CHAPTER FIFTEEN

SUMMARY AND COMPARISON OF PROPERTIES OF THE ACTINIDE AND TRANSACTINIDE ELEMENTS

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15.1 INTRODUCTION

15.1.1 Scope

This chapter is intended to provide a unified view of selected aspects of the physical, chemical, and biological properties of the actinide elements, their typical compounds, and their ions in aqueous solutions. The f-block elements have many unique features, and a comparison of similar species of the lanthanide and actinide transition series provides valuable insights into the properties of both. Comparative data are presented on the electronic configurations, oxidation states, oxidation–reduction (redox) potentials, thermochemical data, crystal structures, and ionic radii of the actinide elements, together with important topics related to their environmental properties and toxicology. Many of the topics in this chapter, and some that are not discussed here, are the subjects of subsequent chapters of this work, which should be consulted for more comprehensive treatments. This chapter provides an opportunity to discuss the biological and environmental aspects of the actinide elements, subjects that were barely mentioned in the first edition of this work and discussed only briefly in the second edition, but have assumed great importance in recent years. This chapter also provides a summary of the chemical properties of the transactinide elements that have been characterized.

15.1.2 The actinide concept

The actinide concept has achieved nearly universal acceptance as a way of integrating the transuranium elements into the periodic table. This concept was first expounded by G. T. Seaborg in 1944 (Seaborg *et al.*, 1949, pp. 1492–524, especially pp. 1517–20) and first enunciated in public on November 16, 1945 (C&E News, 1945). The chemical and electronic evidence that established the actinides as an inner transition series has been recently reviewed (Gruen, 1992). A succinct summary of this important principle will therefore be sufficient here.

The actinide concept considers the elements with atomic numbers 89–103 to be members of a transition series, the first member of which is actinium (atomic number 89). The elements with atomic numbers 89–103 are thus analogs of the lanthanide transition series that starts with lanthanum (atomic number 57) and includes the rare earth elements cerium through lutetium (atomic number 71). It is important, in comparing the lanthanide and actinide transition series, to keep in mind that the electronic configuration of any given element may be significantly different in the gaseous atoms, in ions in solids or solutions, and in the metallic state. In the lanthanide 3+ ions, 14 4f electrons are added in sequence beginning with cerium, atomic number 58 (Table 15.3). In the actinide series, 5f electrons are added successively beginning formally with thorium (atomic number 90) and ending with lawrencium (atomic number 103). Note the qualification 'formally.' No compelling evidence exists to show that thorium metal, or thorium ions in solution or in any of its well-defined compounds, contain 5f electrons. There is convincing evidence that protactinium metal displays 5f electron character, as is expected for the third member of an actinide series (Zachariasen, 1973; Fournier, 1976; Haire *et al.*, 2003).

The subsequent trivalent ions of the actinide series contain their appropriate complements of 5f electrons. Although there are important differences between the actinide and lanthanide elements, there are also striking similarities. The metallic elements and 3+ ions with half-filled f-electron shells, for example, are of special interest because of the enhanced stability of this particular electron configuration. Curium (atomic number 96), with seven 5f electrons in the metal and 3+ species, has magnetic, optical, and chemical properties that are remarkably similar to those of gadolinium (atomic number 64), with seven

4f electrons, as would be expected from the actinide concept. The principal differences between the two transition series arise largely from the lower binding energies and less effective shielding by outer electrons of 5f as compared to 4f electrons. Both the similarities and the differences between the actinide and lanthanide series have had great heuristic value in actinide element research. Further discussion of the electronic structure of the actinide elements is given in Section 15.4. Much more detailed expositions of the actinides as a 5f transition series are given in subsequent chapters.

15.2 SOURCES OF ACTINIDE AND TRANSACTINIDE ELEMENTS

15.2.1 Natural sources

The elements actinium through plutonium occur in nature. Only the elements thorium, protactinium, and uranium are present in amounts sufficient to warrant extraction from natural sources. Thorium and uranium are widely disseminated in the Earth's crust ($\sim$10000 and $\sim$3000 μg kg^{-1} respectively), and, in the case of uranium, in significant concentrations in the oceans (3.3 μg L^{-1}). More importantly, thorium and uranium are found highly enriched in certain mineral formations, and are obtained by conventional mining operations. The richest deposits of uranium are found in northern Saskatchewan, Canada. The annual world production of uranium from uranium ore in the period 1995–2000 was about 35000 metric tons of uranium oxide. Proven uranium reserves were about 3.2 million metric tons, with the richest deposits in Canada, Kazakhstan, USA, and Australia (World Energy Council, 1988). Thorium reserves were estimated at 1.2 million metric tons in 2004 (U.S. Geological Survey, 2002), but this estimate would be much higher if thorium extraction were economically viable; the largest deposits are in India, Australia, and the U.S. Extraction of thorium and uranium from their ores had been practiced for many years before the discovery of the transuranium elements, and an extensive technology exists for the extraction of thorium and uranium from many different types of ores.

Hundreds of thousands of tons of uranium have been processed for isotopic separation. Five grades of isotopically separated uranium are commonly recognized: depleted uranium (less than 0.71% ^{235}U), natural uranium (0.71% ^{235}U), low-enriched uranium (LEU) (0.71–20% ^{235}U), highly enriched uranium (HEU) (20–90% ^{235}U), and weapon-grade uranium (greater than 90% ^{235}U). Of these grades, HEU and weapon-grade uranium are the most important. HEU is produced (almost in equal amounts by gaseous diffusion or centrifuge enrichment) from natural uranium for use in nuclear weapons and for use in commercial nuclear reactors. Worldwide, at the end of 1994, 450 metric tons of HEU (calculated as weapon-grade equivalent) was inside nuclear weapons and 1300 metric tons had been removed from weapons. An additional 20 metric tons exist in civil inventories. This total (1770 metric tons) is slowly decreased (20 metric tons per year in 1996) by blending down of Russian HEU (Albright *et al.*, 1996).

Neptunium (^{237}Np and ^{239}Np) and plutonium (^{239}Pu) are present in extremely minute amounts in nature as a result of natural nuclear reactions with neutrons in uranium ores. The longer-lived ^{244}Pu has been found in the rare earth mineral bastnasite to the extent of 1 part in 10^{18}, and may possibly be a primordial endowment (see Section 15.8.1).

15.2.2 Neutron irradiation

Actinium and protactinium are decay products of the naturally occurring uranium isotope ^{235}U and are present in uranium minerals in such low concentration that recovery from natural sources is a very difficult task. By comparison, it is relatively straightforward to obtain actinium, protactinium, and most of the remaining transuranium elements by neutron irradiation of elements of lower atomic number in nuclear reactors (Seaborg, 1963, 1978; Hyde *et al.*, 1964). Thus, actinium has been produced in multigram quantities by the transmutation of radium with neutrons produced in a high-flux nuclear reactor:

$$^{226}\mathrm{Ra} + \mathrm{n} \rightarrow {}^{227}\mathrm{Ra} + \gamma$$

$$^{227}\mathrm{Ra} \rightarrow {}^{227}\mathrm{Ac} + \beta^-$$

The product actinium can be separated from the precursor radium by solvent extraction or ion exchange, and gram amounts of actinium have been obtained by these procedures. This is not at all an easy task, considering the highly radioactive substances involved and the hazards of radon emission that accompanies these nuclear reactions, but it is preferable by far to extraction from natural sources. Protactinium can be produced by the nuclear reactions:

$$^{230}\mathrm{Th} + \mathrm{n} \rightarrow {}^{231}\mathrm{Th} + \gamma$$

$$^{231}\mathrm{Th} \rightarrow {}^{231}\mathrm{Pa} + \beta^-$$

The amount of ^{231}Pa produced in this way, however, is much less than the amounts (more than 100 g) of protactinium obtained from residues accumulated from the very large-scale extraction of uranium from ores. Because of the extreme tendency of protactinium(v) to form colloidal polymers that are easily adsorbed on solid surfaces, and cannot be removed from aqueous media by solvent extraction, the recovery of protactinium from uranium ore processing residues can only be described as a heroic enterprise.

Neptunium-237 is a long-lived isotope of element 93 that is produced in kilogram amounts. It is formed as a by-product in nuclear reactors when neutrons produced in the fission of uranium-235 react with uranium-238:

$$^{238}\mathrm{U} + \mathrm{n} \rightarrow {}^{237}\mathrm{U} + 2\mathrm{n}$$

$$^{237}\mathrm{U} \rightarrow {}^{237}\mathrm{Np} + \beta^-$$

Neptunium-237 is also formed by neutron capture in uranium-235:

$$^{235}\mathrm{U} + \mathrm{n} \rightarrow {}^{236}\mathrm{U} + \gamma$$

$$^{236}\mathrm{U} + \mathrm{n} \rightarrow {}^{237}\mathrm{U} + \gamma$$

$$^{237}\mathrm{U} \rightarrow {}^{237}\mathrm{Np} + \beta^-$$

The waste solutions from the processing of irradiated uranium fuel usually contain the neptunium, which can be isolated and purified by a combination of solvent extraction, ion exchange, and precipitation techniques.

The strategically important isotope ^{239}Pu is produced by the ton in nuclear reactors. Excess neutrons from the fission of uranium-235 are captured by uranium-238 to yield plutonium-239:

$$^{238}\mathrm{U} + \mathrm{n} \rightarrow {}^{239}\mathrm{U} \rightarrow {}^{239}\mathrm{Np} \rightarrow {}^{239}\mathrm{Pu}$$

Neutrons also cause the uranium nuclei to fission:

$$^{235}\mathrm{U} + \mathrm{n} \rightarrow \text{fission products} + 2.5n + 200\,\mathrm{MeV}$$

After removal from the reactor, the irradiated fuel can be chemically separated to extract the plutonium and also to separate the highly radioactive fission products.

Plutonium produced in nuclear reactors in which the fuel is irradiated for long periods of time contains plutonium isotopes with mass numbers up to 244, formed from ^{239}Pu by successive neutron capture. Industrial-scale processes for the separation and purification of plutonium are described in detail in Chapter 7. Three grades of plutonium are commonly recognized: weapon-grade plutonium (less than 7% ^{240}Pu), fuel-grade plutonium (7–18% ^{240}Pu), and reactor-grade plutonium (more than 18% ^{240}Pu).

Plutonium is an element that was until recently produced in ‘production’ reactors, i.e. reactors that were dedicated to produce nuclear materials for military purposes. More than 260 metric tons of military plutonium have been produced and separated worldwide (Albright *et al.*, 1996). Plutonium is also formed as a by-product of electricity production in all commercial (civilian) nuclear power reactors. As of 2000 the total ‘discharge’ of plutonium (plutonium in and separated from civilian spent fuel) from commercial nuclear power reactors was estimated to be 1380 metric tons, and this amount is predicted to increase by 741 metric tons in the decade 2001–10 (Albright *et al.*, 1996).

Although HEU and weapon-grade plutonium are primarily for military purposes and the lower grades are used in commercial nuclear reactors, enriched uranium and plutonium of all grades are commonly discussed together because ^{235}U and ^{239}Pu are the two primary fissile isotopes and because they have the greatest security risk of potential diversion from peaceful to military or terrorist uses. Therefore, the total inventory must include both military and civilian stocks.

Plutonium has been separated from civilian reactor fuel principally at the B205 reprocessing plant in UK, at three reprocessing plants (UP1, UP2, UP3) in France, at Wiederaufarbeitungsanlage Karlsruhe (WAK) in Germany, and at Tokaimura in Japan. As of 1995, 132 metric tons of civilian plutonium had been removed at these plants. When plutonium separated by other countries is added, the total at the end of 1993 was 145 metric tons, of which 21 metric tons was in use in fast reactors and 17 metric tons in thermal reactors. The world annual separation of civilian plutonium continues at the rate of ca. 16 metric tons per year. By 2010, it is predicted that 437 metric tons will have been separated (Albright *et al.*, 1996).

Worldwide, at the end of 1994, 70 metric tons of plutonium were contained in nuclear weapons and 160 metric tons had been removed from weapons. The world inventory of all types of plutonium was 1160 metric tons at the end of 1994. The majority of this plutonium, 755 metric tons, was unseparated plutonium remaining in spent reactor fuel. This increases at the rate of approximately 70 metric tons per year.

The isotope ^{238}Pu is an important heat source for terrestrial and extraterrestrial applications (Section 15.11.2). The heat is generated by its nuclear alpha-particle decay. This isotope is available in kilogram quantities from the neutron irradiation of neptunium-237:

$$^{237}\mathrm{Np} + \mathrm{n} \rightarrow {}^{238}\mathrm{Np} \rightarrow {}^{238}\mathrm{Pu}$$

followed by chemical separation. Its 87.7 year half-life makes it the best isotope for this purpose. High-level waste from the isolation of plutonium-239 contains much larger quantities of plutonium-238, as well as heavier plutonium isotopes, formed by various nuclear reactions in reactor fuel elements, but the isotopic separation would be difficult and prohibitively expensive. The plutonium in a typical pressurized water reactor (PWR) fuel is approximately 1.3% ^{238}Pu after 33000 MWd ton^{-1} burnup (Albright *et al.*, 1996). As of 2000 approximately 10 metric tons of plutonium-238 exists in stored spent fuel elements and process residues accumulated in the U.S. and by the European Community, mixed with heavier plutonium isotopes (Albright *et al.*, 1996).

The elements americium and curium are obtained as by-products of the large-scale production of plutonium-239, or by the irradiation of plutonium-239 or isotopes of transplutonium elements in special high-neutron-flux reactors. The plutonium in a typical PWR fuel is approximately 14% ^{241}Pu after 33000 MWd ton^{-1} burnup (Albright *et al.*, 1996), producing ^{241}Am by beta decay with a half-life of 13.2 years. Kilogram quantities of americium-241 can be separated from irradiated fuel by a combination of precipitation, ion exchange, and solvent extraction.

Isotopes of curium are also found in waste streams from plutonium-239 production, but in amounts smaller than those of americium. Curium (as ^{242}Cm and ^{244}Cm) is produced in nuclear reactors primarily by the beta decay of ^{242}Am and ^{244}Am, isotopes that were formed by neutron capture in ^{241}Am and ^{243}Am, respectively. The amount of ^{244}Cm accumulated in process wastes and in unprocessed irradiated fuel elements as of 2000 is estimated to be more than 1 metric ton (NEA, 2002). The high specific radioactivity (18.1-year half-life) of ^{244}Cm means that it has to be considered in separation schemes for reprocessing and transmutation, but it decays to low enough levels in a few hundred years that long-term storage is not a concern. Separation and purification of curium and americium is best carried out by the solvent extraction procedures described below because both are present as $3+$ ions, which have similar chemical properties (see Section 15.3.6).

The sequence of neutron captures and beta decays that forms transuranium elements by slow neutron capture starting with plutonium-239 is shown in Fig. 15.1. A high neutron flux is essential to expedite the production of transplutonium elements. Fig. 15.2 shows that, even with a neutron flux in excess of 10^{14} cm^{-1} s^{-1}, years of irradiation may be required to attain useful conversions. Starting with 1 kg of ^{239}Pu, about 1 mg of ^{252}Cf would be present after 5–10 years of continuous irradiation at a neutron flux of 3×10^{14} cm^{-1} · s^{-1}. To increase the production rate, large quantities of ^{239}Pu can first be irradiated in production reactors, followed by continued irradiation in higher-neutron-flux reactors. The High Flux Isotope Reactor (HFIR) at Oak Ridge National

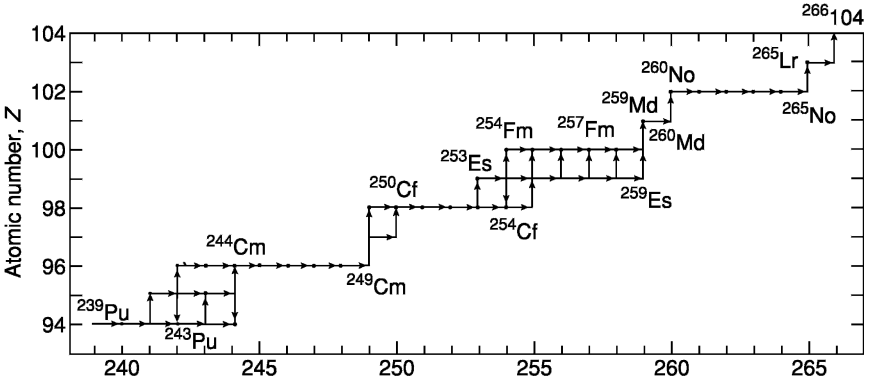


Fig. 15.1 *Nuclear reaction sequence for production of transplutonium elements by intensive slow-neutron irradiation. The principal path is shown by heavy arrows (horizontal, neutron capture; vertical, beta decay). The sequence above ^{258}Fm is a prediction.*

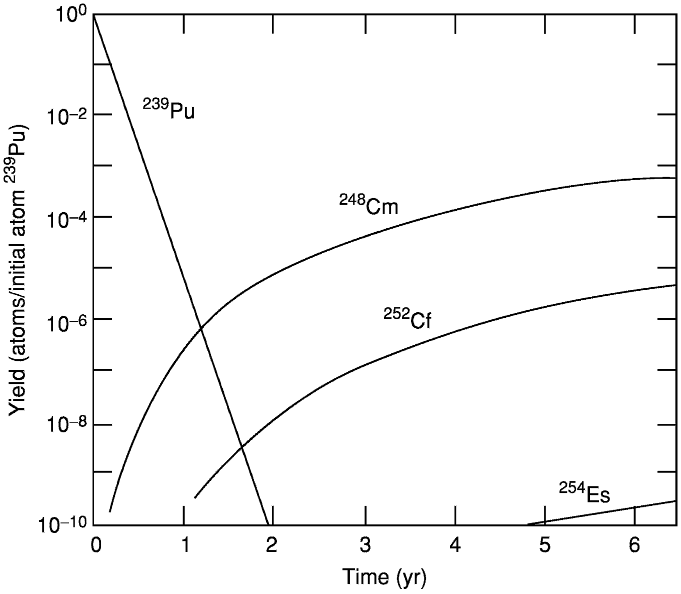


Fig. 15.2 *Production of some transplutonium nuclides by irradiation of* ^{239}*Pu at a neutron flux of* 3×10^{14} cm^{-2} s^{-1}.

Laboratory in Tennessee can provide neutron fluxes of about 2×10^{15} cm$^{-2} \cdot$ s^{-1}. This reactor and tritium-production reactors that were in operation from 1953 to 1993 at the Savannah River Site in South Carolina, have made major contributions to the production of transcurium elements. A special facility, presently called the Radioisotope Engineering Development Center (REDC), was established at Oak Ridge in 1966 to fabricate plutonium targets, to extract transplutonium elements from the highly irradiated targets, and to provide pure samples of transplutonium isotopes as heavy as ^{257}Fm for research and industry. Neutron irradiation cannot be used to prepare the elements beyond fermium (^{257}Fm) because some of the intermediate nuclides have such short half-lives that the low equilibrium concentrations present effectively prevent the formation of significant amounts of the desired isotopes. Thus, only milligram amounts of einsteinium and picogram amounts of fermium can be obtained by protracted neutron irradiation even under the most favorable circumstances. Table 15.1 lists the past production rates of isotopes of elements from curium-248 to fermium-257 in the Oak Ridge HFIR/REDC operation (National Research Council, 1983; Keller *et al.*, 1984; Alexander, 2005). The SM-2 loop reactor in Russia has similar power and flux levels, giving it the potential for producing similar quantities of these transcurium isotopes. Isotopes that are sufficiently long-lived for work in weighable amounts are obtainable at least in

Table 15.1 *Production of transcurium isotopes in the U.S.*[a]

Isotope	*Half-life*	*Amount/year* (1983)	*Amount/campaign* (2004)
^{248}Cm	3.48×10^5 yr	150 mg[b]	100 mg[b]
^{249}Bk	330 d	50 mg	45 mg
^{249}Cf	351 yr	50 mg[c]	<45 mg[c]
^{252}Cf	2.645 yr	500 mg	400 mg
^{253}Es	20.47 d	2 mg[d]	1–2 mg[d]
^{254}Es	275.7 d	3 μg	4 μg
^{257}Fm	100.5 d	1 pg	1 pg

[a] One or two separation campaigns per year until about 1995; one campaign every 18–24 months from about 1995 to 2003.

[b] From alpha decay of ^{252}Cf.

[c] From beta decay of ^{249}Bk.

[d] Mixed with 0.06–0.3% ^{254}Es; chemical separation of ^{253}Cf followed by its beta decay can yield ~200 μg of isotopically pure ^{253}Es.

principle for all of the actinide elements through einsteinium. The elements above einsteinium appear likely to remain amenable to chemical study only by tracer techniques because (except for ^{257}Fm) only isotopes with short half-lives are known, and because it is unlikely that isotopes of the elements beyond einsteinium can be formed in weighable quantities by neutron irradiation or any other process.

Very heavy elements have been detected under circumstances where very intense neutron fluxes were produced. Such is the case for a few microseconds after a thermonuclear explosion. Isotopes of einsteinium and fermium were first discovered in the debris of the first thermonuclear explosion detonated at Eniwetok Atoll in November 1952 (Hyde *et al.*, 1964; Choppin *et al.*, 2002, p. 423). The route whereby elements of high atomic number are formed in the detonation of a thermonuclear device is again multiple neutron capture in ^{238}U, which is a component of the thermonuclear device. Thus, the synthesis of ^{255}Fm in the explosion occurred by way of ^{255}U (formed by the capture of 17 neutrons in ^{238}U) followed by a long sequence of short-lived beta decays that take place after the neutron capture reactions are complete:

$$^{238}\mathrm{U} + 17\mathrm{n} \rightarrow {}^{255}\mathrm{U} \xrightarrow{\beta^-} {}^{255}\mathrm{Np} \xrightarrow{\beta^-} {}^{255}\mathrm{Pu} \overset{\beta^-}{\cdots} {}^{255}\mathrm{Fm}$$

15.2.3 Heavy-ion bombardment

In lieu of the extraordinarily intense neutron fluxes associated with a thermonuclear explosion, synthesis of the transfermium elements in amounts sufficient to study their chemical properties has depended on nuclear reactions of charged particles (i.e. ^{4}He, ^{10}B, ^{12}C, and ^{16}O accelerated to appropriate energies in heavy-ion accelerators) with targets of an actinide element of a lower atomic number. Such syntheses are made very difficult by the limited availability of target materials of high atomic number, by the low reaction yields, and by the difficulties inherent in the separation, isolation, and characterization of very short-lived radioactive isotopes. A distinctive feature of these procedures is that the product nuclide is produced and collected one atom at a time, necessitating isolation and identification procedures that are highly innovative. However, the obstacles have been successfully surmounted, and numerous isotopes of the heaviest actinide elements mendelevium, nobelium, and lawrencium have been produced, their nuclear properties measured, and salient features of their chemical properties established (Ghiorso, 1982 and Chapter 13, this work).

The currently known transactinide elements 104 through 111 were discovered at Berkeley, Dubna, and Darmstadt (see Table 1.1 and Chapter 14) using physical and nuclear techniques for synthesis, separation, and identification. The longest known confirmed half-lives for these elements range from 75 s for Rf to only ~40 ms for Mt. Discoveries of isotopes of Rf and Db with half-lives of seconds to minutes permitted investigations of their chemical properties after 1970. However, the first isotope discovered for element 106, Sg, had a half-life of just under a second, and the first-discovered isotopes of elements 107 through 111 had half-lives of only milliseconds. Nuclear theorists predicted that half-lives of isotopes of these elements near the deformed nuclear shells they calculated to be at $Z = 108$ and $N = 162$ would be stabilized by orders of magnitude. These predictions motivated experimentalists to design suitable production reactions, and in 1994 isotopes of Sg with alpha decay half-lives estimated to be tens of seconds were produced in reactions of the actinide target ^{248}Cm with ^{22}Ne beams and detected by physical means by a Dubna/Lawrence Livermore National Laboratory (LLNL) collaboration. These results helped to substantiate the theoretical predictions and innovative techniques to perform chemical investigations of Sg, Bh, and Hs were undertaken during the period 1997–2003. Isotopes of these elements with half-lives as long as 15–20 s were successfully identified in these studies by observation of their alpha decay to known daughter isotopes. These studies furnished valuable information about the chemical properties of Sg in both gas and aqueous phases, and of Bh and Hs in the gas phase.

Comparison of the observed chemical properties with the proposed lighter homologs in the periodic table confirms their placement in the periodic table as members of a 6d transition series; nevertheless there is some evidence for deviations that may be attributable to the influence of relativistic effects, expected to be strongest in the heaviest elements. To date, no chemical studies have been conducted beyond Hs because longer-lived isotopes of Mt have not yet been identified. A surprising amount of information has been obtained about the oxidation states of the transfermium and transactinide ions in solution even though in many cases only a few atoms or even a single atom at a time was available for study. Discoveries of isotopes of elements 110, 111, and 112 were reported in 1995; for element 110 the reports have been confirmed and the name darmstadtium, symbol Ds, was approved by IUPAC in 2003. The name roentgenium, symbol Rg, for element 111 was approved by IUPAC late in 2004. A consortium of scientists from Dubna and LLNL has reported elements 113 through 116 (Table 1.1), but these have not yet been confirmed at another laboratory. The chemistry of transactinide elements and their predicted chemical and nuclear properties is discussed in Chapter 14.

An exciting frontier is the additional exploration of the chemical properties of the heavier transactinides, especially those beyond element 108 where relativistic effects become ever more important. Effects on chemical bonding have not been investigated satisfactorily even for the beginning of the transactinides. The synthesis of longer-lived isotopes of the elements beyond ^{108}Hs will be required to investigate even their rudimentary chemical properties, e.g. whether element 112 is a noble metal or a rare gas.

