



# Actinide Elements

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## GLOSSARY

**Actinyl ion** Dioxo actinide cations  $\text{MO}_2^+$  and  $\text{MO}_2^{2+}$ .

**Decay chain** A series of nuclides in which each member transforms into the next through nuclear decay until a stable nuclide has been formed.

**Lanthanides** Fourteen elements with atomic numbers 58 (cerium) to 71 (lutetium) that are a result of filling the  $4f$  orbitals with electrons.

**Nuclear fission** The division of a nucleus into two or more parts, usually accompanied by the emission of neutrons and  $\gamma$  radiation.

**Nuclide** A species of atom characterized by its mass number, atomic number, and nuclear energy state. A radionuclide is a radioactive nuclide.

**Primordial radionuclides** Nuclides which were produced during element evolution and which have partly survived since then due to their long half-lives.

**Radioactivity** The property of certain nuclides of showing radioactive decay in which particles or  $\gamma$  radiation are emitted or the nucleus undergoes spontaneous fission.

**Speciation** Characterization of physical and chemical states of (actinide) species in a given (chemical) environment.

**Transactinide elements** Artificial elements beyond the actinide elements, beginning with rutherfordium (Rf), element 104. The heaviest elements, synthesized until now, are the elements 114, 116, and 118. At present, bohrium (Bh), element 107, is the heaviest element which has been characterized chemically; chemical studies of element 108, hassium (Hs), and element 112 are in preparation.

**THE ACTINIDE ELEMENTS** (actinoids) comprise the 14 elements with atomic numbers 90–103, which follow actinium in the periodic table: thorium (Th), protactinium (Pa), uranium (U), neptunium (Np), plutonium (Pu), americium (Am), curium (Cm), berkelium (Bk), californium (Cf), einsteinium (Es), fermium (Fm), mendelevium (Md), nobelium (No), and lawrencium (Lr). The actinides constitute a unique series of elements which are formed by the progressive filling of the  $5f$  electron shell. Although not formally an actinide element, actinium (Ac;

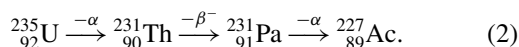
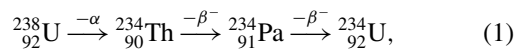
atomic number 89) is usually included in discussions about the actinides.

According to the International Union of Pure and Applied Chemistry (IUPAC), the name actinoid is preferable to actinide because the ending “-ide” normally indicates a negative ion. However, owing to wide current use, “actinide” is still allowed.

## I. DISCOVERY, OCCURRENCE, AND SYNTHESIS OF THE ACTINIDES

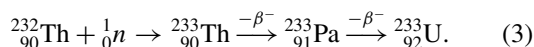
### A. Naturally Occurring Actinides

All of the isotopes of the actinide elements are radioactive, and only four of the primordial isotopes,  $^{232}\text{Th}$ ,  $^{235}\text{U}$ ,  $^{238}\text{U}$ , and  $^{244}\text{Pu}$ , have a sufficient long half-life for there to be any of these isotopes left in nature. Only three actinide elements and actinium were known as late as 1940. In addition to thorium and uranium, protactinium and actinium have been found to exist in uranium and thorium ores due to the  $^{238}\text{U}$  [Eq. (1)] and  $^{235}\text{U}$  [Eq. (2)] decay series:



It was not until 1971 that the existence of primordial  $^{244}\text{Pu}$  in nature in trace amounts was shown by D. C. Hoffman and co-workers.

