hydroxides. In organic solvents, where actinide hydrolysis is not important, organic ligands with softer donors such as dithiophosphinic acids (Pinkerton *et al.*, 1984; Jensen and Bond, 2002), thiacrown ethers (Karmazin *et al.*, 2002), ethylenediamine (Cassol *et al.*, 1990), or tripyrazine (Drew *et al.*, 2000) form actinide complexes that are stable, although weaker than complexes of similar oxygen donor ligands.

The most commonly studied actinide–organic ligand complexes involve ligands bearing carboxylic acid groups. Actinide complexes with simple monocarboxylate ligands (i.e. those that contain no other actinide-binding groups) are not among the stronger actinide complexes (Table 23.22). Compared to common inorganic ligands, the actinide complexes of simple monocarboxylates are somewhat stronger than the equivalent SO_4^{2-} complexes, but weaker than the OH^- or CO_3^{2-} complexes. For acetic acid, the stability constants of the first and second acetate complexes, β_{11} and β_{12}, follow the expected order of effective cation charge and ionic radii for actinides in the different oxidation states. However, the 1:3 acetate complexes of the actinyl(VI) ions are stronger than expected from the stability constants of the An(III) and An(IV) complexes. The thermodynamics of actinide–monocarboxylate complexation are, like those of the simple inorganic ligands, entropy driven, with weakly positive or negative complexation enthalpies. Monocarboxylates with low pK_a values (e.g. dichloroacetate [$pK_a = 1.1$] and trichloroacetate [$pK_a = -0.5$]), form outer sphere complexes with the actinides (Section 23.5).

Table 23.22 *Stability constants of actinide carboxylate and phosphonate complexes in perchlorate media at* 25°C.

		I (M)	*log* β_{11}	*log* β_{12}	*log* β_{13}	*log* β_{14}	*References*
Acetate (ac$^-$) $CH_3CO_2^-$	Pu^{3+}	2[a]	2.02	3.34	–	–	Magon *et al.* (1968)
	Am^{3+}	0.5[a]	1.99	3.28	–	–	Grenthe (1962)
	Cm^{3+}	0.5[a]	2.06	3.09	–	–	Grenthe (1963)
	Th^{4+}	1	3.86	6.97	8.94	10.28[d]	Portanova *et al.* (1975)
	$NpO_2{}^+$	2	0.87	–	–	–	Rizkalla *et al.* (1990b)
	UO_2^{2+}	1	2.42	4.41	6.40	–	Ahrland and Kullberg (1971a)
	NpO_2^{2+}	1[a]	2.31	4.23	6.0	–	Portanova *et al.* (1970)
glycolate $HOCH_2CO_2^-$	Am^{3+}	0.5[a]	2.82	4.86	6.3	–	Grenthe (1962)
	Cm^{3+}	0.5[a]	2.85	4.75	–	–	Grenthe (1963)
	Bk^{3+}	2	2.65	4.69	–	–	Choppin and Degischer (1972)
	Th^{4+}	1	4.11	7.45	10.1	12.0[e]	Di Bernardo *et al.* (1978)
	NpO_2^+	2	1.43	1.90	–	–	Rizkalla *et al.* (1990b)
	UO_2^{2+}	1	2.35	3.97	5.17	–	Di Bernardo *et al.* (1976)
	NpO_2^{2+}	1[a]	2.37	3.95	5.00	–	Portanova *et al.* (1972)
	PuO_2^{2+}	0.1	2.43	3.79	–	–	Eberle and Schaefer (1968)
oxalate $(CO_2)_2^{2-}$	No^{2+}	0.5[b]	1.68		–	–	McDowell *et al.* (1976)
	Am^{3+}	1	4.63	8.35	11.15	–	Sekine (1964)
	Th^{4+}	1	8.23	16.77	22.77	–	Moskvin and Essen (1967)
	Np^{4+}	1	8.19	16.21	–	–	Bansal and Sharma (1964)
	NpO_2^+	1	3.71	6.12	–	–	Tochiyama *et al.* (1992)
	UO_2^{2+}	1[a]	5.99	10.64	11.0	–	Havel (1969)
malonate $CH_2(CO_2)_2^{2-}$	Th^{4+}	1	7.47	12.79	16.3	–	Di Bernardo *et al.* (1977)
	NpO_2^+	1	2.63	4.28	–	–	Jensen and Nash (2001)

Table 23.22 (*Contd.*)

		I (M)	*log* β$_{11}$	*log* β$_{12}$	*log* β$_{13}$	*log* β$_{14}$	*References*
	UO_2^{2+}	1	5.42	9.48	–	–	Di Bernardo *et al.* (1977)
succinate $(CH_2CO_2)_2^{2-}$	Th^{4+}	1	6.44	–	–	–	Di Bernardo *et al.* (1983)
	NpO_2^+	1^c	1.51	2.14	–	–	Stout *et al.* (1989)
	UO_2^{2+}	1	3.85	–	–	–	Bismondo *et al.* (1981)
diglycolate $O(CH_2CO_2)_2^{2-}$	Th^{4+}	1	8.15	14.8	18.2	–	Di Bernardo *et al.* (1983)
	NpO_2^+	1	3.79	–	–	–	Jensen and Nash (2001)
	UO_2^{2+}	1	5.11	7.54	–	–	Di Bernardo *et al.* (1980)
	NpO_2^{2+}	1^a	5.16	–	–	–	Cassol *et al.* (1973)
	PuO_2^{2+}	1^a	4.97	–	–	–	Cassol *et al.* (1973)
phosphonoacetate $O_2CCH_2PO_3H^{2-}$	Th^{4+}	2	8.50	16.05			Nash (1991a)
	UO_2^{2+}	0.1	7.57	14.17			Nash (1993b)
methane-1,1-diphosphonate $CH_2(PO_3H)_2^{2-}$	Th^{4+}	2	8.34	15.44			Nash (1991a)
	UO_2^{2+}	0.1	7.82	13.82			Nash (1993b)
ethane-1,2-diphosphonate $(CH_2PO_3H)_2^{2-}$	UO_2^{2+}	0.1	5.34	8.31			Nash (1993b)

[a] 20°C.
[b] 0.5 M NH_4NO_3, no temperature given.
[c] 23°C.
[d] $\log \beta_{15} = 11.00$.
[e] $\log \beta_{15} = 13.4$.

Multifunctional ligands such as polycarboxylates, hydroxycarboxylates, and aminocarboxylates tend to form stronger actinide complexes than simple monocarboxylates due to the formation of chelate rings through coordination of multiple functional groups. This occurs because the affinity of carboxylate (or phosphonate) groups for actinide ions, and their very favorable complexation entropies, provide an anchor for the complexation of amines, ether oxygens, or other less effective donor atoms within the same ligand. For instance, simple alcohols are not good ligands for actinides in aqueous solution. However, the stability constants of the 1:1 An:L complexes of α-hydroxycarboxylates like glycolate (Table 23.22) and α-hydroxyisobutyrate are stronger than that of acetate because of chelation via the α-hydroxy group (Ahrland, 1986; Stumpf *et al.*, 2002; Toraishi *et al.*, 2002), even though the pK_a values of the carboxylic group would indicate that they are less basic ligands.

Multifunctional ligands also form polynuclear complexes by bridging actinide ions, though this behavior is not unique to actinide cations. In some cases, for example $(UO_2)_2$(edta), $(UO)_2(\text{citrate})_2^{2-}$, or $Th_4(\text{glycolate})_n$ ($n = 8 \pm 1$) (Kozlov and Krot, 1960; Rajan and Martell, 1965; Fraústo da Silva and Simoes, 1968; Toraishi *et al.*, 2002), the polynuclear complexes are well defined and soluble, making measurement of the formation constants of the polynuclear species possible. The likelihood of polynuclear complex formation is usually favored by increasing metal concentrations and decreasing ligand:metal ratios. As the size of the polynuclear complexes increase, their precipitation becomes more likely.

Ethylenediaminetetraacetic acid (H_4edta) and the related multifunctional polyaminocarboxylate ligands are strong, but not very selective, complexants for An(III) and An(IV) cations. Steric constraints make them much poorer ligands for actinyl(V) and actinyl(VI) cations as discussed in Section 23.6. This has led to the use of polyaminocarboxylates as masking agents for interfering An(III) or An(IV) cations in the chemical analysis of actinyl ions. When fully coordinated, the most commonly used polyaminocarboxylate ligands, hexadentate edta^{4-} and dcta^{4-}, and octadentate dtpa^{5-} only partially envelope actinide cations, leaving one or more coordination sites for water molecules (Carey and Martell, 1968; Fried and Martell, 1971; Kimura and Choppin, 1994), or for other small ligands (Pachauri and Tandon, 1975). The strongest polyaminocarboxylate ligands complex An(III) and An(IV) cations over a wide range of acidities (Fig. 23.23). In moderately acidic media (pH 1–3), protonated actinide–polyaminocarboxylate complexes, for example An(Hedta), form. As the pH is increased, fully deprotonated complexes, such as An(edta)^{-} form first, followed by the formation of ternary actinide–hydroxy-polyaminocarboxylate complexes, such as An(OH)(edta)^{2-}, in basic solutions. Increasing the hydroxide concentration further will eventually displace the organic ligand, but for strong polyaminocarboxylate ligands like edta^{4-} this occurs only in the most caustic solutions (>1 M NaOH) (Wang *et al.*, 2003).

Table 23.23 shows that the strength of actinide-polyaminocarboxylate complexes is principally due to large, positive complexation entropies, in common with other inner sphere actinide complexes. However, in contrast to the actinide complexes of inorganic or carboxylate ligands, most actinide–polyaminocarboxylate complexes are strengthened by substantially exothermic complexation enthalpies, which are commonly observed in metal–amine complexation.

Organophosphorus ligands with low water solubility are used widely in organic solvents for chemical separation or purification of the actinides by

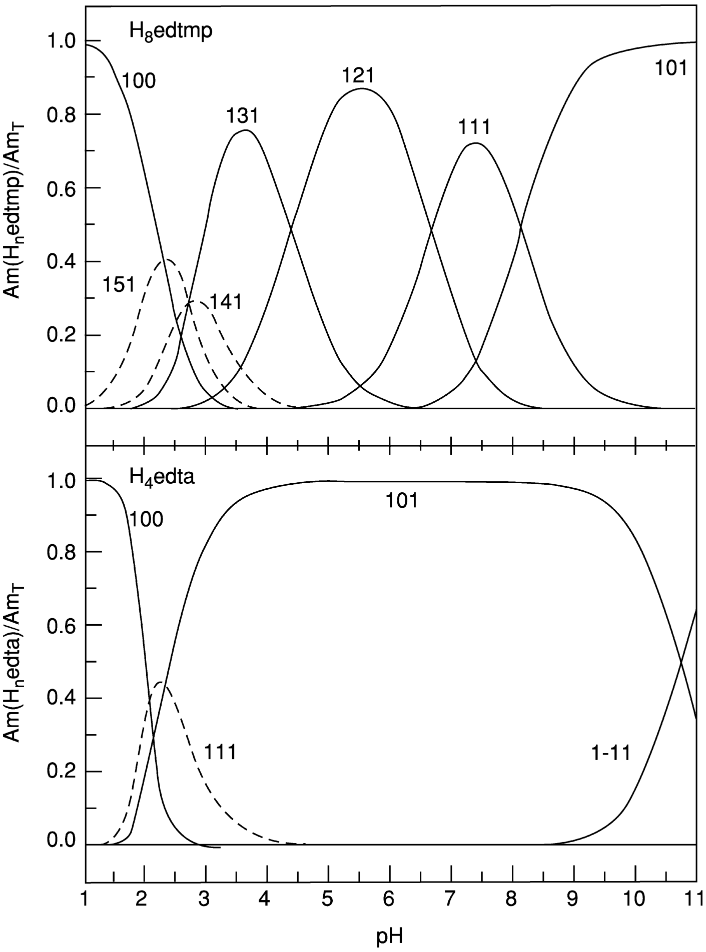


Fig. 23.23 *Speciation of Am(*III*) complexes of ethylenediaminetetraacetic acid* (H_4edta) *and ethylenediaminetetra(methylenephosphonic) acid* (H_8edtmp) *identified by the An:H:L stoichiometry as a function of pH for* 1×10^{-6} M *Am and* 1.2×10^{-4} M *ligand at* $I = 0.1$ M *and* 25°C. *Stability constants from Shalinets* (1972*a,b*).

solvent extraction. Water-soluble organophosphorus ligands based on phosphoric and phosphonic acids, $ROPO_3H_2$ and RPO_3H_2, are also important actinide complexants in nature (Panak *et al.*, 2002a,b) and in chemical separations (see Chapter 24). Compared to carboxylic acids, the phosphonic acids usually form f-element complexes with Gibbs energies of complexation that are larger than expected from the ligand basicity (Nash, 1993b), even when the ligands are partially protonated (e.g. RPO_3H^-) as illustrated in Table 23.22. The methane-1,1-diphosphonic acids, $RCH(PO_3H_2)_2$, analogs of malonic acid,

Table 23.23 *Thermodynamic parameters for actinide acetate and aminopolycarboxylate complexation at* 25°C.

		I (M)	ΔG_{11} (kJmol^{-1})	ΔH_{11} (kJmol^{-1})	ΔS_{11} (JK^{-1}mol^{-1})	*References*
ac$^-$	Am^{3+}	2	−11.2	6.8	60	Rizkalla *et al.* (1989)
	Cm^{3+}	2	−11.7	6.0	57	Choppin *et al.* (1985)
	Th^{4+}	1	−22.0	11.3	112	Portanova *et al.* (1975)
	$UO_2{}^{2+}$	1	−13.8	10.5	82	Ahrland and Kullberg (1971a)
ida^{2-}	Am^{3+}	0.5	−44.9	−4.6	136	Rizkalla *et al.* (1989)
	Th^{4+}	1	−55.3	6.5	207	Di Bernardo *et al.* (1983)
	$NpO_2{}^+$	0.5	−33.2	−16.4	56	Choppin *et al.* (1992a)
		1	−33.6	−16.0	59	Jensen and Nash (2001)
	$UO_2{}^{2+}$	1	−50.1	−2.2	161	Di Bernardo *et al.* (1980)
edta^{4-}	Pu^{3+}	0.1	−103.1	−17.7	287	Fuger and Cunningham (1965)
	Am^{3+}	0.1	−103.7	−19.5	282	Fuger and Cunningham (1965)
		0.5	−95.7	−23.9	241	Rizkalla *et al.* (1989)
	Cm^{3+}	0.5	−96.2	−29.3	225	Choppin *et al.* (1985)
	Th^{4+}	0.1	−132.5	−12.1	404	Kinard *et al.* (1989)
dcta^{4-}	Am^{3+}	0.5	−103.9	−10.8	312	Rizkalla *et al.* (1989)
	Cm^{3+}	0.5	−103.3	−9.7	314	Choppin *et al.* (1987)
dtpa^{5-}	Am^{3+}	0.5	−120.6	−39.5	272	Rizkalla *et al.* (1989)
	Th^{4+}	0.1	−163.8	−12	510	Kinard *et al.* (1989)

$CH_2(CO_2H)_2$, form quite strong complexes. Partially protonated complexes are believed to be a key factor in the strength of these diphosphonate complexes, stabilizing the 1:2 actinide:phosphonate complexes through inter-ligand, intra-complex hydrogen bonding (Nash *et al.*, 1995). The larger anionic charge of the fully deprotonated phosphonic acids, the presence of inter-ligand hydrogen bonding, and the enhanced dehydration of the metal cations on complexation (Jensen *et al.*, 2000b), contribute to the stability of actinide–diphosphonate complexes, as does the strength of the An–O=P bond. Complexation of An(IV) cations by neutral, fully protonated methanediphosphonic acid, $CH_2(PO_3H_2)_2$, persist in 2 M nitric acid at ligand concentrations as low as 0.05 M (Nash, 1991b).

Since monophosphonate and diphosphonate ligands form complexes with actinide ions more readily than the corresponding carboxylates, methylenephosphonic acid derivatives of H_4edta might be expected to be extremely powerful complexants. However, replacing the four acetic acid groups of H_4edta with methylenephosphonic acid groups (H_8edtmp) yields slightly weaker An(III) complexes (Fig. 23.23), although the stability constants indicate that a range of AnH_nedtmp^{n-5} complexes exist in 1 M NaOH for a concentration of 1×10^{-4} M edtmp (Shalinets, 1972b). Inter-ligand hydrogen bonding between the amines and the phosphonates (Jensen *et al.*, 2000b) and steric constraints (Shalinets, 1972c) apparently resist the formation of complexes in these aminomethylenephosphonates.