Some recent theoretical calculations indicate that in addition to the experimentally confirmed island of deformed stability near $Z = 108$, $N = 162$ and the island of spherical stability originally predicted to be around atomic number $Z = 114$ and neutron number $N = 184$, there may be islands of spherical stability around $Z = 120$ and $N = 172$, and $Z = 124$ or 126 and $N = 184$. If the reports by the Dubna/LLNL collaboration of the production in relatively high yield of neutron-rich, long-lived isotopes of elements 112 through 116 in irradiations of ^{244}Pu and other actinide targets with ^{48}Ca projectiles are confirmed, then many isotopes will become available for chemical studies. This would constitute a whole new region of nuclear stability with neutron numbers from $\sim$163 to $\sim$173, which could truly be called a region of 'superheavy elements.' The chemical properties of elements beyond 122 are currently impossible to predict and classify on the basis of the periodic table because the energy spacing for the 7d, 6f, and 5g levels, and later, for the 9s, $9p_{1/2}$, and $8p_{3/2}$ levels become so close and overlapping that clear structures on the basis of pure p, d, f, and g blocks are no longer distinguishable. An international collaborative effort will be required to initiate and implement such a frontier research program.

15.2.4 Atomic weights

The question of atomic weights deserves a brief comment. Many of the radionuclides listed in Table 15.2 can be obtained in high isotopic purity. Compounds of curium, for example, will have different formula weights depending on the particular curium isotope that is present in the compound. Atomic and molecular weights must be calculated from the relative abundances of isotopes present in a given sample.

Table 15.2 *Long-lived actinide nuclides suitable for physical and chemical investigation.*

Element	*Isotope*	*Half-life*
actinium	^{227}Ac	21.772 yr
thorium	^{232}Th	1.405×10^{10} yr
protactinium	^{231}Pa	3.276×10^{4} yr
uranium	^{233}U	1.592×10^{5} yr
	^{238}U^{a}	4.468×10^{9} yr
neptunium	^{236}Np	1.54×10^{5} yr
	^{237}Np	2.144×10^{6} yr
plutonium	^{238}Pu	87.7 yr
	^{239}Pu	2.411×10^{4} yr
	^{240}Pu	6564 yr
	^{242}Pu	3.733×10^{5} yr
	^{244}Pu	8.08×10^{7} yr
americium	^{241}Am	432.2 yr
	^{243}Am	7370 yr
curium	^{244}Cm	18.10 yr
	^{245}Cm	8500 yr
	^{246}Cm	4760 yr
	^{247}Cm	1.56×10^{7} yr
	^{248}Cm	3.48×10^{5} yr
	^{250}Cm	~8300 yr^{b}
berkelium	^{247}Bk^{c}	1380 yr
	^{249}Bk	330 d
californium	^{249}Cf	351 yr
	^{252}Cf	2.645 yr
einsteinium	^{253}Es	20.47 d
	^{254}Es	275.7 d
	^{255}Es	39.8 d
fermium	^{257}Fm	100.5 d

[a] Natural isotopic composition is 99.275% ^{238}U, 0.720% ^{235}U, and 0.005% ^{234}U. Half-life given is for the major constituent ^{238}U.

[b] Produced only in very small amounts from neutron irradiations in thermonuclear explosions.

[c] Produced so far only in tracer quantities from charged particle irradiations.

15.3 EXPERIMENTAL TECHNIQUES

15.3.1 Hazards

All of the actinide elements, with the exception of uranium and thorium, are radioactive to such a degree that handling requires special equipment and shielded facilities (Gmelin, 1973; Choppin *et al.*, 2002, pp. 498–513; this work, Figs. 1.2–1.4) when samples above the tracer level are handled. The special containment and manipulation techniques for work with the actinide elements are necessitated by the potential health hazards to the investigator and other occupants of the laboratory. Containment in the form of hoods and gloved boxes is now standard, and these are available through normal commercial channels. Shielded facilities are more specialized, and, for the most part, are found in laboratories devoted to the study or processing of the actinide elements.

The toxicity of the actinide elements, which requires an absolute barrier between the experiment and the experimenter, is dictated to only a small extent by external radiation hazards. Plutonium-239 is intensely radioactive, emitting 1.4×10^8 alpha particles per milligram per minute. However, the alpha radiation from plutonium-239 can easily be shielded by even a thin sheet of paper. It is the consequences of inhalation and ingestion that make plutonium-239 and most isotopes of the other actinide elements such toxic substances. Plutonium-239, inhaled into the lungs as fine particulate matter, is deposited in the lungs or translocated to the bone, and, over a period of time, may give rise to lung or bone neoplasms (see Section 15.10). The biological properties of the actinide elements are discussed in more detail in Sections 15.9 and 15.10 and in Chapter 31.

15.3.2 Long-lived actinide nuclides

Isotopes sufficiently long-lived for work with weighable amounts are in principle available for all the actinide elements through einsteinium (element 99). Long-lived actinide isotopes particularly suitable for physical and chemical investigations by more or less ordinary laboratory procedures are listed in Table 15.2. Not all of these are available in high isotopic purity. The elements above fermium, it appears, will always require tracer techniques for their investigation. This is not as restrictive a prospect as it may seem, for an astonishing amount of chemical information has been acquired from the few atoms of the heaviest actinide and transactinide elements that have already been prepared.

Most of the chemical studies with plutonium have been carried out with ^{239}Pu, but the isotopes ^{242}Pu and ^{244}Pu are more suitable (but available in very limited quantities) because of their longer half-lives and therefore lower specific activities. The solution chemistry of shorter-lived actinide ions in concentrated aqueous solution is complicated by radiolysis products such as hydrogen peroxide rapidly formed by the high-energy alpha particles produced by radioactive decay. In solid compounds, the high-energy heavy recoil particles can seriously damage or even destroy the crystal lattice. Americium chemistry, often studied with ^{241}Am, which emits about 8×10^9 alpha particles per milligram per minute, has fewer ambiguities when the studies are performed with ^{243}Am, which has a specific alpha activity about 20 times less than ^{241}Am. Much of the early research with curium used the isotopes ^{242}Cm and ^{244}Cm. The heavier curium isotopes, especially ^{248}Cm, obtained in relatively high isotopic purity as the alpha-particle decay daughter of ^{252}Cf, make life much simpler for the investigator, although ^{248}Cm decays in small part by spontaneous fission, which creates a significant neutron hazard. The isotope ^{249}Bk and Cf as a mixture of the isotopes ^{249}Cf, ^{250}Cf, ^{251}Cf, and ^{252}Cf are available from the intense neutron irradiation of lighter elements. The most useful isotope for the study of californium is ^{249}Cf, which can be isolated in pure form from the beta decay of its parent ^{249}Bk. The isotope ^{253}Es (half-life 20.47 days), another product of intense neutron irradiation, is used to study the chemical properties of einsteinium, but the longer-lived ^{254}Es (half-life 275.7 days) would be more useful for work with macroscopic quantities. However, it is not produced initially free of ^{253}Es. There are severe problems in working with weighable amounts of berkelium, californium, and einsteinium because of their intense radioactivity. Spontaneous fission is an important mode of decay for ^{252}Cf (half-life 2.645 years): 1 μg of this isotope emits approximately 1.4×10^8 neutrons min^{-1}. Californium produced in the highest-flux reactors contains sufficient ^{252}Cf to cause very severe handling and shielding problems because of the spontaneous-fission neutron flux. Remote control manipulation is essential when more than a few micrograms of ^{252}Cf are used. While spontaneous fission makes for problems in chemical studies, ^{252}Cf provides very convenient neutron and fission fragment sources, which have important scientific, medical, and industrial uses (see Sections 15.11.3 and 15.11.4).

15.3.3 Tracer techniques

Investigations may be carried out on the tracer level, where solutions are handled in ordinary-sized laboratory equipment, but where the substance studied is present in extremely low concentrations. Concentrations of the radioactive species of the order of 10^{-12} M or much less are not unusual in tracer work with radioactive nuclides. A much larger amount of a suitably chosen nonradioactive host or carrier is subjected to chemical manipulation, and the behavior of the radioactive species (as monitored by its radioactivity) is determined relative to the behavior of the carrier. Thus the solubility of an actinide compound can be judged by whether the radioactive ion is carried by a precipitate formed by the nonradioactive carrier. Interpretation of such studies is made difficult by the adsorption of radioactive ions on vessel walls or colloidal particles in solution. Tracer studies provide information on the oxidation states of ions and complex-ion formation, and are used in the development of liquid–liquid solvent extraction and chromatographic separation procedures. Tracer techniques are not applicable to solid state or to most spectroscopic studies. Despite the difficulties inherent in tracer experiments, these methods continue to be used with the heaviest actinide and transactinide elements, where only a few to a few score atoms may be available (Benes and Majer, 1980).

15.3.4 Ultramicrochemical manipulations

Chemistry under the microscope often provides an alternative to tracer techniques. It is possible to work with microgram or even smaller amounts of material in very small volumes of solution not visible to the naked eye at ordinary concentrations, say 10^{-1} M to 10^{-3} M. Ultramicrochemical investigations yield results of normal validity, but skill, experience, a good microscope, and much patience are necessary to carry out such experiments. X-ray diffraction methods can be applied to microgram or even smaller samples of solid compounds. Many actinide element compounds have been identified and their molecular formulas established on samples of a few micrograms synthesized directly in the capillary that is subsequently used to record the X-ray diffraction pattern. With milligram amounts, operations can be readily carried out in a conventional manner. Most of the chemical results described in this book were obtained on about the milligram scale by semi-micro procedures. With highly radioactive isotopes (e.g. ^{253}Es), the microgram scale may still be preferred even when larger amounts of material are available. In the past, usable X-ray diffraction patterns were difficult to obtain from highly radioactive crystals because of radiation damage. Such problems are considerably ameliorated when smaller samples and modern methods of obtaining X-ray diffraction patterns are used.

15.3.5 Ion-exchange chromatography

Separations based on ion exchange have contributed to the science and technology of actinides in a variety of ways. In particular, the development of ion-exchange materials based on functionalized polymers (with well-characterized and reproducible properties) have enabled important procedures for both analysis and purification of actinides. Both cation-exchange resins containing (in particular) sulfonic and carboxylic acid groups, and anion-exchange resins with quaternary ammonium or methylpyridinium groups have been employed to separate actinides or to separate actinides from fission product lanthanides. Inorganic ion-exchange materials also have been used in actinide separations, particularly for waste management purposes. In this chromatographic technique (see Chapter 24), actinides, either as cations or anionic coordination complexes, are partitioned between a mobile aqueous phase and the solid resin phase. Actinide ions in the III, IV, V, and VI oxidation states are sorbed to different degrees and in different orders on cation and anion-exchange resins. The selectivity of separations is often determined by the complexants present in the mobile phase.

Ion-exchange separations can be rapid and selective and offer the inherent enhanced separation efficiency of being operable in a chromatographic mode. Because the elution order and approximate peak positions can be predicted with considerable confidence, ion exchange has been the key to the discovery of the transcurium elements. The power of the method can be judged from Fig. 15.3,

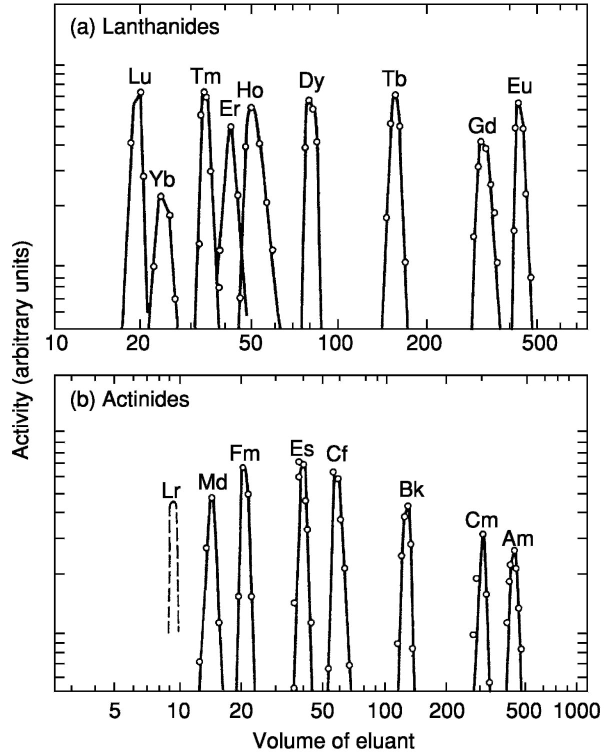


Fig. 15.3 *Elution of tripositive lanthanide and actinide ions on Dowex* 50 *cation-exchange resin and ammonium* α*-hydroxyisobutyrate eluant.* Lr^{3+} *band* (*dashed line*) *was predicted.*

which compares the order of elution of the trivalent lanthanide and actinide ions from the cation-exchange resin Dowex 50 (a copolymer of styrene and divinylbenzene containing sulfonic acid groups). The eluting agent is an aqueous solution of ammonium α-hydroxyisobutyrate. In this system elution occurs in the inverse order of atomic number for both lanthanide and actinide elements. The order of elution is determined by the relative stability of the aqueous complexes formed in the mobile phase. As a result, the differences between these adjacent metal ions are correlated with the variation of ionic radius with atomic number. There are many similarities between the 4f and 5f series of elements, but few parallels are more striking than those observed for the trivalent ions in ion exchange.

15.3.6 Liquid–liquid extraction

Liquid–liquid (or solvent) extraction is a separation technique that depends on the partition of ions between two immiscible liquid phases, one of which is usually an acidic aqueous solution (see Chapter 24). Under most circumstances, the organic phase contains a strongly lipophilic extracting agent that interacts with a metal cation to form an electroneutral lipophilic complex. Among the most important actinide extractants are tri(*n*-butyl)phosphate (TBP) (basis of the PUREX process), bis(2-ethylhexyl)phosphoric acid, octyl(phenyl)-*N*,*N*-diisobutyl-carbamoylmethylphosphine oxide (basis of the TRUEX process), and *N*,*N*-dimethyl-*N*′,*N*′-dibutyl-2-hexoxyethylmalonamide (basis of the DIAMEX process). Tertiary (e.g. tricaprylamine or trilaurylamine) or quaternary amines (e.g. tricaprylammonium chloride) can also accomplish effective and selective separations of actinide ions through the formation of lipophilic ion pairs of actinide ions associated with enough normally hydrophilic anions (like Cl^- or NO_3^-) to create an anionic coordination complex. As is the case for ion exchange, the most effective separations in solvent extraction are those relying on the differences in actinide oxidation states. Some classes of solvent extraction reagents are capable of the separation of the individual trivalent actinide cations, as in the ion exchange example above. In recent years, solvent extraction reagents capable of efficiently separating trivalent actinides from fission product lanthanides have emerged. Separations are achieved because the partition coefficients of individual actinide ions in a mixture are significantly different. For production purposes, solvent extraction enables rapid and efficient separations when applied in a countercurrent multistage process. Solvent extraction is widely used for actinide element separations both in laboratory investigations and on a large industrial scale.

15.3.7 Column partition chromatography

A technique closely related to liquid–liquid extraction, also discussed in Chapter 24, is column partition chromatography, sometimes referred to as extraction chromatography. Partition chromatography is essentially a solvent extraction system in which one of the liquid phases is made stationary by adsorption on a solid support. The other liquid phase is mobile. Extraction chromatographic materials are usually (but not always) employed for analytical separations using column chromatography, which significantly increases separation efficiency. Either the aqueous or the organic phase can be immobilized. The aqueous phase can be made stationary by adsorption on silica gel, diatomaceous earth, or 5–10 μm diameter microspheres of silica. The same extracting agents that are used in ordinary solvent extraction can be used in partition chromatography. The organic phase can be adsorbed on beads (50–200 μm in diameter) of poly(vinylchloride), poly(tetrafluoroethylene), poly(monochlorotrifluoroethylene), or other solid support. When the stationary phase is organic, the technique is referred to as reversed-phase partition chromatography. This technique is widely used in radioanalytical chemistry, though its application to large-scale separation of actinides from dissolved spent fuel has been considered.

15.4 ELECTRONIC CONFIGURATION

15.4.1 General considerations

Establishing the electronic configuration of the elements and their ions has historically been a primary objective in physical and chemical research. This stems from the conviction that it ought to be possible to deduce *a priori* many of the properties of an element and its compounds from a detailed knowledge of its electronic configuration, a goal that is still approaching full realization. There are other reasons why such information is of particular interest in actinide chemistry. The f-block elements have unusual electronic configurations, and the comparative aspects of lanthanide and actinide electronic structures, as manifested in the chemical and physical properties of homologous elements, is a matter of keen interest. The striking similarities and differences between corresponding elements of the two series provide important insights into the contributions that the valence-electron quantum numbers make to the physical and chemical properties of the f-block elements.

Information relevant to the electronic configuration can be obtained from X-ray absorption spectroscopy, atomic emission spectroscopy (AES), X-ray photoelectron spectroscopy, paramagnetic susceptibility measurements, electron paramagnetic resonance, electronic transition spectroscopy, transmission electron microscopy, X-ray and neutron crystallography, and atomic-beam experiments. Discussions of the theoretical and experimental aspects of atomic spectroscopy, magnetic properties, crystal structures of solids, and electronic absorption spectroscopy are found in the later chapters of this work.

15.4.2 Spectroscopic studies

In AES and inductively coupled plasma mass spectrometry (ICP-MS) the wavelengths of light emitted from a vaporized atom in an excited electronic state are used as a 'signature' of the atomic number of the atom. These techniques are now used routinely for elemental analyses of research, industrial, and environmental materials, but AES was essentially the technique used originally to characterize the electronic properties of actinides. In an electrical discharge most of the species produced are electrically neutral atoms, but among them are small numbers of ionized species that have lost one, two, or three of their valence electrons. Because the spectra result from changes in the quantum numbers of the valence electrons present in the atom or ion, it is possible in principle to make deductions about the electronic energy levels of the emitting species. In practice, however, there are very severe problems in the interpretation of the emission spectra of the actinide elements. In the free atoms in the gas phase, the valence electrons interact strongly with the 5f electrons and also with each other. Each 5f level is split by these interactions to give many energy levels that are more widely split than the 5f levels themselves. The result is an enormous number of lines in the emission spectra of actinide elements. In the uranium spectrum, 100000 lines have been measured, and between 5000 and 20000 lines have been measured for each of the elements from plutonium to berkelium. The number of assigned lines varies considerably but is much smaller, from about 2500 for uranium to about 100 for curium. The ground electronic configurations of neutral actinium, thorium, uranium, americium, berkelium, californium, and einsteinium were determined by atomic spectroscopy. The ground electronic structures of protactinium, neptunium, plutonium, curium, and fermium were deduced from atomic-beam experiments (Gmelin, 1973; see Chapter 16).

The dominant features of the electronic transition spectra of actinide ions in solution or in solid crystals arise for the most part from transitions within the $5f^N$ subshell. However, in the gas phase the predominant population consists of neutral atoms, which possess all of their valence electrons and therefore experience more interactions between the 5f electrons and the d- and s-shell valence electrons. The 5f electrons in actinide ions, either in crystals or in solution, are perturbed to a lesser extent because valence electrons in the 6d and 7s subshells are missing, and the 5f electrons are shielded from the electric fields of other ions by the remaining 6s and 6p electrons. The electronic transition spectra of actinide ions in solution therefore provide more information about the structure of the 5f levels, but the free-atom spectra provide more information about the interactions between the 5f and the valence electrons.

15.4.3 Electronic structure

Table 15.3 shows the assignments of the configuration (beyond the radon structure) of the ground-state gas-phase neutral atom of each of the elements from actinium to lawrencium, as well as the configurations of the singly charged, doubly charged, and triply charged gaseous atoms. Included for comparison are the ground-state neutral-atom and triply charged electronic configurations (beyond the xenon structure) of the 4f lanthanide elements and the configurations of the 3+ ions of both series. The similarities between the lanthanide and actinide elements were recognized from very early work on the actinides. It can be seen from Table 15.3 that the incorporation of the 14 5f electrons into the elements of the actinide series is not as regular as in the 4f series, especially in the actinide elements preceding curium.

The atomic spectra indicate quite clearly that the 6d levels of thorium in the gas-phase neutral atom are lower in energy than the 5f levels. As in other transition series, the relative energy levels of the electron shell being filled become lower as successive electrons are added, and, in the elements following thorium, the 5f shell appears clearly to be of lower energy than the 6d shell. Triply ionized Th^{3+} has one 5f electron in the gas phase as the ground configuration with the 6d configuration $\sim$1.25 eV higher. But in the very few molecular Th^{3+} compounds synthesized to date, the 6d configuration is stabilized by the

Table 15.3 *Electronic configurations of f-block and transactinide atoms and ions.*[a]

		Lanthanide series				*Actinide series*				
Element	*Gaseous atom*	M^{3+}(g)	M^{3+}(aq)	*Element*	*Gaseous atom*	M^{+}(g)	M^{2+}(g)	M^{3+}(g)	M^{3+}(aq)	M^{4+}(g)
La	$5d6s^2$			Ac	$6d7s^2$	$7s^2$	$7s$			
Ce	$4f5d6s^2$	$4f$	$4f$	Th	$6d^27s^2$	$6d7s^2$	$5f6d$	$5f$		
Pr	$4f^36s^2$	$4f^2$	$4f^2$	Pa	$5f^26d7s^2$	$5f^27s^2$	$5f^26d$	$5f^2$		$(5f)$
Nd	$4f^46s^2$	$4f^3$	$4f^3$	U	$5f^36d7s^2$	$5f^37s^2$		$5f^3$	$5f^3$	$5f^2$
Pm	$4f^56s^2$	$4f^4$	$4f^4$	Np	$5f^46d7s^2$			$5f^4$	$5f^4$	$(5f^3)$
Sm	$4f^66s^2$	$4f^5$	$4f^5$	Pu	$5f^67s^2$	$5f^67s$	$5f^6$	$5f^5$	$5f^5$	$(5f^4)$
Eu	$4f^76s^2$	$4f^6$	$4f^6$	Am	$5f^77s^2$	$5f^77s$	$5f^7$	$5f^6$	$5f^6$	$(5f^5)$
Gd	$4f^75d6s^2$	$4f^7$	$4f^7$	Cm	$5f^76d7s^2$	$5f^77s^2$	$5f^8$	$5f^7$	$5f^7$	$(5f^6)$
Tb	$4f^96s^2$	$4f^8$	$4f^8$	Bk	$5f^97s^2$	$5f^97s$	$5f^9$	$5f^8$	$5f^8$	$(5f^7)$
Dy	$4f^{10}6s^2$	$4f^9$	$4f^9$	Cf	$5f^{10}7s^2$	$5f^{10}7s$	$5f^{10}$	$5f^9$	$5f^9$	$(5f^8)$
Ho	$4f^{11}6s^2$	$4f^{10}$	$4f^{10}$	Es	$5f^{11}7s^2$	$5f^{11}7s$	$5f^{11}$	$5f^{10}$	$5f^{10}$	$(5f^9)$
Er	$4f^{12}6s^2$	$4f^{11}$	$4f^{11}$	Fm	$5f^{12}7s^2$			$5f^{11}$	$5f^{11}$	$(5f^{10})$
Tm	$4f^{13}6s^2$	$4f^{12}$	$4f^{12}$	Md	$5f^{13}7s^2$			$5f^{12}$	$5f^{12}$	$(5f^{11})$
Yb	$4f^{14}6s^2$	$4f^{13}$	$4f^{13}$	No	$5f^{14}7s^2$		$(5f^{14})$	$5f^{13}$	$5f^{13}$	$(5f^{12})$
Lu	$4f^{14}5d6s^2$	$4f^{14}$	$4f^{14}$	Lr	$(5f^{14}6d7s^2$ or $5f^{14}7s^27p)$			$5f^{14}$	$5f^{14}$	$(5f^{13})$
				Rf	$(5f^{14}6d^27s^2)$					$(5f^{14})$
				Db	$(6d^37s^2)$	$(6d7s^2)$	$(7s^2)$			
				Sg	$(6d^47s^2)$	$(6d^27s^2)$	$(6d^3)$			
				Bh[e]	$(6d^57s^2)$	$(6d^37s^2)$	$(6d^37s)$			
				Hs	$(6d^67s^2)$	$(6d^47s^2)$	$(6d^37s^2)$			
				109	$(6d^77s^2)$	$(6d^57s^2)$	$(6d^57s)$			
				110	$(6d^87s^2)$	$(6d^67s^2)$	?			
				111	$(6d^97s^2)$	$(6d^77s^2)$	?			
				112	$(6d^{10}7s^2)$	$(6d^87s^2)$	?			

[a] Configurations from Chapters 14 and 16. Predicted configurations are given in parentheses.