Uranium was the first actinide element to be discovered. M. H. Klaproth showed in 1789 that pitchblende contained a new element and named it uranium after the then newly discovered planet Uranus. Uranium is now known to comprise 2.1 ppm of the Earth's crust, which makes it about as abundant as arsenic or europium. It is widely distributed, with the principal sources being in Australia, Canada, South Africa, and the United States. The two most important oxide minerals of uranium are uraninite ( $\text{U}_3\text{O}_8$ ; 50–90% uranium), a variety of which is called pitchblende, and carnotite ( $\text{K}_2(\text{UO}_2)(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$ ; 54% uranium). A very common uranium mineral is autunite ( $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ ,  $n = 8\text{--}12$ ). Natural uranium consists of 99.3%  $^{238}\text{U}$  and 0.72% of the fissionable isotope  $^{235}\text{U}$ . A third important isotope,  $^{233}\text{U}$ , does not occur in nature but can be produced by thermal-neutron irradiation of  $^{232}\text{Th}$  [Eq. (3)]:



This process converts thorium to fissionable fuel in a breeder reactor.

Thorium was discovered by J. J. Berzelius in 1828 when he isolated a new oxide from a Norwegian ore then known as thorite. He named the oxide thoria, and the metal he ob-

tained by reduction of its tetrachloride with potassium he named thorium. (Later, in 1841, B. Peligot used the same method to prepare uranium metal for the first time.) Thorium constitutes 8.1 ppm of the Earth's crust and is thus as abundant as boron. Converted by neutron irradiation to  $^{233}\text{U}$ , it could yield an amount of neutron-fissile material several hundred times the amount of the naturally occurring fissile uranium isotope  $^{235}\text{U}$ . The principal thorium ore is monazite, a mixture of rare-earth and thorium phosphates containing up to 30%  $\text{ThO}_2$ . Monazite sands are widely distributed throughout the world. In Canada thorium is recovered from uranotorite (a mixed thorium-uranium silicate accompanied by pitchblende) as a co-product of uranium. Rarer minerals thorianite (90%  $\text{ThO}_2$ ) and thorite ( $\text{ThSiO}_4$ ; 62% thorium) have been found in the western United States and New Zealand. Natural thorium is 100%  $^{232}\text{Th}$ .

In 1913 protactinium was discovered by K. Fajans and O. Göhring, who identified  $^{234\text{m}}\text{Pa}$  as an unstable member of the  $^{238}\text{U}$  decay series. They named the new element brevium because of its short half-life of 1.15 min. In 1918 the longer-lived isotope  $^{231}\text{Pa}$ , with a half-life of 32,800 years, was identified independently by two groups, O. Hahn and L. Meitner, and F. Soddy and J. A. Cranston, as a product of  $^{235}\text{U}$  decay. Since the name brevium was obviously inappropriate for such a long-lived radioelement, it was changed to protactinium, thus naming element 91 as the parent of actinium. Protactinium is one of the rarest of the naturally occurring elements. Although not worth extracting from uranium ores, protactinium becomes concentrated in residues from uranium processing plants.

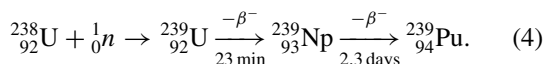
Actinium was discovered by A. Debierne in 1899. Its name is derived from the Greek word for beam or ray, referring to its radioactivity. The natural occurrence of the longest lived actinium isotope  $^{227}\text{Ac}$ , with a half-life of 21.77 years, is entirely dependent on that of its primordial ancestor,  $^{235}\text{U}$ . The natural abundance of  $^{227}\text{Ac}$  is estimated to be  $5.7 \cdot 10^{-10}$  ppm. The most concentrated actinium sample ever prepared from a natural raw material consisted of about 7  $\mu\text{g}$  of  $^{227}\text{Ac}$  in less than 0.1 mg of  $\text{La}_2\text{O}_3$ .

### B. Synthetic Actinides

Stimulated by the discovery of the neutron in 1932 by J. Chadwick and the first synthesis of artificial radioactive nuclei using  $\alpha$  particle-induced nuclear reactions in 1934 by F. Joliot and I. Curie, many attempts were made to produce transuranium elements by neutron irradiation of uranium. In 1934, E. Fermi and later O. Hahn, L. Meitner, and F. Strassmann reported that they had created transuranium elements. But in 1938, O. Hahn and F. Strassmann showed that the radioactive species produced by neutron

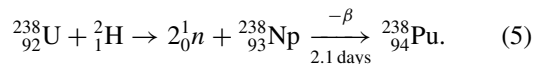
irradiation of uranium were in fact fission fragments resulting from the nuclear fission of uranium! Thus, the early search for transuranium elements led to one of the greatest discoveries of the 20th century.