Anionic carboxylate and organophosphorus-based ligands are among the most studied organic actinide complexants in aqueous solution, but the actinide complexes of a variety of other organic ligands also have been studied. Stable actinide complexes form in weakly acidic aqueous solution (pH 3–6) with neutral ligands like tpen (Fig. 23.18), or polyamino(2-hydroxyalkyl) ligands (Jarvis *et al.*, 1992; Jarvis and Hancock, 1994; Jensen *et al.*, 2000a). The pK_a values of these neutral ligands are low enough that An(III), An(IV), or An(VI) cations can effectively compete with protons for the ligand binding sites in acidic solutions. However, the hydroxide concentration in nearly neutral solutions is sufficient to displace these neutral organic ligands and precipitate actinide hydroxides.

Competition of protons for the actinide binding sites is not a hindrance to the binding of crown ether ligands (e.g. 15-crown-5 or 18-crown-6, Fig. 23.18). Yet without chelating by other complexing groups such as carboxylic acids incorporated into the crown ether, these ligands are weak actinide complexants in aqueous solution (Brighli *et al.*, 1985), most likely forming outer sphere complexes (Guilbaud and Wipff, 1993b). In contrast, even the simplest phenol-based calix[5]- and calix[6]-arene macrocyclic ligands (Fig. 23.18) form strong actinyl(VI) complexes ($\log\beta_{11} = 19$ for UO_2^{2+} at 25°C, $I = 0.1$ M) with a selectivity ratio for UO_2^{2+} over divalent transition metal cations that exceeds 10^{10} (Shinkai *et al.*, 1987).

Naturally occurring ligands that efficiently bind metal cations are found throughout the biosphere. Hard transition metal cations are vital for many biological processes and there are many natural ligands that regulate their biochemistry. The actinides are also hard cations and the charge to radius ratio of the tetravalent actinides is similar to that of one of the most biologically important metal ions, Fe(III). Consequently, ligands that efficiently bind iron are expected to be efficient ligands for actinides. Desferrioxamine siderophores, a class of polyhydroxamic acid ligands used by microbes to scavenge and transport Fe(III), have proven to be equally efficient ligands for Pu(IV) (Jarvis and Hancock, 1991). X-ray crystallography of the Pu(IV) complex of desferrioxamine E shows that the Pu is nine-coordinated with three water molecules and six desferrioxamine oxygens in the inner coordination sphere (Neu *et al.*, 2000). Interestingly, the ligand is only slightly deformed when it complexes Pu(IV) rather than Fe(III), despite the 0.08 Å difference in ionic radii (CN = 6).

The complexing strength of naturally occurring hydroxamic and catechol (1,2-dihydroxybenzene) groups that siderophores use to sequester Fe(III) have led to the design of catecholamide and hydroxypyridone ligands that strongly complex An(III) and An(IV) cations (Raymond, 1985). These ligands are highly selective for An(IV) over Fe(III) both *in vitro* (Romanovski *et al.*, 1999; Zhao *et al.*, 1999) and *in vivo* (Stradling *et al.*, 1992; Xu *et al.*, 1995), and are more efficient reagents for Pu decontamination than the polyaminocarboxylate, diethylenetriaminepentaacetate (dtpa^{5-}).

Humic and fulvic acids are naturally occurring polyelectrolytes resulting from the decay of natural matter. Their composition varies with the local geology, hydrology, and biology, resulting in fulvic acids with molecular weights as low as 300 and humic acids with molecular weights in excess of 100 000 (Choppin and Allard, 1985). These materials contain alcoholic, phenolic, and carboxylic acid groups, which result in an affinity for metal ion complexation. Actinide ions may interact with these ligands either through binding in specific sites (Marinsky, 1976) or through a generalized 'territorial' binding where the cation is attracted by multiple functional groups within one area of the ligand (Manning, 1979). Different modeling approaches have been proposed to calculate the stability constants for metal ions bound by these ligands (Choppin and Labonne-Wall, 1997). Stability constants of certain humic and fulvic acid complexes have been reported for the most common actinides (Choppin and Allard, 1985; Kim and Sekine, 1991; Moulin *et al.*, 1992; Kim *et al.*, 1993; Marquardt and Kim, 1998). In addition to complexation of actinide cations, humic and fulvic acids can also be redox active, reducing the hexavalent NpO_2^{2+} and PuO_2^{2+} (Dahlman *et al.*, 1976; Choppin, 1988; Jainxin *et al.*, 1993; Yaozhong *et al.*, 1993), and pentavalent PuO_2^+ (André and Choppin, 2000) and NpO_2^+ (Marquardt *et al.*, 1996). Both their redox and complexation properties can lead to significant effects on actinide behavior in environmental systems.

23.8 TERNARY COMPLEXES

In aqueous solution, most actinide–ligand complexes could be considered ternary complexes, as they have three components, an actinide ion (component 1), one or more ligands (component 2) and some number of inner sphere water molecules (component 3). It is common, however, to consider such metal cation + ligand anion + coordinated water complexes as a binary metal–ligand complexes. Therefore, our discussion of ternary (or mixed) complexes is limited to three-component complexes, such as AnX_qY_p or $AnO_2X_qY_p$, where X and Y are different ligands but not H_2O. Such ternary complexes may also have coordinated water molecules and varying degrees of protonation of the ligands. Bimetallic complexes, $An_nM_mX_q$ also are considered ternary complexes, but solution studies on such bimetallic complexes of actinide cations are rare (Stemmler *et al.*, 1996; Dodge and Francis, 1997). Despite the large literature on actinide–ligand complexation and the large number of possible complexes of actinide ions in their various oxidation states, with two different ligands, the number of detailed experimental studies on ternary actinide complexation is limited.

The combination of the low polarity and hydrophobicity of organic solvents often results in the formation of ternary complexes in these solvents. As a consequence, the best documented and most extensively studied actinide ternary complexes are those present in the organic phases of liquid–liquid (solvent) extraction systems, which are described in detail in Chapter 24. In organic solvents, the ternary actinide complexes often form with neutral organophilic ligands, required to provide solubility, and anions, required to balance the positive charge of the actinide cations, in the inner coordination sphere. However, complexes containing different anions and no neutral ligands are also well known in such solvents (Ferraro and Peppard, 1963).

Ternary complexes of actinide salts have been important in actinide separations for more than a century, since the initial use of the extraction of $UO_2(NO_3)_2(Et_2O)_2$ into diethylether to purify uranium (Péligot, 1842). Industrial scale processing of the tetravalent and hexavalent actinides was built on this foundation, substituting methylisobutylketone, dibutylcarbitol (dibutoxydiethylene glycol), or tri(*n*-butyl)phosphate (and similar organophosphate-based ligands) for diethylether. The tri(*n*-butyl)phosphate (TBP) systems are particularly important since they have been adopted internationally for processing nuclear fuel in the PUREX process (Choppin *et al.*, 2002). When actinides are extracted from nitric acid solutions into organic solutions containing TBP, the complexes $AnO_2(NO_3)_2(TBP)_2$ are formed in the organic phase for the hexavalent actinides, while the tetravalent actinides have the form $An(NO_3)_4(TBP)_p$ ($p = 2$ or 3). The nitrate groups are directly coordinated to the central actinide cation as bidentate ligands.

Given the propensity of the actinides to undergo hydrolysis reactions (Section 23.3), the single largest class of ternary complexes in aqueous solution are the mixed hydroxides, $An(OH)_qL_p$, which are readily encountered even in weakly acidic solutions for some species. This class of complexes was first reported almost 50 years ago (Hök-Bernström, 1956). The most extensively studied ternary actinide complexes remain the hydroxycarbonates, $An(OH)_q(CO_3)_p$ and $AnO_2(OH)_q(CO_3)_p$. The structural features and the formation constants of An^{3+}, An^{4+}, AnO_2^+, and AnO_2^{2+} hydroxycarbonates have been reported (Clark *et al.*, 1995). The hydroxycarbonates of the pentavalent and hexavalent actinyl ions (Neck *et al.*, 1997; Szabó *et al.*, 2000) exhibit some solubility. In contrast, the neutral hydroxycarbonates, $An(OH)(CO_3)$, are the solubility-limiting species in near neutral aqueous solutions in equilibrium with atmospheric carbon dioxide when other ligands are absent (Bernkopf and Kim, 1984; Silva and Nitsche, 1984; Standifer and Nitsche, 1988; Felmy *et al.*, 1990). Neutral 1:1:1 $An(OH)(CO_3)$ species do not exist in significant amounts in the solution phase (Felmy *et al.*, 1990; Meinrath and Kim, 1991). Simple, mononuclear hydroxycarbonate complexes, as well as polynuclear species with average stoichiometries of $Th_{16}(OH)_{20}(CO_3)_{16}^{12+}$ and $Th_8(OH)_{20}(CO_3)_2^{8+}$ have been reported at low metal concentrations (Grenthe and Lagerman, 1991).

Ternary U(VI)–fluoride–carboxylate ligand complexes have been used for systematic studies of the rates and mechanisms of intermolecular and intramolecular exchange reactions. Multinuclear NMR and potentiometric investigations of the complexes revealed a variety of stoichiometries and structures that depend on the nature of the carboxylic acid (Smith, 1959; Szabó *et al.*, 1997; Aas *et al.*, 1998; Szabó and Grenthe, 2000; Szabó, 2002). The presence of two types of ligands ($X = F^-$, $Y = RCOO^-$) and a variety of coordination geometries usually gave rise to a number of different ternary complexes that were simultaneously present in the solutions. In the presence of carbonate or glycolate ligands, the formation of dinuclear ternary complexes, $(UO_2)_2F_q(gly)_p^{4-q-p}$ and $(UO_2)_2F_q(CO_3)_p^{4-q-2p}$, was reported. Although a variety of species were present in the solutions studied, the rate constants and the activation parameters for fluoride exchange were not strongly dependent on the identity of the carboxylate ligand, even for chelating ligands containing other coordinating groups (e.g. picolinic acid, glycine, and *N*-(phosphonomethyl) glycine). Coordination of negatively charged carboxylate ligands (Y^{z-}) has little effect on the equilibrium constants for fluoride complexation by $UO_2Y_q^{2-qz}$ in contrast to fluoride complexation by $UO_2(H_2O)_q^{2+}$ (Aas *et al.*, 1998).

The small amount of quantitative information regarding ternary complexes in aqueous solution limits attempts to model the chemical speciation of actinides in chemical systems when many different ligands are present. Nevertheless, the regularity of electrostatic bonding in actinide complexes (Section 23.4) makes estimation of the formation constants possible, allowing evaluation of the possible importance of a hypothesized species to determine if additional experimental work would be justified. The thermodynamic parameters for the formation of simple 1:1:1 An(X)(Y) ternary complexes often can be estimated from the parameters of the binary AnX and AnY complexes (Grenthe and Puigdomenech, 1997); however, the uncertainty in an estimated formation constant for these complexes can approach an order of magnitude. The most accurate estimated equilibrium constants for the formation of ternary complexes should include corrections for the appropriate change in the effective charge of the actinide caused by the complexation of the first ligand and for the decrease in the number of available coordination sites, which is an entropic (statistical) factor.

23.9 CATION–CATION COMPLEXES

Most studies of actinide complexation have involved interaction of actinide cations with neutral or anionic ligands as nearly all of the known complexes are with such ligands. However, the cationic, *trans*-dioxoactinide(V) (i.e. actinyl(V)), species form weak complexes with polyvalent metal cations in non-complexing, acidic solutions, as first observed for the complexes of NpO_2^+ with UO_2^{2+} (Sullivan *et al.*, 1961). Cation–cation complexes of UO_2^+ (Newton and Baker, 1962), PuO_2^+ (Newton and Burkhart, 1971), and AmO_2^+ (Rykov and Frolov, 1975) with various cations have also been reported. Actinyl(v) cations are not the only dioxocation species that form cation–cation complexes. A complex of pentavalent *cis*-dioxovanadium(v), VO_2^+, with oxovanadium(iv), VO^{2+}, also has been reported (Madic *et al.*, 1983b).The formation of cation–cation complexes is not an inherent property of all actinyl ions. The presence of a pentavalent actinyl(v) cation is required to form cation–cation complexes. The actinyl(vi) cations, which have the same structure as the actinyl(v) cations, form cation–cation complexes only with an actinyl(v) cation.

The nature of the species formed in cation–cation complexes has been a focus of investigation since their discovery. Three different models have been proposed. In one model, cation–cation complexes were treated as products of incomplete redox reactions accompanied by the formation of electron–hole pairs in the solvent (Rykov and Frolov, 1972a, 1974). However, this model postulated the formation of solvated electrons, which are not observed in the EPR spectrum of the Np(v)−U(vi) complex (Madic *et al.*, 1979). Another model proposed that the cation–cation complexes are polynuclear, ligand-bridged complexes (Guillaume *et al.*, 1982; Nagasaki *et al.*, 1992) by analogy with oligomeric AnO_2^{2+} hydroxides such as $(UO_2)_2(OH)_2$. However, cation–cation complexes are stable in acidic solutions (2 M $HClO_4$), and it is not apparent why water molecules or perchlorate anions would be effective bridging ligands for polynuclear species requiring participation of AnO_2^+ cations, as these cations generally form comparatively weak complexes with normal ligands.

In the model most used, the cation–cation complexes are the result of bonding between AnO_2^+ cations either as inner sphere (Sullivan, 1962) or outer sphere complexes (Stout *et al.*, 1993). Although the actinyl(v) cations possess a formal +1 charge, the effective charge of the actinide atom is approximately +2.2 (Choppin and Rao, 1984). This observation implies that each of the -yl oxygen atoms has a residual negative charge of ca. –0.6 that allows them to form moderately weak electrostatic bonds with other cations (Vodovatov *et al.*, 1979). Relativistic spin–orbit configuration interaction calculations on NpO_2^+ resulted in a value for the residual negative charge of −0.48 on each of the neptunyl(v) oxygens while the calculated residual charge on the oxygen atoms of neptunyl(vi) was −0.17 (Matsika and Pitzer, 2000). If the residual negative charge on the oxygen atoms of actinyl(vi) cations is indeed so much smaller than it is for the actinyl(v) cations, the formation of cation–cation complexes by actinyl(v) ions but not by actinyl (vi) ions can be understood.

However, a different explanation for the lack of actinyl(vi) cation–cation complexes is required if the empirical effective positive charges on the actinyl (vi) (ca. +3.2) and actinyl(v) (ca. +2.2) cations are more accurate reflections of the electron distribution in the actinyl cations than are these theoretically computed electron distributions. The effective positive charges measured for the pentavalent and hexavalent actinyl cations (Choppin and Rao, 1984) predict that the -yl oxygen atoms of actinyl cations carry approximately the same partial negative charge, –0.6, regardless of the oxidation state of the actinyl cation. Therefore, the attractive electrostatic force between the negatively charged -yl oxygen atoms and a given cation would be the same for both oxidation states. Under this model, the lack of actinyl(VI) cation–cation complexes must be attributed to the cancellation of the attractive electrostatic force between the cation and the -yl oxygen atoms by the larger repulsive force between the effective +3.2 charge of the central hexavalent actinide atom and the positive charge of the other cation.

Regardless of which mechanism is correct, the formally cationic actinyl(v) ions can assume the normal role of ligands, forming electrostatic bonds with other cations through the actinyl oxygen atoms, which carry a substantial, partial negative charge.

The actual structures of cation–cation complexes in solution can be surmised from the combination of several different lines of structural evidence. The magnetic splitting of the Np Mössbauer spectra of $NpO_2^+ - Cr^{3+}$ and $NpO_2^+ - Rh^{3+}$ adsorbed on cation exchange resin were interpreted as being consistent with axially symmetric NpO_2^+ (Karraker and Stone, 1977). Wide angle X-ray scattering measurements of solutions containing either $NpO_2^+ - NpO_2^+$ or $NpO_2^+ - UO_2^{2+}$ cation–cation complexes show a peak at 4.2 Å in the radial distribution function, which was assigned as the distance between nearest neighbor actinide atoms in the cation–cation complexes (Guillaume *et al.*, 1983). Also, inner sphere $NpO_2^+–NpO_2^+$ cation pairs have been observed in a number of crystalline neptunyl(v) complexes (Cousson *et al.*, 1984; Tomilin *et al.*, 1986; Grigor'ev *et al.*, 1993a–c, 1995). In the solid state, two structural motifs for $NpO_2^+ - NpO_2^+$ complexes, the staggered and the 'T-shaped' dimers (Fig. 23.24), with significantly different cation–cation distances, have been observed. The Np–Np distances of the T-shaped dimers, like those observed in $NpO_2ClO_4 \cdot 4H_2O$, 4.20 Å (Grigor'ev *et al.*, 1995), are excellent matches for the X-ray scattering results from aqueous solutions of $NpO_2^+ - NpO_2^+$ complexes (Guillaume *et al.*, 1983). Polymeric NpO_2^+ cation–cation structures have not been observed in solution. Taken together, these experiments confirm the T-shaped solution phase coordination geometry initially suggested by Sullivan (1962) and imply that these are inner sphere complexes.