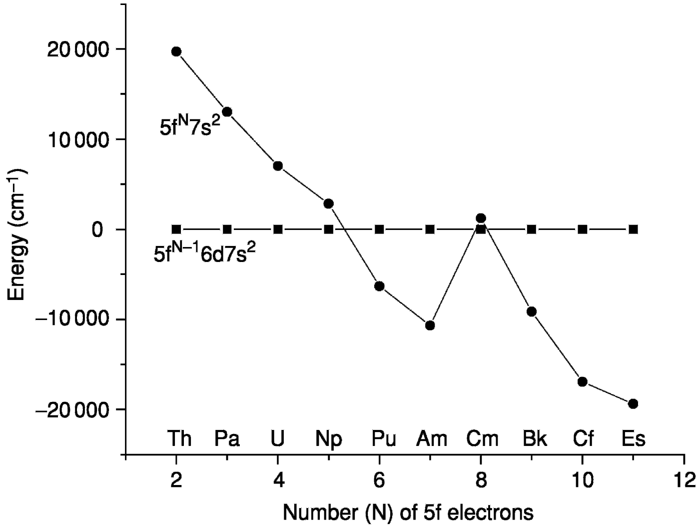
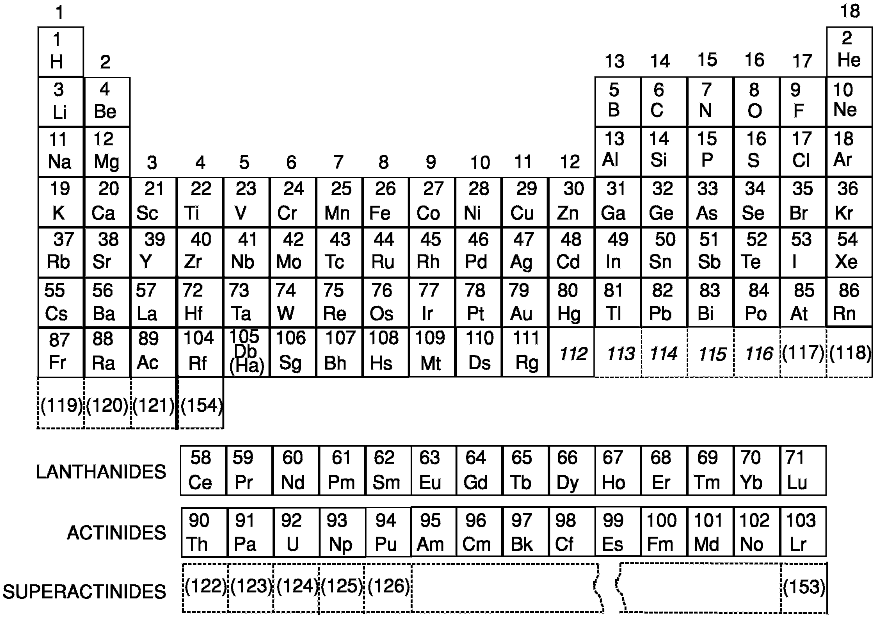


Fig. 15.4 *Relative energies of the* $5f^N7s^2$ *and* $5f^{N-1}6d7s^2$ *electron configurations in the gaseous actinide atoms showing the stabilization of the* $5f^N7s^2$ *as the atomic number* Z $(Z = 88 + N)$ *increases.*

ligand field relative to the 5f configuration, and is found to be the ground configuration. For the elements beyond neptunium, the electronic configurations of the 4f and 5f elements strongly resemble each other. That the relative energy levels of the outer d- and s-shell electrons relative to the 5f electrons are not identical to those observed in the 4f block elements is not unexpected. Fig. 15.4 represents the relative energies of electron configurations that interchange 5f and 6d electrons for most of the actinide elements; as the curves intersect, inversion of behavior is inevitable.

15.4.4 Position in the periodic table

Before 1944, the elements thorium, protactinium, and uranium were assigned positions in the periodic table immediately below the elements hafnium, tantalum, and tungsten. It became evident that to accommodate the transuranium elements in the periodic table would require a radically new arrangement. The arguments for positioning them as a new ‘actinide’ transition series, similar to the rare earths, became strong by 1944 but experimental data to support this view were still scanty. With the passage of time the evidence in favor of a new transition series has become very convincing. Fig. 15.5 shows a modern periodic table, which not only includes the actinide elements as a transition series, but also indicates the location of the transactinides and a new superactinide transition series that may never be discovered.



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	1 H																	2 He
	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
	87 Fr	88 Ra	89 Ac	104 Rf	105 Db (Ha)	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	*112*	*113*	*114*	*115*	*116*	(117)	(118)
	(119)	(120)	(121)	(154)														
LANTHANIDES				58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
ACTINIDES				90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	
SUPERACTINIDES				(122)	(123)	(124)	(125)	(126)									(153)	

Fig. 15.5 *Modern periodic table showing predicted locations of many undiscovered transuranium elements (atomic numbers in parentheses). For element* 105 *two symbols are shown. The official IUPAC name is dubnium (Db), adopted in* 1997. *Hahnium (Ha) is also shown; this name also was used for a number of years after the discovery of this element.*

15.5 OXIDATION STATES

15.5.1 Ions in aqueous solution

Tables 15.4 and 15.6 list the oxidation states of the actinide elements and the color of the actinide ions, respectively. It is clear that the actinide oxidation states are far more variable than those of the lanthanides. The close proximity of the energy levels of the 7s, 6d, and 5f electrons almost guarantees multiple oxidation states for the actinide ions, at least in the first half of the actinide series. The multiplicity of oxidation states, coupled with the hydrolytic behavior of the ions, make the chemical behavior of the elements from protactinium to americium among the most complex of the elements in the periodic table.

In Table 15.4, the most stable states are shown in bold type and the more unstable states are indicated by parentheses. Oxidation states that have been claimed to exist, but not independently substantiated, are indicated with question marks. The most unstable oxidation states have only been observed in solid compounds, or produced as transient species in solution by pulse radiolysis (Sullivan *et al.*, 1976a,b, 1982; Gordon *et al.*, 1978). In this very interesting technique, a beam of energetic electrons is injected into an aqueous

Table 15.4 *The oxidation states of the actinide elements.*

Atomic No.	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Element	*Ac*	*Th*	*Pa*	*U*	*Np*	*Pu*	*Am*	*Cm*	*Bk*	*Cf*	*Es*	*Fm*	*Md*	*No*	*Lr*
Oxidation states															
													1?		
		(2)					(2)			(2)	(2)	2	2	**2**	
	3	(3)	(3)	3	3	3	**3**	**3**	**3**	**3**	**3**	**3**	**3**	3	**3**
		4	4	4	4	**4**	4	4	4	4	4?				
			5	5	**5**	5	5	5?		5?					
				6	6	6	6	6?							
					7	7	7?								
						8?									

Bold type, most stable; ( ), unstable; ?, claimed but not substantiated.

Table 15.5 *The oxidation states of the transactinide elements.*

Atomic No.	104	105	106	107	108	109	110	111	112
Element	*Rf*	*Db*	*Sg*	*Bh*	*Hs*	*Mt*	*Rg*		
Oxidation states									
								–1 ?	
							0 ?		**0 ?**
						1 ?		**3 ?**	
							2 ?		2 ?
	3	(3)	(3)	**3**	**3**	**3 ?**		**5** ?	
	4	4	4	4	**4**		4 ?		**4 ?**
		5	5	5					
			6		6	**6 ?**	6 ?		
				7					
					8				

Bold type, most stable; ( ), unstable; ?, predicted but not experimentally substantiated.

solution of the ion (for actinides, mainly the 3+ ions) under investigation. When N_2O is present in the reaction mixture, the hydrated electrons formed by the injection of the electrons into water are converted into OH radicals, which are strong oxidants. If *t*-butanol is present in place of nitrous oxide, the OH radicals are scavenged, and only the hydrated electron, $e^-(aq)$, a powerful reducing agent, is formed. The reactions of these reagents with actinide ions are followed spectrophotometrically. Reaction of the 3+ ions in 0.1 M perchloric acid with $e^-(aq)$ forms Am(II), Cm(II), and Cf(II). When OH radicals react, Am(IV) and Cm(IV), but no Cf(IV), are produced. All of the 2+ and 4+ species are transient. The 2+ species disappear with rate constants of about 10^5 s^{-1} by what appears to be a first-order process. Am(II), Cm(II), and Cf(II) have half-lives of the order of 5–20 μs. Am(IV) appears to be appreciably more stable and has a half-life of about 1 ms. Pulse radiolysis has been shown to be a widely applicable method for producing ionic species in oxidation states that are difficult or impossible to access by conventional chemical procedures.

With the exception of thorium and protactinium, all of the actinide elements show a 3+ state in aqueous solution, although the 3+ state does not become the preferred or stable oxidation state under ordinary conditions until americium is reached. Stable organometallic compounds of Th(III) have been characterized and have a $6d^1$ configuration as the ground state (Blake *et al.*, 2001). A stable 4+ state is observed in the elements thorium through plutonium and in berkelium. Am(IV) can be stabilized in aqueous media by very strong complexing agents such as carbonate, tungstophosphate and tungstosilicate heteropolyanions. The 5+ oxidation state is well established for the elements protactinium through americium, and the 6+ state in the elements uranium through americium. The 4+ state in curium is confined to a few solid compounds, particularly CmO_2 and CmF_4, and appears to be present in a stable complex ion that exists in concentrated cesium fluoride solution. The Cf(IV) state is limited to the solid compounds CfO_2, CfF_4, a complex oxide $BaCfO_3$, and in tungstophosphate solutions; the oxidation of Cf(III) to Cf(IV) in strong carbonate solutions is a disputed topic.

The 2+ oxidation state first appears at americium in a few solid compounds and then at californium in the second half of the series. The II oxidation state becomes increasingly more stable in proceeding to nobelium. Md(II) and No(II) have been observed in aqueous solution and this appears to be the most stable oxidation state for nobelium. Am(II) has not only been encountered in solid compounds, but also in electrochemical and pulse radiolysis experiments in acetonitrile solution. The formation of Bk(IV) is associated with enhanced stability of the half-filled 5f configuration ($5f^7$), and the No(II) state reflects the stability of the full 5f shell ($5f^{14}$). The increase in the stability of the lower oxidation states of the heavier actinide elements relative to the lanthanides may be the result of stronger binding of the 5f (and 6d) electrons in the elements near the heavy end of the actinide series. Claims have been advanced that all the elements from plutonium to nobelium can be prepared in the 2+ state, and that this is a stable oxidation state for the elements fermium to nobelium (Mikheev, 1984). There has been no confirmation of these claims. The findings from pulse radiolysis show that even the 2+ state of the actinides preceding einsteinium are transient species, and have very short lifetimes (Gordon *et al.*, 1978; Sullivan *et al.*, 1982). Mendelevium has been reported to possess a stable 1+ oxidation state (Mikheev, 1984), but the evidence for monovalent ions of the actinide elements is doubtful. (See chapter 13.)

The transactinide elements rutherfordium through hassium have been studied by innovative chemical techniques, in particular thermochromatography (by which the relative volatilities of halides of elements 104–108 have been determined). The resulting oxidation states are shown in Table 15.5.

15.5.2 Ion types

Actinide ions in the same oxidation state have essentially the same coordination environments. In aqueous solutions at a $\mathrm{pH} < 3$, four structural types of actinide cations exist. Formulas and colors of these ions are listed in Table 15.6. Only simple (uncomplexed) ions are listed. The ions of the type M^{3+} or M^{4+}, as is the case for cations with a high charge, show a strong inclination to solvation, hydrolysis, and polymerization (see Section 15.5.3). For the actinide elements in higher oxidation states (U through Am), the effective charge on the simple ion is decreased by the formation of oxygenated species of the general type MO_2^+ and MO_2^{2+}. The actinyl ions MO_2^+ and MO_2^{2+} are remarkably stable, having strong covalently bonded O=M=O ions, and persisting as a unit through a great variety of chemical transformations. Infrared spectroscopy shows conclusively that the ion MO_2^{2+} exists as a symmetrical, linear or very nearly linear, group. Crystallographic studies have shown that in solids UO_2^{2+} have four, five, or six ligands, typically in an equatorial plane perpendicular to the O=U=O axis; X-ray scattering in dilute perchloric acid solution shows UO_2^{2+} coordinated to five water molecules (Neuefeind *et al.*, 2004). The stability and linearity of the MO_2^{2+} ions are understood from theoretical bonding arguments (Zhang and Pitzer, 1999; Hay *et al.*, 2000). The corresponding 5+ state actinyl ions, AnO_2^+ (An = U, Np, Pu, Am), have the same symmetrical linear structure but with weaker metal–oxygen bonds. There is a regular decrease in the strength of the metal–oxygen bond with increasing atomic number in the actinyl ions from uranium to americium. The 7+ oxidation state, found in some

Table 15.6 *Ion types and colors for actinide ions in aqueous solution.*

Element	M^{3+}	M^{4+}	MO_2^+	MO_2^{2+}	$MO_4(OH)_2^{3-}$ (*alkaline soln.*)
actinium	colorless				
thorium		colorless			
protactinium		colorless	colorless		
uranium	red	green	color unknown	yellow	
neptunium	blue to purple	yellow-green	green	pink to red	dark green
plutonium	blue to violet	tan to orange	reddish-purple	yellow to pink-orange	dark green
americium	pink or yellow	color unknown	yellow	rum-colored	
curium	pale green	color unknown			
berkelium	green	yellow			
californium	green				

compounds of neptunium and plutonium in alkaline aqueous solution, contains in some cases tetroxo species $MO_4(OH)_2^{3-}$ (Williams *et al.*, 2001). The existence of Am(VII), even in alkaline media, is still a matter of debate (see Chapter 8). In acid solution, actinide ions in the 7+ oxidation state oxidize water rapidly.

Reduction potentials for the actinide elements are shown in Fig. 15.6. These show standard potentials in volts in aqueous acidic solution relative to the standard hydrogen electrode. The measured potentials were determined by electrochemical cells at or near equilibrium, and enthalpy of reaction measurements coupled with entropy measurements or estimates. Species not found in aqueous solution, but whose thermodynamic properties have been estimated, are indicated in parentheses.

The M^{4+}/M^{3+} and the MO_2^{2+}/MO_2^{+} couples are reversible, and, as expected, rapid reactions occur with one-electron oxidizing and reducing agents when no bond breaking or making takes place. The MO_2^{+}/M^{3+}, MO_2^{+}/M^{4+}, and MO_2^{2+}/M^{4+} couples are not reversible, presumably because of the barrier introduced by formation and rupture of covalent ‘yl’ bonds and the subsequent reorganization of the solvent shell, and also because some of these are two-electron reductions.

A summary of qualitative information about the oxidation–reduction characteristics of the actinide ions is presented in Table 15.7. The disproportionation and redox reactions of UO_2^{+}, Pu^{4+}, PuO_2^{+}, and AmO_2^{+} are especially complex, and, despite extensive study, many aspects of these reactions still remain to be explored. In the case of plutonium, the situation is especially complicated, because ions in all four oxidation states 3+, 4+, 5+, and 6+ can exist simultaneously in aqueous solution in comparable concentrations. The kinetics of the redox reactions of the actinide elements were reviewed by Newton (1975) and are presented in Chapter 23. Mechanisms of redox reactions involving uranium species are discussed in Chapter 5.

15.5.3 Hydrolysis and polymerization

All metal cations in aqueous solution interact extensively with the solvent water, and to a lesser or greater extent exist as hydrated cations (Baes and Mesmer, 1976; Burgess, 1978). The more highly charged the naked cation, the greater the extent of interaction with the solvent. Aquo cations, especially those of 4+, 3+, and small 2+ ions, act as acids in solution:

$$M(OH_2)_x^{n+} \rightarrow M(OH_2)_{x-1}(OH)^{(n-1)+} + H^+$$

This reaction illustrates the increase in acidity caused by hydrolysis of water as a protic ligand coordinated to metal cations. Because the acidity of water coordinated to 3+ and 4+ species is the more strongly enhanced the higher the charge on the metal cation, actinide elements in their most frequently encountered oxidation states undergo extensive hydrolytic reactions. Th^{4+}(aq) begins to hydrolyze to $Th(OH)^{3+}$ below pH 2. At higher pH, more hydrolyzed and

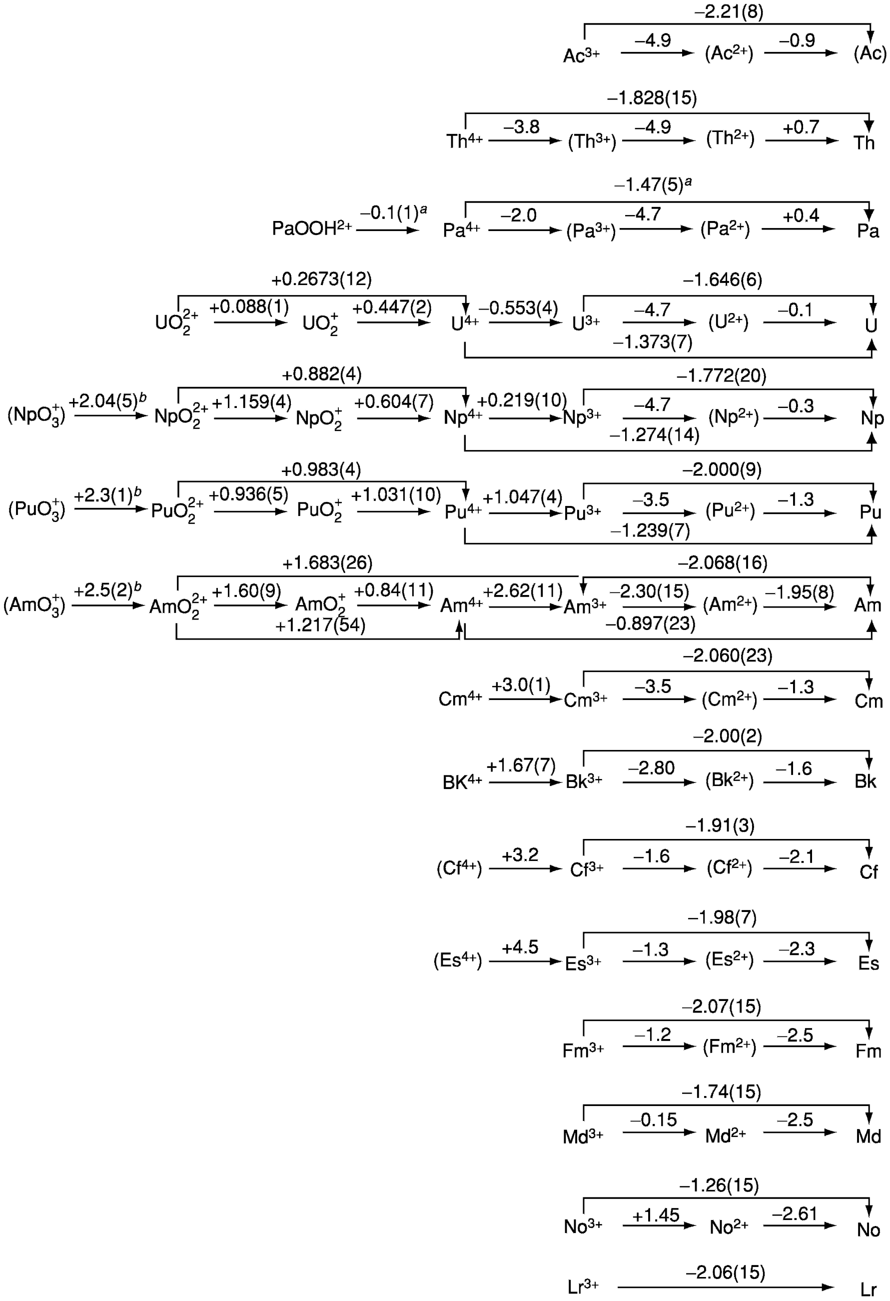


Fig. 15.6 *Standard reduction potentials diagrams for the actinide ions. Values in volts versus standard hydrogen electrode; footnote a indicates that the solvent is* 1 M *HCl, footnote b refer to the potentials in* 1 M *$HClO_4$.*

Table 15.7 *Stability of actinide ions in aqueous solution (usually acidic).*

Ion	*Stability*
Md^{2+}	stable to water, but readily oxidized
No^{2+}	stable
Ac^{3+}	stable
U^{3+}	oxidizes to U^{4+} and reduces water; aqueous solutions evolve H_2 on standing
Np^{3+}	stable to water, but easily oxidized by air to
Pu^{3+}	stable to water and air, but easily oxidized to Pu^{4+}
Am^{3+}	stable; can be oxidized with difficulty
Cm^{3+}	stable
Bk^{3+}	stable; can be oxidized to Bk^{4+}
Cf^{3+}	stable
Es^{3+}	stable
Fm^{3+}	stable
Md^{3+}	stable, but rather easily reduced to Md^{2+}
No^{3+}	easily reduced to No^{2+}
Lr^{3+}	stable
Th^{4+}	stable
Pa^{4+}	stable to water, but readily oxidized
U^{4+}	stable to water, but slowly oxidized by air to UO_2^{2+}
Np^{4+}	stable to water, but slowly oxidized by air to NpO_2^+
Pu^{4+}	stable in concentrated acid, e.g. 6 M HNO_3, but disproportionates to Pu^{3+} and PuO_2^{2+} at lower acidities
Am^{4+}	known in solution only in presence of strong complexants
Cm^{4+}	known in solution only in presence of strong complexants
Bk^{4+}	marginally stable; easily reduced to Bk^{3+}
Pa^{5+}	stable, hydrolyses readily
UO_2^+	disproportionates to U^{4+} and UO_2^{2+}; most nearly stable at pH 2–4
NpO_2^+	stable; disproportionates only at high acidities
PuO_2^+	tends to disproportionate to Pu^{4+} and PuO_2^{2+} (ultimate products); most nearly stable at very low acidities
AmO_2^+	disproportionates in strong acid to Am^{3+} and AmO_2^{2+}; reduces fairly rapidly under the action of its own a radiation at lower acidities (as ^{241}Am isotope)
UO_2^{2+}	stable; difficult to reduce
NpO_2^{2+}	stable; easy to reduce
PuO_2^{2+}	stable; easy to reduce; reduces slowly under the action of its own alpha radiation (as ^{239}Pu isotope)
AmO_2^{2+}	easy to reduce; reduces fairly rapidly under the action of its own alpha radiation (as ^{241}Am isotope)
$NpO_4(OH)_2^{3-}$	observed only in alkaline solution
$PuO_4(OH)_2^{3-}$	observed only in alkaline solution; oxidizes water

polymerized Th(IV) species begin to predominate. The mononuclear Pa(IV) species $PaO^{2+}(aq)$ or $Pa(OH)_2^{2+}(aq)$ have been claimed to exist at low concentrations; however, polymers are already evident at protactinium concentrations well below micromolar and in tracer experiments. U(IV) begins to undergo hydrolysis in aqueous solution above pH 2.9, and, at somewhat higher pH, is largely present as hydrolyzed and polymerized species. $U(OH)^{3+}$ has been identified as the predominant U(IV) species in solution at low uranium concentrations and moderate acidities. Pu(IV) requires strongly acid conditions to exist as a simple Pu^{4+}(aq) ion. Even in moderately acid solutions, Pu(IV) hydrolyzes extensively, and may form polymers of high molecular weight. The actinyl ions typical of the 5+ and 6+ states presumably are formed with great speed whenever oxidation to the 5+ and 6+ states occurs in water. Once the uranyl, neptunyl, plutonyl, and americyl ions are formed, the only practical way to remove the coordinated oxygen atoms is by reduction to the 4+ or 3+ state. Although uranyl nitrate can be obtained as an anhydrous compound, in this form it is coordinatively unsaturated, and it is usually encountered as the hexahydrate or coordinated to equivalent ligands.

It is well known that aquo cations of heavy elements in the 3+ oxidation state or higher readily lose protons to form hydroxo complexes. Subsequent condensation reactions between the hydroxo complexes can then form polynuclear species in which the metal ions are linked through hydroxo (M–OH–M) or oxo (M–O–M) bridges. For the formation of polynuclear species, the pH range is critical; at too low a pH the ion will exist as the simple aquo cation, and at too high a pH the hydrous oxide or hydroxide precipitates. The actinide ions with oxidation number 4+ are particularly prone to hydrolysis and polymerization, but the MO_2^{2+} oxo cations also have considerable tendencies toward polynuclear ion formation. Among the 4+ cations, Th(IV), U(IV), and especially Pu(IV) form polymeric species. Th(IV) has a very complicated solution chemistry and, except in strong acid solutions, polynuclear species are easily generated in which Th(IV) ions are cross-linked by hydroxo bridges. Similarly, U(IV) forms polynuclear aggregates that may contain both hydroxo and oxo bridges. The $U(OH)^{3+}$ ion, which predominates in acidic solutions and low uranium concentrations, rapidly undergoes polymerization in solutions of moderate or low acidity. The formation of very large polymers occurs with U(IV) at much lower ligand numbers than is the case for Th(IV). The hydrolytic behavior of the Np(IV) ion is similar to that of Pu(IV), although Np^{4+} is an appreciably weaker acid.

The hydrated Pu(IV) ion is a stronger acid than the U(IV) ion, and it is exceptionally prone to polymer formation. As hydrolysis proceeds and before actual precipitation occurs, positively charged polymers of colloidal dimensions with molecular weights as high as 10^{10} have been observed. Although all of the polynuclear species of the actinide ions are of scientific interest, the polymers of Pu(IV) have attracted the most attention because of practical considerations. The effect of concentration, acidity, temperature, and ionic strength on polymer formation are ill-defined, and, as the Pu(IV) polymers are very stable and depolymerization is not at all easily affected, unpredictable behavior of Pu(IV) solutions can pose major problems and create potentially serious hazards, such as criticality, in nuclear fuel processing.

The actinyl ions MO_2^+ and MO_2^{2+} are considerably less acidic than are the 4+ state monomeric ions, and therefore have a smaller tendency to undergo hydrolysis. Hydrolysis decreases in the order $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^+$. This trend follows the expected decreasing ratio of charge to ion size as the determining factor in hydrolysis.

The order of acidity for the 4+ species is $Pu^{4+} \approx Np^{4+} > U^{4+} \gg Th^{4+}$ (Neck and Kim, 2001). The similar hydrolytic behavior of Np^{4+} and Pu^{4+} cannot be understood simply in terms of charge-to-size considerations. On the basis of increasing charge and decreasing ionic size, it is expected that the degree of hydrolysis for a series of ions of any charge in the actinide series would increase with atomic number. This hydrolytic behavior of Np(IV) implies that additional, and as yet unidentified, factors make important contributions to the interaction of the actinide ions with water.