The first transuranium element, neptunium, was discovered in 1940 by E. M. McMillan and P. H. Abelson. They were able to chemically separate and identify element 93 formed in the following reaction sequences [Eq. (4)]:



They showed that element 93 has chemical properties similar to those of uranium and not those of an eka-rhenium as suggested on the basis of the periodic table of that time. To distinguish it from uranium, element 93 was reduced by  $\text{SO}_2$  and precipitated as a fluoride. This new element was named neptunium after Neptune, the planet discovered after Uranus. In 1952, trace amounts of  ${}^{237}\text{Np}$  were found in uranium of natural origin, formed by neutron capture in uranium.

It was obvious to the discoverers of neptunium that  ${}^{239}\text{Np}$  should  $\beta$  decay to the isotope of element 94 with mass number 239, but they were unable to identify it. However, up to the end of 1940, G. T. Seaborg, E. M. McMillan, J. W. Kennedy, and A. C. Wahl succeeded in identifying  ${}^{238}\text{Pu}$  in uranium, which was bombarded with deuterons produced in the 60-in. cyclotron at the University of California in Berkeley [Eq. (5)]:



Element 94 was named plutonium after the planet discovered last, Pluto. In 1941, the first 0.5  $\mu\text{g}$  of the fissionable isotope  ${}^{239}\text{Pu}$  were produced by irradiating 1.2 kg of uranyl nitrate with cyclotron-generated neutrons. In 1948, trace amounts of  ${}^{239}\text{Pu}$  were found in nature, formed by neutron capture in uranium. In chemical studies, plutonium was shown to have properties similar to uranium and not to osmium as suggested earlier. The actinide concept advanced by G. T. Seaborg, to consider the actinide elements as a second  $f$  transition series analogous to the lanthanides, systematized the chemistry of the transuranium elements and facilitated the search for heavier actinide elements. The actinide elements americium (95) through fermium (100) were produced first either via neutron or helium-ion bombardments of actinide targets in the years between 1944 and 1955.

Element 96, curium, was produced in 1944 by the bombardment of  ${}^{239}\text{Pu}$  with helium ions in the Berkeley 60-in. cyclotron, and soon after it was found that  ${}^{241}\text{Pu}$ , formed from  ${}^{239}\text{Pu}$  by two successive neutron captures in a nuclear reactor, decays under  $\beta^-$  particle emission to give  ${}^{241}\text{Am}$ . Earlier attempts to produce and chemically separate ameri-

cium and curium failed, believing that they would have chemical properties similar to uranium, neptunium, and plutonium. Once it was recognized that these elements, according to G. T. Seaborg's actinide concept, might have properties similar to europium and gadolinium, the use of proper chemical procedures led to success. By analogy to europium (named after Europe) and gadolinium (named after Johan Gadolin, a Finnish rare-earth chemist), for elements 95 and 96 the names americium after the continent of America and curium to honor Pierre and Marie Curie were proposed. The elements with the atomic numbers 97 and 98 at first could not be produced by irradiation with neutrons, because  $\beta^-$  decaying isotopes of curium were not known. By 1949 sufficient amounts of  ${}^{241}\text{Am}$  and  ${}^{242}\text{Cm}$  had been accumulated to make it possible to produce elements 97 and 98 in helium-ion bombardments. The  $\alpha$  particle-emitting species produced in the bombardments could be identified as isotopes of elements 97 and 98, which were named berkelium and californium after the city and state of discovery.