The stability constants for the formation of cation–cation complexes are invariably small. Typical constants reported for the equilibrium

$$AnO_2^+ + M^{z+} \rightleftarrows AnO_2M^{(z+1)+}$$

range from 0.1 to 16 M^{-1} in aqueous solution, depending on the cations involved and the ionic strength. In organic media the equilibrium constants may be much larger (Rykov and Frolov, 1972b; Musikas, 1986). The enthalpies and entropies

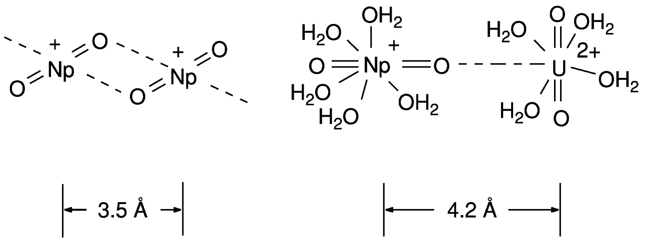


Fig. 23.24 *Inner sphere cation–cation interactions showing staggered* NpO_2^+ – NpO_2^+ *and T-shaped* NpO_2^+ – UO_2^{2+} *complexes.*

Table 23.24 *Thermodynamic parameters of aqueous* NpO_2^+*–cation complexes at* 25°C. *Data taken from Sullivan* (1964), *Murmann and Sullivan* (1967), *Madic* et al. (1979), *and Stout* et al. (1993).

Cation	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})	*Ionic strength* (M)
Cr^{3+}	−2.96	−14	−38	8.0
Rh^{3+}	−2.37	−15	−42	8.0
NpO_2^{2+}	−2.01	0	+9	7
UO_2^{2+}	−2.72	−12	−34	6.0
NpO_2^+	−0.9	0	+3	6.0

of complexation in aqueous solutions also are relatively small (Table 23.24). Such small or negative ΔH and ΔS values often indicate outer sphere complexation (Choppin, 1997). However, the reported ΔH and ΔS values also would be in agreement with the accumulated structural data and the formulation of the complexes as inner sphere, $O{=}An{=}O^+{-}M^{z+}$, complexes if the hydration sphere about the resulting complex is more ordered than the hydration spheres of the individual cations are (Stout *et al.*, 1993).

The redox reaction rates of AnO_2^+ ions are often influenced by complex formation with other cations present in the solution. Despite the small stability constants of these complexes (<10), the oxidation of AnO_2^+ by several agents is slowed by the formation of cation–cation complexes. The stabilities of the complexes of AnO_2^+ with UO_2^{2+} decrease in the sequence $UO_2^+ > NpO_2^+ > AmO_2^+ > PuO_2^+$, with a stability constant of $\beta = 16$ for the most stable complex, $UO_2^+ - UO_2^{2+}$. The complexes $NpO_2^+ - UO_2^{2+}$ and $NpO_2^+ - NpO_2^{2+}$ have about the same stability (Madic *et al.*, 1979). Because the $UO_2^+ - UO_2^{2+}$ complex undergoes redox disproportionation at a much slower rate than the simple UO_2^+ aquo ion, solutions of the relatively unstable uranium(V) are significantly stabilized in the presence of UO_2^{2+}.

23.10 KINETICS OF REDOX REACTIONS

The redox reactions of the lighter actinides, which often have several oxidation states of almost equal reduction potentials (e.g. plutonium, Fig. 23.1) are particularly challenging systems. The An(IV)–An(III) and the An(VI)–An(V) couples involve simple electron loss or gain (Newton, 1975; Sullivan and Nash, 1986). The An(VI)–An(IV) and An(V)–An(IV) redox half-reactions include metal–oxygen bond formation or rupture, as well as electron gain or loss, because of the dioxo structure of the actinyl(V) and actinyl(VI) cations. The redox behavior of the actinides is complicated further by the possibility of disproportionation reactions at macro (but not at micro) concentrations.

23.10.1 Electron exchange reactions

Examples of reactions where the An–O bonds in the actinyl ions are not broken are processes such as

$$\mathrm{An(1)^{3+} + An(2)O_2^{2+} \rightleftarrows An(1)^{4+} + An(2)O_2^{+}}$$

where An(1) and An(2) denote actinide ions that retain their structures (e.g. $\mathrm{An(1)}^{z+}$ or $\mathrm{An(2)O_2^{z+}}$). A number of such reactions, involving uranium, neptunium, and plutonium as reductants and oxidants, have been carefully studied (Table 23.25) (Fulton and Newton, 1970). Though these reactions are fast, the rates vary within wide limits; for example, the oxidation of $\mathrm{U^{3+}}$ by $\mathrm{UO_2^{2+}}$ or $\mathrm{Np^{3+}}$ by $\mathrm{NpO_2^{2+}}$, respectively, are extremely fast while that of $\mathrm{Np^{3+}}$ by $\mathrm{UO_2^{2+}}$ or of $\mathrm{Pu^{3+}}$ by $\mathrm{NpO_2^{2+}}$ are much slower. The difference is not due to the fact that the latter reactions involve different actinides, since the oxidation of $\mathrm{Pu^{3+}}$ by $\mathrm{PuO_2{}^{2+}}$ is even slower than the $\mathrm{Np^{3+} + UO_2^{2+}}$ and the $\mathrm{Pu^{3+} + NpO_2^{2+}}$ reaction rates.

The rates of reaction are closely connected with the Gibbs energies, enthalpies, and entropies of activation (ΔG^*, ΔH^*, and ΔS^*). These have been determined from the temperature dependence of the rate constants and are listed in Table 23.25 for the formation of the activated complex $[\mathrm{An(1)An(2)O_2^{5+}}]^*$ along with the equilibrium thermodynamic reaction values ΔG°, ΔH°, and ΔS° for the redox reaction.

The equilibrium values of the entropy changes, ΔS°, are practically the same in all the reactions. This is because the hydration of the actinide ions in a particular oxidation state is fairly independent of the particular element involved. The values of ΔS° are very negative, implying that the formation of strongly hydrated $\mathrm{M^{4+}}$ ions brings about a considerable net increase of order in the solutions. However, the values of ΔH°, and, consequently, the values of ΔG°, differ considerably between the various systems in such a way that the fastest reactions are also the most exothermic. The reactions rate constants, k, do not decrease monotonically as the reactions become less exothermic.

The activation parameters provide insight into the source of the large differences in the reaction rates. The three reactions $U^{3+} + UO_2^{2+}$, $Np^{3+} + NpO_2^{2+}$, and $Pu^{3+} + PuO_2^{2+}$ are all first order in each of the reactants and independent of H^+ in the range of acidities measured (0.04–0.6 M, 0.01–0.1 M, and 0.1–1.0 M perchloric acid, respectively, at constant ionic strength) (Newton and Fulton, 1970). This implies that the reactions proceed via an activated complex $[An(1)An(2)O_2^{5+}]^*$. The reaction $Pu^{3+} + NpO_2^{2+}$, also progresses through formation of this activated complex. Since the rate depends upon the acidity, a parallel reaction path via a hydrolyzed complex $[Pu(OH)NpO_2^{4+}]^*$ was proposed (Fulton and Newton, 1970). In the case of $Np^{3+} + UO_2^{2+}$, the conditions are complicated by the presence of two parallel reactions following the initial reaction (Newton, 1970):

$$Np^{3+} + UO_2^{+} + 4H^{+} \rightarrow Np^{4+} + U^{4+} + 2H_2O$$

and

$$2UO_2^{+} + 4H^{+} \rightarrow UO_2^{2+} + U^{4+} + 2H_2O$$

At high acidities, these reactions are fast, despite the need to break the U–O -yl bonds in UO_2^+. As the reaction proceeds in 1.0 M acid, the concentration of uranyl(V) reaches a maximum, then decreases, while the concentration of uranium(IV) produced by the reaction of Np^{3+} with UO_2^+ steadily increases after a slow beginning. The activation parameters listed in Table 23.25 refer to the activated complexes $[An(1)An(2)O_2^{5+}]^*$.

The rates of the two fastest reactions are due to different causes. For $U^{3+} + UO_2^{2+}$, the rate is due to the less negative activation entropy while for $Np^{3+} + NpO_2^{2+}$, it is due to the less endothermic enthalpy. The values of ΔH^* are not very different for $U^{3+} + UO_2^{2+}$ and $Pu^{3+} + PuO_2^{2+}$, but the values of ΔS^* are quite different. The faster rates of the mixed systems $Np^{3+} + UO_2^{2+}$ and $Pu^{3+} + NpO_2^{2+}$ compared to $Pu^{3+} + PuO_2^{2+}$ are due primarily to the favorable values of ΔH^*.

23.10.2 Reactions of An–O bond breakage

Redox reactions in which An–O bonds are broken or formed are represented by

$$An(1)^{4+} + An(2)O_2^{2+} + 2H_2O \rightleftarrows An(1)O_2^{+} + An(2)O_2^{+} + 4H^{+}$$

in Table 23.26. Analogous to the oxidation of An^{3+} (Table 23.25), the rates have a first-order dependence on the concentrations of each of the actinide reactants. However, the rates of the An^{4+} oxidations also depend upon the H^+ concentrations with exponents that vary from –1 to –3. For some reactions, a non-integral exponent is found, indicating alternative paths with different orders of dependence on the acidity. The apparent second-order rate constants are generally much smaller than the rate constants of the An^{3+} oxidation reactions.

Table 23.25 *Rate constants* (M^{-1} s^{-1}), *activation parameters, and thermodynamic equilibrium parameters for the reaction* $An(1)^{3+} + An(2)O_2^{2+} \rightarrow An(1)^{4+} + An(2)O_2^{+}$ *in* 1.0 M $HClO_4$ *at* 25°C *from Fulton and Newton* (1970).

Reaction	k (M^{-1} s^{-1})	ΔG^* (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (J K^{-1}mol^{-1})	ΔG^o (kJ mol^{-1})	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1}mol^{-1})
$U^{3+} + UO_2^{2+}$	5.5×10^4	46.0	18.1	−93	−67	−112	−151
$Np^{3+} + NpO_2^{2+}$	1.05×10^5	44.4	4.2	−134	−95	−141	−159
$Pu^{3+} + PuO_2^{2+}$	2.7×10^0	70.5	20.2	−169	6.3	−40	−151
$Np^{3+} + UO_2^{2+}$	3.9×10^1	64.4	10.9	−178	8.6	−36	−151
$Pu^{3+} + NpO_2^{2+}$	3.55×10^1	64.2	14.6	−166	−15	−61	−153

Table 23.26 *Apparent second-order rate constants, activation parameters, and thermodynamic equilibrium parameters for the reaction* $An(1)^{4+} + An(2)O_2^{2+} + 2H_2O \rightarrow An(1)O_2^{+} + An(2)O_2^{+} + 4H^{+}$ *in perchlorate media with* 1.0 M H^{+} *at* 25°C. *Data from Masters and Schwartz* (1961), *Newton and Baker* (1965), *Sullivan* et al. (1960), *Hindman* et al. (1954), *Newton and Montag* (1976), *and Rabideau* (1957).

Reaction	I (M)	n^a	k (M^{-1} s^{-1})	ΔG^* (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (J K^{-1}mol^{-1})	ΔG^o (kJ mol^{-1})	ΔH^o (kJ^{-1}mol^{-1})	ΔS^o (J K^{-1}mol^{-1})
$U^{4+} + UO_2^{2+}$	2	−3	4×10^{-7}	111	157	152	51.4	111	198
$U^{4+} + NpO_2^{2+}$	2	−1	22	66.9	76.1	31	−54.0	7.1	205
$U^{4+} + PuO_2^{2+}$	2	−1(−2)	3.1	69.5	73.6	14	−32.6	28.9	205
$Np^{4+} + NpO_2^{2+}$	2	−2(−1)	5×10^{-2}	80.8	102.9	74	−38.5	31.4	234
$Np^{4+} + PuO_2^{2+b}$	1	−2(−3)	7.5×10^{-4}	93	129	125	−17.2	–	–
$Pu^{4+} + PuO_2^{2+}$	1	−3	2×10^{-7}	111	158	159	24.3	79.5	184

[a] Order of the hydrogen ion dependence; if more than one reaction path was observed, the order of the less important path is given in parentheses.

[b] $T = 30$°C.

The strong tendency for hydrolysis of An^{4+} sets a lower limit on the acidity of the solutions which can be investigated, ca. 0.1 M.

Inverse acidity dependence is displayed by the reactions $U^{4+} + UO_2^{2+}$ and $Pu^{4+} + PuO_2^{2+}$, which have similar slow rates and almost equal activation parameters, indicating they proceed along analogous paths. By contrast, $U^{4+} + NpO_2^{2+}$ and $U^{4+} + PuO_2^{2+}$, which also display inverse linear acidity dependence, are the fastest of these reactions with similar values for the activation parameters. The large increase in the rate is due to the much more favorable values of ΔH^*. The values of ΔS^* are less favorable, reducing somewhat the influence of the more favorable values of ΔH^*.

Generally, the slow rates of An^{4+} oxidation are due to very positive values of ΔH^*. Positive values of ΔS^* favor the process but are insufficient to compensate for the influence of ΔH^*. Both the ΔH^* and ΔS^* values of An^{4+} oxidation differ significantly from those of An^{3+} oxidations (Table 23.25).

These trends are even more marked in the thermodynamic equilibrium parameters in Tables 23.25 and 23.26 for the two types of reactions. The values of ΔS° are negative in An^{3+} oxidation reactions due to the formation of the strongly hydrated An^{4+} ions but they are positive for the oxidation reactions in the An^{4+} systems as this reaction is accompanied by release of water from the inner coordination sphere of the tetravalent cation. By contrast, the An^{3+} oxidations are exothermic, while the An^{4+} oxidations are endothermic. Thus, ΔH° opposes ΔS° in both sets of reactions and the result is a mixture of values for the Gibbs energy changes of these oxidation reactions.

23.10.3 Redox disproportionation reactions

The disproportionation of actinyl(V) ions, AnO_2^+, is the reverse of the $An^{4+} + AnO_2^{2+}$ oxidation–reduction reactions. In Table 23.27, the rates and activation parameters of the disproportionation reactions of UO_2^+, NpO_2^+, and PuO_2^+ are listed. These rates vary from UO_2^+ reacting quite rapidly to NpO_2^+

Table 23.27 *Apparent second order rate constant and activation parameters for the disproportionation reaction* $2AnO_2^+ + 4H^+ \rightarrow An^{4+} + AnO_2^{2+} + 2H_2O$ *in perchlorate media,* $[H^+] = 1.0$ M *at* 25°C *from Ahrland* (1986).

	I (M)	n[a]	k (M^{-1} s^{-1})	ΔG^* (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})
UO_2^+	2	1	4×10^{2}	60	46	−46
NpO_2^+	2	2	9×10^{-9}	119	72	−159
PuO_2^+	1	1	3.6×10^{-3}	87	79	−24

[a] Acid dependence of the rate constant.

reacting extremely slowly. The fast reaction rate of UO_2^+ is due to a low value of ΔH^* while the slow rate of $NpO_2{}^+$ is due, to a large negative value of ΔS^*.

For both the redox and the disproportionation reactions, the lower the charge of the activated complex, the lower the ΔS^* value. For the formation of AnO_2^+ ions, the more negative the exponent of the hydrogen dependence, the more positive the ΔS^* value. For the disproportionation reactions, the more positive the exponent of the hydrogen dependence, the more negative the ΔS^* value. All of the AnO_2^+ ions listed disproportionate at a faster rate in D_2O (Rabideau, 1957; Hindman *et al.*, 1959). Also, the reaction rates of MO_2^+ ions are often influenced by complex formation with cations present in the reaction. These cation–cation complexes are discussed in Section 23.9. Their formation results in a slower rate of oxidation of the AnO_2^+ species by a number of oxidizing agents.