The actinyl(V) ions, which carry the low charge of 1+, are weak acids, with the singular exception of Pa(V). The protactinyl(V) ion is a much stronger acid than its successors in the actinide series and, in fact, the least hydrolyzed species of Pa(V) appears to be $PaO(OH)^{2+}$. In both its 4+ and 5+ oxidation states, protactinium shows a very unusual tendency to hydrolyze. Experience with protactinium chemistry in extremely dilute acidic solutions indicates that Pa(V) is already extensively hydrolyzed. The chemical investigation of protactinium at any level is rendered extremely difficult by the formation of intractable polymers. The use of strong complexing agents such as fluoride circumvents some of these difficulties.

The actinyl(VI) ions all undergo hydrolysis to an appreciable extent. Hydrolysis of UO_2^{2+} even in dilute solution results in almost total conversion to polynuclear species. These are small polymers, containing fewer than five uranium atoms. The tendency to form polymers of colloidal dimensions thus appears to be much diminished in the actinyl(VI) ions relative to the actinide(IV) ions. Precipitation occurs gradually or rapidly, depending on the kinetics of colloidal aggregation. The strong inclination to form insoluble precipitates after only a small amount of hydrolysis makes characterization of the water-soluble polymers of the actinyl ions a difficult challenge.

15.5.4 Complex-ion formation

The tendency to form complex ions in solution is to a considerable extent an expression of the same forces that lead to hydrolysis. The high positive charge on a bare 3+ or 4+ ion provides a strong driving force for interaction with nucleophiles. Water is only one example of such a nucleophilic ligand. Other nucleophiles that may be present in a solution can compete for coordination to the electrophilic cation to form complex ions. In most cases of complex formation, water molecules directly bound to the metal cation are displaced by the entering ligand to form an inner-sphere complex that may or may not contain water still bound to the metal ion. Alternatively, ligands may form hydrogen bonds to water molecules of the outer hydrate shell to form outer-sphere complexes. Strong complexes are for the most part of the inner-sphere type. For inorganic anions, the complexing power of the actinide cations is in the order fluoride > nitrate > chloride > perchlorate for the singly charged anions, and carbonate > oxalate > sulfate for doubly charged anions. The stability of the complexes for a given ligand follows the order $M^{4+} > MO_2^{2+} \approx M^{3+} > MO_2^{+}$. For ions of the same charge, the stability of the complex increases with decreasing ionic radius in the first half of the actinide series. Many irregularities are encountered in the series of ions of uranium through americium, just as in the hydrolytic behavior of the tetravalent actinides. Overall, however, the stability of the actinide complexes increases as the ratio of effective charge to ionic radius increases. As a general rule, the actinide ions form somewhat more stable complexes than do the homologous lanthanide ions.

The phosphate anion PO_4^{3-} and organic phosphates are powerful complexing agents for actinide ions. The phosphate anion acts as a bridge between metal ions to form aggregates that are insoluble in water. The M^{4+} and MO_2^{2+} ions form complexes with many organic phosphates, either neutral or anionic, that are preferentially soluble in nonpolar aliphatic hydrocarbons. Typical of such ligands are TBP and dibutyl phosphate (DBP). Phosphine oxides are also potent coordinating ligands. Oxygen-containing donor compounds such as the ketones, diisopropyl ketone or methyl isobutyl ketone, and the ethers, diethyl ether, ethyleneglycol diethyl ether, or diethyleneglycol dibutyl ether, act likewise and are good complexing agents for actinide ions. All of these ligands have oxygen atoms with lone electron pairs not otherwise engaged in chemical bonding that can act as electron donors in coordination interactions. Complexes with such reagents have been used on a very large scale in the extraction and separation of the actinide elements by liquid–liquid extraction. In recent years, extractants containing soft donor atoms (nitrogen, sulfur) have received much attention, especially as they offer great potential for the separation of trivalent actinides from the chemically similar lanthanides. Among other compounds, polyaza and dithiophosphinic acid derivatives are investigated extensively. The reader is referred to Chapter 24 for a discussion of the comparative merits of various extractant systems.

Chelating ligands form strong complexes with actinide ions. Examples of such are the β-diketones, the tropolones, 8-hydroxyquinoline and its derivatives, and ethylenediaminetetraacetic acid (EDTA), among many others. In its enol form, acetylacetone, a typical diketone, forms very strong complexes with M^{4+} ions. Even though these complexes have significant water solubility, they are easily and completely extracted by benzene, carbon tetrachloride, or similar nonpolar solvents. The acetylacetone complexes of the MO_2^{2+} actinyl ions form weaker complexes that show little preference for a nonpolar organic phase. The structure of the diketone can be modified to enhance the preferential solubility of the metal complex for the organic phase. The most important of such modified diketone chelating agents is 2-thenoyltrifluoroacetone ($C_4H_3COCH_2COCF_3$), which has been widely used to extract plutonium from aqueous solutions into nonpolar solvents. Tropolone ($C_7H_6O_2$, 2-hydroxy-2,4,6-cycloheptatrien-1-one) is a seven-membered cyclic carbon compound containing a keto carbonyl function and a weakly acid hydroxyl group, both of which are able to form strong complexes with highly charged metal cations. EDTA is an effective sequestering agent for the actinide ions in aqueous solutions. The strongest EDTA complexes are formed by M^{4+}. The strength of the EDTA complexes with M^{3+} ions increases steadily from Pu^{3+} to Cf^{3+}. Possibly for steric reasons, EDTA interacts in a different way with actinyl(VI) ions; in these systems EDTA is a bridging ligand, and gives rise to linear polynuclear complexes.

There is a great deal more to be said about the actinide ions in solution, about hydrolytic phenomena, and about complex-ion formation. For a comprehensive and authoritative treatment of these important subjects, the reader is referred to Chapters 23 and 24.

15.6 THE METALLIC STATE

The actinide metals pose some of the most interesting problems in actinide research and, in fact, in all of materials science. Many actinide compounds behave in a perfectly conventional way (except for radioactivity), and have properties that can be safely inferred from lanthanide chemistry or the chemistry of similar compounds of well-studied elements. For no category of materials is this less true than for the actinide metals and intermetallics. Many of the actinides in their elemental state and in intermetallic compounds are unique. They have metallurgical properties that are unprecedented in conventional metals, and their properties cannot be described by conventional theories of the metallic state. The theoretical framework of the metallic state has been broadened to accommodate this group of unusual metals, and this led to a better understanding of complex phenomena not only in the actinide series but also in such complex materials as high-temperature superconductors (Santini *et al.*, 1999; Sarrao *et al.*, 2002).

15.6.1 Preparation

The actinide metals are highly electropositive and may react, especially on surfaces and in finely divided form, with water vapor, oxygen, nitrogen, and hydrogen. The chemical reactivity and radioactivity of most of the actinides makes confinement in atmosphere-controlled gloved boxes compulsorily. For some of the heavier actinide metals, shielding is required because of gamma rays or because of neutrons released by spontaneous fission. The actinide elements form very stable oxides and fluorides, so that vigorous reducing agents and high temperatures are necessary for their reduction to the metals. The earliest preparations of the actinide metals were carried out by reduction of the anhydrous actinide tri- or tetrafluoride with the appropriate alkali or alkaline earth metal at high temperature. For submilligram amounts this is still the method of choice, especially with lithium or barium as reductants. Alternatively, especially at the industrial scale, the actinide oxide is reduced at high temperature with lanthanum or thorium metal. All of the starting materials must be as pure as possible to yield a pure product. Reduction of the oxide is the preferred route to milligram-to-gram amounts of Ac, Am, Cm, Bk, Cf, and submilligram amounts of Es (Heathman and Haire, 1998). Uranium, thorium, and plutonium metals are obtained from appropriate industrial-scale operations.

Much modern research on the metallic state requires very pure metals. Depending on the nature of the impurities, the actinide metals can be purified by volatilization of the impurities in a very high vacuum, by volatilization of the metal itself to form films of very pure metal, or by electrodeposition from molten salt baths. Very pure protactinium and thorium metals can be obtained by the van Arkel process, which consists of converting the crude metal to the volatile iodide by reaction with elemental iodine at an elevated temperature, and decomposing the gaseous metal iodide on a hot filament (Müller and Spirlet, 1985). This process produces exceptionally pure metals, which have been used for such demanding purposes as superconductivity measurements that require metals of the highest purity.

15.6.2 Crystal structures

The crystal structures, phase transformations, and metallic radii of the actinide metals are listed in Table 15.8, together with melting points, densities, and enthalpies of sublimation. The crystal structures of metallic protactinium, uranium, neptunium, and plutonium are complex, have no counterparts among the lanthanide metals, and resemble the 3d transition metals more closely than the lanthanides. The lanthanide metals show a generally uniform hexagonal close-packed (hcp) or face-centered cubic (fcc) crystal structure pattern at low temperatures, and body-centered cubic (bcc) at high temperatures. The lighter actinide elements have a bcc structure at the melting point, which changes to fcc in the elements after plutonium. For the actinide elements americium through einsteinium, the characteristic crystal structures at all temperatures below the melting point are the fcc and double hexagonal close-packed (dhcp) structures. In uranium, neptunium, and plutonium, complex crystal structures are observed at low temperatures.

The differences between the actinide and lanthanide metals can be rationalized by a consideration of the differences between the 4f and 5f electron shells (Santini *et al.*, 1999). In the 4f series, all the 4f electrons (added after cerium) are buried in the interior of the electron cloud. The 4f electrons thus experience relatively little interaction with valence electrons in the outer shells. The maxima in the 4f radial charge density occur well inside the usual interatomic distances in solids, and consequently the 4f electron properties of the free atoms are

Table 15.8 *Selected properties of actinide metals.*[a]

Element	*Melting point* (K)	*Enthalpy of sublimation at* 298.15 K (kJ mol^{-1})	*Lattice symmetry*	*Temperature range* (K)	*Lattice constants*[b]				*X-ray density* (g cm^{-3})	*Z* (*atoms per unit cell*)	*Metallic radius CN* 12 (Å)[d]
					a_0 (Å)	b_0 (Å)	c_0 (Å)	β (deg)			
actinium	1323 ± 50	418 ± 20	fcc		5.315				10.01	4	1.878
thorium		602 ± 6	α, fcc	below 1633	5.0842				11.724	4	1.798
	2023 ± 10		β, bcc	1633–2023	4.11 (1723 K)					2	~1.80
protactinium		570 ± 10	α, bcc tetrag.	below 1443	3.929		3.241		15.37	2	1.642
	1845 ± 20		β, bcc or fcc	1443–1845							
uranium		533 ± 8	α, orthorh.	below 941	2.854	5.870	4.955		19.04	4	1.542
			β, tetrag.	941–1049	5.656 (5) (995 K)	10.759 (5)	10.759 (5)		18.11	30	1.548
	1408 ± 2		γ, bcc	1049–1408	3.524 (2) (1078 K)				18.06	2	1.548
neptunium		465.1 ± 3.0	α, orthorh.	below 553	6.663 (293 K)	4.723	4.887		20.48	8	1.503
			β, tetrag.	553–849	4.897 (586 K)		3.388		19.38	4	1.511
	912 ± 3		γ, bcc	849–912	3.518 (873 K)				18.08	2	1.53
plutonium		349.0 ± 3.0	α, monocl.	below 397.6	6.183 (294 K)	4.822	10.963	101.79	19.85	16	1.523
			β, monocl.	397.6–487.9	9.284 (463 K)	10.463	7.859	93.13	17.71	34	1.571
			γ, orthorh.	487.9–593.1	3.159 (508 K)	5.768	10.162		17.15	8	1.588
			δ, fcc	593.1–736.0	4.637 (593 K)				15.92	4	1.640
			δ′, bcc tetrag.	736.0–755.7	3.34 (738 K)		4.44		16.03	2	1.640
	913.0 ± 2.0		ε, bcc	755.7–913.0	3.6361 (763 K)				16.51	2	1.592
americium		283.8 ± 1.5	α, dhcp	below 1042	3.47		11.25		13.67	4	1.730
			β, fcc	1042–1350	4.89				13.69	4	1.730
	1449 ± 5		γ, bcc?	1350–1449	unknown						
curium		384 ± 10	α, dhcp	below 1568	3.500(3)[c]		11.34(1)[c]		13.5	4	1.743
	1619 ± 50		β, fcc	1568–1619	5.065				12.7	4	1.782
berkelium		310 ± 10	α, dhcp	below 1250	3.416 (3)		11.069 (7)		14.79	4	1.704
	1323 ± 50		β, fcc	1250–1323	4.997(4)				13.24		1.767
californium		196 ± 10	α, dhcp	below ~973	3.384		11.040		15.1	4	1.691
	1173 ± 30		β, fcc	~973–1173	4.78				15.1	4	1.69
einsteinium	1133	130 ± 10	fcc	ambient	5.75				8.84	4	2.03

[a] Chapter 21, Table 21.1, which contains additional data.

[b] At 298.15 K, unless otherwise stated.

[c] Stevenson, J. N. and Peterson, J. R. (1979) *J. Less Common Metals*, **66**, 201–10.

[d] Zachariasen, W. H. (1973) *J. Inorg. Nucl. Chem.* 35, 3487–97. Zachariasen adjusted high-temperature radii to room temperature. For Ac, Cf, and Es see Chapter 2, 11, 12 respectively.

retained in the metallic as well as ionic lanthanide solids. Cerium is the only 4f metal that does not conform to this generalization, presumably because its 4f electron shell is not yet fully stabilized. The actinide 5f electrons behave quite differently. For the early members of the actinide series, the 5f electrons have a greater radial distribution than do their 4f homologs. The first few 5f electrons are not confined to the core of the atom, and they can therefore interact or mix with the other valence electrons to affect interatomic interactions in the solid state. Beyond plutonium, all the 5f electrons are localized within the atomic core, and the resemblance between the f-block elements becomes closer. Americium is the first actinide metal whose crystal structure resembles that of the lanthanide metals. In the transcurium metals, the resemblance to the lanthanide metals becomes increasingly strong. The room temperature crystal structure for the elements for Am to Cf is dhcp, just as it is in the light lanthanides (see Table 15.8).

A natural consequence of the increase in nuclear charge along the actinide series for a given oxidation state is an increasing tendency for the 6d and 7s electrons to experience less shielding from the nuclear charge. This leads to a contraction of the atomic radius. Shielding of the valence electrons from the nucleus is also diminished by delocalization of the 5f electrons in the early part of the actinide series. In metals, the atomic radius expands significantly when the 5f electrons are localized in the core, which occurs at americium and curium. The transition from delocalized to localized f-electron behavior at americium is clearly reflected in the complex chemical and physical properties of uranium, neptunium, and especially plutonium metals in the crossover region of the actinide series. Recent experiments have shown that americium metal exhibits delocalized 5f electron behavior and a structure similar to alpha uranium under high pressure (Lindbaum *et al.*, 2003).

15.6.3 Polymorphic transformations

Protactinium, uranium, neptunium, and plutonium metal have complex structures unlike anything encountered in the lanthanide metals (see Table 15.8). For example, plutonium metal is unique among metals, having no fewer than six allotropic modifications between room temperature and its melting point at 913.0 K. A remarkable phenomenon occurs as plutonium metal is heated. Plutonium metal undergoes a 26% volume increase going from room temperature through the α, β, γ, and δ phases with increasing temperature. However as the temperature continues to increase the δ and δ' phases undergo a contraction with a concomitant increase in density. An immense effort has been expended to map the phase transformations in uranium and plutonium metals and their alloys because of their great importance in nuclear technology. Details of the electronic properties of the actinide metals can be found in Chapter 21 and in Lam *et al.* (1974) and Spirlet (1982). The metallurgy of Pu and its phase transitions are discussed in Chapter 7.

15.6.4 Electronic structures

We have noted in Section 15.6.2 the effects of localized and delocalized 5f electrons on the crystal structures and phase transformations of the actinide metals. These effects are observed in many materials, but perhaps most clearly in the actinide metals. The basis for the differences observed for localized and delocalized 5f electrons has been discussed briefly in Section 15.4, but because of their importance in the metallic state some additional discussion of the electronic state in the actinide metals is appropriate. The classical d-electron or d-block transition series and the f-block elements have as a principal feature of their electronic architecture the filling of the 3d, 4d, and 5d electron shells for the d-block series, and the 4f and 5f energy levels in the lanthanide and actinide series. The f electrons occupy energy levels or orbitals closer to the nucleus of the atom than do the outer s and p valence electrons. In the lanthanide elements beyond cerium, the 4f levels are highly localized and, because overlap between the levels is minimal, these energy levels are not broadened to any appreciable extent by 4f–4f interactions. Nor do the 4f electrons mix significantly with the d, s, or p valence electrons. In the d-block metals, the d-electron levels have significant overlap with other d-electrons; the d-electrons also mix or hybridize with s and p levels. The extensive mixing of the d, s, and p orbitals in d-block elements generates broad energy bands whose existence is reflected in the magnetic and electrical properties of the d-block transition metals.

The electronic properties of the 5f elements are intermediate between those of the d-block elements and the 4f elements. At the beginning of the actinide series, the 5f electrons interact strongly with each other, and the band character of the delocalized (itinerant) 5f electrons inhibits the development of magnetism. As the 5f shell is filled, the 5f electrons become increasingly localized and the energy levels fall so that they are well below the Fermi band level. The transition from delocalized to localized 5f electrons takes place in the vicinity of plutonium, as shown in schematic fashion in Fig. 15.7. In the crossover region, which extends from uranium to americium, the electronic behavior is especially complicated because the energy differences between localized and delocalized 5f electrons is small. Comparatively small perturbations can convert the localized 5f electrons into mobile electrons with a band structure, or the reverse. This delicate balance near the middle of the actinide series gives rise to unusual crystal structures, unusual thermodynamic and mechanical properties, multiple valence states, and collective phenomena such as magnetism, superconductivity, and valence fluctuations. So complex are the phenomena near the middle of the actinide series that modern theories of the metallic state have serious difficulties in dealing with them, a situation that is under active study and may well turn out to be not the least valuable contribution that the study of the actinide elements will have made to the understanding of the solid state (Albers, 2001).

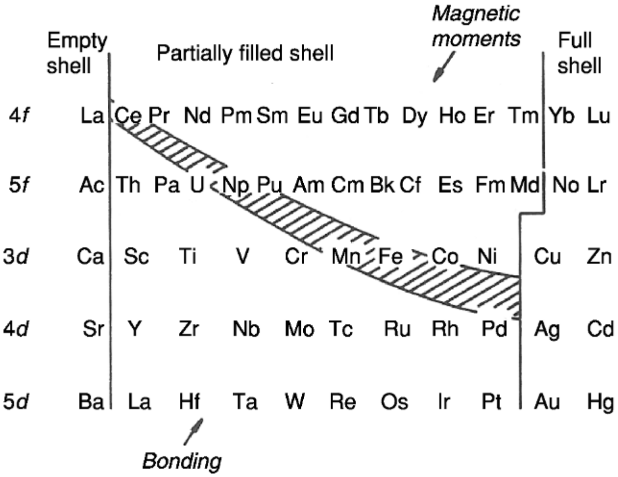


Fig. 15.7 *Transition metals (f- and d-series) showing the crossover from delocalized (bonding) to localized (magnetic moments) f- and d-electron behavior. From Smith and Kmetko* (1983), *with permission.*

One of the most powerful techniques for the elucidation of the electronic states of the actinide elements is the application of high pressure (Benedict, 1984; Haire *et al.*, 2004). The early actinides at 1 atm exhibit complex phase structures due to the behavior of the itinerant (nonlocalized) 5f electrons. The transplutonium elements do not have 5f itineracy contributing to the bonding and show complex phase behavior under high pressures. For americium metal, these 5f electrons become delocalized at high pressures, and the same crystal structures found for the light actinides are obtained (Lindbaum *et al.*, 2003). Pressure also affects the superconducting transition temperature and the magnetic properties of the actinide metals. Similarly, large pressure effects have been observed in actinide alloys and compounds (Heathman and Haire, 1998; Haire *et al.*, 2004).

15.6.5 Superconductivity

Superconductivity in the actinide metals is closely related to the degree of delocalization of the 5f electrons. Highly localized 5f electrons, which are characteristic of the latter portion of the actinide series, are associated with temperature-dependent paramagnetism and the absence of superconductivity. Delocalized 5f electrons participate in chemical bonding, show small temperature-independent magnetic moments, and are conducive to superconductivity. Protactinium metal becomes superconducting at 1.4 K, thorium metal at 1.368 K, and uranium metal at 0.68 K. These three elements have delocalized (itinerant) 5f electrons. Neptunium and plutonium, especially the latter, are anomalous. The 5f electrons in americium are localized, but americium metal is superconducting at 0.625 K, because its spin and orbital angular momenta cancel one another and its magnetic moment at low temperature is almost zero. The transamericium actinide metals all contain strongly localized 5f electrons, are not superconductors, and have large magnetic moments at low temperatures. Plutonium is not superconducting, but the intermetallic compound $PuCoGa_5$ shows a superconducting transition at $T_c = 18.5$ K. This surprising result is attributed to the presence of a local magnetic moment in the normal state. The superconductivity in this compound is of an unconventional type and could be due to magnetically mediated superconductivity. Thus the transuranics appear to represent a promising area of superconductor research, intermediate between known heavy fermion materials and the high-temperature superconductors derived from copper oxides (Sarrao *et al.*, 2002).

15.7 SOLID COMPOUNDS

15.7.1 Introductory remarks

Thousands of compounds of the actinide elements have been prepared (Gmelin, 1972; Müller and Blank, 1975; Müller and Lindner, 1975; Shannon, 1976). Compounds that have special scientific or technological importance are described in the preceding chapters on the chemistry of the individual actinide elements, and in a systematic way in Chapter 22. In the past few years there have been important additions to the roster of actinide compounds and new chemical phenomena that are particularly characteristic of, although perhaps not entirely confined to, the chemical behavior of the actinide compounds, and these are commented on here.

15.7.2 Binary compounds

Table 15.9 lists the binary hydrides, oxides, and halides of the actinide elements along with their melting points, color, and crystallographic parameters. The properties of the hydrides and oxides in Table 15.9 are for compounds that are stoichiometric or come close to the indicated stoichiometric composition. The methods of preparation of the compounds in Table 15.9 are essentially classical procedures adapted to a micro- or semi-microscale and to the radioactivity of the actinide elements (Müller, 1983). There are claims in the literature for the synthesis of actinide halides in which the actinide element is in an unusually high or low oxidation state. Reports of the synthesis of the higher-valent actinide fluorides PuF_5, EsF_4, AmF_6, and CmF_6 have not been confirmed. Following the discovery of the lanthanide dihalides $NdCl_2$ and $TmCl_2$, the dichlorides, dibromides, and diiodides of americium and californium have been prepared. These studies were reviewed by Morss and Edelstein (1984).