Elements 99 and 100, named einsteinium and fermium to honor Albert Einstein and Enrico Fermi, were unexpectedly synthesized in the first U. S. thermonuclear explosion in 1952. The successive capture of numerous neutrons by  ${}^{238}\text{U}$  and subsequent  $\beta^-$  decay chains ended in the  $\beta$  stable nuclides  ${}^{253}\text{Es}$  and  ${}^{255}\text{Fm}$ . From tons of coral collected at the explosion area, hundreds of atoms of the new elements could be separated and positively identified. Further attempts to produce still heavier elements in underground nuclear tests or in high-flux nuclear reactors failed.  ${}^{257}\text{Fm}$  is the heaviest nuclide which can be produced using neutron-capture reactions, owing to the very short half-lives of the heavier fermium isotopes and their spontaneous fission instead of  $\beta^-$  decay. To produce element 101, mendelevium, only about  $10^9$  atoms of  ${}^{253}\text{Es}$  were made available for a bombardment with helium ions in the Berkeley 60-in. cyclotron. For the first time an element was discovered in "one-atom-at-a-time" experiments on the basis of only 17 produced atoms recoiling from the einsteinium target. The discoverers of element 101, A. Ghiorso, B. G. Harvey, G. R. Choppin, S. G. Thompson, and G. T. Seaborg, suggested the name mendelevium in honor of the Russian chemist Dmitri I. Mendelev, who was the first to use a periodic system of the elements to predict the chemical properties of undiscovered elements.

The synthesis of element 102 was even more complicated, because a fermium target to apply the bombardment with helium ions was not available. In order to make use of lighter target elements, heavier ions had to be accelerated. The discovery of element 102 was first reported in 1957 by an international group working at the Nobel Institute of Physics in Stockholm. The name nobelium in honor of

Alfred Nobel was immediately accepted by the IUPAC. However, experiments at Berkeley and the Kurchatov Institute in Moscow showed that the original Swedish claim to have prepared element 102 was in error. Attempts to synthesize and identify isotopes of element 102 in heavy ion bombardments of actinide targets dragged on for many years at the laboratories in Berkeley and Dubna, Russia. Thus, scientists from Berkeley suggested that the credit for the discovery should be shared. But, in 1993 the IUPAC-IUPAP Transfermium Working Group concluded that the Dubna laboratory finally achieved an undisputed synthesis.

Also, the discovery of element 103, the last actinide element, was contested by Berkeley and Dubna for a long time. At Berkeley mixtures of californium isotopes were bombarded with boron ions, whereas at Dubna the bombardment of americium targets with oxygen ions was applied. Finally, both groups accepted the conclusion of the Transfermium Working Group, that full confidence was built up over a decade with credit for discovery of element 103 attaching to work in both Berkeley and Dubna. The name lawrencium after E. O. Lawrence, the inventor of the cyclotron, suggested by A. Ghiorso and co-workers from Berkeley and accepted by IUPAC, was finally recommended by IUPAC in 1997 together with the names for the transactinide elements up to element 109.

Table I summarizes the discovery or synthesis of all of the actinide elements.

## II. RADIOACTIVITY AND NUCLEAR REACTIONS OF ACTINIDES

All isotopes of the actinides and actinium are radioactive. Table II presents data on several of the most available and important of these. The unstable, radioactive actinide nuclei decay by emission of  $\alpha$  particles, electrons, or positrons ( $\beta^-$  or  $\beta^+$  decay, respectively). Alternatively to the emission of a positron, the unstable nucleus may capture an electron of the electron shell of the atom (symbol  $\epsilon$ ). In most cases the radioactive decay leads to an excited state of the new nucleus, which gives off its excitation energy in the form of one or several photons ( $\gamma$  rays). In some cases a metastable state results that decays independently of the way it was formed. Spontaneous fission (symbol sf) is another mode of radioactive decay, which was discovered in 1940 by G. N. Flerov and K. A. Petrzhak.