23.10.4 Effect of complexation

All reactions discussed so far take place between hydrated metal ions in noncomplexing perchlorate media. In the presence of complex formation with anions, the reaction rates usually increase significantly. This was noticed initially for chloride and sulfate solutions. For example, plutonium(IV) disproportionates about five times faster in hydrochloric acid than in perchloric acid of the same concentration (Rabideau and Cowan, 1955). A study of sulfate media containing Np(IV), Np(V), and Np(VI) revealed that the rate of formation of neptunium(V) depends upon the concentration of the complexes $NpSO_4^{2+}$ and NpO_2SO_4, while disproportion depends upon the concentration of HSO_4^- (Sullivan *et al.*, 1957). For both reactions, the rate laws are not simple. With increasing sulfate concentration, the rate of formation initially increases, reaches a maximum, then decreases. The maximum coincides with the maximum concentration of $NpSO_4^{2+}$ as the higher sulfate complexes have no catalytic effect. The rate of disproportionation, by contrast, is a monotonically increasing function of the concentration of HSO_4^-. Table 23.28 lists the parameters for the reduction reactions of NpO_2^{2+} by complexing anions.

In the disproportionation of americium(V), analogous catalytic effects have been observed (Coleman *et al.*, 1963). In perchloric acid, the reaction

$$3AmO_2^+ + 4H^+ \rightleftarrows 2AmO_2^{2+} + Am^{3+} + 2H_2O$$

occurs, with a rate dependence on the hydrogen ion between 2 and 3. At 76°C, and an acidity of 2 M, the rates in nitric, hydrochloric, and sulfuric acids are 4, 4.6, and 24 times as great as that in perchloric acid. Similar effects have also been found for several other systems.

Comparison of the rate constants for the reaction of $[(NH_3)_6Co]^{3+}$ and $[(NH_3)_5CoX]^{2+}$ ($X = N_3^-, F^-, Cl^-, ac^-, Br^-, CN^-$, or NCS^-) with U^{3+} indicate that these reactions proceed by an inner sphere mechanism. The activation parameters for the analogous reaction of Np^{3+} with $(NH_3)_5RuX^{3+}$ ($X = H_2O$

Table 23.28 *Rate constant and activation parameters for the reduction of Np*(VI). *Data from Rao and Choppin* (1984), *Kim and Choppin* (1988), *and Choppin and Kim* (1989).

Reductant	*pH*	T (°C)	k_1 (s^{-1})	ΔH^* ($kJ\,mol^{-1}$)	ΔS^* ($J\,K^{-1}\,mol^{-1}$)
Dicarboxylic acids ($I = 0.10$ M NaCl)					
oxalic acid	1.1	33.7	1.30×10^{-3}	90 ± 7	-7 ± 21
malonic acid	2.2	34.2	2.70×10^{-3}	70 ± 10	-64 ± 25
methylmalonic acid	2.4	34.7	1.06×10^{-4}	88 ± 9	-16 ± 29
dimethylmalonic acid	3.0	35.2	3.10×10^{-5}	43 ± 13	-183 ± 33
succinic acid	3.0	34.0	1.50×10^{-4}	66 ± 9	-103 ± 42
maleic acid	3.0	35.9	1.00×10^{-4}	87 ± 12	-43 ± 42
phthalic acid	3.0	34.1	5.20×10^{-5}	38 ± 8	-209 ± 25
fumaric acid	3.0	23.1	1.80×10^{-5}	37 ± 23	-209 ± 84
Hydroxylic acids (I = 1.0 M NaCl)					
kojic acid	4.6	25.0	1.6	83 ± 3	34 ± 1
tropolone		25.0	70.8	67 ± 3	15 ± 12

and NH_3) (Espenson and Wang, 1970; Lavallee *et al.*, 1973) supported this proposal, indicating formation of a seven-coordinate Ru(III) intermediate. Other bridging ligands such as SO_4^{2-}, ClO_4^-, Cl^-, etc. have an accelerating effect on the reaction rate. This was attributed to a reduction in the cation–cation electrostatic repulsion through the formation of the intermediate $An^{3+}–X^{x-}–M^{z+}$.

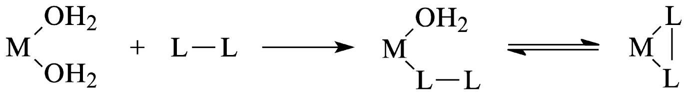
23.11 KINETICS OF COMPLEXATION REACTIONS

The complexation and dissociation of actinide cations with anions of simple structure are more rapid than the analogous rates of reaction of the d-transition cations. These fast reaction rates are due to the strongly ionic nature of most actinide–ligand bonds, which results in a wide range of hydration and coordination numbers and symmetries. This structural versatility arises from the lack of strong crystal-field effects in 5f electronic configurations as well as from the relatively large ionic radii of these cations as the coordination numbers and symmetries are determined by steric and electrostatic factors (see Sections 23.4 and 23.6).

The complexation reactions usually proceed by the Eigen mechanism (Diebler and Eigen, 1959; Eigen and Tamm, 1962; Eigen, 1963). This mechanism involves two steps, the rapid formation of an outer sphere association complex (i.e. an ion pair) and the subsequent rate-determining step in which the ligand displaces one or more water molecules.

$$M(H_2O)_q^{m+} + L^{z-} \rightleftarrows M(H_2O)_q^{m+}\text{–}L^{z-} \rightleftarrows M(H_2O)_{q-1}L^{(m-z)} + H_2O$$

The actual ligand-interchange step may be dissociative or associative in character. For multidentate ligands, the associative steps with replacement of two-coordinated water can be represented as



In the absence of any steric constraints, formation of the first M–L bond, generally, but not always, leads to rapid ring closure. As the chain distance separating the two donor atoms of the ligand increases, the rate (or probability) of ring closure decreases (Wilkins, 1974, Burgess, 1978). This is reflected in a decrease in $\log\beta_{11}$ and a deviation from linearity in plots of $\log\beta_{11}$ versus ΣpK_a (see Section 23.6). In some systems it is uncertain whether this increase in donor separation is accompanied by a change from chelation to monodentation. Microscopic reversibility requires that complex dissociation reactions follow the formation pathway in reverse. Complex dissociation is typically investigated by addition of a competing metal ion or of a chelating agent that binds more strongly to the cation. Complex dissociation reactions are often catalyzed by H^+ in acidic solution. A variety of experimental techniques have been used to study actinide complexation kinetics. These include stopped-flow spectrophotometry, pulse radiolysis, temperature-jump, NMR, solvent extraction separation methods, and conventional spectrophotometry.

According to the Eigen mechanism for complexation, the rate of solvent water exchange represents an upper limit to the rate of complex formation. Such rates are not available for the trivalent actinides but have been discussed for the chemically analogous lanthanides. Cossy *et al.* (1989) have reported that the second-order rate constants for water exchange are directly proportional to the cation radii of trivalent lanthanides. The water exchange rates for Am(III)–Cf(III) are estimated to range from 1×10^9 to 1×10^8 $\text{M}^{-1}\ \text{s}^{-1}$ assuming a linear correlation with the lanthanides based on cation radius (Nash and Sullivan, 1998). Kiener *et al.* (1976) report that the water exchange rates for UO_2^{2+} are complex. Exchange rates for tetravalent and for pentavalent actinide cations have neither been reported, nor can they be estimated reliably. Bardin *et al.* (1998) have reported NMR data that give a first order rate constant for water exchange by UO_2^{2+} in d_6-acetone of $1 \times 10^6\ \text{s}^{-1}$ at 25°C.

The complexation kinetics of multidentate ligands are slower than for monodentate ligands due to the changes in ligand structural characteristics during the reactions. The aminopolycarboxylates have been used commonly in actinide separations, and, as a result, their kinetics of complexation with the An(III) cations have been studied in more depth than for any other An(III)–ligand system. Such studies usually involve metal exchange in which the An(III) cation displaces a trivalent lanthanide from complexation with an aminopolycarboxylate complex. For the reaction of An(III) with the Eu(III)–ethylenediaminetetraacetate complex (D'Olieslager *et al.*, 1970; Williams and Choppin, 1974), the rate was shown to be described by the equation:

$$\begin{aligned}\text{Rate} = {} & (k_a[\mathrm{Eu(edta)}][\mathrm{H}][\mathrm{An}]/[\mathrm{Eu}] + k_b[\mathrm{Eu(edta)}][\mathrm{An}]) \\ & - (k_c[\mathrm{An(edta)}][\mathrm{H}] + k_d[\mathrm{An(edta)}][\mathrm{Eu}])\end{aligned} \tag{23.14}$$

in which the ionic charges are omitted for simplicity. The specific rate constants k_a and k_c are associated with the hydrogen ion catalyzed forward and reverse terms, while k_b and k_d are specific rate constants for the respective acid-independent terms.

Below about pH 6 the hydrogen-catalyzed paths dominate the reaction. In these paths, the metal complex is protonated in a series of proton additions, leading ultimately to the decomposition of the complex and hence to metal exchange. The alternate acid-independent path in the exchange mechanism has been described by a metal ion-catalyzed decomposition of the complex in which the ligand serves as a bridge between the entering and exiting metal ions. The exchange reactions can be represented as follows ($\mathrm{Y} = \mathrm{edta}^{4-}$).

(A) *Acid-dependent mechanism*

$$\begin{tikzcd}[column sep=large]
\mathrm{EuY + H} \arrow[r, shift left, "\text{Fast}"] & \mathrm{EuYH} \arrow[l, shift left] \arrow[r, "\text{Slow}"] & {[\mathrm{EuYH}]^*} \arrow[r, shift left, "\text{Fast}"] & \mathrm{Eu + H_xY + An} \arrow[l, shift left] \arrow[d, shift right] \\
& \mathrm{AnY + H} \arrow[r, shift left, "\text{Fast}"] & \mathrm{AnYH} \arrow[l, shift left] & {[\mathrm{AnYH}]^*} \arrow[l, "\text{Slow}"'] \arrow[u, shift right, "\text{Fast}"']
\end{tikzcd}$$

(B) *Acid-independent mechanism*

$$\begin{tikzcd}[column sep=large]
\mathrm{EuY + An} \arrow[r, shift left, "\text{Fast}"] & \mathrm{EuY{-}An} \arrow[l, shift left] \arrow[r, "\text{Slow}"] & {[\mathrm{EuYAn}]^*} \arrow[d, "\text{Fast}"] \\
& \mathrm{AnY + Eu} \arrow[r, shift left, "\text{Fast}"] & \mathrm{Eu\text{-}YAn} \arrow[l, shift left]
\end{tikzcd}$$

The formation and dissociation reactions of other aminopolycarboxylate complexes of Ln and An cations follow these general mechanisms. The rates of metal ion exchange for the trivalent actinides (Am, Cm, Bk, Cf) with $\mathrm{Eu(edta)}^-$ indicate a similar dependence on acidity and, in cases where an acetate buffer was used, an additional dependence on free acetate concentration (Choppin and Williams, 1973; Williams and Choppin, 1974).

The rates of formation and dissociation of the Am(III) complex with dcta^{4-} (*trans*-1,2-diaminocyclohexane-*N*,*N*,*N′*,*N′*-tetraacetate, Fig. 23.18) were determined using stopped-flow spectrophotometry to study the formation reaction and conventional spectrophotometry for the decomposition reaction (Sullivan *et al.*, 1978). The experimental results are consistent with the interpretation that a precursor between Am(III) and the ligand is formed. The rate-determining step in the reaction was postulated to be the formation of a bond between Am(III) and an imino nitrogen of dcta^{4-}.

The dissociation of the $\mathrm{Am(dcta)}^-$ complex was studied by the metal ion exchange technique using Cu^{2+}, as was reported in an analogous study of the

Ln(dcta)$^-$ chelates (Nyssen and Margerum, 1970). No dependence on the copper concentration was observed, implying that any reaction rates measured were pertinent to either acid-induced or spontaneous dissociation of the complex. The results agree with studies on the rate of dissociation of trivalent actinides with a variety of aminopolycarboxylate complexants studied by solvent extraction or ion exchange separation techniques at radiotracer concentrations of the metal ion (D'Olieslager *et al.*, 1970; Choppin and Williams, 1973; El-Rawi, 1974; Williams and Choppin, 1974; Muscatello *et al.*, 1989). The rate-determining step for complex formation is an acid-dependent intramolecular process that appears to be limited by the rate of formation of An(iii) bonding to the amine nitrogen. The activation parameters for the reaction were reported to be $E_a = +59.0$ kJmol^{-1} and $\Delta S^* = -19$ JK^{-1}mol^{-1} (Sullivan *et al.*, 1978).

The rate of dissociation of trivalent actinide (Am, Cm, Bk, Cf) complexes with the aminopolycarboxylate ligands hedta^{3-} (*N*-hydroxyethylethylenediaminetriacetate) and tmdta^{4-} (trimethylenediaminetetraacetate) have been measured (El-Rawi, 1974; Muscatello *et al.*, 1989). As in the case for the edta complexes, the rate of the acid-catalyzed dissociation decreases with increasing cation atomic number (Fig. 23.25), which is consistent with a simple electrostatic model for the interactions of both lanthanides and actinides. The dissociation rate of Am(dcta)$^-$ was observed to be more similar to that of the isoelectronic Eu(dcta)$^-$ than to the dissociation rate of Nd(dcta)$^-$, whose cationic radius (and, hence, electrostatic attraction for the ligand) is closest to that of Am^{3+}.

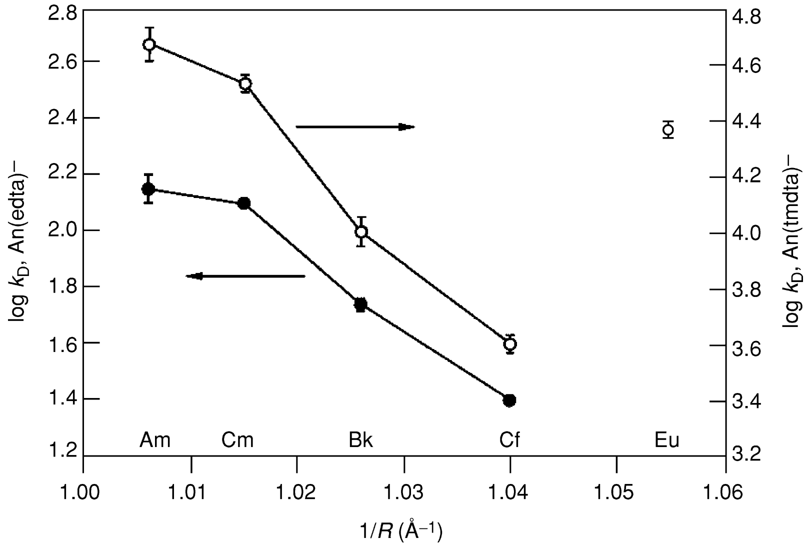


Fig. 23.25 *Correlation of the rate constant of the acid dependent dissociation pathway,* k_D, *of* MY^- (Y = *edta*$^{4-}$ *or tmdta*$^{4-}$) *and the reciprocal of the cation radius* ($CN = 6$).

Table 23.29 *Rate constants* ($\mathrm{M}^{-1}\ \mathrm{s}^{-1}$, 25°C) *for the reaction*

$$An^{3+} + HY^{3-} \underset{k_D}{\overset{k_F}{\rightleftharpoons}} AnY^{-} + H^{+}.$$

	tmdta^{4-}		*dcta*$^{4-}$		*edta*$^{4-}$	
Metal ion	$10^{-7}\,k_F$	$10^{-4}\,k_D$	$10^{-8}\,k_F$	k_D	$10^{-10}\,k_F$	$10^{-2}\,k_D$
Am	5.5 ± 0.9	4.78 ± 0.49	1.2	4.4	0.59	1.39
Cm	8.8 ± 1.2	3.52 ± 0.22	2.4	2.8	1.0	1.10
Bk	8.8 ± 1.6	0.95 ± 0.10	–	–	1.2	0.57
Cf	1.3 ± 1.0	0.39 ± 0.02	–	–	0.85	0.25
Eu	3.2 ± 0.4	2.29 ± 0.13	0.34	3.2	0.32	2.28

This result suggests a possible minor covalent contribution in the binding of Am(III) to the amine (Nash and Sullivan, 1998).

The dissociation rate constants for the trivalent actinide complexes with tmdta^{4-}, as seen in Fig. 23.25, are about two orders of magnitude larger than for the corresponding An(edta)$^{-}$ complexes. This is most probably due to the greater lability of the Am–N bonds in the six member N–Am–N ring of the tmdta complex when compared to the lability of the Am–N bonds in the five-membered N–Am–N ring of the edta chelate.