Table 15.9 *Properties and crystal structure data for some important actinide binary compounds. References are in Chapters 2–12.*

Compound	*Color*	*Melting point* (°C)	*Symmetry*	*Space group or structure type*	*Lattice parameters* a_0 (Å)	b_0 (Å)	c_0 (Å)	β (deg)	*Density* (g cm^{-3})
ThH_2	black		tetragonal	$I4/mmm$	4.055		4.965		9.50
Th_4H_{15}	black		cubic	$I\bar{4}3d$	9.116				8.25
α-PaH_3	gray		cubic	$Pm3n$	4.150				10.87
β-PaH_3	black		cubic	β-W ($Pm3n$)	6.648				10.58
α-UH_3	?		cubic	β-W	4.160				11.12
β-UH_3	black		cubic	β-W	6.6444				10.92
NpH_2	black		fcc	fluorite ($Fm3m$)	5.343				10.41
NpH_3	black		trigonal	NpF_3 ($P\bar{3}c1$)	6.51		6.72		9.64
PuH_2	black		fcc	fluorite	5.359				10.40
PuH_3	black		trigonal	NpF_3	6.55		6.76		9.61
AmH_2	black		fcc	fluorite	5.348				10.64
AmH_3	black		trigonal	NpF_3	6.53		6.75		9.76
CmH_2	black		fcc	fluorite	5.322				10.84
CmH_3	black		trigonal	NpF_3	6.528		6.732		10.06
BkH_2	black		fcc	fluorite	5.248				11.57
BkH_3	black		trigonal	NpF_3	6.454		6.663		10.44
Ac_2O_3	white		hexagonal	La_2O_3 ($P\bar{3}m1$)	4.07		6.29		9.19
Pu_2O_3	?		cubic	$Ia3$	11.03				10.44
Pu_2O_3	black	2085	hexagonal	La_2O_3 ($P\bar{3}m1$)	3.841		5.958		11.47
Am_2O_3	tan		hexagonal	La_2O_3 ($P\bar{3}m1$)	3.817		5.971		11.77
Am_2O_3	reddish brown		cubic	$Ia3$	11.03				10.57
Cm_2O_3	white to faint tan	2260	hexagonal	La_2O_3 ($P\bar{3}m1$)	3.792		5.985		12.17
Cm_2O_3	light green		monoclinic	Sm_2O_3($C2/m$)	14.282	3.641	8.883	$\beta = 100.29$	11.90
Cm_2O_3	white		cubic	$Ia3$	11.002				10.80
Bk_2O_3	light green		hexagonal	La_2O_3 ($P\bar{3}m1$)	3.754		5.958		12.47
Bk_2O_3	yellow-green		monoclinic	$C2/m$	14.197	3.606	8.846	$\beta = 100.23$	12.20
Bk_2O_3	yellowish brown		cubic	$Ia3$	10.998				11.66
Cf_2O_3	pale green		hexagonal	La_2O_3 ($P\bar{3}m1$)	3.72		5.96		12.69
Cf_2O_3	lime green		monoclinic	$C2/m$	14.12	3.591	8.809	$\beta = 100.34$	12.37

Table 15.9 (*Contd.*)

Compound	*Color*	*Melting point* (°C)	*Symmetry*	*Space group or structure type*	*Lattice parameters*				*Density* (g cm^{-3})
					a_0 (Å)	b_0 (Å)	c_0 (Å)	β (deg)	
Cf_2O_3	pale green		cubic	I*a*3	10.839				11.39
Es_2O_3	white		hexagonal	La_2O_3 ($P\bar{3}m1$)	3.7		6.0		12.7
Es_2O_3	white		monoclinic	C2/*m*	14.1	3.59	8.80	$\beta = 100$	12.4
Es_2O_3	white		cubic	I*a*3	10.766				11.79
ThO_2	white		f. c. cubic	fluorite	5.592				10.00
PaO_2	black		f. c. cubic	fluorite	5.509				10.45
UO_2	black or brown		f. c. cubic	fluorite	5.4704				10.95
NpO_2	apple green		f. c. cubic	fluorite	5.4334				11.14
PuO_2	yellow-green		f. c. cubic	fluorite	5.3960				11.46
AmO_2	black		f. c. cubic	fluorite	5.374				11.68
CmO_{2-x}	black		f. c. cubic	fluorite	5.358				11.92
BkO_2	yellowish-brown		f. c. cubic	fluorite	5.3315				12.31
CfO_{2-x}	black		f. c. cubic	fluorite	5.310				12.46
Pa_2O_5	white		cubic	fluorite-related	5.446				11.14
Np_2O_5	dark brown		monoclinic	$P2_1/c$	4.183	6.584	4.086	$\beta = 90.32$	8.18
α-U_3O_8	black-green	1150 (dec)	orthorhombic	C2*mm*	6.716	11.960	4.147		8.39
β-U_3O_8	black-green		orthorhombic	C*mcm*	7.069	11.445	8.303		8.32
γ-UO_3	orange	650 (dec)	orthorhombic	F*ddd*	9.813	19.93	9.711		7.80
$AmCl_2$	black		orthorhombic	$PbCl_2$ (P*bnm*)	8.963	7.573	4.532		6.78
$CfCl_2$	red-amber		?						
$AmBr_2$	black		tetragonal	$SrBr_2$ (P4/*n*)	11.592		7.121		7.00
$CfBr_2$	amber		tetragonal	$SrBr_2$	11.500		7.109		7.22
β-ThI_2	gold		hexagonal	$P6_3/mmc$	3.97		31.75		7.45
AmI_2	black	~700	monoclinic	EuI_2 ($P2_1/c$)	7.677	8.311	7.925	$\beta = 98.46$	6.60
CfI_2	violet		hexagonal	CdI_2($P\bar{3}m1$)	4.557		6.992		6.63
CfI_2	violet		rhombohedral	$CdCl_2$ ($R\bar{3}$/m)	7.434			$\alpha = 35.83$	6.58

$\mathrm{AcF_3}$	white		trigonal	$\mathrm{LaF_3}$ ($P\bar{3}c1$)	7.41		7.53	7.88
$\mathrm{UF_3}$	black	dispropor-tionates above 1000	trigonal	$\mathrm{LaF_3}$	7.173		7.341	8.95
$\mathrm{NpF_3}$	purple		trigonal	$\mathrm{LaF_3}$	7.129		7.288	9.12
$\mathrm{PuF_3}$	purple	1425	trigonal	$\mathrm{LaF_3}$	7.092		7.254	9.33
$\mathrm{AmF_3}$	pink	1393	trigonal	$\mathrm{LaF_3}$	7.044		7.225	9.53
$\mathrm{CmF_3}$	white	1406	trigonal	$\mathrm{LaF_3}$	7.014		7.194	9.85
$\mathrm{BkF_3}$	yellow-green		orthorhombic	$\mathrm{YF_3}$ ($Pnma$)	6.70	7.09	4.41	9.70
$\mathrm{BkF_3}$	yellow-green		trigonal	$\mathrm{LaF_3}$	6.97		7.14	10.15
$\mathrm{CfF_3}$	light green		orthorhombic	$\mathrm{YF_3}$	6.653	7.039	4.393	9.88
$\mathrm{CfF_3}$	light green		trigonal	$\mathrm{LaF_3}$	6.945		7.101	10.28
$\mathrm{AcCl_3}$	white		hexagonal	$\mathrm{UCl_3}$	7.62		4.55	4.81
$\mathrm{UCl_3}$	green	835	hexagonal	$P6_3/m$	7.452		4.328	5.51
$\mathrm{NpCl_3}$	green	~800	hexagonal	$\mathrm{UCl_3}$	7.413		4.282	5.60
$\mathrm{PuCl_3}$	emerald green	760	hexagonal	$\mathrm{UCl_3}$	7.394		4.243	5.71
$\mathrm{AmCl_3}$	pink or yellow	715	hexagonal	$\mathrm{UCl_3}$	7.382		4.214	5.87
$\mathrm{CmCl_3}$	white to pale green	695	hexagonal	$\mathrm{UCl_3}$	7.374		4.185	5.95
$\mathrm{BkCl_3}$	green	603	hexagonal	$\mathrm{UCl_3}$	7.382		4.127	6.02
α-$\mathrm{CfCl_3}$	green	545	orthorhombic	$\mathrm{TbCl_3}$ ($Cmcm$)	3.859	11.748	8.561	6.07
β-$\mathrm{CfCl_3}$	green		hexagonal	$\mathrm{UCl_3}$	7.379		4.090	6.12
$\mathrm{EsCl_3}$	white to orange		hexagonal	$\mathrm{UCl_3}$	7.40		4.07	6.20
$\mathrm{AcBr_3}$	white		hexagonal	$\mathrm{UBr_3}$	8.06		4.68	5.85
$\mathrm{UBr_3}$	red	730	hexagonal	$P6_3/m$	7.942		4.441	6.54
$\mathrm{NpBr_3}$	green		hexagonal	$\mathrm{UBr_3}$	7.919		4.392	6.65
$\mathrm{NpBr_3}$	green		orthorhombic	$\mathrm{TbCl_3}$ ($Cmcm$)	4.109	12.618	9.153	6.67
$\mathrm{PuBr_3}$	green	681	orthorhombic	$\mathrm{TbCl_3}$	4.097	12.617	9.147	6.72
$\mathrm{AmBr_3}$	white to pale yellow		orthorhombic	$\mathrm{TbCl_3}$	4.064	12.661	9.144	6.85
$\mathrm{CmBr_3}$	pale yellow-green	625 ± 5	orthorhombic	$\mathrm{TbCl_3}$	4.041	12.700	9.135	6.85

Table 15.9 (*Contd.*)

Compound	*Color*	*Melting point* (°C)	*Symmetry*	*Space group or structure type*	*Lattice parameters* a_0 (Å)	b_0 (Å)	c_0 (Å)	β (deg)	*Density* (g cm^{-3})
$BkBr_3$	light green		monoclinic	$AlCl_3$ (C2/*m*)	7.23	12.53	6.83	$\beta = 110.6$	5.604
$BkBr_3$	light green		orthorhombic	$TbCl_3$	4.03	12.71	9.12		6.95
$BkBr_3$	yellow green		rhombohedral	$FeCl_3$ $(R\bar{3})$	7.66			$\alpha = 56.6$	5.54
$CfBr_3$	green		monoclinic	$AlCl_3$	7.215	12.423	6.825	$\beta = 110.7$	5.673
$CfBr_3$	green		rhombohedral	$FeCl_3$	7.58			$\alpha = 56.2$	5.77
$EsBr_3$	straw		monoclinic	$AlCl_3$	7.27	12.59	6.81	$\beta = 110.8$	5.62
β-ThI_3			orthorhombic	C*ccm*	8.735	20.297	14.661		
UI_3	black		orthorhombic	$TbCl_3$ (C*mcm*)	4.334	14.024	10.013		6.78
NpI_3	brown		orthorhombic	$TbCl_3$	4.30	14.03	9.95		6.82
PuI_3	green		orthorhombic	$TbCl_3$	4.33	13.95	9.96		6.92
AmI_3	pale yellow		hexagonal	BiI_3 $(R\bar{3})$	7.42		20.55		6.35
AmI_3	yellow		orthorhombic	$TbCl_3$	4.28	13.94	9.974		6.95
CmI_3	white		hexagonal	BiI_3	7.44		20.40		6.40
BkI_3	yellow		hexagonal	BiI_3	7.584		20.87		6.02
CfI_3	red-orange		hexagonal	BiI_3	7.587		20.81		6.05
EsI_3	amber to light yellow		hexagonal	BiI_3	7.53		20.84		6.18
ThF_4	white	1068	monoclinic	UF_4 (C2/*c*)	13.049	11.120	8.538	$\beta = 126.31$	6.20
PaF_4	reddish-brown		monoclinic	UF_4	12.88	10.88	8.49	$\beta = 126.4$	6.38
UF_4	green	1036	monoclinic	C2/*c*	12.7941	10.7901	8.3687	$\beta = 126.25$	6.71
NpF_4	green		monoclinic	UF_4	12.68	10.66	8.34	$\beta = 126.3$	6.86
PuF_4	brown or pink		monoclinic	UF_4	12.59	10.69	8.29	$\beta = 126.0$	7.05
AmF_4	tan		monoclinic	UF_4	12.56	10.58	8.25	$\beta = 125.9$	7.23
CmF_4	light gray-green		monoclinic	UF_4	12.50	10.49	8.18	$\beta = 126.1$	7.36
BkF_4	pale yellow-green		monoclinic	UF_4	12.396	10.466	8.118	$\beta = 126.33$	7.55
CfF_4	light green		monoclinic	UF_4	12.38	10.44	8.12	$\beta = 126.2$	7.57

$\alpha\text{-ThCl}_4$	white		tetragonal	$I4_1/a$	6.408		12.924		
$\beta\text{-ThCl}_4$	white	770	tetragonal	UCl_4 ($I4_1/amd$)	8.491		7.483		
$PaCl_4$	greenish-yellow		tetragonal	UCl_4	8.377		7.481		4.72
UCl_4	green	590	tetragonal	$I4_1/amd$	8.3018		7.4813		4.87
$NpCl_4$	red-brown	518	tetragonal	UCl_4	8.266		7.475		4.96
$\alpha\text{-ThBr}_4$	white		tetragonal	$I4_1/a$	6.737		13.601		5.94
$\beta\text{-ThBr}_4$	white		tetragonal	UCl_4	8.971		7.912		
$PaBr_4$	orange-red		tetragonal	UCl_4	8.824		7.957		5.90
UBr_4	brown	519	monoclinic	$C2/m$	10.92	8.69	7.05	$\beta = 93.9$	5.55
$NpBr_4$	dark red	464	monoclinic	$C2/m$	10.89	8.74	7.05	$\beta = 94.19$	
ThI_4	yellow	556	monoclinic	$P2_1/n$	13.216	8.068	7.766	$\beta = 98.68$	6.00
PaI_4	black								
UI_4	black		monoclinic	$C2/c$	13.967	8.472	7.510	$\beta = 90.54$	
PaF_5	white		tetragonal	$I\bar{4}2d$	11.53		5.19		
$\alpha\text{-UF}_5$	grayish white		tetragonal	$I4/m$	6.5259		4.4717		5.81
$\beta\text{-UF}_5$	pale yellow		tetragonal	$I\bar{4}2d$	11.469		5.215		6.45
NpF_5			tetragonal	$I4/m$	6.53		4.45		
$PaCl_5$	yellow	306	monoclinic	$C2/c$	8.00	11.42	8.43	$\beta = 106.4$	
$\alpha\text{-UCl}_5$	brown		monoclinic	$P2_1/n$	7.99	10.69	8.48	$\beta = 91.5$	3.81
$\beta\text{-UCl}_5$	red-brown		triclinic	$P\bar{1}$	7.07	9.65	6.35	$\alpha = 89.10$; $\beta = 117.36$; $\gamma = 108.54$	
$\alpha\text{-PaBr}_5$			monoclinic	$P2_1/c$	12.64	12.82	9.92	$\beta = 108$	
$\beta\text{-PaBr}_5$	orange-brown		monoclinic	$P2_1/n$	9.385	12.205	8.95	$\beta = 91.1$	
UBr_5	brown		triclinic	$P\bar{1}$	7.449	10.127	6.686	$\alpha = 89.25$; $\beta = 117.56$; $\gamma = 108.87$	5.07
PaI_5	black		orthorhombic	unknown	7.22	21.2	6.85		
UF_6	white	64.02 at 151.6 kPa	orthorhombic	$Pnma$	9.924	8.954	5.198		5.06
NpF_6	orange	55	orthorhombic	$Pnma$	9.909	8.997	5.202		5.00
PuF_6	reddish-brown	52	orthorhombic	$Pnma$	9.888	8.961	5.202		5.085
UCl_6	dark green	178	hexagonal	$P\bar{3}m1$	10.95		6.016		3.594

15.7.3 Other compounds

The actinide M^{3+} ions in aqueous solution resemble the tripositive lanthanide ions in their precipitation reactions, allowing for differences in the redox properties of early members of the actinide series. The chloride, bromide, nitrate, bromate, and perchlorate anions form water-soluble salts, which can be isolated as hydrated solids by evaporation. The acetates, iodates, and iodides are somewhat less soluble in water. The sulfates are sparingly soluble in hot solutions, and somewhat more soluble in the cold. Insoluble precipitates are formed with hydroxide, fluoride, carbonate, oxalate, and phosphate anions. Precipitates formed from aqueous solution are usually hydrated, and the preparation of anhydrous salts from the hydrates without formation of hydrolyzed species can only be accomplished with difficulty. The actinide(IV) ions resemble Ce(IV) in forming fluorides and oxalates that are insoluble even in acid solution. The nitrates, sulfates, perchlorates, and sulfides are all water-soluble. The 4+ state actinide ions form insoluble iodates and arsenates even in rather strong acid solution. The actinyl(V) ions can be precipitated as the insoluble potassium salts from concentrated carbonate solutions. Actinyl(VI) ions in solutions containing high concentrations of acetate ions form an insoluble crystalline double salt, $NaAnO_2(O_2CCH_3)_3$ (An = actinide). The hydroxides or hydrous oxides of any of the actinide ions in all oxidation states are insoluble in water. Some complex oxides such as $M^I_2U_2O_7$ or $M^{II}U_2O_7$(with $M^I = Na, NH_4\ldots; M^{II} = Mg\ldots$) can be precipitated from moderately alkaline solutions. The actinyl(VII) ions NpO_5^{3-} and PuO_5^{3-} exist as $MO_4(OH)_2^{3-}$ in alkaline solution, from which they can be precipitated by several di- and tripositive cations.

Actinide(IV) ions form insoluble peroxy compounds with hydrogen peroxide in moderately acid solution. The solid peroxy compounds incorporate inorganic anions such as sulfate, nitrate, or chloride that may be present in the solution. Phosphates, arsenates, cyanides, cyanates, thiocyanates, selenocyanates, sulfites, selenates, selenites, tellurates, and tellurites of some actinides have all been prepared, but our knowledge of these compounds is far from thorough.

15.7.4 Oxides and nonstoichiometric systems

There are many inorganic compounds whose composition is not necessarily expressible as the ratio of small whole numbers. Instead, they exist over a range of compositions. Compounds of variable composition often have electrical, magnetic, and thermal properties that are exceedingly sensitive to the exact composition. Nonstoichiometry is purely a solid-state phenomenon, which is associated with vacancies and/or interstitial ions in or near cation or anion sites in a crystal lattice (Anderson, 1970). Electrical neutrality in the crystal must of course be maintained, and deviations from exact stoichiometry can only exist if compensated by a change in the oxidation state of another constituent of the crystal. Nonstoichiometry is therefore encountered in binary and ternary compounds of transition elements with hydrogen, oxygen, chalcogens, pnictogens, carbon, silicon, and boron. The presence of a metallic ion in more than one oxidation state in a crystal endows nonstoichiometric compounds with a variety of interesting properties: they may be highly colored; they may show metallic electrical conductivity, or they may be semiconductors; they frequently show marked catalytic activity; and they may differ significantly in chemical reactivity from the stoichiometric compounds of the same elements. Nonstoichiometric compounds are important as transistors, thermistors, rectifiers, ionic electrical conductors, thermoelectric generators, photodetectors, and other electronic and optical devices. The actinide elements, because of the multiplicity of oxidation states that they can assume, are particularly prone to the formation of nonstoichiometric systems. This is especially true for the elements uranium through curium. The oxide systems illustrate many of the salient features of nonstoichiometry in actinide element chemistry.

The first actinide element to form nonstoichiometric oxides is protactinium. It is also the first of the actinide elements to have two readily accessible oxidation states. The black dioxide PaO_2 is obtained by reduction of Pa_2O_5 with hydrogen or carbon. Intermediate phases with the composition $PaO_{2.18\text{–}2.20}$, $PaO_{2.33}$, $PaO_{2.40\text{–}2.42}$, and $PaO_{2.42\text{–}2.44}$ have been identified by X-ray crystallography. Pa_2O_5 itself occurs in several crystal modifications determined by the method and temperature of preparation. The black color of PaO_2 indicates that it is probably nonstoichiometric and the white color of Pa_2O_5 indicates that it is stoichiometric.

The complexity of the uranium–oxygen system is awesome. In the composition range UO_2 to UO_3 there are close to a dozen phases, many of which exist in several crystal modifications. UO_3 itself occurs in six polymorphs. The complex phase relationships result from the easy change in oxidation state of the uranium as additional oxygen is introduced into the UO_2 lattice. The additional oxygen incorporated in hyperstoichiometric UO_{2+x} is distributed at random into vacant lattice sites. The original fluorite structure is distorted, but remains recognizably the same phase over a range of compositions. The stoichiometric range of a phase is a measure, at a particular temperature and oxygen pressure, of its ability to accommodate randomly distributed oxygen without change in the long-range order of a crystal. When random incorporation is no longer possible, additional oxygen is ordered in a superlattice structure, and a new phase appears, possibly because of variable composition. In the uranium–oxygen system such an abrupt transformation occurs at the composition $UO_{2.4}$. Six more phases occur between $UO_{2.4}$ and UO_3.

Only two neptunium oxide phases, with compositions of NpO_2 to $NpO_{2.5}$, are known. The composition of the latter oxide is consistent with the well-known stability of the Np(v) state. Plutonium has two oxides corresponding to the oxidation states 3+ and 4+, and an oxide of intermediate composition, $PuO_{1.61}$. Despite the existence of stable 6+ states for both neptunium and plutonium, no binary oxide corresponding to the 6+ oxidation state is known for neptunium but hyperstoichiometric PuO_{2+x} does appear to exist (Haschke *et al.*, 2000). Recent spectroscopic evidence indicates that it contains Pu(v) rather than Pu(vi) (Conradson *et al.*, 2004).

For the transplutonium elements through fermium, the 3+ oxidation state is the stable one, and the actinide elements following plutonium have (or should have, for Fm–Lr) oxides of the composition An_2O_3. All of the transplutonium elements to californium also form oxides in which the actinide elements have the formal oxidation state 4+, which is consistent with the known ability of these elements to assume oxidation states higher than 3+. The relative ease of formation of the transplutonium dioxides from $MO_{1.5}$ is in the order $BkO_2 > AmO_2 > CmO_2 > CfO_2$. Curium and californium are also reported to form intermediate oxides of the composition $CmO_{1.714}$ and $CfO_{1.714}$. In the case of $CfO_{1.714}$, this is the highest oxide that can be prepared in air or in oxygen at 1 atm pressure. The oxide systems of the transcalifornium elements still remain to be explored. By comparison, the nonstoichiometric compounds of the actinides elements with the chalcogenides and pnictides have only received a modest amount of study.

15.7.5 Crystal structures and ionic radii

The vast accumulation of crystallographic structural data, especially structures of ionic compounds solved by single-crystal diffractometry, has provided the basis for the determination of the ionic radii of monatomic ions in several coordination numbers. Actinide ionic radii for coordination number 6 are presented in Table 15.10. Ionic radii for the lanthanide series are listed for comparison. For both the 3+ and 4+ ions of the actinide series, the ionic radii decrease with increasing atomic number, a phenomenon that is caused by decreased shielding by f-electrons of the outer valence electrons from the increasing nuclear charge. This behavior, termed ‘actinide contraction,’ is very similar to the corresponding ‘lanthanide contraction.’ As a consequence of the ionic character of most actinide compounds, and the similarity of the ionic radii for a given oxidation state, analogous compounds of lanthanide and actinide ions with similar ionic radii are generally isostructural. In the series UBr_3, $NpBr_3$, $PuBr_3$, and $AmBr_3$, for example, the structural type changes with increasing atomic number, which is consistent with the contraction in ionic radius and with lanthanide tribromides that have similar Ln^{3+} ionic radii (Brown, 1968; Eick, 1994). The extraordinary stability of the fluorite-type MO_2 structure is responsible for the existence of such compounds as PaO_2, AmO_2, CmO_2, and CfO_2, despite the relative instability of the 4+ oxidation state of these elements in solution and in many solids. The actinide contraction and the isostructural relationships among the compounds of 4f and 5f elements are particularly convincing examples of evidence for the actinide elements as a 5f transition series.

Table 15.10 *Ionic radii of lanthanides and actinides* (*coordination number* 6) (*Shannon*, 1976, *except as noted*).

No. of 4f or 5f electrons	*Lanthanide series*						*Actinide series*					
	2+ *ion*	*Radius* (Å)	3+ *ion*	*Radius* (Å)	4+ *ion*	*Radius* (Å)	2+ *ion*	*Radius* (Å)	3+ *ion*	*Radius* (Å)	4+ *ion*	*Radius* (Å)
0			La^{3+}	1.032	Ce^{4+}	0.87			Ac^{3+}	1.12	Th^{4+}	0.94
1			Ce^{3+}	1.01	Pr^{4+}	0.85			Th^{3+}		Pa^{4+}	0.90
2			Pr^{3+}	0.99					Pa^{3+}	1.04	U^{4+}	0.89
3			Nd^{3+}	0.983					U^{3+}	1.025	Np^{4+}	0.87
4	Nd^{2+}	1.20[a]	Pm^{3+}	0.97					Np^{3+}	1.01	Pu^{4+}	0.86
5			Sm^{3+}	0.958					Pu^{3+}	1.00	Am^{4+}	0.85
6	Sm^{2+}	1.18[a]	Eu^{3+}	0.947					Am^{3+}	0.975	Cm^{4+}	0.84[b]
7	Eu^{2+}	1.17	Gd^{3+}	0.938	Tb^{4+}	0.76	Am^{2+}	1.16[a]	Cm^{3+}	0.97	Bk^{4+}	0.83
8			Tb^{3+}	0.923					Bk^{3+}	0.96	Cf^{4+}	0.821
9			Dy^{3+}	0.912					Cf^{3+}	0.95	Es^{4+}	0.81[c]
10	Dy^{2+}	1.07	Ho^{3+}	0.901			Cf^{2+}	1.14[d]	Es^{3+}	0.93[b]		
11			Er^{3+}	0.890					Fm^{3+}			
12			Tm^{3+}	0.880					Md^{3+}			
13	Tm^{2+}	1.03	Yb^{3+}	0.868					No^{3+}			
14	Yb^{2+}	1.02	Lu^{3+}	0.861			No^{2+}	1.05[e]	Lr^{3+}			

[a] Corrected to coordination number 6 using Fig. 2 of Shannon (1976).

[b] Shannon (1976) gives 0.85 Å, which is not consistent with lattice parameters of dioxides (Table 15.9).

[c] Chapter 12.

[d] Mean of values of Chapter 11 (0.01 smaller than IR(Eu^{2+}) and David (1984) (1.125 Å), both for coordination number 6.

[e] Estimated by David (1984).

15.7.6 Organoactinide compounds

When the first edition of this book was in preparation (1956), the prospects of an organoactinide chemistry, i.e. compounds containing an actinide–carbon bond, were judged to be very dim. At this time of writing, the situation is very different. A rich organometallic chemistry of the actinide elements has come into existence in the last four decades, so luxuriant in fact that presenting a concise summary that does justice to the subject is not possible. This field of inquiry is one of the most active and important in current actinide element research (see Chapters 25 and 26). Not only are new organoactinide compounds with remarkable properties appearing, but studies of their structure and physical properties by the use of nuclear magnetic resonance (NMR), optical and vibrational spectroscopy, photoelectron spectroscopy, crystallography, and many other physical and chemical techniques are contributing valuable information on the electronic structure and the nature of chemical bonding in the 5f elements, subjects that are of great importance in every aspect of actinide element chemistry.

The large size and the generally ionic bonding for the 5f ions result in different reactivities and coordination with the same ligands as compared to the d-transition series. In addition, the early actinides, uranium, neptunium, and plutonium in particular, have stable oxidation states ranging from trivalent to hexavalent, which introduces a range of possible organometallic compounds with varying formal charge on the metal ion. Due to the relatively easy availability of thorium and uranium starting materials and the low specific activity of the naturally occurring isotopes of these elements, most of the work to date has been done with thorium and uranium. Only a few organometallic compounds of the transuranium elements have been characterized.

The best known covalent organometallic compound of a transition metal, $Fe(C_5H_5)_2$ (ferrocene), was synthesized in 1951 (Keally and Pauson, 1951). The main group elements were well known to form compounds in which covalent metal–carbon bonds were formed, but transition metals were widely regarded as incapable of forming stable bonds of this kind. The first stable transition-metal organometallic compounds were derivatives of cyclopentadiene, C_5H_6. Its anion, cyclopentadienide ion (Cp^-), is aromatic and possesses 6 π electrons capable of coordination to vacant d-orbitals on a transition metal. In 1956, uranium, newly recognized as a member of a 5f transition element series, became the first of the actinide elements to yield a stable cyclopentadienyl (Cp) compound, tris(cyclopentadienyl)uranium chloride, Cp_3UCl (Reynolds and Wilkinson, 1956). A decade was to pass before the first transuranium organometallic derivative, tris(cyclopentadienyl)neptunium chloride, was prepared (Baumgartner *et al.*, 1965). Since then, hundreds of organometallic derivatives of the actinide metals have been prepared. Among these are compounds containing other π-donor ligands, such as indenyl and cyclooctatetraenyl groups. The introduction of bulky alkyl- and silyl-substituted derivatives of these π-donor ligands has extended the scope of these reactions and allowed the isolation of discrete molecular entities because the large ionic radii of the actinide ions require sterically demanding ligands so that only one or a few coordinatively unsaturated sites are available for reaction. These compounds provide an excellent environment for the study of chemical bonding in the f-block elements.

Cyclopentadienyl organoactinide compounds can be prepared by a variety of reactions (Marks and Fischer, 1979). One method for actinides in the 3+ and 4+ oxidation states is by reaction of potassium or sodium cyclopentadienide with the anhydrous actinide halide (AnX_n) in an organic solvent such as tetrahydrofuran (THF), toluene, or diethyl ether:

$$AnX_4 + 4KCp \rightarrow AnCp_4 + 4KX$$

$$AnX_4 + 3KCp \rightarrow Cp_3AnX + 3KX$$

$$AnX_3 + 3KCp \rightarrow AnCp_3 + 3KX$$

The actinide compounds are recovered from the reaction mixture by extraction with an appropriate organic solvent, and can be further purified by sublimation in a good vacuum when the volatility of the compound permits. The actinide cyclopentadienylides can also be prepared by metathesis in the molten phase by heating the actinide halide with beryllium or magnesium cyclopentadienides. The tris(cyclopentadienyl) compounds are strong Lewis acids and form adducts with many Lewis bases. They are ionic substances, although the bonding has more covalent character than in the corresponding lanthanide compounds. All of the actinide(III) compounds, with the exception of the uranium compound, are soluble in organic solvents, are reasonably stable, and are appreciably volatile, but all are sensitive to air. The tetrakiscyclopentadienyl complexes are soluble in organic solvents and moderately stable to air; they are not, however, appreciably volatile.

Compounds of the type Cp_3AnX, where the actinide element is in the 4+ oxidation state and X is an anion, have been prepared in large numbers and with a great variety of anions. Evidence has been adduced that the uranium tris (cyclopentadienyl) chloride ionizes in oxygen-free water to form the UCp_3^+ and Cl^- ions. The halide ion (X^-) in compounds of the type Cp_3AnX can be exchanged in solution by reaction with KX′. Anions (X'^-) that can be introduced include not only other halides, but also sulfate, perchlorate, nitrate, thiocyanate, etc., and also more exotic anions such as BH_4^-, BPh_3CN^-, $Co_3(CO)_{10}^-$, and OR^- (where R is an alkyl or other organic entity). These compounds have been subjected to structural analysis as well as examination by modern spectroscopic techniques. NMR spectroscopy has shown that the hydrogen atoms in the borohydride derivatives are all equivalent. The crystal structure indicates that in the BH_4^- anion there are two structurally distinct hydrogen atoms, bridging and terminal atoms. The equivalence of the hydrogen atoms on the NMR timescale demonstrates the existence of a rapid internal dynamic exchange process. The NMR studies have not only revealed unusual features of the structure of the organometallic compounds but have also contributed to the theory of NMR paramagnetic chemical shifts by virtue of the magnetic properties of the 5f electrons in the compounds.

The discovery in 1968 by Streitwieser and coworkers (Streitwieser and Muller-Westerhof, 1968; Seyferth, 2004) that the dianion of cyclooctatetraene (COT), $C_8H_8^{2-}$, can act as a ligand to the actinide elements signaled an important new development in organoactinide chemistry. The first compound of this class was uranocene, prepared by reaction of UCl_4 with potassium salt of COT:

$$UCl_4 + 2K_2(COT) \rightarrow U(COT)_2 + 4KCl$$

Subsequently, the corresponding compounds of Th, Pa, Np, and Pu have been prepared. All have a sandwich structure in which two planar COT dianion rings enclose a metal atom. Uranocene is the most intensively studied of these compounds. It is exceedingly reactive toward oxygen, but it reacts only slowly with water or acetic acid. Unlike the cyclopentadienyl compounds of the actinides, all reactions with strong electrophiles completely decompose uranocene. The nature of the bonding in the actinide bis-cyclooctatetraene compounds has naturally attracted much interest. From crystal structure data, ionic bonding seems plausible, but photoelectron, NMR, and Mössbauer spectroscopy all suggest substantial covalency. This conclusion is reinforced by *ab initio* calculations on this series of molecules. NMR has been especially useful in studying ligand-exchange reactions, in mapping the electron spin distribution, and in exploring the dynamic processes in these compounds.

Attempts to prepare organometallic compounds that contain a direct metal–carbon bond were made in the very early days of the Manhattan Project, with the objective of producing compounds sufficiently volatile to be useful in isotope separation by diffusion or electromagnetic separation methods. All products prepared by the reactions then available for the synthesis of σ metal–carbon bonds gave products that were unstable at room temperature. The first cyclopentadienyl compound containing a true σ metal–carbon bond was obtained by alkylation of tris(cyclopentadienyl) uranium(IV) chloride (Brandi *et al.*, 1973; Gebala and Tsutsui, 1973; Marks *et al.*, 1973):

$$UCp_3Cl + RLi \rightarrow UCp_3R + LiCl$$

where R = methyl, and many other straight- and branched-chain alkyl groups, unsaturated alkenes such as allyl and vinyl, aromatic radicals such as phenyl, tolyl, or benzyl, or many other functional groups. Analogous compounds of thorium, but not of the other actinide elements, have also been reported. The structure of the UCp_3R compounds is basically a distorted tetrahedron with the three cyclopentadienyl rings at three of the corners, and the sigma bonded alkyl group at the fourth corner on the three-fold axis of rotation of the molecule. The NMR spectra are very informative about the structure, the spin delocalization of U(IV), and the structural dynamics of the molecule. At room temperature the three cyclopentadienyl rings are magnetically equivalent, but at low temperature the equivalence vanishes because of restricted rotation about the uranium–carbon σ bond.

The chemistry of the actinide–carbon σ bond has been studied intensively. The Cp_3AnR (and alkyl- or silyl-substituted Cp) compounds are extremely sensitive to air, have high thermal stability, and completely lack any tendency for β-hydride elimination by the alkyl moiety. Hydrogen elimination is a common process in d-block organometallic compounds, and its complete suppression in the actinide hydrocarbyl derivatives is noteworthy. Uranium(IV) and thorium(IV) bis(pentamethylcyclopentadienyl) dichlorides can be readily alkylated with lithium reagents in diethyl ether solutions to yield the air-sensitive but thermally stable bis(pentamethylcyclopentadienyl) actinide dialkyls. These actinide hydrocarbyls are highly reactive. Hydrogenolysis yields organoactinide hydrides; this constituted the first preparation of a member of this class of compounds. The dialkyls also show remarkable reactivity with carbon monoxide at low temperatures to form metal–oxygen and carbon–carbon double bonds, reactions that are of interest in catalysis.

A complete review of the present state of organometallic chemistry of the actinides (including the details and references to the work described here) is presented in Chapter 25 and the use of organoactinide compounds in catalysis is given in Chapter 26. Chapter 17 covers the bonding in organometallic compounds of the actinides as described by *ab initio* calculations.

15.8 ENVIRONMENTAL ASPECTS OF THE ACTINIDE ELEMENTS

The development of a large-scale nuclear power industry and the detonation of nuclear weapons in the atmosphere have created worldwide anxiety about the long-term consequences arising from the introduction of transuranium elements into the atmosphere, the hydrosphere, and the biosphere. The radioactive nature of the transuranium elements, and the relatively long half-lives of many of these radionuclides, provide ample reasons for concern. In this section, a summary of the distribution and migration of the actinide elements in the environment is presented. In the preparation of this section we have made extensive use of a number of reviews (Walters *et al.*, 1983; Allard *et al.*, 1984; Bidoglio *et al.*, 1984; Scoppa, 1984; Silva and Nitsche, 1995; Runde, 2000; Choppin *et al.*, 2002, 2003; this work, Chapter 22). A summary of the environmental research on the transuranium elements conducted under the auspices of the U.S. Department of Energy to 1980 provides a comprehensive and authoritative guide to the voluminous literature on the subject (Hanson, 1980).

15.8.1 Actinide elements of natural origin

Several of the actinide elements are natural constituents of the Earth's crust. Of these, thorium and uranium are relatively common and, in the aggregate, occur in enormous quantities in the lithosphere. Uranium and thorium, in fact, are present in the Earth's crust to a larger extent than such familiar elements as mercury, bismuth, tin, cadmium, and silver, and in about the same concentration as lead. The uranium concentration is estimated at 1–10 $\mu g\ g^{-1}$ (1–10 ppm) in the igneous rocks of the Earth's crust; some sedimentary rocks contain much more, as also do some granites. The concentration of thorium in igneous rock is somewhat higher than that of uranium, in the range 5–20 $\mu g\ g^{-1}$ (Hedrick, 1999). The uranium content of seawater is 3.3 $\mu g\ L^{-1}$; thorium concentrations in water are much lower ($6 \times 10^{-4}\ \mu g\ L^{-1}$) (Allard *et al.*, 1984). Estimates of about 10^{14} tons for the uranium content of the Earth's crust (to a depth of 20 km) have been made, and about 10^{10} tons of uranium may be contained in the Earth's oceans. Other naturally occurring radioactive elements, which are all decay progeny of long-lived thorium or uranium isotopes, are present in the lithosphere and oceans to much smaller extents: protactinium and radium have an abundance of about 10^{-12} mass percent, and the remaining radioactive isotopes as little as several orders of magnitude less. The concentration of radioactive nuclides in secular equilibrium with the progenitors of the natural uranium and thorium decay series is determined by the half-lives of the daughter radionuclides, and, unless concentrated by some geochemical process, they will be present in very small concentrations. Radioactivity is a primeval endowment of the world we inhabit.

Neptunium and plutonium are found in nature in minute amounts, formed by nuclear reactions with fission neutrons in uranium. The ratio of $^{239}Pu/^{238}U$ is on the order of 10^{-12} (see Chapter 7, Table 7.3). Longer-lived ^{244}Pu, which may be primordial in origin, is present in the rare earth mineral bastnasite to the extent of 1 part in 10^{18} (Hoffman *et al.*, 1971). The amount of the naturally occurring plutonium isotopes are so small that for all practical purposes any of the transuranium elements encountered in the environment must be taken as man-made.

There is convincing evidence that some uranium ores have in past geological epochs sustained natural chain reactions. Some samples of pitchblende, U_3O_8, from the Oklo Mine in Gabon, Africa, have a ^{235}U content distinctly lower than the natural average of 0.72%. Some samples contained less than 0.5% ^{235}U, and other elements in these samples had isotopic compositions that varied considerably from the norm. For example, some of the pitchblende from the Oklo Mine had an unusually high content of ^{143}Nd, and an equally unusually low content of ^{142}Nd. Fission-product neodymium contains a high percentage of ^{143}Nd, whereas ^{142}Nd is not formed in the fission of ^{235}U. A high ^{143}Nd content is found in ore that has a low ^{235}U content. These observations strongly suggest that in some remote bygone age, ^{235}U had undergone fission, a conclusion supported by the unusual isotopic compositions of elements in the ore, indicating they were produced by fission. It is not likely that similar natural 'reactors' are in operation today. Fissile ^{235}U has a much shorter half-life than ^{238}U. In the early days of the Earth, the ^{235}U content of uranium minerals relative to ^{238}U was therefore higher. The age of the Oklo deposit has been established at 1.74×10^9 years. Calculation indicates that the ^{235}U content of the Oklo pitchblende 1.74×10^9 years ago was about 3%. At this concentration of fissile material, water suffusing the ore deposit could have brought regions of the deposit to criticality, and a slow or intermittent chain reaction could have ensued. It is believed that other concentrated uranium ore deposits could have achieved supercriticality in the presence of water as a neutron moderator $(2\text{–}3) \times 10^9$ years ago. Such chain reactions conceivably played an important part in early geological events. It is interesting to note that the fission products produced at Oklo over an estimated period of 10^6 years are still retained in the rock in which they were formed more than a billion years ago (Maurette, 1976; Casas *et al.*, 2004).

15.8.2 Man-made actinides

In terms of amount, by far the most significant of the synthetic actinide elements is plutonium. Commercial nuclear power reactors produce approximately 70 metric tons per year worldwide of a mixture of plutonium isotopes as a by-product. About 1380 metric tons of plutonium was estimated to be in the world plutonium inventory in 2000, mostly still in unprocessed spent fuel assemblies from nuclear reactors (Albright *et al.*, 1996). Plutonium produced for nuclear weapons is mainly ^{239}Pu, but plutonium produced as a by-product of energy production contains substantial amounts of ^{240}Pu, ^{241}Pu, and ^{242}Pu and small amounts of ^{238}Pu (Albright *et al.*, 1996, p. 20).

The plutonium in the terrestrial environment (at or near the Earth's surface and in ocean sediment) is due, in decreasing order of importance, to the testing of nuclear weapons in the atmosphere, the reentry into the atmosphere and disintegration of satellites equipped with ^{238}Pu power sources, and the processing of irradiated nuclear reactor fuel.

(a) Nuclear weapons testing

A total of approximately 7700 kg of plutonium has been released in atmospheric and underground nuclear explosions. During the period 1950–63, when testing nuclear weapons in the atmosphere was regarded as acceptable practice by the USSR and the U.S., 4400 kg of plutonium, primarily ^{239}Pu and ^{240}Pu, were injected into the atmosphere in 543 acknowledged atmospheric detonations, mostly as plutonium oxide (Kim, 1986; Hobart, 1990). More than 99% of this has by now been redeposited on Earth; 10.87 PBq of ^{239,240}Pu has been deposited on the ocean (UNSCEAR, 2000); the concentration varies greatly as a function of latitude, longitude, and depth (Nakano and Povinec, 2003). The highest Pu concentrations in the ocean near the end of the 20th century were ~ 0.1 Bq m^{-3} in the vicinity of Eniwetok and Bikini atolls at a depth of about 800 m. Of the original 12.8 PBq (1.28×10^{16} Bq, 3.5×10^{5} Ci) of plutonium originally present in the atmosphere of the Northern Hemisphere, about 37 TBq (1000 Ci) remain, a decrease by a factor of 1000 or more (Olivier *et al.*, 2004). Another 1.4 metric tons of plutonium have been deposited in the ground in the course of surface and subsurface testing of nuclear devices (Allard *et al.*, 1984). When more recent weapons tests are included, approximately 6 metric tons of plutonium have been deposited in the Earth's environment from weapons tests that peaked in 1963 (Allard *et al.*, 1984; Olivier *et al.*, 2004).

(b) Disintegration of satellites

Plutonium that is highly enriched in ^{238}Pu has been released into the atmosphere, largely the result of the disintegration over the Indian Ocean in 1964 of a Transit satellite (Table 15.12) carrying a nuclear power source (Nenot and Metivier, 1984).

(c) Nuclear fuel processing and storage

The amount of plutonium in the environment resulting from nuclear reactors and fuel reprocessing operations is small. Measurements in the waters of the Seine Bay (taken near the La Hague fuel reprocessing plant) indicated a plutonium concentration of about 10000 times less than the concentration of natural uranium (Nenot and Metivier, 1984). Since that time the amounts of plutonium released from all these sources has been much smaller. However, there is a potential for future release from stored spent nuclear fuel: Examination of accelerated commercial spent fuel corrosion products by electron microscopy showed that U–Pu enriched layers exist in the corroded fuel and that some of the plutonium may be present as soluble and mobile Pu(v) (Buck *et al.*, 2004).

What complicates the environmental situation is that plutonium is not the only transuranium element produced in nuclear reactors. Americium and curium are also formed by multiple neutron capture (see Fig. 15.1). The amounts of long-lived actinides in spent fuel as a function of time after removal from a reactor are shown in Table 15.11. The elements americium and curium formed in the reactor undergo radioactive decay to produce radioactive daughter species (Allard *et al.*, 1984):

$$^{245}\mathrm{Cm} \rightarrow {}^{241}\mathrm{Pu} \rightarrow {}^{241}\mathrm{Am} \rightarrow {}^{237}\mathrm{Np} \rightarrow {}^{233}\mathrm{U} \rightarrow {}^{229}\mathrm{Th}$$

$$^{242}\mathrm{Am} \rightarrow {}^{242}\mathrm{Cm} \rightarrow {}^{238}\mathrm{Pu} \rightarrow {}^{234}\mathrm{U} \rightarrow {}^{230}\mathrm{Th} \rightarrow {}^{226}\mathrm{Ra}$$

$$^{243}\mathrm{Am} \rightarrow {}^{239}\mathrm{Pu} \rightarrow {}^{235}\mathrm{U} \rightarrow {}^{231}\mathrm{Pa} \rightarrow {}^{227}\mathrm{Ac}$$

Table 15.11 *Long-lived actinides in spent fuels*[a] (*Allard* et al., 1984).

Nuclide	*Half-life*[b] (yr)	*Activity* (GBq/ton U) *after*		
		40 yr	100 yr	1000 yr
^{229}Th	7.340×10^3	–	–	0.006
^{230}Th	7.538×10^4	0.018	0.048	0.74
^{231}Pa	3.276×10^4	0.001	0.002	0.011
^{232}U	68.9	0.78	0.44	–
^{233}U	1.592×10^5	0.003	0.007	0.15
^{234}U	2.455×10^5	52	67	89
^{235}U	7.038×10^8	0.52	0.52	0.52
^{236}U	2.3415×10^7	10	10	10
^{238}U	4.468×10^9	12	12	12
^{237}Np	2.144×10^6	16	19	48
^{239}Pu	2.411×10^4	1.1×10^4	1.1×10^4	1.1×10^4
^{240}Pu	6.564×10^3	1.4×10^4	1.4×10^4	1.3×10^4
^{241}Pu	14.35	9.3×10^5	5.2×10^4	12
^{242}Pu	3.733×10^5	110	110	110
^{241}Am	432.2	1.8×10^5	1.9×10^5	4.4×10^4
^{243}Am	7.37×10^3	0.0012	0.0012	0.0011

[a] PWR, 38 000 MW d ton^{-1} U.

[b] Appendix II, this work.

The effect of radioactive decay of the americium and curium is an increase in the intensity of radioactivity with time after removal from the reactor. For a period from 10 to 10^3–10^4 years after discharge from the reactor, the environmental hazards will be preponderantly due to ^{241}Am; from 10^4 to 10^5 years the nuclides ^{239}Pu and ^{240}Pu will be the principal actinides present; and for the period after 10^6 years, ^{237}Np will be the principal actinide present. The chemical properties of uranium, neptunium, plutonium, and americium thus determine the mode and extent of dispersion of alpha-emitting radionuclides introduced into the environment from nuclear operations. Table 15.12 indicates the amounts of transuranium elements released into the atmosphere as of 1980. The disposal of low-level waste streams from nuclear fuel reprocessing in the sea is estimated to add considerably less than 0.1 kg (0.3 TBq) per year of plutonium to the environmental inventory (Allard *et al.*, 1984).

15.8.3 Actinides in the hydrosphere

From the discussion of ions in solution and their redox and hydrolytic properties in Section 15.5, it can be inferred that the transuranium elements in a marine (ocean) environment will tend to form insoluble compounds. Under the redox conditions that obtain in the ocean, the stable oxidation states of plutonium,

Table 15.12 *Transuranium elements released to the atmosphere* (*Allard* et al., 1984; *LANL*, 2000, *pp.* 36–47).

Nuclide	*Amount* (TBq)
$^{238}Pu^{a}$	890^{b}
^{239}Pu	5.7×10^{3}
^{240}Pu	7.7×10^{3}
^{241}Pu	3.6×10^{5c}
^{241}Am	1.2×10^{4d}

[a] Half-life 87.7 years.

[b] Including 590 TBq from a SNAP 9A radionuclide battery in a Transit satellite that vaporized upon reentering the atmosphere in April 1964.

[c] Largely decayed to ^{241}Am.

[d] Largely from ^{241}Pu.

americium, and curium are expected to be Pu(iv), Pu(v), Am(iii), and Cm(iii). Under reducing conditions, neptunium is expected to be in the Np(iv) state and to behave much as does Pu(iv). Under oxidizing conditions, however, the neptunyl(v) ion, NpO_2^+, will be the stable species, and the similar Pu(v) ion PuO_2^+ predominates; these ionic species have smaller tendency to undergo hydrolysis or to form strong complexes than do the 4+ state ions or other actinyl ions in the 6+ oxidation state (Orlandini *et al.*, 1986). Plutonium and the other transplutonium elements in the 3+ and 4+ oxidation states readily undergo hydrolysis at the normal pH of marine waters to form hydroxides and oxides that are essentially insoluble in water. However, these ions form strong complexes with oxygen-containing ligands, which may change their redox potentials significantly, and this may render them oxidizable. The overall effect of the formation of higher oxidation states and complex ions is to produce actinide ions that are more soluble in water. The carbonate ion in particular is important because it is present in natural waters; it forms soluble complexes that stabilize the higher oxidation states of neptunium and plutonium. Allard *et al.* (1984) made a detailed analysis of the interaction of the transuranium elements with natural complexing agents as a function of concentration and pH, and calculated solubilities in water that may be expected for these elements under various conditions. Because natural conditions vary a great deal, it is difficult to make precise generalizations, but general trends can be discerned without too much difficulty. The transuranium actinides under most conditions form insoluble species that result in actinide enrichment in bottom sediments. The tendency to form strong complexes with water-insoluble oxygen-containing ligands (e.g. the exoskeletons of marine organisms) is another route for the removal of the transuranium actinides from the water column to the bottom sediments. The nature of the chemical forms in which the actinide elements occur in marine sediments, and the chemical processes that occur between seawater and sediments, are topics of active research (Morse and Choppin, 1986; McCubbin *et al*., 2002).

The availability of ocean transuranium elements to marine organisms has received attention. Plutonium is accumulated quite efficiently by benthic (sea-bottom) algae and invertebrates and by plankton. While it is a fairly straightforward matter to determine the plutonium content of harvested organisms, it is not so simple to decide the route by which the plutonium entered or just where in the organism the plutonium is retained. Transfer of plutonium in the water to starfish can take place via ingested food, but it can also occur by adsorption on the surface of the organism. The high concentration of plutonium in starfish appears to be due largely to the strong affinity of polymeric plutonium hydrosols or simple plutonium ions for the mucus sheath that coats the organism. Neptunium, as the NpO_2^+ ion, is rapidly accumulated and excreted by marine zooplankton, but appears, on the basis of limited observations, to be less available than either plutonium or americium.

The transfer rate of americium from sediments containing it in insoluble form is low, and it appears for the most part to be adsorbed on the exterior of bivalve molluscs, *Polychaeta* (marine worms), and isopods (crustaceans). In the presence of higher concentrations of carbonate (Atlantic sediments containing 83% carbonate as compared to Pacific sediments containing only 8% carbonate), the transfer of americium to living organisms increased several fold (Scoppa, 1984). Experiments in which the marine environment was simulated show that the accumulation of ^{241}Am by tiny crustaceans (krill) occurred mainly by adsorption on the exoskeleton, and that only a small amount of americium was retained by the krill after molting. Americium sorbed on diatoms ingested by krill was not assimilated and was excreted in a short time.

Based on a limited amount of data acquired in the Irish Sea near the reprocessing plant at Sellafield, UK, invertebrates and algae accumulate higher concentrations of curium than do the edible parts of fish. The behavior of californium has been studied in a preliminary way in seawater, sediments, and plankton (Scoppa, 1984). Cf(iii) is rapidly adsorbed by particulate matter and sediments with distribution coefficients of 10^4 to 10^5. It is also taken up rapidly by marine zooplankton. The relative order of uptake by krill is Cf(iii) > Am(iii) > Pu(v+vi) > Np(v). Assimilation and incorporation of Cf(iii) by the zooplankton in the internal tissues is extremely low in these organisms, and take-up is most likely due to adsorption on the surface of the organisms.

Actinide elements have been released into freshwater (rivers and lakes) as a result of subsurface plumes from leaking waste tanks or other storage of nuclear wastes at former military reactor processing sites. At the Hanford site (Washington state, USA) several tons of uranium, accompanied by other radionuclides, has contaminated the vadose zone. Synchrotron X-ray spectroscopy and diffraction studies of borehole samples showed uranium to be present in the U(vi) solids that are known forms. These solids make it unlikely that uranium is migrating in the vadose zone but will make it difficult to remove the uranium as a remediation option (Catalano *et al.*, 2004).

15.8.4 Actinide sorption and mobility

Polymeric actinide ions carry a positive charge, and are easily scavenged by negatively charged surfaces. As depolymerization is a very slow process even in strong acid solution, the Pu(IV) polymer is an attractive candidate for an explanation of the ease with which it is removed and the tenacity with which it is retained by clays or soils. Many minerals, especially clays with zeolitic channels and cages, have ion-exchange properties. Ion-exchange sites firmly bind the simple actinide ions in the III and IV oxidation states, and binding of the actinyl ions in the 5+ and 6+ states is considerably weaker. Plutonium is strongly sorbed on many minerals in the pH range normally encountered in the environment under both oxidizing and reducing conditions.