In contrast to the tmdta complex, the acid-dependent rate constant for the acid dissociation of the Am(dcta)$^{-}$ complex is $\log k_D = 0.64$, which is two orders of magnitude smaller than that for Am(edta)$^{-}$ (Sullivan *et al.*, 1978). This was attributed to the structural effect of the rigidity of the cyclohexyl ring. Table 23.29 lists the values for both the formation and dissociation rate constants for actinide(III) complexes of tmdta^{4-}, dcta^{4-}, and edta^{4-} from Muscatello *et al.* (1989).

23.12 SUMMARY

Although the aqueous complexes of the actinide elements has been a topic of continual interest for over half a century, puzzles remain to be solved and opportunities abound because such complexes are central to understanding the environmental, biological, and separations chemistry of the actinides. Historically, most of this work has involved studies of complexation strength, and to a lesser extent, studies of the kinetics of reactions. Many different techniques have been used. Unfortunately, the utility of such thermodynamic and kinetic measurements diminishes the farther system conditions deviate from those used in the laboratory measurements. The presence of new kinetic pathways, unforeseen equilibria, or solid phases that were not encountered in the laboratory studies can dominate the aqueous speciation when the concentrations of the solution components or pH values are significantly different from the conditions that have been studied. For instance, the U–O bonds of the UO_2^{2+} cation are quite inert in acidic aqueous solutions with a half-life for oxygen exchange of 4×10^4 h in 1 M perchloric acid (Gordon and Taube, 1961), but in 3.5 M tetramethylammonium hydroxide, the exchange is complete in minutes (Clark *et al.*, 1999). As a result, other techniques for studying actinide complexes, such as NMR, fluorescence spectroscopy, and EXAFS have become increasingly important sources of extra-thermodynamic information on dissolved actinide complexes in recent years.

While the information available on the solution complexation of the actinide elements covers a range of actinide ions, oxidation states, and ligands, it can usually be understood by several straightforward principles. The actinide cations are hard Lewis acids that interact preferentially with ligands that are hard Lewis base donors, in aqueous solution, forming strongly electrostatic bonds. Thus, the complexes generally become more stable as the effective charge of the actinide cation or ligand increases and as the size of the actinide cation decreases, if metal- or ligand-centered steric constraints are not important. This is best characterized for the An(III) and An(IV) oxidation states. However, the limited number of actinide cations that are stable in several of the oxidation states from 3+ to 6+, and the short half-lives of the *trans*-californium elements limit the number of actinide species that can be studied by many techniques for use in systematic, empirical comparisons of the metal ion properties. The electrostatic model of actinide–ligand bonding can be very useful despite its simplicity. However, accurate, quantitative, and non-empirical predictions of the strength and structure of actinide complexes are currently only possible for the simplest ligands because of ligand- and solvent-centered effects.

Many areas of actinide complexation chemistry remain relatively unexplored. Topics in actinide complexation which are only beginning to be defined include actinide complexation by neutral ligands in aqueous solutions, the formation of ternary complexes, and the behavior of actinide complexes in alkaline solutions. In addition, studies of ligands that are capable of stabilizing difficult to attain oxidation states; studies of ligands with well defined, pre-organized actinide binding sites; and studies of actinide–selective soft donor ligands have the potential to create new perspectives in actinide chemistry.

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REFERENCES

Aas, W., Moukhamet-Galeev, A., and Grenthe, I. (1998) *Radiochim. Acta*, **82**, 77–82.

Åberg, M. (1969) *Acta Chem. Scand.*, **23**, 791–810.

Åberg, M. (1970) *Acta Chem. Scand.*, **24**, 2901–15.

Åberg, M., Ferri, D., Glaser, J., and Grenthe, I. (1983a) *Inorg. Chem.*, **22**, 3986–9.

Åberg, M., Ferri, D., Glaser, J., and Grenthe, I. (1983b) *Inorg. Chem.*, **22**, 3981–5.

Ahrland, S. (1949) *Acta Chem. Scand.*, **3**, 1067–76.

Ahrland, S. and Kullberg, L. (1971a) *Acta Chem. Scand.*, **25**, 3677–91.

Ahrland, S. and Kullberg, L. (1971b) *Acta Chem. Scand.*, **25**, 3457–70.

Ahrland, S. and Kullberg, L. (1971c) *Acta Chem. Scand.*, **25**, 3471–83.

Ahrland, S. (1986) in *Chemistry of the Actinide Elements,* 2nd edn, vol. 2 (eds. J. J. Katz, G. T. Seaborg, and L. R. Morss), Chapman&Hall, New York, pp. 1480–546.

Ahrland, S., Hefter, G., and Norén, B. (1990) *Acta Chem. Scand.*, **44**, 1–7.

Alcock, N. W. and Esperås, S. (1977) *J. Chem. Soc., Dalton Trans.,* 893–6.

Allard, B., Kipatsi, H., and Liljenzin, J. (1980) *J. Inorg. Nucl. Chem.*, **42**, 1015–27.

Allard, B. and Rydberg, J. (1983) in *Plutonium Chemistry* (eds. W. T. Carnall and G. R. Choppin) (ACS Symp. Ser. 216), American Chemical Society, Washington, DC, pp. 275–95.

Allen, P. G., Bucher, J. J., Clark, D. L., Edelstein, N. M., Ekberg, S. A., Gohdes, J. W., Hudson, E. A., Kaltsoyannis, N., Lukens, W. W., Neu, M. P., Palmer, P. D., Reich, T., Shuh, D. K., Tait, C. D., and Zwick, B. D. (1995) *Inorg. Chem.*, **34**, 4797–807.

Allen, P. G., Bucher, J. J., Shuh, D. K., Edelstein, N. M., and Reich, T. (1997) *Inorg. Chem.*, **36**, 4676–83.

Allen, P. G., Bucher, J. J., Shuh, D. K., Edelstein, N. M., and Craig, I. (2000) *Inorg. Chem.*, **39**, 595–601.

André, C. and Choppin, G. R. (2000) *Radiochim. Acta*, **88**, 613–16.

Antonio, M. R., Williams, C. W., and Soderholm, L. (1998) *J. Alloys Compd.*, **271–273**, 846–9.

Antonio, M. R., Soderholm, L., Williams, C. W., Blaudeau, J.-P., and Bursten, B. E. (2001) *Radiochim. Acta*, **89**, 17–25.

Antonio, M. R., Williams, C. W., and Soderholm, L. (2002) *Radiochim. Acta*, **90**, 851–6.

Appelman, E. H., Kostka, A. G., and Sullivan, J. C. (1988) *Inorg. Chem.*, **27**, 2002–5.

Awasthi, S. P. and Sundaresan, M. (1981) *Indian J. Chem.*, **20A**, 378–81.

Baes, C. F. Jr, Norman, J., Meyer, N. J., and Roberts, C. E. (1965) *Inorg. Chem.*, **4**, 518–27.

Baes, C. F. Jr and Mesmer, R. E. (1976) *The Hydrolysis of Cations,* John Wiley, New York.

Bansal, B. M. L. and Sharma, H. D. (1964) *J. Inorg. Nucl. Chem.*, **26**, 799–805.

Bardin, N., Rubini, P., and Madic, C. (1998) *Radiochim. Acta*, **83**, 189–94.

Beck, M. T. (1968) *Coord. Chem. Rev.*, **3**, 91–113.

Beitz, J. V. and Hessler, J. P. (1980) *Nucl. Technol.*, **51**, 169–77.

Beitz, J. V., Bowers, D. L., Doxtader, M. M., Maroni, V. A., and Reed, D. T. (1988) *Radiochim. Acta*, **44/45**, 87–93.

Beitz, J. V. (1991) *Radiochim. Acta*, **52/53**, 35–9.

Beitz, J. V. (1994) *J. Alloys Compd.*, **207/208**, 41–50.

Bennet, D. A., Hoffman, D. C., Nitsche, H., Russo, R. E., Torres, R. A., Baisden, P. A., Andrews, J. E., Palmer, C. E. A., and Silva, R. J. (1992) *Radiochim. Acta*, **56**, 15–19.

Bernkopf, M. F. and Kim, J. I. (1984) *Hydrolyse-Reaktionen und Karbonat Komplexierung von Dreiwertigen Americium im NatÜrlichen Aquatischen System,* Institut fÜr Radiochemie, Technical University Munich Report RCM-02884.

Bismondo, A., Cassol, A., Di Bernardo, P., Magon, L., and Tomat, G. (1981) *Inorg. Nucl. Chem. Lett.*, **17**, 79–81.

Bjerrum, N. (1926) Kgl. Danske Vidensk. Selskab. Math.-fysike Medd, **7**(9), 1–48.

Bleaney, B., Llewellyn, P. M., and Jones, D. A. (1956) *Proc. Phys. Soc.*, **B69**, 858–60.

Bockris, J. O'M. and Reddy, A. K. D. (1970) *Modern Electrochemistry,* vol. I, Plenum Press, New York.

Bockris, J. O'M. and Saluja, P. P. S. (1972a) *J. Phys. Chem.*, **76**, 2140–51.

Bockris, J. O'M. and Saluja, P. P. S. (1972b) *J. Phys. Chem.* **76**, 2298–310.

Borkowski, M., Krejzler, J., and Siekierski, S. (1994) *Radiochim. Acta*, **65**, 99–103.

Born, M. (1920) *Z. Phys.*, **1**, 45–8.

Brand, J. R. and Cobble, J. W. (1970) *Inorg. Chem.*, **9**, 912–17.

Bratsch, S. G. (1983) *Chem. Phys. Lett.*, **98**, 113–17.

Bratsch, S. G. and Lagowski, J. J. (1985a) *J. Phys. Chem.*, **89**, 3310–16.

Bratsch, S. G. and Lagowski, J. J. (1985b) *J. Phys. Chem.*, **89**, 3317–19.

Bratsch, S. G. and Lagowski, J. J. (1986) *J. Phys. Chem.*, **90**, 307–12.

Brendler, V., Geipel, G., Bernhard, G., and Nitsche, H. (1996) *Radiochim. Acta*, **74**, 75–80.

Brennan, J. G., Stults, S. D., Andersen, R. A., and Zalkin, A. (1987) *Inorg. Chim. Acta*, **139**, 201–2.

Brennan, J. G., Green, J. C., and Redfern, C. M. (1989) *J. Am. Chem. Soc.*, **111**, 2373–7.

Brighli, M., Fux, P., Lagrange, J., and Lagrange, P. (1985) *Inorg. Chem.*, **24**, 80–4.

Brown, D. (1972) in *MTP International Review of Science, Lanthanides and Actinides*, Inorganic Chemistry, Ser. 1, vol. 7 (ed. K. W. Bagnall), University Park Press, Baltimore, MD, pp. 87–137.

Brown, P. L., Sylva, R. N., and Ellis, J. (1985) *J. Chem. Soc.*, *Dalton Trans.*, 723–30.

Brüchle, W., Schädel, M., Scherer, U. W., Kratz, J. V., Gregorich, K. E., Lee, D., Nurmia, M., Chasteler, R. M., Hall, H. L., Henderson, R. A., and Hoffman, D. C. (1988) *Inorg. Chim. Acta*, **146**, 267–76.

Bünzli, J.-C. G., Metabanzoulou, J.-P., Froidevaux, P., and Jin, L. (1990) *Inorg. Chem.*, **29**, 3875–81.

Burgess, J. (1978) *Metal Ions in Solution,* John Wiley, New York.

Burns, J. H., Baldwin, W. H., and Stokely, J. R. (1973) *Inorg. Chem.*, **12**, 466–9.

Butler, R. N. and Symons, M. C. R. (1969) *Trans. Faraday Soc.*, **65**, 945–9.

Caceci, M. S. and Choppin, G. R. (1983a) *Radiochim. Acta*, **33**, 101–4.

Caceci, M. S. and Choppin, G. R. (1983b) *Radiochim. Acta*, **33**, 113–14.

Carey, G. H. and Martell, A. E. (1968) *J. Am. Chem. Soc.*, **90**, 32–8.

Carnall, W. T. (1989) *J. Less Common Metals*, **156**, 221–35.

Carugo, O. and Castellani, C. B. (1992) *Inorg. Chim. Acta*, **191**, 115–20.

Cassol, A., Magon, L., Tomat, G., and Portanova, R. (1972a) *Inorg. Chem.*, **11**, 515–19.

Cassol, A., Magon, L., Portanova, R., and Tondello, E. (1972b) *Radiochim. Acta*, **17**, 28–32.

Cassol, A., Di Bernardo, P., Portanova, R., and Magon, L. (1973) *Inorg. Chim. Acta*, **7**, 353–8.

Cassol, A., Di Bernardo, P., Portanova, R., Tolazzi, M., Tomat, G., and Zanonato, P. (1990) *Inorg. Chem.*, **29**, 1079–84.

Cauchetier, P. and Guichard, C. (1973) *Radiochim. Acta*, **19**, 137–46.

Chatterjee, A., Maslen, E. N., and Watson, K. J. (1988) *Acta Cryst. B*, **44**, 381–6.

Chaudhuri, N. K., Sawant, R. M., and Sood, D. D. (1999) *J. Radioanal. Nucl. Chem.*, **240**, 993–1011.

Chierice, G. O. and Neves, E. A. (1983) *Polyhedron*, **2**, 31–5.

Choppin, G. R. and Strazik, W. F. (1965) *Inorg. Chem.*, **4**, 1250–4.

Choppin, G. R. and Schneider, J. K. (1970) *J. Inorg. Nucl. Chem.*, **32**, 3283–8.

Choppin, G. R. (1971) *Pure Appl. Chem.*, **27**, 23–41.

Choppin, G. R. and Degischer, G. (1972) *J. Inorg. Nucl. Chem.*, **34**, 3473–7.

Choppin, G. R. and Williams, K. R. (1973) *J. Inorg. Nucl. Chem.*, **35**, 4255–69.

Choppin, G. R. and Unrein, P. J. (1976) in *Transplutonium Elements* (eds. W. Müller and R. Lindner), North-Holland, Amsterdam, pp. 97–107.

Choppin, G. R. and Ensor, D. D. (1977) *J. Inorg. Nucl. Chem.*, **39**, 1226–7.

Choppin, G. R. (1983) *Radiochim. Acta*, **32**, 43–53.

Choppin, G. R. and Rao, L. F. (1984) *Radiochim. Acta*, **37**, 143–6.

Choppin, G. R. and Allard, B. (1985) in *Handbook on the Physics and Chemistry of the Actinides,* vol. 3 (eds. A. J. Freeman and C. Keller), Elsevier, New York, pp. 407–29.

Choppin, G. R., Liu, Q., and Sullivan, J. C. (1985) *Inorg. Chem.*, **24**, 3968–9.

Choppin, G. R., Rizkalla, E. N., and Sullivan, J. C. (1987) *Inorg. Chem.*, **26**, 2318–20.

Choppin, G. R. and Yao, K. (1988) *Inorg. Chim. Acta*, **147**, 131–3.

Choppin, G. R. (1988) *Radiochim. Acta*, **44/45**, 23–8.

Choppin, G. R. and Kim, W. H. (1989) *Radiochim. Acta*, **48**, 153–7.

Choppin, G. R. (1991) *J. Radioanal. Nucl. Chem.*, **147**, 109–16.

Choppin, G. R., Rao, L. F., Rizkalla, E. N., and Sullivan, J. C. (1992a) *Radiochim. Acta*, **57**, 173–5.

Choppin, G. R., Khalili, F. I., and Rizkalla, E. N. (1992b) *J. Coord. Chem.*, **26**, 243–50.

Choppin, G. R. (1993) *Thermochim. Acta*, **227**, 1–7.

Choppin, G. R. and Rizkalla, E. N. (1994) in *Handbook on the Physics and Chemistry of Rare Earths,* vol. 18 (eds. K. A. Gschneidner Jr, L. Eyring, G. R. Choppin, and G. H. Lander), Elsevier, New York, pp. 559–90.

Choppin, G. R. (1997) *J. Alloys Compd.*, **249**, 9–13.

Choppin, G. R. and Labonne-Wall, N. (1997) *J. Radioanal. Nucl. Chem.*, **221**, 67–71.

Choppin, G. R., Liljenzin, J., and Rydberg, J.-O. (2002) *Radiochemistry and Nuclear Chemistry,* 3rd edn, Butterworth-Heinemann, Woburn, MA, p. 653.

Choppin, G. R. (2003) *Radiochim. Acta*, **91**, 645–9.