The overall effect of ion exchange and other sorption processes by solid phases is to remove actinides at tracer concentrations from an aqueous phase. The uptake on solids is in the same sequence as the order of hydrolysis: Pu(IV) > U(VI) > Am(III) > Np(V).

Assimilation in plants commonly declines in the order: Np(V) > U(VI) > Am (III) > Pu(IV), Np(IV). Both phenomena are evidently contingent on the species formed by hydrolysis: the easily immobilized species are also assimilated with difficulty by plants. The uptake of actinides by living organisms from solid phase is minor, and this is also the case for actinide elements immobilized on food. Of the 4400–7700 kg of plutonium that came to Earth after atmospheric testing of nuclear weapons, the total amount fixed in the world population is estimated to be less than 1 g (Allard *et al.*, 1984). Allard *et al.* (1984) conclude from the available evidence that plutonium in the environment is not concentrated in the food chain. Surface-adsorbed actinides appear to be the major mechanism for the introduction of transuranium elements into the terrestrial food chain even though the actinides are not actually incorporated into the internal tissues of the organisms (Teale and Brown, 2003). The enrichment of actinides in the food chain to humans is minimized by discrimination against the absorption of actinides by organisms at higher levels in the food chain. Thus, it is unlikely that the concentration of plutonium in a human being will significantly exceed the concentration in natural waters, regardless of the mode of ingestion.

Organic and inorganic particles or colloids to which actinide elements are attached constitute a major mode of dissemination of the actinide elements in the environment. Natural waters contain particulate silt and organic matter, which may or may not be living. Transport of actinide elements adsorbed on particulate matter will then depend on particle size, water flow, and factors other than the chemical properties of the actinide species themselves.

Living organisms can also act as carriers even if the actinide elements are not actually incorporated into the tissues of the organism.

15.8.5 Nuclear waste disposal

The fate of actinide elements introduced into the environment is not merely a scientific issue. The disposal of the by-products of the nuclear power industry has become a matter of industrial and public concern. For each 1000 kg of uranium fuel irradiated in a typical nuclear reactor for a 3 year period, about 50 kg of uranium are consumed. In addition to a large amount of energy evolved as heat, 35 kg of radioactive fission products and 15 kg of plutonium and transplutonium elements are produced. Many of the fission-product nuclides are stable or are short-lived radionuclides that decay to stable isotopes, but others are highly radioactive for decades or longer. All of the fission products are isotopes of elements whose chemical properties are well understood. The transuranium elements produced in the reactor by neutron capture, however, have unique chemical properties, which are reasonably well understood but are not easily inferred by extrapolation from the chemistry of the classical elements. Plutonium is fissile and can be recycled as a nuclear fuel in conventional or breeder reactors, but the transplutonium elements are not fissile to the extent of supporting a nuclear chain reaction, and in any event they are produced in amounts too small to be of interest for large-scale uses. The transplutonium elements must therefore be secured and stored.

The exact form in which fission products and heavy elements are extracted from spent fuel elements is determined by the chemical process used to treat the spent fuel. In the past, most fuel reprocessing has been by solvent extraction, and it is probable that solvent extraction will continue to be the most widely used processing procedure, at least until new reactor types are introduced. Solvent extraction is efficient in separating uranium, fission products, and transuranium elements, but large volumes of liquid waste streams with rather low but not negligible levels of radioactivity are generated in the process. The plutonium is generally separated from the transplutonium elements, leaving a complex mixture of fission products and americium, curium, and transcurium elements, which as they decay form isotopes of neptunium, uranium, and natural radioactive elements. These must be immobilized and stored in a way and in places where no geological or man-made catastrophe will release the radioactive material into the environment, even over an enormously long timespan.

Many schemes have been considered for disposal of both fission products and actinide elements. These proposals has been discussed by Choppin *et al.*, 2002, pp. 599–640), National Academy of Sciences (1995), and Van Tuyle *et al.* (2002) among others. Nuclear 'incineration,' the transmutation of excess plutonium and the 'minor actinides' neptunium, americium, and curium (which are the predominant source of radioactivity from spent fuel after about 600 years) in nuclear reactors after their separation from other components of spent fuel, is a realistic option pursued in several countries. Prolonged neutron irradiation in a conventional fission nuclear reactor, or possibly in a fast breeder reactor, will transmute long-lived actinide isotopes, especially excess weapons plutonium, to short-lived radioactive or stable isotopes faster than they will be formed from the uranium or uranium–plutonium mixed oxide (MOX) fuel in the reactor, especially if the nuclear fuel is an 'inert matrix' ceramic oxide that has no uranium. The actinide elements subjected to nuclear incineration in a reactor must be free of lanthanide fission products, as some of these have very large cross sections for neutron capture and thus could adversely affect the neutron economy of a nuclear reactor. A drawback of reactor incineration is that some plutonium is bred; this drawback can be mitigated by the use of uranium-free 'inert matrix fuels' that are ceramic oxides such as yttria stabilized zirconia or zirconates. These fuels are inert in the sense that the fuel cannot breed plutonium (Degueldre and Yamashita, 2003).

Another transmutation scheme is accelerator transmutation of long-lived nuclear wastes. An accelerator generates high neutron fluxes by spallation. These neutrons drive a subcritical reactor to fission the long-lived actinide isotopes without breeding additional plutonium. This technology can transmute fissile ^{235}U and ^{239}Pu, as well as the isotopes ^{237}Np, ^{241}Pu, and ^{241}Am that dominate both the long-term heat load and radiotoxicity of the waste.

Immobilization and disposal in appropriate geological formations has received the most attention. The first step in immobilization is to convert the liquid waste streams from fuel processing into dry solids by evaporation or some other drying process. The dry residue is calcined to convert the radioactive mix to metal oxides. In this form the calcined oxides are leachable and can easily become airborne. Their thermal conductivity is low, and good heat conductivity is essential to dissipate the heat liberated by radioactive decay. A great variety of glassy and crystalline matrices have been explored. Prime requirements are stability to radiation and to chemical attack by or to solubility in water, since exposure to groundwater is a possibility that must be guarded against in any subterranean repository. Borosilicate glasses are preferred matrices in most countries, and in fact France (La Hague) and the U.S. (Savannah River plant) have glass melters that have been in operation for one or more decades (CEA, 2002). Additional encapsulation of the solidified waste is generally considered mandatory, and for this purpose corrosion-resistant metals such as copper or C-22 alloy (UNS 06022, a nickel–chromium–molybdenum–tungsten alloy) have been selected for waste canisters.

The requirements for a geological repository are quite stringent. The repository must be sited in a region of high geological stability, free of earthquakes and volcanic activity. The chosen stratum must be free of vents to the surface, and it must have little or no groundwater circulation. It is important that the geological formation have good heat conduction properties to enable heat evolved by radioactive decay, which is very substantial, to be conducted away rapidly enough to prevent destruction of the containment by high temperature. Rock salt, granite, and clay all have their proponents. Disposal in the Arctic ice caps and burial in deep seabeds also have been considered. Rock salt formations, at least in the U.S., appear to be the geological stratum of choice for transuranic wastes. Unaltered rock salt formations of great age and of unquestionable seismic stability are known. Rock salt has exceptionally good heat transfer properties. Extremely dry salt domes that have existed for more than 100 million years without appreciable alteration exist in many places. Salt is plastic, and holes and fractures in the salt bed will self-seal. As long as the surface layers are not breached by drilling, and that provision is made in repository design for the corrosive properties of brine, rock salt domes appear to have most of the features required for a secure repository.

Clays likewise have desirable properties. The migration rate of fission products and actinides through clay is very slow and, once adsorbed in such a matrix, the transuranium elements are effectively immobilized. However, clay deposits frequently are percolated by water, and it is difficult to guarantee that even a bed dry for geological epochs will remain that way. Still, even radionuclides that enter underground water are readily removed and immobilized by ion exchange on clays and other minerals. A very good example of efficient and extraordinarily effective immobilization of radioactive fission products by natural processes is found in the Oklo mineral formation, where the products of a natural chain reaction have remained in close proximity to their point of origin although the rock formation has been suffused repeatedly by water in the past billion years (see Section 15.8.1). Although there are unanswered questions about nuclear repositories, there are many reasons to expect that the technical problems in nuclear waste disposal can be solved satisfactorily. Indeed, most of the necessary technology has been in existence for some time, and a high level of technical sophistication has been available for many years (Topp, 1982). It seems likely that interim or monitored retrieval storage will be the method of choice for the storage of nuclear waste. Storage of this kind is easier to prove safe and could be useful for a century or more.

15.9 BIOLOGICAL BEHAVIOR OF THE ACTINIDE ELEMENTS

15.9.1 General considerations

In this section we have made extensive use of several authoritative reviews (Bulman, 1980; Raymond and Smith, 1981; Nenot and Metivier, 1984; Banaszak *et al.*, 1999; Gorden *et al.*, 2003) that emphasize aspects of importance in the biological behavior of the actinide elements, both in the ecosphere and in humans. None of the elements heavier than iodine (atomic number 53) is, so far as is known, essential to life, and an intrusion by any of them into living organisms is generally regarded as a noxious event best avoided. Studies on the heavier elements tend to be sparse or fragmentary except where special circumstances apply, e.g. mercury or lead. Were it not for the long-lived radioactivity of the actinide elements, it is likely that they too would attract little interest. Uranium, neptunium, plutonium, and americium are regarded as the major health hazards among the actinide elements, and thus have been the focus of research activity (Thompson, 1982). Recently, interest in the oxidation–reduction and coordination of neptunium with microorganisms and their organic by-products (e.g. humic and fulvic acids) has reawakened and is now a theme in bioremediation research because Np(v) appears to be the most mobile of the actinide ionic species (Songkasiri *et al.*, 2002). This, coupled with the realization that long-lived ^{237}Np formed by the radioactive decay of ^{241}Pu (via the decay sequence

$$^{241}\mathrm{Pu} \xrightarrow{\beta^-} {}^{241}\mathrm{Am} \xrightarrow{\alpha} {}^{237}\mathrm{Np}$$

in nuclear waste) makes ^{237}Np the major contributor to the radioactivity of nuclear waste at times greater than 10^5 years, has stimulated new interest in the biological properties of neptunium. A comprehensive treatment of the behavior of actinides in animals and man is found in chapter 31.

15.9.2 State of actinide elements in body fluids

The forms in which plutonium, americium, and curium occur in blood and urine are continuing topics of major concern, for they are intimately involved in transport in the body after ingestion and in subsequent excretion. Boocock and Popplewell (1965) found that plutonium injected intravenously into the rat was bound in the blood serum to transferrin, a protein produced in the liver that transports iron between tissues and bone marrow. Pu(iv) in the blood is rapidly and firmly bound to transferrin. By far the greater part of the plutonium is captured by transferrin, but small amounts are believed to be complexed by citrate ion or low-molecular-weight carbohydrates or peptides. This may reflect a complex equilibrium situation, or may be an indication that more than one ionic species of plutonium in more than one oxidation state is present. The binding of plutonium to transferrin is strong, but Fe(iii) can displace it, and plutonium is not bound by iron-saturated transferrin. Bicarbonate ion is required to bind iron to transferrin, and this is also the case for plutonium. The half-life for the removal of transferrin-bound iron and plutonium from the circulation is the same. The exact nature of the binding sites remains unknown, and whether the same site is used for binding iron and plutonium is unsettled. Transferrin contains a sialic acid component (an oligo- or polysaccharide containing an acidic sugar, *N*-acetylneuraminic acid), which is an excellent complexing agent for metal ions. However, destruction of the polysaccharide moiety inhibits the binding of Pu(iv) but not of Fe(iii), suggesting a more complicated binding site situation than at first anticipated. Pu(iv) shows remarkable similarity to Fe(III) in its coordination behavior, attributed by Raymond *et al.* (1984) to similar ratios of charge to ionic radius for Pu(IV) (4.6e Å^{-1}) and Fe(III) (4.2e Å^{-1}). The 3+ ions of americium, curium, and the transcurium elements bind very weakly, if at all, to transferrin. Instead, the actinide(III) ions present in biological fluids are weakly associated with various plasma proteins. Uranium, present as the uranyl ion UO_2^{2+}, which has a much diminished tendency to form complex ions as compared to uranium in lower oxidation states, is found in the blood in roughly equal amounts associated with protein and as uranyl carbonate complex ions. U(IV), however, binds strongly to protein and is excreted very slowly.

Such studies as are available indicate that plutonium, americium, and curium are cleared through the kidneys and excreted in the urine as citrate complexes, whereas uranyl ion is excreted as a bicarbonate complex. Although there is by now a considerable body of information on the rate of excretion of plutonium in the urine as influenced by a variety of additives and presumptive therapeutic agents, much remains to be learned about the chemistry of the elimination of the actinide elements through the kidney.

Plutonium, americium, and curium are cleared from the liver through bile, which is the principal source of these elements in feces. The clearance of the actinide elements through the feces, however, constitutes only a very small fraction of the radioactivity transported in mammals. Transport of the actinide elements also appears to take place in lymph fluid. This is presumed to be the mode of transport of plutonium introduced in a wound. Plutonium as a simple ion in the lymphatic system moves with the fluid flow, but plutonium as a colloid or as particulate matter is transported in lymphocytes whose function is to scavenge ingested particulate matter. Plutonium in the fluid phase of the lymph migrates as a transferrin complex (Bulman, 1980). The behavior of plutonium and the transplutonium elements in the lymphatic system may well have an important bearing on the decorporation of ingested actinide elements, but too little information is available to make any definitive declarations on this point.

15.9.3 Uptake of actinide elements in the liver

Actinide elements are rapidly cleared from the body fluids. As is usual in the removal of xenobiotics, the first repository is the liver. According to Bulman (1980), the mechanism by which plutonium, americium, and curium are removed from the blood and trapped in the liver is not well understood. The actinide elements bound by transferrin are transferred in the liver to ferritin, an iron storage protein, but nothing is known about the transfer process. It might be expected that actinide element colloids would be taken up by endocytosis, the process of cellular uptake or internalization by which particles, macromolecules, and fluid droplets are removed from the bloodstream and incorporated into living cells. However, the literature does not support this view. Endocytosis (or pinocytosis as the process is also known) is not considered to play an important part in the incorporation of actinide elements into liver cells (Taylor, 1972). What seems well established is the critical role of phospholipids in the uptake of the actinide elements by the liver. Actinide(iii) and (iv) ions are complexed strongly by phosphates in simple aqueous systems. Th(iv) likewise interacts strongly with phospholipids (Boocock and Popplewell, 1965; Barton, 1968). Such behavior for other actinides ions in the 3+ and 4+ oxidation states would not be unexpected. Phospholipids could thus act as ionophores in the concentration of the actinide elements in the liver. The evidence in support of this hypothesis is mostly indirect. Based on the behavior of Fe(iii) and the uptake of plutonium in animals treated so as to have a much higher than normal concentration of phospholipids in the liver, there is reason to suppose that phospholipids cause concentration of plutonium by the liver. Thioacetamide characteristically increases the accumulation of acidic phospholipids in the liver, and this compound is found to cause a 2.5-fold increase in the uptake of Pu(iv) by the liver. The effect of various phospholipids on the liquid–liquid partition of Pu(iv), Am(iii), and Cm(iii) between water and water-immiscible organic solvents provides additional evidence of the ionophore capabilities of phospholipids. Nevertheless, the exact nature of the receptors involved in actinide uptake (if indeed there are specific receptors) remains to be established.

Several research groups have provided evidence that plutonium, americium, and curium are taken up by lysosomes in the liver. Lysosomes are specialized parts of cells or organelles in which an important part of the cellular metabolism is carried out. The lysosome is surrounded by a single membrane and contains a complex mixture of hydrolytic enzymes; together these enzymes are able to dismantle proteins, nucleic acids, polysaccharides, and lipids to their component parts. The actinide elements not translocated from the liver remain associated with the lysosomes, possibly bound to the iron storage proteins ferritin and hemosiderin. Lysosomes are associated with endocytosis and at least a fraction of the lysosomes are formed by endocytosis. If the main part of the actinide uptake is really associated with liver lysosomes, then it may be premature to exclude endocytosis as a primary event in liver uptake of actinide ions. A substantial association of the cellular actinide content with mitochondria is also probable.

A body of evidence indicates that, within 3 days of administration, considerable amounts of plutonium are bound to lysosomal ferritin, and similar findings have been reported for americium and curium administered as monomeric citrates (Boocock *et al.*, 1976). Americium has been reported to associate with lysosomal ferritin and lipofuscin, a yellow-brown pigment that accumulates in aging cells. Lipofuscin contains phospholipids and is known to bind metal ions.

15.9.4 Uptake of actinides by bone

The ultimate fate of plutonium that is not excreted promptly after administration or ingestion is deposition in the bone and other mineralized tissues. Whether the mineralization is phosphate- or carbonate-based appears to be immaterial. In cartilaginous fish, plutonium is concentrated in the skeleton to a significant extent, and in fish with a bony skeleton, the plutonium concentration in the soft tissues may be less than 1% of that in the skeleton. The uptake of actinide elements from the body fluids by bone is a slow process, because of the strong binding of plutonium by transferrin. Autoradiography of bone shows quite different patterns of deposition for plutonium and americium compared to the deposition of radioactive calcium. Calcium deposition is uniform, whereas actinide deposition is irregular. The lack of uniformity in the distribution of the actinides deposited in bone may be related to variations in the pH of the bone surface, or to different concentrations of citrate ion at different locations on the bone surface.

Glycoprotein has been suggested as the important agent in the fixation of plutonium, but glycoprotein is less important for americium or curium (Mahlum, 1967). Glycoproteins that have a high acidic amino acid content bind plutonium *in vitro*. Calcium ion is required for plutonium fixation, which suggests that calcium nucleation sites are necessary for plutonium uptake. Phospholipids have also been implicated in the process, and a lysosome–inositol triphosphatide complex that plays an important part in a model of bone calcification is known to complex Pu(IV), Am(III), and Cm(III) from citrate solutions or plasma (Bulman and Griffin, 1980). Eventually the plutonium in bone accumulates in immobilized deposits of hemosiderin, which, unlike the iron storage protein ferritin, is insoluble in aqueous media. Hemosiderin contains a large core of iron hydroxides and phosphates, and is the repository of the iron content of heme liberated by the catabolism of hemoglobin. Hemosiderin deposits are located close to the surfaces of the bone in the reticuloendothelial cells of the bone marrow (Durbin, 1975). Once plutonium is incorporated into bone, it is not totally immobilized, but the rate at which it leaves the bone is slow and the process by which it is released is unknown. The half-time for the spontaneous removal of plutonium from bone has been estimated as 65–130 years (Bulman, 1980). Release of plutonium from hemosiderin should not be taken to imply that the mobile plutonium will be excreted through the kidney. More probably, it will be bound to transferrin and recycled into the liver and bone.

15.9.5 Bioremediation of actinides from the environment

Biological treatments of organic, agricultural, and domestic wastes have been in use for centuries and are used very widely. Bioremediation of such wastes is usually ecologically and economically preferable to chemical treatment. These wastes can be converted to harmless and sometimes beneficial products. Although the biotreatment of metals, especially radioactive metals, cannot decrease the elemental composition of the metal or the specific activity of radionuclides in waste, it can increase the concentration of metallic species to facilitate their removal from the environment or cause the metal to precipitate to prevent its migration. Therefore the bioremediation of actinides requires microbial interactions that changes the actinide's complexation behavior or oxidation state.

Thomas and McCaskie (1996) demonstrated that microorganisms (especially *Pseudomonas*) can hydrolyze the widely used extractant TBP into phosphate and also precipitate U(VI) as a uranyl phosphate, thereby breaking down an organophosphorus pollutant and immobilizing a dissolved actinide. Microbes can serve as reducing agents to convert mobile actinides, e.g. U(VI), Np(V), and Pu(VI) to readily precipitated tetravalent ions. Banaszak *et al.* (1999) presented the redox couples of many important electron transport coenzymes and showed how these coenzymes can catalyze the reduction of actinide ions via sulfate reduction, Fe(III)/Fe(II) reduction, or other electron transfer processes at pH 7. Reductants that can reduce Fe(III) to Fe(II), or are more reducing, can reduce U(VI) to U(IV), Np(V) to Np(IV), and Pu(V) to Pu(IV) or Pu(III). The more reduced actinide ions can be precipitated, a process referred to as biomineralization. Bioremediation research utilizes the disciplines of microbiology, enzymology, actinide chemistry, and environmental science (NABIR, 2003).

15.10 TOXICOLOGY OF THE ACTINIDE ELEMENTS

Although plutonium has been known since 1940 and has been manufactured and handled on a large scale, there have been few cases of injury to workers and the average intakes by most workers have been consistently low. In recent years, information has become available from Russia where there have been instances of high-level exposure to plutonium with a reported increase in lung cancer deaths compared to other workers whose exposure was within occupational limits (see Section 15.10.3). Most of the information about the toxicity of plutonium has been learned from animal experimentation. The application of information acquired in this way to human toxicology can only be estimated by extrapolation (Clarke *et al.*, 1996). The information available about the other actinide elements is much less abundant, and some generalizations must be accepted with reservations.

15.10.1 Ingestion and inhalation

Any of the actinide elements in the environment can enter the human body by ingestion, by inhalation of particulate matter, by passage through the skin, or by accidents accompanied by forcible introduction of the actinide into the body. Absorption through the intestinal tract appears to be one of the least important routes for the incorporation of plutonium and the transplutonium elements. Plutonium has not been found to concentrate in the food chain (see Section 15.8.4); however, solubilizing ligands have been found to increase the uptake of plutonium and americium into plants, presenting a possible means of their introduction into the food chain (Francis, 1973; Bulman, 1978; Vyas and Mistry, 1983). Plutonium itself is not very bioavailable as it does not readily pass through the intestinal wall when ingested. Unbroken skin presents an essentially impermeable barrier to the passage of actinide ions. Likewise, the fate of plutonium deposited in an open wound is largely dependent on the chemical state of the plutonium. If the plutonium is in a soluble form such as a citrate complex, it will rapidly reach the circulatory system and form a transferrin complex. If it is deposited in a wound as an insoluble compound, translocation is slower (Clarke *et al.*, 1996). The toxic effects and ability of Pu (IV) to form strong complexes with bone and tissue is similar to the behavior of Fe(III). The currently available treatments for chelation therapy to extract actinides that have been introduced into the body are most effective if administered within hours of exposure. After this point, the actinides can be incorporated into bone and tissues, rendering them fixed (Durbin *et al.*, 1998).

By far the most likely (and serious) mode of entry for plutonium into the body is inhalation of insoluble particulate matter into the lungs. Factors that influence the translocation of plutonium oxides from the lung to other parts of the body include particle size, chemical composition, lung burden, calcination temperature, and isotopic composition (Lataillade *et al.*, 1995). Extremely small particles (1 nm in diameter) of PuO_2 are quickly absorbed from the lung and enter the circulation as low-molecular-weight complexes. Large particles (0.025–0.22 μm) clear very slowly. AmO_2 made by calcination of americium oxalate at 650°C was observed to be removed so rapidly from the lung as to raise questions whether the compound should continue to be considered insoluble. It is possible that the americium dioxide preparation was actually americium hydroxide polymer, and it may be that small deviations from stoichiometry could have a considerable effect on the rate of dissolution and removal from the lung. Variations in stoichiometry are expected to be much more prominent in plutonium than in americium, which may be responsible for the surprising differences in the behavior of the oxides of these actinide elements. Curium dioxide behaves quite similarly to americium dioxide, but there is at least one important and puzzling difference between the two. While americium dioxide does not bind to protein, curium dioxide does (Bulman, 1980). In the absence of information about the stoichiometry of the actinide oxide, or the preparations used in the experiments, it is difficult to ascertain whether it is particle size or deviations from stoichiometry that are responsible for the biological behavior of the actinide oxides. Many questions about the behavior of actinide particulates in the lung remain, and the answers could have implications for other lung pathologies. It has been found that $^{238}PuO_2$ clears the lung much faster than does $^{239}PuO_2$ (NCRP, 2001). The magnitude of the difference is clearly beyond the range of ordinary isotope effects, and must be attributed to the increased radiation damage incurred by the oxide particles from the more energetic alpha particles emitted by the shorter-lived radionuclide ^{238}Pu (Bulman, 1980).

15.10.2 Acute toxicity of plutonium

There is general agreement that the chemical toxicity of plutonium is inconsequential compared to the radiotoxicity, or the effects caused by its alpha radiation (Bulman, 1980; Nenot and Metivier, 1984; Clarke *et al.*, 1996; Voelz, 2000; Guilmette, 2001). By far, the greatest risk from plutonium is the long-term possibility to develop cancer. One way to compare risks between two materials is by a comparison of relative limits on concentration in air of the two substances. These limits are extrapolated from experimental observations with animals. The limit in air for plutonium is referred to as the derived air concentration (C_{DAC}). This is the concentration in air which, if breathed alone for one work year, would irradiate 'reference man' to the limits for occupational exposure, and is 0.006 μCi cm^{-3} for ^{239}Pu (4×10^{-4} μg m^{-3}). Comparing plutonium-239 to most materials handled on the small industrial scale shows plutonium-239 to be a very toxic material. Its toxicity per unit mass is similar to that of long-lived fission products such as strontium-90 and cesium-137 but less than that of short-lived fission products such as iodine-121 (Clarke *et al.*, 1996).