Choppin, G. R. and Wall, D. E. (2003) *J. Radioanal. Nucl. Chem.*, **255**, 47–52.

Clark, D. L., Hobart, D. E., and Neu, M. P. (1995) *Chem. Rev.*, **95**, 25–48.

Clark, D. L., Conradson, S. D., Keogh, D. W., Palmer, P. D., Scott, B. L., and Tait, C. D. (1998) *Inorg. Chem.*, **37**, 2893–9.

Clark, D. L., Conradson, S. D., Donohoe, R. J., Keogh, D. D., Morris, D. E., Palmer, P. D., Rogers, R. D., and Tait, C. D. (1999) *Inorg. Chem.*, **38**, 1456–66.

Coleman, J. S., Keenan, T. K., Jones, L. H., Carnall, W. T., and Penneman, R. A. (1963) *Inorg. Chem.*, **2**, 58–61.

Combes, J.-M., Chisholm-Brause, C. J., Brown, G. E. Jr, Parks, G. A., Conradson, S. D., Eller, P. G., Triay, I. R., Hobart, D. E., and Meijer, A. (1992) *Environ. Sci. Technol.*, **26**, 376–82.

Cossy, C., Barnes, A. C., Enderby, J. E., and Merbach, A. E. (1989) *J. Chem. Phys.*, **90**, 3254–60.

Coulter, L. V., Pitzer, K. S., and Latimer, W. M. (1940) *J. Am. Chem. Soc.*, **62**, 2845–51.

Cousson, A., Dabos, S., Abazli, H., Nectoux, F., Pagès, M., and Choppin, G. R. (1984) *J. Less Common Metals*, **99**, 233–40.

Cramer, R. E., Maynard, R. B., Paw, J. C., and Gilje, J. W. (1983) *Organometallics*, **2**, 1336–40.

Creaser, I., Heckel, M. C., Neitz, R. J., and Pope, M. T. (1993) *Inorg. Chem.*, **32**, 1573–8.

D'Olieslager, W., Choppin, G. R., and Williams, K. R. (1970) *J. Inorg. Nucl. Chem.*, **32**, 3605–10.

Dahlman, R. C., Bondietti, E. A., and Eyman, L. D. (1976) in *Actinides in the Environment* (ed. A. M. Friedman) (ACS Symp. Ser. 35), American Chemical Society, Washington, DC, pp. 47–81.

David, F., Fourest, B., and Duplessis, J. (1985) *J. Nucl. Mater.*, **130**, 273–9.

David, F. (1986) *J. Less Common Metals*, **121**, 27–42.

David, F. H. and Vokhmin, V. (2003) *New J. Chem.*, **27**, 1627–32.

Decambox, P., Mauchien, P., and Moulin, C. (1989) *Radiochim. Acta*, **48**, 23–8.

De Carvalho, R. G. and Choppin, G. R. (1967) *J. Inorg. Nucl. Chem.*, **29**, 725–35.

Dem'yanova, T. A., Stepanov, A. V., Babauer, A. S., and Aleksandruk, V. M. (1986) *Radiokhimiya*, **28**, 494–8.

Den Auwer, C., Charbonnel, M. C., Presson, M. T., Madic, C., and Guillaumont, R. (1997) *Polyhedron*, **16**, 2233–8.

Denecke, M. A., Reich, T., Bubner, M., Pompe, S., Heise, K. H., Nitsche, H., Allen, P. G., Bucher, J. J., Edelstein, N. M., and Shuh, D. K. (1998) *J. Alloys Compd.*, **271–273**, 123–7.

Denning, R. G., Green, J. C., Hutchings, T. E., Dallera, C., Tagliaferri, A., Giarda, K., Brookes, N. B., and Braicovich, L. (2002) *J. Chem. Phys.*, **117**, 8008–20.

Di Bernardo, P., Bismondo, A., Portanova, R., Traverso, O., and Magon, L. (1976) *Inorg. Chim. Acta*, **18**, 47–50.

Di Bernardo, P., Di Napoli, V., Cassol, A., and Magon, L. (1977) *J. Inorg. Nucl. Chem.*, **39**, 1659–63.

Di Bernardo, P., Roncari, E., Mazzi, U., Bettella, F., and Magon, L. (1978) *Thermochim. Acta*, **23**, 293–302.

Di Bernardo, P., Tomat, G., Bismondo, A., Traverso, O., and Magon, L. (1980) *J. Chem. Res. M*, 3144–71.

Di Bernardo, P., A., Cassol, G., Tomat, A., Bismondo, and L. Magon, (1983) *J. Chem. Soc., Dalton Trans.*, 733–5.

Diamond, R. M., Street, K., and Seaborg, G. T. (1954) *J. Am. Chem. Soc.*, **76**, 1461–9.

Diebler, H. and Eigen, M. (1959) *Z. Phys. Chem.* (Frankfurt), **20**, 299–309.

Docrat, T. I., Mosselmans, J. F. W., Charnock, J. M., Whiteley, M. W., Collison, D., Livens, F. R., Jones, C., and Edmiston, M. J. (1999) *Inorg. Chem.*, **38**, 1879–82.

Dodge, C. J. and Francis, A. J. (1997) *Environ. Sci. Technol.*, **31**, 3062–7.

Drago, R. S. and Wayland, B. B. (1965) *J. Am. Chem. Soc.*, **87**, 3571–7.

Drew, M. G. B., Iveson, P. B., Hudson, M. J., Liljenzin, J. O., Spjuth, L., Cordier, P.-Y., Enarsson, Å., Hill, C., and Madic, C. (2000) *J. Chem. Soc., Dalton Trans.*, 821–30.

Eberle, S. H. and Schaefer, J. B. (1968) *Inorg. Nucl. Chem. Lett.*, **4**, 283–7.

Eigen, M. and Tamm, K. (1962) *Z. Elektrochem.*, **66**, 93–107, 107–21.

Eigen, M. (1963) *Ber. Bunsenges Phys. Chem.*, **67**, 753–62.

Eigen, M. and Wilkins, R. G. (1965) *Adv. Chem. Ser.*, **49**, 55–67.

El-Rawi, H. (1974) *Complexing Kinetics of Transplutonium Elements*, Institut für Radiochemie, Kernforschungszentrum, Karlsruhe Report KFK-1927.

Ensor, D. D. and Choppin, G. R. (1980) *J. Inorg. Nucl. Chem.*, **42**, 1477–80.

Ernst, S. and Jezowska-Trzebiatowska, B. (1975a) *J. Phys. Chem.*, **79**, 2113–16.

Ernst, S. and Jezowska-Trzebiatowska, B. (1975b) *Z. Phys. Chem.* (Leipzig), **256**, 330–6.

Espenson, J. H. and Wang, R. T. (1970) *J. Chem. Soc., Chem. Commun.,* 207–8.

Fanghänel, T. and Kim, J. I. (1994) *Radiochim. Acta*, **66/67**, 81–7.

Felmy, A. R., Rai, D., and Fulton, R. W. (1990) *Radiochim. Acta*, **50**, 193–204.

Ferraro, J. R. and Peppard, D. F. (1963) *Nucl. Sci. Eng.*, **16**, 389–400.

Fourest, B., Duplessis, J., and David, F. (1984) *Radiochim. Acta*, **36**, 191–5.

Fratiello, A., Lee, R. E., and Schuster, R. E. (1970a) *Inorg. Chem.*, **9**, 391–2.

Fratiello, A., Kubo, V., Lee, R. E., and Schuster, R. E. (1970b) *J. Phys. Chem.*, **74**, 3726–30.

Fraústo da Silva, J. J. R. and Simoes, M. L. S. (1968) *Talanta*, **15**, 609–22.

Fried, A. R. and Martell, A. E. (1971) *J. Am. Chem. Soc.*, **93**, 4695–700.

Fuger, J. and Cunningham, B. B. (1965) *J. Inorg. Nucl. Chem.*, **27**, 1079–84.

Fuger, J. and Oetting, F. L. (1976) *The Chemical Thermodynamics of Actinide Elements and Compounds,* part 2, *The Actinide Aqueous Ions*, International Atomic Energy Agency, Vienna.

Fuger, J. (1982) in *Actinides in Perspective* (ed. N. M. Edelstein), Pergamon Press, New York, pp. 409–31.

Fuger, J., Khodakovsky, I. L., Sergeyava, E. I., Medvedev, V. A., and Navratil, J. D. (1992) *The Chemical Thermodynamics of Actinide Elements and Compounds,* part 12, *The Actinide Aqueous Inorganic Complexes*, International Atomic Energy Agency, Vienna.

Fulton, R. B. and Newton, T. W. (1970) *J. Phys. Chem.*, **74**, 1661–9.

Garnov, A. Y., Krot, N. N., Bessonov, A. A., and Perminov, V. P. (1996) *Radiochemistry*, **38**, 402–6.

Gaunt, A. J., May, I., Helliwell, M., and Richardson, S. (2002) *J. Am. Chem. Soc.*, **124**, 13350–1.

Giffaut, E. and Vitorge, P. (1993) in *Scientific Basis for Nuclear Waste Management XVI,* vol. 294 (eds. C. G. Interrante and R. T. Pabalan), Materials Research Society, Pittsburg, PA, pp. 747–51.

Gordon, G. and Taube, H. (1961) *J. Inorg. Nucl. Chem.*, **19**, 189–91.

Gordon, S., Mulac, W. A., Schmidt, K. N., and Sjoblom, R. K. (1978) *Inorg. Chem.*, **17**, 294–6.

Grenthe, I. (1962) *Acta Chem. Scand.*, **16**, 1695–712.

Grenthe, I. (1963) *Acta Chem. Scand.*, **17**, 1814–15.

Grenthe, I. (1964) *Acta Chem. Scand.*, **18**, 283–92.

Grenthe, I. and Lagerman, B. (1991) *Acta Chem. Scand.*, **45**, 231–8.

Grenthe, I., Fuger, J., Konings, R. J. M., Lemire, R. J., Muller, A. B., Nguyen-Trung, C., and Wanner, H. (1992) *Chemical Thermodynamics of Uranium,* North-Holland, Amsterdam.

Grenthe, I. and Lagerman, B. (1993) *Radiochim. Acta*, **61**, 169–76.

Grenthe, I. and Puigdomenech, I. (1997) *Modelling in Aquatic Chemistry,* Nuclear Energy Agency/Organisation for Economic Cooperation and Development, Paris.

Grigor'ev, M. S., Gulev, B. F., and Krot, N. N. (1986) *Radiokhimiya*, **28**, 690–4; *Sov. Radiochem.*, **28**, 630–3.

Grigor'ev, M. S., Baturin, N. A., Budantseva, N. A., and Fedoseev, A. M. (1993a) *Radiokhimiya*, **35**(2), 29–38; *Sov. Radiochem.*, **35**, 151–6.

Grigor'ev, M. S., Charushnikova, I. A., Krot, N. N., Yanovskii, A. I., and Struchkov, Y. T. (1993b) *Radiokhimiya*, **35**(4), 31–7; *Sov. Radiochem.*, **35**, 39–48.

Grigor'ev, M. S., Charushnikova, I. A., Krot, N. N., Yanovskii, A. I., and Struchkov, Y. T. (1993c) *Radiokhimiya*, **35**(4), 24–30; *Sov. Radiochem.*, **35**, 388–93.

Grigor'ev, M. S., Baturin, N. A., Bessonov, A. A., and Krot, N. N. (1995) *Radiochemistry*, **37**, 12–4.

Gritmon, T. F., Goedken, M. P., and Choppin, G. R. (1977) *J. Nucl. Inorg. Chem.*, **39**, 2021–3.

Gross, J. and Keller, C. (1972) *J. Inorg. Nucl. Chem.*, **34**, 725–38.

Guilbaud, P. and Wipff, G. (1993a) *J. Inclusion Phenom. Mol. Recognit. Chem.*, **16**, 169–88.

Guilbaud, P. and Wipff, G. (1993b) *J. Phys. Chem.*, **97**, 5685–92.

Guillaumont, R. (1966) *Rev. Chim. Minér.*, **3**, 339–73.

Guillaumont, R. (1968) *Bull. Soc. Chim. Fr.*, 168–70.

Guillaumont, R., Bouissières, G., and Muxart, R. (1968) *Actinides Rev.*, **1**, 135–63.

Guillaumont, R., Fanghänel, T., Fuger, J., Grenthe, I., Neck, V., Palmer, D., and Rand, M. H. (2003) *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium,* Elsevier, Amsterdam.

Guillaume, B., Begun, G. M., and Hahn, R. L. (1982) *Inorg. Chem.*, **21**, 1159–66.

Guillaume, B., Hahn, R. L., and Narten, A. H. (1983) *Inorg. Chem.*, **22**, 109–11.

Gusev, N. I. (1971) *Russ. J. Phys. Chem.*, **45**, 1268–71, 1455–7, 1575–6.

Gusev, N. I. (1972) *Russ. J. Phys. Chem.*, **46**, 1034–7, 1657–9.

Gusev, N. I. (1973) *Russ. J. Phys. Chem.*, **47**, 52–5, 184–7, 687–90, 1309–12.

Habenschuss, A. and Spedding, F. H. (1979a) *J. Chem. Phys.*, **70**, 2797–806.

Habenschuss, A. and Spedding, F. H. (1979b) *J. Chem. Phys.*, **70**, 3758–64.

Habenschuss, A. and Spedding, F. H. (1980) *J. Chem. Phys.*, **73**, 442–50.

Halperin, J. and Oliver, J. H. (1983) *Radiochim. Acta*, **33**, 29–33.

Hancock, R. D. and Marsicano, F. (1980) *Inorg. Chem.*, **19**, 2709–14.

Hancock, R. D. and Martell, A. E. (1989) *Chem. Rev.*, **89**, 1875–914.

Hancock, R. D. (1992) in *Perspectives in Coordination Chemistry* (eds. A. F. Williams, C. Floriani, and A. E. Merbach), Springer-Verlag, New York, pp. 129–51.

Hancock, R. D. and Martell, A. E. (1996) *J. Chem. Educ.*, **73**, 654–63.

Harmon, H. D., Peterson, J. R., McDowell, W. J., and Coleman, C. F. (1972a) *J. Inorg. Nucl. Chem.*, **34**, 1381–97.

Harmon, H. D., Peterson, J. R., Bell, J. T., and McDowell, W. J. (1972b) *J. Inorg. Nucl. Chem.*, **34**, 1711–19.

Havel, J. (1969) *Collect. Czech. Chem. Commun.*, **34**, 3248–65.

Hay, P. J., Martin, R. L., and Schreckenbach, G. (2000) *J. Phys. Chem. A*, **104**, 6259–70.

Hefter, G. (1974) *Coord. Chem. Rev.*, **12**, 221–39.

Hietanen, S. (1954) *Acta Chem. Scand.*, **8**, 1626–42.

Hietanen, S. (1956) *Acta Chem. Scand.*, **10**, 1531–46.

Hietanen, S. and Sillen, L. G. (1968) *Acta Chem. Scand.*, **22**, 265–80.

Hinchey, R. J. and Cobble, J. W. (1970) *Inorg. Chem.*, **9**, 922–6.

Hindman, J. C., Sullivan, J. C., and Cohen, D. (1954) *J. Am. Chem. Soc.*, **76**, 3278–80.

Hindman, J. C., Sullivan, J. C., and Cohen, D. (1959) *J. Am. Chem. Soc.*, **81**, 2316–19.

Hinton, J. F. and Amis, E. S. (1971) *Chem. Rev.*, **71**, 627–74.

Hök-Bernström, B. (1956) *Acta Chem. Scand.*, **10**, 163–73.

Howatson, J., Grev, D. M., and Morosin, B. (1975) *J. Inorg. Nucl. Chem.*, **37**, 1933–5.

Huheey, J. E. (1976) *Inorganic Chemistry,* Harper and Row, New York.

Hulet, E. K., Lougheed, R. W., Baisden, P. A., Landrum, J. H., Wild, J. F., and Lundqvist, R. F. D. (1979) *J. Inorg. Nucl. Chem.*, **41**, 1743–7.

Inoue, Y. and Tochiyama, O. (1985) *Bull. Chem. Soc. Jpn.*, **58**, 2228–33.

Itagaki, H., Nakayama, S., Tanaka, S., and Yamawaki, M. (1992) *Radiochim. Acta*, **58/59**, 61–6.

Jainxin, T., Yaozhong, C., and Zhangji, L. (1993) *Radiochim. Acta*, **61**, 73–5.

Jarvis, N. V. and Hancock, R. D. (1991) *Inorg. Chim. Acta*, **182**, 229–32.

Jarvis, N. V., de Sousa, A. S., and Hancock, R. D. (1992) *Radiochim. Acta*, **57**, 33–9.

Jarvis, N. V. and Hancock, R. D. (1994) *Radiochim. Acta*, **64**, 15–22.

Jensen, M. P. and Choppin, G. R. (1998) *Radiochim. Acta*, **82**, 83–8.

Jensen, M. P., Morss, L. R., Beitz, J. V., and Ensor, D. D. (2000a) *J. Alloys Compd.*, **303/304**, 137–41.

Jensen, M. P., Beitz, J. V., Rogers, R. D., and Nash, K. L. (2000b) *J. Chem. Soc., Dalton Trans.*, 3058–64.

Jensen, M. P. and Nash, K. L. (2001) *Radiochim. Acta*, **89**, 557–64.

Jensen, M. P. and Bond, A. H. (2002) *J. Am. Chem. Soc.*, **124**, 9870–7.

Johansson, G. (1968) *Acta Chem. Scand.*, **22**, 399–409.

Johansson, L. (1971) *Acta Chem. Scand.*, **25**, 3569–76.

Johansson, G., Magini, M., and Ohtaki, H. (1991) *J. Solution Chem.*, **20**, 775–92.

Johnson, D. A. (1982) *Some Thermodynamic Aspects of Inorganic Chemistry,* 2nd edn, Cambridge University Press, Cambridge.

Jones, A. D. and Choppin, G. R. (1969) *Actinides Rev.*, **1**, 311–36.

Kaltsoyannis, N. (2000) *Inorg. Chem.*, **39**, 6009–17.

Karmazin, L., Mazzanti, M., and Pécaut, J. (2002) *Chem. Commun.*, 654–5.

Karraker, D. G. and Stone, J. A. (1977) *Inorg. Chem.*, **16**, 2979–80.

Keenan, T. K. and Kruse, F. H. (1964) *Inorg. Chem.*, **3**, 1231–2.

Kepert, C. J., Skelton, B. W., and White, A. H. (1999) *Aust. J. Chem.*, **52**, 617–20.

Khalili, F. I., Choppin, G. R., and Rizkalla, E. N. (1988) *Inorg. Chim. Acta*, **143**, 131–5.

Khopkar, P. K. and Mathur, J. N. (1974) *J. Inorg. Nucl. Chem.*, **36**, 3819–25.

Kiener, C., Folcher, G., Rigny, P., and Virlet, J. (1976) *Can. J. Chem.*, **54**, 303–12.

Kim, J. I. and Kanellakopulos, B. (1989) *Radiochim. Acta*, **48**, 145–50.

Kim, J. I. and Sekine, T. (1991) *Radiochim. Acta*, **55**, 187–92.

Kim, J. I., Wimmer, H., and Klenze, R. (1991) *Radiochim. Acta*, **54**, 35–41.

Kim, J. I., Rhee, D. S., Wimmer, H., Buckau, G., and Klenze, R. (1993) *Radiochim. Acta*, **62**, 35–43.

Kim, W. H. and Choppin, G. R. (1988) *Inorg. Chem.*, **27**, 2771–3.

Kimura, T. and Choppin, G. R. (1994) *J. Alloys Compd.*, **213–214**, 313–17.

Kimura, T., Choppin, G. R., Kato, Y., and Yoshida, Z. (1996) *Radiochim. Acta*, **72**, 61–4.

Kimura, T. and Kato, Y. (1998) *J. Alloys Compd.*, **271–273**, 867–71.

Kinard, W. F. and Choppin, G. R. (1974) *J. Inorg. Nucl. Chem.*, **36**, 1131–4.

Kinard, W. F., Grant, P. M., and Baisden, P. A. (1989) *Polyhedron*, **8**, 2385–8.

Kirby, H. W. (1959) *The Radiochemistry of Protactinium*, U.S. Atomic Energy Commission Report NAS-NS 3016. (*The Radiochemistry of...*" series can be found at http://lib-www.lanl.gov/radiochemistry/elements.htm).

Klenze, R., Kim, J. I., and Wimmer, H. (1991) *Radiochim. Acta*, **52/53**, 97–103.

Kobashi, A. and Choppin, G. R. (1988) *Radiochim. Acta*, **43**, 211–15.

Kolarich, R. T., Ryan, V. A., and Schuman, R. P. (1967) *J. Inorg. Nucl. Chem.*, **29**, 783–97.

Kolbe, W. and Edelstein, N. M. (1971) *Phys. Rev. B*, **4**, 2869–75.

Kosyakov, V. N., Timofeev, G. A., Erin, E. A., Andreev, V. I., Kopytov, V. V., and Simakin, G. A. (1977) *Sov. Radiochem.*, **19**, 418–23.

Kozlov, A. G. and Krot, N. N. (1960) *Russ. J. Inorg. Chem.*, **5**, 954–6.

Kraus, K. A. and Dam, J. R. (1949) in *The Transuranium Elements* (eds. G. T. Seaborg, J. J. Katz, and W. M. Manning), Natl. Nucl. En. Ser., Div. IV, 14B, part 1, McGraw-Hill, New York, pp. 528–49.

Kraus, K. A. and Holmberg, R. W. (1954) *J. Phys. Chem.*, **58**, 325–30.

Kraus, K. A., Moore, G. E., and Nelson, F. (1956) *J. Am. Chem. Soc.*, **78**, 2692–4.

Krot, N. N., Ermolaev, N. P., and Gel'man, A. D. (1962) *Russ. J. Inorg. Chem.*, **7**, 1062–6.

Krot, N. N., Shilov, V. P., Nikolaevskii, V. B., Pikaev, A. K., Gel'man, A. D., and Spitsyn, V. I. (1974) *Dokl. Acad. Sci. USSR*, **217**(3), 525–7.

Laidler, K. J. (1956) *Can. J. Chem.*, **34**, 1107–13.

Laubscher, A. E. and Fouché, K. F. (1971) *J. Inorg. Nucl. Chem.*, **33**, 3521–35.

Lavallee, D. K., Lavallee, C., Sullivan, J. C., and Deutsch, E. (1973) *Inorg. Chem.*, **12**, 570–4.

Lemire, R. J., Fuger, J., Nitsche, H., Rand, M. H., Potter, P., Rydberg, J., Spahiu, K., Sullivan, J. C., Ullman, W. J., Vitorge, P., and Wanner, H. (2001) *Chemical Thermodynamics of Neptunium and Plutonium,* Elsevier, New York.

Lundqvist, R. (1974) in *Proc. Int. Solvent Extr. Conf. 1974,* vol. 1 (ed. G. V. Jeffreys), Society of Chemical Industry, London, pp. 469–76.

Lundqvist, R., Hulet, E. K., and Baisden, P. A. (1981) *Acta Chem. Scand.*, **35A**, 653–61.

Madic, C., Guillaume, J. C., Morisseau, J. C., and Moulin, J. P. (1979) *J. Inorg. Nucl. Chem.*, **41**, 1027–31.

Madic, C., Hobart, D. E., and Begun, G. M. (1983a) *Inorg. Chem.*, **22**, 1494–503.

Madic, C., Begun, G. M., Hobart, D. E., and Hahn, R. L. (1983b) *Radiochim. Acta*, **34**, 195–202.

Magon, L., Cassol, A., and Portanova, R. (1968) *Inorg. Chim. Acta*, **2**, 285–8.

Makarova, T. P., Sinitsyna, G. S., Stepanov, A. V., Shestakova, I. A., and Shestakov, B. I. (1972) *Sov. Radiochem.*, **14**(4), 555–7.

Manning, G. S. (1979) *Acc. Chem. Res.*, **12**, 443–9.

Manning, T. J. (1996) *J. Chem. Educ.*, **73**, 661–3.

Marcus, Y. (1966) *J. Inorg. Nucl. Chem.*, **28**, 209–19.

Marcus, Y. and Bomse, M. (1970) *Israel. J. Chem.*, **8**, 901–11.

Marcus, Y. and Loewenschuss, A. (1986) *J. Chem. Soc., Faraday Trans.*, **82**, 2873–86.

Marinsky, J. A. (1976) *Coord. Chem. Rev.*, **19**, 125–71.

Marks, A. P. and Drago, R. S. (1975) *J. Am. Chem. Soc.*, **97**, 3324–9.

Marquardt, C., Herrmann, G., and Trautmann, N. (1996) *Radiochim. Acta*, **73**, 119–25.

Marquardt, C. and Kim, J. I. (1998) *Radiochim. Acta*, **81**, 143–8.

Martell, A. E., Smith, R. M., and Motekaitis, R. J. (1998) *Critically Selected Stability Constants of Metal Complexes Database Version 5.0,* NIST Standard Reference Data, Gaithersburg, MD.

Masci, B., Nierlich, M., and Thuéry, P. (2002) *New J. Chem.*, **26**, 120–8.

Masters, B. J. and Schwartz, L. L. (1961) *J. Am. Chem. Soc.*, **83**, 2620–4.

Matonic, J. H., Scott, B. L., and Neu, M. P. (2001) *Inorg. Chem.*, **40**, 2638–9.

Matsika, S. and Pitzer, R. M. (2000) *J. Phys. Chem. A*, **104**, 4064–8.

McDowell, W. J., Keller, Jr, O. J. Dittner, P. E., Tarrant, J. R., and Case, G. N. (1976) *J. Inorg. Nucl. Chem.*, **38**, 1207–10.

Meinrath, G. and Kim, J. I. (1991) *Radiochim. Acta*, **53**, 29–34.

Miguirditchian, M. (2003) PhD Dissertation, Paris XI University, Orsay.

Mikhailov, V. A. (1969) *Russ. J. Inorg. Chem.*, **14**, 1119–24.

Mikheev, N. B., Spitsyn, V. I., Kamenskaya, A. N., Konovalova, N. A., Rumer, I. A., Auerman, L. N., and Podorozhnyi, A. M. (1977) *Inorg. Nucl. Chem. Lett.*, **13**, 651–6.

Mikheev, N. B., Spitsyn, V. I., Kamenskaya, A. N., Mikulski, J., and Petryna, T. (1980) *Radiochem. Radioanal. Lett.*, **43**, 85–92.

Milic, N. B. (1981) *J. Chem. Soc.*, *Dalton Trans.*, 1445–9.

Milic, N. B. and Suranji, T. M. (1982) *Can. J. Chem.*, **60**, 1298–303.

Moll, H., Denecke, M. A., Jalilehvand, F., Sandström, M., and Grenthe, I. (1999) *Inorg. Chem.*, **38**, 1795–9.

Moll, H., Reich, T., Hennig, C., Rossberg, A., Szabó, Z., and Grenthe, I. (2000) *Radiochim. Acta*, **88**, 559–66.

Moon, H.-C. (1989) *Bull. Korean Chem. Soc.*, **10**, 270–2.

Morgenstern, A. and Kim, J. I. (1996) *Radiochim. Acta*, **72**, 73–7.

Moriyama, H., Kitamura, A., Fujiwara, K., and Yamana, H. (1999) *Radiochim. Acta*, **87**, 97–104.

Moriyama, H., Fujiwara, K., and Yamana, H. (2002) *J. Nucl. Sci. Technol.*, Suppl. **3**, 246–50.

Morse, J. W. and Choppin, G. R. (1991) *Rev. Aquat. Sci.*, **4**, 1–22.

Morss, L. R. (1976) *Chem. Rev.*, **76**, 827–41.

Morss, L. R. and McCue, M. C. (1976) *J. Chem. Eng. Data*, **21**, 337–41.

Morss, L. R. (1985) in *Standard Potentials in Aqueous Solutions* (eds. A. J. Bard, R. Parsons and J. Jordan), Marcel Dekker, New York, pp. 587–629.

Morss, L. R., Nash, K. L., and Ensor, D. D. (2000) *J. Chem. Soc.*, *Dalton Trans.*, 285–91.

Moskvin, A. I. and Essen, L. N. (1967) *Russ. J. Inorg. Chem.*, **12**, 359–62.

Moulin, V., Tits, J., and Ouzounian, G. (1992) *Radiochim. Acta*, **58–59**, 179–90.

Münze, R. (1972) *J. Inorg. Nucl. Chem.*, **34**, 661–8.

Murmann, R. K. and Sullivan, J. C. (1967) *Inorg. Chem.*, **6**, 892–900.

Muscatello, A. C., Choppin, G. R., and D'Olieslager, W. (1989) *Inorg. Chem.*, **28**, 993–7.

Musikas, C., Cuillerdier, C., Livet, J., Forchioni, A., and Chachaty, C. (1983) *Inorg. Chem.*, **22**, 2513–18.

Musikas, C. (1984) in *International Symposium on Actinide/Lanthanide Separations* (eds. G. R. Choppin, J. D. Navratil, and W. W. Schulz), World Scientific, Philadelphia, pp. 19–30.

Musikas, C. (1986) *J. Less Common Metals*, **122**, 107–23.

Nagasaki, S., Kinoshita, K., Enokida, Y., and Suzuki, A. (1992) *J. Nucl. Sci. Technol.*, **29**, 1100–7.

Nash, K. L. and Cleveland, J. M. (1983) in *Plutonium Chemistry* (eds. W. T. Carnall and G. R. Choppin) (ACS Symp. Ser. 216), American Chemical Society, Washington, DC, pp. 251–62.

Nash, K. L. and Cleveland, J. M. (1984a) *Radiochim. Acta*, **37**, 19–24.

Nash, K. L. and Cleveland, J. M. (1984b) *Radiochim. Acta*, **36**, 129–34.

Nash, K. L. (1991a) *Radiochim. Acta*, **54**, 171–9.

Nash, K. L. (1991b) *Eur. J. Solid State Inorg. Chem.*, **28**, 389–92.

Nash, K. L. (1993a) *Solvent Extr. Ion Exch.*, **11**, 729–68.

Nash, K. L. (1993b) *Radiochim. Acta*, **61**, 147–54.

Nash, K. L., Rao, L. F., and Choppin, G. R. (1995) *Inorg. Chem.*, **34**, 2753–8.

Nash, K. L. and Sullivan, J. C. (1998) *J. Alloys Compd.*, **271–273**, 712–18.

Neck, V., Kim, J. I., and Kanellakopulos, B. (1992) *Radiochim. Acta*, **56**, 25–30.

Neck, V., Fanghänel, T., and Kim, J. I. (1997) *Radiochim. Acta*, **77**, 167–75.

Neck, V. and Kim, J. I. (2000) *Radiochim. Acta*, **88**, 815–22.

Neck, V. and Kim, J. I. (2001) *Radiochim. Acta*, **89**, 1–16.

Nelson, D. M. and Lovett, M. B. (1978) *Nature*, **276**, 599–601.

Neu, M. P., Matonic, J. H., Ruggiero, C. E., and Scott, B. L. (2000) *Angew. Chem.*, **39**, 1442–4.

Newton, T. W. and Baker, F. B. (1962) *Inorg. Chem.*, **1**, 368–77.

Newton, T. W. and Baker, F. B. (1965) *Inorg. Chem.*, **4**, 1166–70.

Newton, T. W. (1970) *J. Phys. Chem.*, **74**, 1655–61.

Newton, T. W. and Fulton, R. B. (1970) *J. Phys. Chem.*, **74**, 2797–801.

Newton, T. W. and Burkhart, M. J. (1971) *Inorg. Chem.*, **10**, 2323–6.

Newton, T.W. (1975) *The Kinetics of the Oxidation–Reduction Reactions of Uranium, Neptunium, Plutonium, and Americium in Aqueous Solutions*, U.S. ERDA TID-26506.

Newton, T. W. and Montag, T. (1976) *Inorg. Chem.*, **15**, 2856–61.

Newton, T. W. and Sullivan, J. C. (1985) in *Handbook on the Physics and Chemistry of the Actinides,* vol. 3 (eds. A. J. Freeman and C. Keller), Elsevier, New York, pp. 387–406.

Nugent, L. J., Baybarz, R. D., Burnett, J. L., and Ryan, J. L. (1973a) *J. Phys. Chem.*, **77**, 1528–39.

Nugent, L. J., Burnett, J. L., and Morss, L. R. (1973b) *J. Chem. Thermodyn.*, **5**, 665–78.

Nyssen, G. A. and Margerum, D. W. (1970) *Inorg. Chem.*, **9**, 1814–20.

Pachauri, O. P. and Tandon, J. P. (1975) *J. Inorg. Nucl. Chem.*, **37**, 2321–3.

Palmer, D. A. and Nguyen-Trung, C. (1995) *J. Solution Chem.*, **24**, 1281–91.