All data on the chemical toxicity of plutonium are derived from animal experiments. On the assumption that ions of similar size and charge will have similar toxicological properties, which is reasonable in this situation, to produce a similar change in an adult human liver would require the intravenous injection of about 200 mg of plutonium (Bulman, 1980). Further evidence supports this conclusion. The amount of material that causes death in 50% of animals after n days is known as the $\mathrm{LD}_{50}(n)$ value. The $\mathrm{LD}_{50}(30)$ value obtained from studies on dogs after intravenous injection of plutonium is about 0.32 mg per kg of tissue. When extrapolated to a human of 70 kg, the $\mathrm{LD}_{50}(30)$ value is about 22 mg (Voelz, 2000). Neptunium-237 injected into rats intravenously at 3 mg kg^{-1} induces short-term subacute changes in the liver, but is nowhere near as toxic as strychnine. There is substantial evidence that the chemical toxicity of plutonium is comparable to that of neptunium, and that plutonium is not an extraordinarily virulent chemical poison. The toxic manifestations of plutonium are due to long-term effects of radiation damage from its radioactive decay.

The acute toxicity of uranium in the form of the uranyl ion varies considerably with the experimental animal; the acute dose in the rabbit and guinea-pig is in the range 0.1–0.3 mg kg^{-1}, and in mice it may be as much as 20–25 mg kg^{-1} (Bulman, 1980). Differences in toxicity in different species have been attributed to differences in diet that result in the excretion of urine of widely differing pH. Herbivores excrete very acidic urine, which interferes with the formation of carbonate and citrate complexes of uranyl ion. These are the forms in which uranium is cleared through the kidneys. Under conditions that lower the carbonate and citrate concentrations, uranium clears the organism more slowly, and a given dose of uranium in a herbivore appears to have a higher toxicity than in an organism that can eliminate uranium more rapidly. Acute toxic symptoms produced in yeast by uranyl salts appear to be a result of the suppression of glucose metabolism by interaction of the uranyl ion with the cell surface. Reagents such as phosphate that complex uranyl ion strongly reverse the inhibition of respiratory activity (Bulman, 1980). The small amount of data gathered from human studies indicates that the renal injury is consistent to what is seen in animal models (Diamond, 1989).

15.10.3 Long-term effects of ingested plutonium

The maximum allowed dose of ^{239}Pu in humans was referred to as maximum permissible body burden and was set at 0.65 μg for radiation workers from 1953 to 1977. The International Commission on Radiation Protection published a series of reports between 1977 and 1988 that effectively decreased the lifetime body burden of ^{239}Pu to 0.5 μg (0.05 Sv) for U.S. radiation workers; these values are approximate because dose calculations must be made for internal deposition of each isotope to specific organs (Voelz, 2000). A population of 26 white male workers at Los Alamos National Laboratory who acquired plutonium body burdens between 260 and 8510 Bq (0.1–3.7 μg if pure ^{239}Pu) during World War II was followed for 50 years. As of 1994, seven persons were dead compared with the expected 16 deaths based on mortality rates for white males in the U.S. in the general population and age group. Comparing the mortality rate of the exposed workers with that of 876 unexposed Los Alamos workers of the same period, the mortality rate of the exposed workers is not elevated. As of 1995, the 16 living white males had diseases and physical changes expected of a male population with a median age of 72 years. Out of 26 white male workers, eight had been diagnosed as having one or more cancers, within the expected range for a similar, unexposed population. The cause of death in three of the seven deceased men was cancer of the prostate, lung, and bone; however mortality from all cancers was not statistically elevated (Voelz *et al.*, 1997).

Long-term chromosomal analyses of British plutonium workers who had more than 20% of the maximum permissible body burden of ^{239}Pu (doses greater than 0.25 Sv) showed no evidence for induction of persistent transmissible genomic instability (Whitehouse and Tawn, 2001). However, some Russian workers have been exposed to much higher levels of plutonium at the Mayak nuclear facility (among 2283 plutonium workers from 1948 to 1958, the mean accumulated dose was 8 Sv for males and 14 Sv for females). An increased risk of lung, liver, and bone cancers was associated with these higher exposures (Tokarskaya *et al.*, 1997; Koshurnikova *et al.*, 1998; Gilbert *et al.*, 2000; Voelz, 2000; Grogan *et al.*, 2001). In many cases, the ingrowth of ^{241}Am from decay of ^{241}Pu that is present in most plutonium samples is actually the largest contributor to the dose from inhaled or ingested plutonium (Hisamatsu and Takizawa, 2003).

Most of the available information on the effects of plutonium in mammals has come from animal experiments. Low doses of radiation in the lungs of rats produce three types of cancer: sarcomas (10%), bronchoalveolar cancers (40%), and bronchogenic cancers (50%). The lowest dose at which a significant increase in lung cancers occurs is 37 Bq g^{-1} of lung tissue for inhaled insoluble plutonium compounds. The mode of distribution of plutonium in the lung has a large effect, and whether the plutonium was acquired in a single exposure or by multiple exposures is also a factor that is important in subsequent pathology. In the dose range 0.06–37 kBq kg^{-1} of bone, an osteosarcoma incidence from 31% to 100% has been observed in dogs. Organisms experiencing rapid bone growth are more sensitive to osteosarcomas from plutonium than are adults. Liver appears to be less sensitive to alpha radiation than either lung or bone. The effects of ingested plutonium on the blood are largely due to irradiation of the hematopoietic tissues where blood cells are formed. No leukemia has ever been detected in dogs. In humans exposed to plutonium, stable chromosomal aberrations in the blood have been seen. Finally, no hereditary diseases have been observed in the progeny of animals whose bodies contained plutonium (Nenot and Metivier, 1984; ICRP, 1986).

15.10.4 Removal of actinide elements from the body

Once plutonium has gained access to the bloodstream, there is no normal physiological process that will eliminate it rapidly from the body. Foreign chemicals or organic poisons that are introduced into the body are converted in the liver by oxidation and conjugation into compounds that can be excreted. Heavy metals are either deposited in insoluble form or else they become complexed to body constituents, and no such metabolic elimination pathway exists. Plutonium retention is not absolute, but the excretion rate is so slow that in a normal lifespan only a fraction of the deposited actinide will be removed from the body. Early attempts to increase the rate of plutonium excretion were based on competitive displacement by innocuous metal ions of a size and charge that would enable them to compete successfully with Pu(IV) for binding sites or crystal lattice sites. Zirconyl(IV) citrate was found to accelerate considerably the excretion of injected plutonium, but only if the zirconium was administered within a very short time after the plutonium. Zirconyl citrate appears to be reasonably effective in displacing Pu(IV) from the bloodstream but not from body tissues. Other hydrous metal oxides such as those of thorium or aluminum minimize deposition of plutonium in bone, but increase the amount of plutonium deposited in the liver. Therapeutic approaches along these lines have therefore fallen into disuse.

The only practical strategy for increasing the excretion of plutonium is based on the use of chelating agents to form water-soluble complexes of plutonium

(ICRP, 1990). Citrate and ascorbate are effective complexing agents to a degree, but are metabolized too rapidly to be of practical utility. Useful therapeutic agents have been sought among the numerous chelating agents that have been synthesized for ion sequestration purposes, particularly derivatives and analogs of EDTA. EDTA itself is quite effective in accelerating the excretion of plutonium, provided it is administered within a short time after plutonium ingestion, but it is much less effective when the interval between ingestion and therapy is of the order of weeks (Schubert, 1955; Durbin, 1973; Vaughn *et al.*, 1973). Of the considerable number of derivatives and analogs of EDTA that have received attention, the most successful is diethylenetriaminepentaacetic acid (DTPA). This compound has one carboxyl group more available for chelation than EDTA, making it an octadentate ligand system capable of fully complexing Pu(IV) in its preferred coordination geometry, thus significantly enhancing the stability of the complex. DTPA administered promptly in a single dose after plutonium ingestion causes the excretion of about 90% of the plutonium in the following 6 days as compared to less than 5% excretion in controls; when pigs were used as the experimental animal (Taylor, 1978). To achieve such good results, DTPA must be administered within 30 min after plutonium injection in beagles. A delay in the administration of DTPA for as little as 2 h results in only 15% of the injected plutonium being excreted during the first day. Delayed treatment with multiple doses of DTPA is effective in removing moderate amounts of plutonium from the pig. In these experiments, it was observed that the principal source of the excreted plutonium was the soft tissues, and that removal of plutonium from the bone did not proceed to the point where the number of bone tumors formed was significantly reduced (James and Taylor, 1971). DTPA is also limited in that it must be administered as the calcium or zinc salt to prevent toxicity from the depletion of these essential divalent metals. Additional details on the use of DTPA can be found elsewhere (Rosenthal and Lindenbaum, 1967; Smith, 1972; Durbin, 1973; Vaughn *et al.*, 1973; Bruenger *et al.*, 1991; Durbin *et al.*, 1998). Many other chelating agents related in structure to EDTA and DTPA (for example, citrate and nitrilotriacetic acid, NTA) have been studied, but none of these are significantly better performers. Increasing the number of carboxyl groups does not improve decorporation, and the replacement of oxygen functions by sulfur or phosphorus analogs degrades their performance.

The *in vivo* situation of chelating agents is much more complicated than sequestration of alkaline earth ions in a detergent solution, or in laboratory systems arranged for the measurements of complexation constants. It has been recognized for some time (Schubert, 1955) that, because the calcium-ion concentration in serum is much greater than that of other metal ions, unless a chelating agent has a much lower affinity for calcium ion than for another metal ion, the chelating agent will exist predominantly as the calcium complex in the circulatory system. The apparent efficacy of a chelating agent is thus increased by a low affinity for calcium ion as well as by an enhanced affinity for plutonium. A foreign metal ion will be partitioned between natural chelators engaged in the transport or metabolic activities of metal ions and any chelating agents that may be introduced for therapeutic purposes. The naturally occurring iron sequestering agent desferrioxamine (DFO) is a very much weaker complexing agent for calcium ion than is DTPA, and even though it does not bind much more strongly to Fe(III) than does DTPA, it is much more effective in removing iron from the body, presumably because of its lower affinity for calcium ion. Whereas DFO is more efficient in plutonium removal than DTPA, provided it is administered within an hour after injection of plutonium, its efficacy decreases more rapidly than that of DTPA as the time interval between plutonium incorporation and therapy increases. Combined use of DTPA and DFO appears to remove the greatest amount of plutonium. The presumption is that plutonium ion liberated from the Pu(IV)–DFO complex is recomplexed and excreted as the DTPA complex before irreversible deposition of the plutonium can occur. Once plutonium has been deposited in insoluble form or incorporated into bone, no known therapeutic approach is efficacious. Inhalation of insoluble plutonium can only be countered by repeated pulmonary lavage with isotonic saline solution (Nenot and Metivier, 1984).

While conventional chelating agents have received by far the most attention in search for effective decorporation of plutonium, other work has aimed at the development of new more selective ligand systems. Raymond *et al.* (1982) have undertaken a search for new chelating agents that would bind strongly to and be specific for actinide ions. They have adopted a biomimetic approach in which compounds are modeled after the powerful and highly specific siderophores, natural iron sequestering agents used by microorganisms to acquire Fe(III) from the environment. Ligands have been generated which incorporate hydroxamic acid, hydroxypyridonate (HOPO), catecholamide (CAM), and terephthalamide (TAM) chelating subunits analogous to those found in the siderophores into a variety of backbones (Gorden *et al.*, 2003). The rationale behind their design method was that by introducing several coordinating functional groups, enough binding sites on the ligand are provided to occupy all of the coordination sites on the metal ion. Enterobactin, a hexadentate siderophore containing three CAM subunits, has the largest formation constant and complexation ability for Fe(III). An octadentate system should be more selective for the larger Pu(IV) ion. The metal ion is then encapsulated, so to speak, by the chelating agent, preventing deposition, increasing solubility and hence, excretion. Siderophore-like systems have also been explored by other researchers to see if they have the potential to introduce Pu or the actinides into the food chain (Ruggiero *et al.*, 2002).

The Raymond–Durbin collaboration has developed a large number of new ligands. Many of these have been tested in mice as actinide decorporation agents. Of these, the best chelating systems for Pu(IV) were, as expected, octadentate ligand systems, e.g. the Pu(IV)–HOPO molecule in Fig. 15.8 , but many

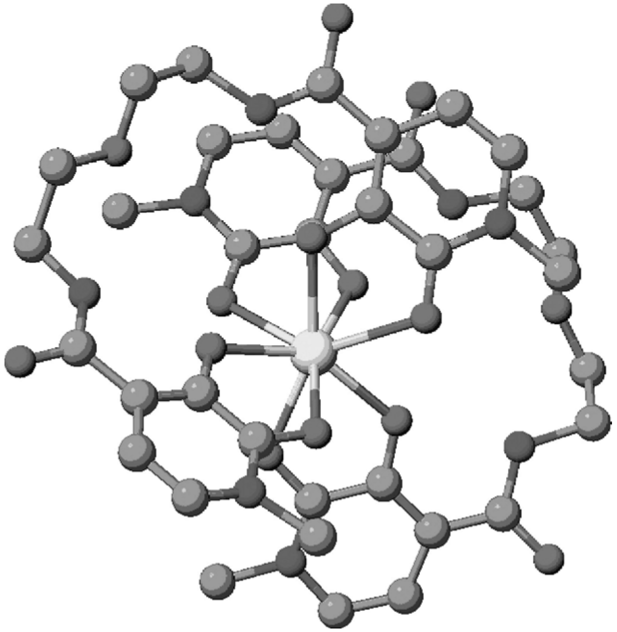


Fig. 15.8 *Molecular structure of Pu*(IV)-(5-*LIO-Me*-3,2-*HOPO*)$_2$ *generated from crystallographic data showing octadentate coordination about the Pu*(IV) *ion. The geometric arrangement of the ligands about the Pu ion is best described as a distorted bicapped trigonal prism* (*Gorden* et al., 2005).

questions remain about the importance of denticity, binding group acidity, backbone flexibility, and solubility in the development of a highly effective, orally bioavailable chelator of low toxicity. Octadentate HOPO systems have been shown to be as much as 40% more effective in mice than an equimolar amount of $CaNa_3$–DTPA, the current clinical drug of choice, as well as to be orally active. Other systems have also been demonstrated to be effective for the chelation of Am(III) as well as U(VI), Th(IV), and Np(IV/V), for which DTPA is not effective (Gorden *et al.*, 2003). Preliminary *in vitro* studies suggest that these complexes are also capable of redissolving Pu(IV) or Am(III) after it has deposited in bone mineral (Guilmette *et al.*, 2003).

15.11 PRACTICAL APPLICATIONS OF THE ACTINIDE ELEMENTS

The principal application of the actinide elements is in the production of nuclear energy. Although this is by far the most important use for any of the actinide elements, a surprising number of other uses have been found. These include the use of short-lived (tens of years) actinide isotopes as portable power supplies for satellites; in ionization smoke detectors; in the therapy of cancer; in neutron radiography; in mineral prospecting and oil-well logging; as neutron sources in nuclear reactor start-up; and as neutron sources in a variety of analytical procedures, the most important of which are neutron activation analysis and heavy-ion desorption mass spectroscopy.

15.11.1 Nuclear power

The practical importance of the actinide elements derives from the discovery of nuclear fission by Hahn and Strassmann in 1939. Atoms of one naturally occurring isotope (0.72% abundance) of uranium, ^{235}U, split into two approximately equal fragments by the capture of a neutron, an event that releases an enormous amount of energy. Approximately 2.5 neutrons are released per fission event, making it possible to initiate an explosive chain reaction in the pure fissile isotope; alternatively, controlled fission in a nuclear reactor can be used to provide heat to generate electricity. The plutonium isotope ^{239}Pu is produced in chain-reacting nuclear reactors by capture of excess neutrons in nonfissionable ^{238}U. Plutonium-239 itself is also fissionable with slow (essentially zero-energy) neutrons. The naturally occurring thorium isotope ^{232}Th, which does not undergo fission, can be converted by neutron capture to ^{233}U, which is a fissionable nuclide. The complete utilization of nonfissionable ^{238}U (through conversion to fissionable ^{239}Pu) and nonfissionable ^{232}Th (through conversion to fissionable ^{233}U) can be accomplished by breeder reactors. The fissile isotopes ^{233}U, ^{235}U, and ^{239}Pu constitute an enormous, effectively inexhaustible, energy resource. The future of nuclear power, however, is clouded by technological and social problems. The technical problems relate to the safety of nuclear reactors, to the ability to prevent access of radioactive substances to the environment, and to the prevention of the diversion of plutonium for the clandestine manufacture of nuclear weapons. We adhere to the school of thought that believes the technological problems of safe nuclear energy and environmental contamination are soluble problems. Indeed, many of these problems have already been solved, and those that remain do not require the discovery of new or unheard of scientific principles for their solution. The social, economic, and political problems are another matter. The fully justified fear of nuclear war is projected onto nuclear power, as if nuclear power and nuclear war were synonymous, and as if the fear of nuclear war could be exorcised by abolishing nuclear power. Prevention of nuclear war and the proliferation of nuclear weapons can only be accomplished by international statesmanship, not by a refusal to make use of the limitless energy that can be supplied by fission.

Some countries (France and Japan are notable examples) have embraced nuclear power, with the probable result that they will have a future economic advantage in world trade from the cheaper electric power that nuclear energy can provide. Nuclear power promises a more prosperous future, but whether the promise becomes a reality in many additional countries will depend on the solution of the social, economic, and international problems that enmesh the issue of nuclear energy.

15.11.2 Portable power sources

Radioactive decay is accompanied by the evolution of heat, and radioactive nuclides can therefore be used as portable heat sources. One gram of ^{238}Pu produces about 0.56 W of thermal power, primarily from its 87.7 year alpha decay, and this isotope of plutonium has found use in space vehicles to drive thermoelectric power units. Several satellites with ^{238}Pu generators that produce 25 W have been deployed in space. Several of the Apollo spacecrafts carried a ^{238}Pu generator that produced 73 W of electrical power, fueled with 2.6 kg of ^{238}Pu in the form of PuO_2, to run the scientific experiments of some Apollo lunar expeditions. The satellite that sent the amazing photographs of Jupiter and the outer planets back to Earth used a 50 W ^{238}Pu power supply for this purpose. Space Nuclear Auxiliary Power (SNAP) thermoelectric power units containing 54 kg of plutonium-238 provide the nuclear-powered energy in the Cassini–Huygens 1966–2005 mission to Saturn and its moon Titan (see Chapter 7, section 7.2, of this book). This space probe is expected to accompany Saturn for 4 years. Much smaller ^{238}Pu generators were implanted as human cardiac pacemakers beginning in 1970; although chemical battery and electronics technologies have rendered nuclear pacemakers obsolete, several nuclear pacemakers have been in operation for over 30 years (see Chapter 7, section 7.2, of this book and section 15.11.4).

15.11.3 Neutron sources

The radionuclide americium-241 emits alpha particles, which produce neutrons by an (α,n) nuclear reaction with light elements. A mixture of americium-241 with beryllium produces 1.0×10^7 neutrons per second per gram of ^{241}Am. A large number of ^{241}Am–Be sources are in daily use worldwide in oil-well logging operations to measure the amount of oil produced in a given period of time. These sources have also been used to measure the water content of soils, and to monitor process streams in industrial plants. ^{241}Am itself has extensive uses in dissipating static electrical charges and in smoke detectors, where it functions to ionize air.

The radioactive decay of the nuclide californium-252 is largely by alpha emission, but part of the decay is by spontaneous fission. ^{252}Cf thus provides an intense neutron source: 1 g emits 2.4×10^{12} neutrons per second. ^{252}Cf is the only commercially available nuclide that can be fabricated into small neutron sources that produce an intense neutron flux over a useful period of time. The physical size of these sources is considerably smaller than alpha neutron sources, and less space must be provided in the ^{252}Cf sources to accommodate gaseous products. Since ^{252}Cf neutron sources became available in 1975, a surprising variety of industrial and scientific uses have been developed for them (Martin *et al.*, 2000).

One of the largest uses of these sources is in reactor start-up operations. Before achieving criticality, a neutron source is inserted into the reactor to allow instrument calibration and observation of the approach to criticality. ^{252}Cf sources are used in reactor start-up all over the world because of the high neutron flux that can be obtained and their small size (<1 cm^3), which is very advantageous in the start-up procedure. ^{252}Cf neutron sources are used in the nuclear power industry as fuel-rod scanners, a procedure in which the amount and uniformity of the fissile material in the fuel rod is measured. This is the second largest industrial application of californium neutron sources.

Applications to neutron activation analysis constitute another important use of ^{252}Cf neutron sources. Neutron capture in many elements forms radioactive species that then decay with highly characteristic γ-ray emissions. This analytical procedure is very sensitive and specific, and is widely used for the analysis of trace elements. Neutron activation finds use in uranium borehole logging to make accurate determinations of the uranium concentrations in boreholes, and as little as 100 ppm of U_3O_8 can be detected by this procedure. Other industrial uses for ^{252}Cf sources are in the continuous monitoring of the sulfur and ash content of coal on a moving conveyor belt at the rate of 50 metric tons h^{-1}. Batch analysis of the vanadium content of crude oil is still another application of neutron activation analysis.

15.11.4 Medical and other applications

Americium-241 has found use in the diagnosis of thyroid disorders, because the 59.6 keV γ-rays allow determination of iodine in the thyroid by X-ray fluorescence (Reiners *et al.*, 1998). Americium-241 is used worldwide in ionization smoke detectors because it emits alpha particles, has a relatively long half-life, and decays to ^{237}Np, which has a much longer half-life. Household smoke detectors contain a small quantity (<35 kBq, approximately 200 μg) of ^{241}Am as AmO_2. Ionization smoke detectors in public or commercial buildings contain up to 2 MBq of ^{241}Am. The nearly monoenergetic alpha particles and 59.6 keV γ-rays of ^{241}Am have made it useful in thickness gauges and radiography (see Chapter 8, section 8.3, of this book).

Miniature power generators using ^{238}Pu have been developed for use in heart pacemakers. The pacemaker itself is a device planted in the chest and connected to the heart muscles; a programmed electrical pulse is periodically administered, which assures regularity in the heartbeat. A typical nuclear-powered heart pacemaker contains about 160 mg of ^{238}Pu encased in a tantalum–iridium–platinum alloy. Several thousand such devices were in use worldwide by 1980 and some remain in use in 2005, having been functioning for over 30 years (see Section 7.2). Heart pacemakers that operate from chemical batteries have a limited life, and must be replaced periodically by a surgical procedure, but they have replaced nuclear pacemakers since about 1980 because of their efficiency and safety (Parsonnet, 2005).

Actinium-225 is used in alpha-particle generators for tumor radiotherapy (see Chapter 2, section 2.9.3, of this book). Californium-252 attracted early attention as a possible therapeutic agent in cancer treatment. The general impression formed from early work was that neutron therapy was inferior to X-ray therapy. More recent studies, however, indicate that neutron irradiation may have advantages over X-rays or γ-rays in certain situations. In the period 1976–82, several hundred cancer cases were treated by neutron irradiation supplied by ^{252}Cf (Murayama, 1991). Although not a cure, ^{252}Cf neutron therapy appears to have promise in the treatment of pelvic cancer and in brachytherapy (short exposure therapy). Sources containing ≤ 30 μg of ^{252}Cf as a Cf_2O_3 wire in a Pd matrix have been prepared by the Radiochemical Engineering Development Center of Oak Ridge National Laboratory (Martin *et al.*, 1997). Neutron sources have also been prepared by the Research Institute of Atomic Reactors (RIAR), Dimitrovgrad, Russia (Karelin *et al.*, 1997). Neutrons appear to have particular utility in tumors whose oxygen supply is impaired, and which, as a consequence, are relatively insensitive to X-rays or γ-rays. While the applications of neutrons in the treatment of cancer are still experimental, there is a possibility that further clinical studies may well find a use for the neutron-emitting californium isotopes in therapy.

ABBREVIATIONS

AES	atomic emission spectroscopy
Bq	SI derived unit of radioactivity, 1 disintegration per second
CAM	catecholamide
Ci	Curie = 3.7×10^{10} disintegrations per second = 3.7×10^{10} Bq.
Cp	cyclopentadienyl, C_5H_5
CEA	Commission de l'Energie Atomique
COT	cyclooctatetrene, C_8H_8
DFO	desferrioxamine
DIAMEX	DIAMide EXtraction process used to separate the lanthanides and the "minor actinides" Np, Am, Cm from fission products
DTPA	diethylenetriaminepentaacetic acid
EDTA	ethylenediaminetetraacetic acid
HEU	highly enriched uranium (20–90% ^{235}U)
HFIR	High Flux Isotope Reactor
HOPO	hydroxypyridonate
ICP-MS	inductively-coupled plasma mass spectroscopy
IUPAC	International Union of Pure and Applied Chemistry
LEU	low enriched uranium (0.7–20% ^{235}U)

LLNL	Lawrence Livermore National Laboratory
MOX	Mixed oxide fuel (usually UO_2-PuO_2 solid solution)
MWd	Megawatt-days
NMR	nuclear magnetic resonance
NTA	nitrilotriacetic acid
PBq	petabequerel (1×10^{15} Bq)
PUREX	Plutonium uranium reduction extraction
PWR	pressurized water reactor
RIAR	Research Institute of Atomic Reactors
REDC	Radioisotope Engineering Development Center
SNAP	Space Nuclear Auxiliary Power
Sv	Sievert (derived SI unit of equivalent dose used for radiation protection purposes); 1 Sv = 1 J kg^{-1} = 100 rem
TAM	terephthalamide
TBP	tri(*n*-butyl)phosphate
TBq	terabecquerel (1×10^{12} Bq)
THF	tetrahydrofuran

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