Panak, P. J., Booth, C. H., Caulder, D. L., Bucher, J. J., Shuh, D. K., and Nitsche, H. (2002a) *Radiochim. Acta*, **90**, 315–21.

Panak, P. J., Knopp, R., Booth, C. H., and Nitsche, H. (2002b) *Radiochim. Acta*, **90**, 779–83.

Passynskii, A. (1938) *Acta Phys. Chim. USSR*, **8**, 385–418.

Patil, S. K., Ramakrishna, V. V., and Rananiah, M. V. (1978) *Coord. Chem. Rev.*, **25**, 133–71.

Péligot, E. (1842) *Ann. Chim. Phys. Ser. 3*, **5**, 1–6.

Pepper, M. and Bursten, B. E. (1991) *Chem. Rev.*, **91**, 719–41.

Peretrukhin, V. F., David, F., and Maslennikov, A. (1994) *Radiochim. Acta*, **65**, 161–6.

Perrin, A. (1976) *Acta Crystallogr. B*, **32**, 1658–61.

Pinkerton, A. A., Pisaniello, D. L., and Zonnevijlle, F. (1984) *Inorg. Chim. Acta*, **82**, 153–6.

Pocev, S. and Johansson, G. (1973) *Acta Chem. Scand.*, **27**, 2146–60.

Portanova, R., Tomat, G., Magon, L., and Cassol, A. (1970) *J. Inorg. Nucl. Chem.*, **32**, 2343–8.

Portanova, R., Tomat, G., Magon, L., and Cassol, A. (1972) *J. Inorg. Nucl. Chem.*, **34**, 1768–70.

Portanova, R., Di Bernardo, P., Traverso, O., Mazzocchin, G. A., and Magon, L. (1975) *J. Inorg. Nucl. Chem.*, **37**, 2177–9.

Rabideau, S. W. and Cowan, H. D. (1955) *J. Am. Chem. Soc.*, **77**, 6145–8.

Rabideau, S. W. (1957) *J. Am. Chem. Soc.*, **79**, 6350–3.

Rabideau, S. W. and Masters, B. J. (1961) *J. Phys. Chem.*, **65**, 1256–61.

Rai, D., Strickert, R. G., Moore, D. A., and Ryan, J. L. (1983) *Radiochim. Acta*, **33**, 201–6.

Rai, D., Felmy, A. R., Sterner, S. M., and Moore, D. A. (1997) *Radiochim. Acta*, **79**, 239–47.

Rajan, K. S. and Martell, A. E. (1965) *Inorg. Chem.*, **4**, 462–9.

Rao, L. F. and Choppin, G. R. (1984) *Inorg. Chem.*, **23**, 2351–4.

Rao, L., Jiang, J., Zanonato, P. L., Di Bernardo, P., Bismondo, A., and Garnov, A. Y. (2002) *Radiochim. Acta*, **90**, 581–8.

Rapko, B. M., Duesler, E. N., Smith, P. H., Paine, R. T., and Ryan, R. R. (1993) *Inorg. Chem.*, **32**, 2164–74.

Raymond, K. (1985) in *Environmental Inorganic Chemistry* (eds. K. J. Irgolic and A. E. Martell), VCH Publishers, Deerfield Beach, FL, pp. 331–47.

Reynolds, J. G., Zalkin, A., Templeton, D. H., and Edelstein, N. M. (1977) *Inorg. Chem.*, **16**, 1090–6.

Rinaldi, P. L., Khan, S. A., Choppin, G. R., and Levy, G. C. (1979) *J. Am. Chem. Soc.*, **101**, 1350–1.

Rizkalla, E. N., Sullivan, J. C., and Choppin, G. R. (1989) *Inorg. Chem.*, **28**, 909–11.

Rizkalla, E. N., Nectoux, F., Dabos-Seignon, S., and Pagès, M. (1990a) *Radiochim. Acta*, **51**, 151–5.

Rizkalla, E. N., Nectoux, F., Dabos-Seignon, S., and Pagès, M. (1990b) *Radiochim. Acta*, **51**, 113–17.

Rizkalla, E. N. and Choppin, G. R. (1994) in *Handbook on the Physics and Chemistry of Rare Earths,* vol. 18 (eds. K. A. Gschneidner Jr, L. Eyring, G. R. Choppin, and G. H. Lander), Elsevier, New York, pp. 529–58.

Romanovski, V. V., White, D. J., Xu, J. D., Hoffman, D. C., and Raymond, K. N. (1999) *Solvent Extr. Ion Exch.*, **17**, 55–71.

Ryan, J. L. (1960) *J. Phys. Chem.*, **64**, 1375–85.

Ryan, J. L. (1961) *J. Phys. Chem.*, **65**, 1856–9.

Rykov, A. G., Vasil'ev, V. Y., and Blokhin, N. B. (1971) *Russ. J. Inorg. Chem.*, **16**, 1539–40.

Rykov, A. G. and Frolov, A. A. (1972a) *Sov. Radiochem.*, **14**, 737–40.

Rykov, A. G. and Frolov, A. A. (1972b) *Sov. Radiochem.*, **14**, 729–36.

Rykov, A. G., Andreichuk, N. N., and Vasil'ev, V. Y. (1973) *Sov. Radiochem.*, **15**, 350–5.

Rykov, A. G. and Frolov, A. A. (1974) *Sov. Radiochem.*, **16**, 786–92.

Rykov, A. G. and Frolov, A. A. (1975) *Sov. Radiochem.*, **17**, 189–91.

Samhoun, K., David, F., Hahn, R. L., O'Kelley, G. D., and Tarrant, J. R. (1979) *J. Inorg. Nucl. Chem.*, **41**, 1749–54.

Sandino, A. and Bruno, J. (1992) *Geochim. Cosmochim. Acta*, **56**, 4135–45.

Šcavnicar, S. and Prodic, B. (1965) *Acta Crystallogr.*, **18**, 698–702.

Schedin, U. (1975) *Acta Chem. Scand.*, **29A**, 333–44.

Schmidt, K. H., Gordon, S., Thompson, R. C., and Sullivan, J. C. (1980) *J. Inorg. Nucl. Chem.*, **43**, 611–15.

Sekine, T. (1964) *J. Inorg. Nucl. Chem.*, **26**, 1463–5.

Sekine, T. (1965) *Bull. Chem. Soc. Jpn.*, **38**, 1972–8.

Sekine, T., Hasegawa, Y., and Ihara, N. (1973) *J. Inorg. Nucl. Chem.*, **35**, 3968–70.

Shalinets, A. B. (1972a) *Sov. Radiochem.*, **14**(2), 285–9.

Shalinets, A. B. (1972b) *Sov. Radiochem.*, **14**(2), 279–84.

Shalinets, A. B. (1972c) *Sov. Radiochem.*, **14**(1), 18–25.

Shalinets, A. B. and Stepanov, A. V. (1972) *Radiokhimiya*, **14**, 280–3; *Sov. Radiochem.*, **14**, 290–3.

Shannon, R. D. (1976) *Acta Crystallogr.*, **32A**, 751–67.

Shcherbakov, V. A., Jorga, E. V., and Mashirov, L. G. (1974) *Sov. Radiochem.*, **16**, 286–7.

Shcherbakov, V. A. and Shcherbakova, L. L. (1976) *Radiokhimiya*, **18**, 207–10; *Sov. Radiochem.*, **18**, 188–90.

Sherif, F. G. and Awad, A. M. (1961) *J. Inorg. Nucl. Chem.*, **19**, 94–100.

Shilov, V. P. (1976) *Sov. Radiochem.*, **18**, 567–8.

Shilov, V. P., Stepanova, E. S., and Krot, N. N. (1976) *Sov. Radiochem.*, **18**, 310–13.

Shinkai, S., Koreishi, H., Ueda, K., Arimura, T., and Manabe, O. (1987) *J. Am. Chem. Soc.*, **109**, 6371–6.

Siddall, T. H. and Stewart, W. E. (1967) *Inorg. Nucl. Chem. Lett.*, **3**, 279–84.

Silva, R. J. and Nitsche, H. (1984) in *NRC Nuclear Waste Geochemistry* (eds. D. H. Alexander and G. F. Birchard), NUREG/CR-0052, U.S. Nuclear Regulatory Commission, Washington, DC, pp. 70–93.

Silva, R. J., Bidoglio, G., Rand, M. H., Robouch, P. B., Wanner, H., and Puigdomenech, I. (1995) *Chemical Thermodynamics of Americium,* Elsevier, New York.

Smith, T. D. (1959) *J. Inorg. Nucl. Chem.*, **11**, 314–19.

Spence, R. (1968) *Talanta*, **15**, 1307–9.

Spencer, S., Gagliardi, L., Handy, N. C., Ioannou, A. G., Skylaris, C. K., Willetts, A., and Simper, A. M. (1999) *J. Phys. Chem. A*, **103**, 1831–7.

Spitsyn, V. I., Gelman, A. D., Krot, N. N., Mefodiyeva, M. P., Zacharova, F. A., Komkov, Y. A., Shilov, V. P., and Smirnova, V. I. (1968) *J. Inorg. Nucl. Chem.*, **31**, 2733–45.

Stadler, S. and Kim, J. I. (1988) *Radiochim. Acta*, **44–45**, 39–44.

Standifer, E. M. and Nitsche, H. (1988) *Lanthanide Actinide Res.*, **2**, 383–4.

Starý, J. (1966) *Talanta*, **13**, 421–37.

Stemmler, A. J., Kampf, J. W., and Pecoraro, V. L. (1996) *Angew. Chem. Int. Edn. Eng.*, **35**, 2841–3.

Stepanov, A. V. (1971) *Russ. J. Inorg. Chem.*, **16**, 1583–6.

Stout, B. E., Caceci, M. S., Nectoux, F., and Pagès, M. (1989) *Radiochim. Acta*, **46**, 181–4.

Stout, B. E., Choppin, G. R., Nectoux, F., and Pagès, M. (1993) *Radiochim. Acta*, **61**, 65–7.

Stradling, G. N., Gray, S. A., Ellender, M., Moody, J. C., Hodgson, A., Pearce, M., Wilson, I., Burgada, R., Bailly, T., Leroux, Y. G. P., Elmanouni, D., Raymond, K. N., and Durbin, P. W. (1992) *Int. J. Radiat. Biol.*, **62**, 487–97.

Stumpf, T., Fanghänel, T., and Grenthe, I. (2002) *J. Chem. Soc., Dalton Trans.*, 3799–804.

Sullivan, J. C. and Hindman, J. C. (1954) *J. Am. Chem. Soc.*, **76**, 5931–4.

Sullivan, J. C., Cohen, D., and Hindman, J. C. (1955) *J. Am. Chem. Soc.*, **77**, 6203–4.

Sullivan, J. C., Cohen, D., and Hindman, J. C. (1957) *J. Am. Chem. Soc.*, **79**, 4029–34.

Sullivan, J. C., Zielen, A. J., and Hindman, J. C. (1960) *J. Am. Chem. Soc.*, **82**, 5288–92.

Sullivan, J. C., Hindman, J. C., and Zielen, A. J. (1961) *J. Am. Chem. Soc.*, **83**, 3373–8.

Sullivan, J. C. (1962) *J. Am. Chem. Soc.*, **84**, 4256–9.

Sullivan, J. C. (1964) *Inorg. Chem.*, **3**, 315–19.

Sullivan, J. C. and Zielen, A. J. (1969) *Inorg. Nucl. Chem. Lett.*, **5**, 927–31.

Sullivan, J. C., Gordon, S., Cohen, D., Mulac, W. A., and Schmidt, K. H. (1976) *J. Phys. Chem.*, **80**, 1684–6.

Sullivan, J. C., Nash, K. L., and Choppin, G. R. (1978) *Inorg. Chem.*, **17**, 3374–7.

Sullivan, J. C. and Nash, K. L. (1986) in *Inorganic and Bioinorganic Reaction Mechanisms,* vol. 4 (ed. A. G. Sykes), Academic Press, London, pp. 185–213.

Sullivan, J. C., Choppin, G. R., and Rao, L. F. (1991) *Radiochim. Acta*, **54**, 17–20.

Sutton, J. (1952) *Nature*, **169**, 235–6.

Swift, T. J. and Sayre, W. G. (1966) *J. Chem. Phys.*, **44**, 3567–74.

Szabó, Z., Aas, W., and Grenthe, I. (1997) *Inorg. Chem.*, **36**, 5369–75.

Szabó, Z. and Grenthe, I. (2000) *Inorg. Chem.*, **39**, 5036–43.

Szabó, Z., Moll, H., and Grenthe, I. (2000) *J. Chem. Soc., Dalton Trans.*, 3158-61.

Szabó, Z. (2002) *J. Chem. Soc., Dalton Trans.*, 4242–7 .

Tochiyama, O., Inoue, Y., and Narita, S. (1992) *Radiochim. Acta*, **58/59**, 129–36.

Tochiyama, O., Siregar, C., and Inoue, Y. (1994) *Radiochim. Acta*, **66/67**, 103–8.

Tomilin, S. V., Volkov, Y. F., Kapshukov, I. I., and Rykov, A. G. (1981) *Sov. Radiochem.*, **23**, 570–4, 574–8, 695–9.

Tomilin, S. V., Volkov, Y. F., Melkaya, R. F., Spiryakov, V. O., and Kapshukov, I. I. (1986) *Sov. Radiochem.*, **28**(3), 272–8.

Toraishi, T., Farkas, I., Szabó, Z., and Grenthe, I. (2002) *J. Chem. Soc., Dalton Trans.*, 3805–12.

Tsushima, S. and Suzuki, A. (2000) *J. Mol. Struct.* (*THEOCHEM*), **529**, 21–5.

Vallet, V., Wahlgren, U., Schimmelpfennig, B., Moll, H., and Szabó, Z., Grenthe, I. (2001) *Inorg. Chem.*, **40**, 3516–25.

Vallet, V., Wahlgren, U., Szabó, Z., and Grenthe, I. (2002) *Inorg. Chem.*, **41**, 5626–33.

Vdovenko, V. M., Romanov, G. A., and Shcherbakov, V. A. (1963) *Sov. Radiochem.*, **5**, 624–7.

Vodovatov, V. A., Mashirov, L. G., and Suglobov, D. N. (1979) *Sov. Radiochem.*, **21**(6), 711–16.

Wahlgren, U., Moll, H., Grenthe, I., Schimmelpfennig, B., Maron, L., Vallet, V., and Gropen, O. (1999) *J. Phys. Chem. A*, **103**, 8257–64.

Walch, P. F. and Ellis, D. E. (1976) *J. Chem. Phys.*, **65**, 2387–92.

Wang, Z., Felmy, A. R., Xia, Y. X., and Mason, M. J. (2003) *Radiochim. Acta*, **91**, 329–37.

Werner, A. (1913) *Neu Anschauungen auf dem Gebiet der anorganischen Chemie,* 3rd edn, Vieweg Sohn, Braunschweig.

Wilkins, R. (1974) *The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes,* Allyn and Bacon, Boston.

Williams, K. R. and Choppin, G. R. (1974) *J. Inorg. Nucl. Chem.*, **36**, 1849–53.

Williams, C. W., Blaudeau, J.-P., Sullivan, J. C., Antonio, M. R., Bursten, B. E., and Soderholm, L. (2001) *J. Am. Chem. Soc.*, **123**, 4346–7.

Wimmer, H., Kim, J. I., and Klenze, R. (1992) *Radiochim. Acta*, **58/59**, 165–71.

Xu, J., Kullgren, B., Durbin, P. W., and Raymond, K. N. (1995) *J. Med. Chem.*, **38**, 2606–14.

Yaozhong, C., Bingmei, T., and Zhangji, L. (1993) *Radiochim. Acta*, **62**, 199–201.

Yusov, A. B. and Shilov, V. P. (1999) *Radiochemistry*, **41**, 1–23.

Yusov, A. B. and Fedoseev, A. M. (2003) *Russ. J. Coord. Chem.*, **29**, 582–90.

Zhao, P. H., Romanovski, V. V., Whisenhunt, D. W., Hoffman, D. C., Mohs, T. R., Xu, J. D., and Raymond, K. N. (1999) *Solvent Extr. Ion Exch.*, **17**, 1327–53.

Zhu, Y., Chen, J., and Jiao, R. (1996) *Solvent Extr. Ion Exch.*, **14**, 61–8.

Zielen, A. J. (1959) *J. Am. Chem. Soc.*, **81**, 5022–8.

Zielen, A. J. and Cohen, D. (1970) *J. Phys. Chem.*, **74**, 394–405.