The numerous radionuclides present in thorium and uranium ores are members of genetic correlated radioactive decay series, which are represented in Fig. 1. In all of these decay series, only  $\alpha$  and  $\beta^-$  decay are observed. With emission of an  $\alpha$  particle ( ${}^4_2\text{He}$ ), the atomic number

is reduced by 2, the mass number by 4. With emission of a  $\beta^-$  particle, the mass number remains unchanged, whereas the atomic number increases by 1. As a result, in these decay series the mass number can differ only by multiples of 4 and there are four such families, designated  $4n + 0$  (thorium series),  $4n + 1$  (neptunium series),  $4n + 2$  (uranium or uranium-radium series), and  $4n + 3$  (actinium series). The neptunium series is missing in nature. It was probably present in nature for some million years after the genesis of the elements, but decayed due to the relatively short half-life of  ${}^{237}\text{Np}$ , compared with the age of the Earth (about  $5 \cdot 10^9$  years). Each series contains a number of short-lived nuclides, and the final members of each series are stable nuclides.  $\alpha$  Decay is the dominant decay mode of long-lived heavy nuclei with atomic numbers  $Z > 83$ . With increasing atomic numbers spontaneous fission begins to compete with  $\alpha$  decay. For  ${}^{238}\text{U}$  the probability of spontaneous fission is about  $10^{-4}\%$  of that of  $\alpha$  decay and is already about 90% for  ${}^{256}\text{Fm}$ .

The radioactive decay is the simplest form of a nuclear reaction according to equation [Eq. (6)]:

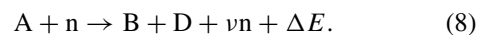


This is a mononuclear reaction. In nuclear science, however, binuclear reactions are generally understood by the term “nuclear reaction.” They are described by the general equation [Eq. (7)]:



where A is the target nuclide, x is the projectile, B is the product nuclide, and y is the particle or photon emitted. Equations (3)–(5) are examples for neutron- and deuteron-induced nuclear reactions. With heavy ions (heavier than  $\alpha$  particles) as projectiles, the heaviest actinides have been synthesized. Targets made from heavy actinide nuclides such as  ${}^{248}\text{Cm}$  and  ${}^{249}\text{Bk}$  have been used to synthesize several transactinide elements in heavy-ion reactions.

Nuclear fission of actinides is, without doubt, the most important nuclear reaction. Nuclear fission by thermal neutrons may be described by the general equation [Eq. (8)]:



The fission products B and D have mass numbers in the range between about 70 and 160, the number of neutrons emitted is  $\nu \approx 2\text{--}3$ , and the energy set free by fission is  $\Delta E \approx 200$  MeV. This energy is relatively high, because the binding energy per nucleon is higher for the fission products than for the actinide nuclei. In the case of nuclei with even proton and odd neutron numbers, such as  ${}^{233}\text{U}$ ,  ${}^{235}\text{U}$ , and  ${}^{239}\text{Pu}$ , the binding energy of an additional neutron is particularly high, and the barrier against fission is easily surmounted. Therefore, these nuclides have high fission yields for fission by thermal neutrons.

**TABLE I** Discovery or Synthesis of Actinide Elements

Atomic number	Element	Symbol	Investigators	Source or synthesis	Isotope first discovered	Most stable isotope	Source of name
89	Actinium	Ac	A. Debierne (1899)	Uranium ore	$^{227}\text{Ac}$	$^{227}\text{Ac}$	Greek word for ray
90	Thorium	Th	J. J. Berzelius (1828)	Thorium ore	$^{232}\text{Th}$	$^{232}\text{Th}$	Scandinavian god of war, Thor
91	Protactinium	Pa	K. Fajans, O. Göhring (1913)	Uranium ore concentrates	$^{234}\text{Pa}$	$^{234}\text{Pa}$	Parent of actinium
92	Uranium	U	M. H. Klaproth (1789)	Pitchblende	$^{238}\text{U}$	$^{238}\text{U}$	Planet Uranus
93	Neptunium	Np	E. M. McMillan, P. Abelson (1940)	Bombardment of uranium with neutrons: $^{238}_{92}\text{U} + {}^1_0n \rightarrow$ $^{239}_{92}\text{U} \xrightarrow[23\text{ min}]{-\beta^-} {}^{239}_{93}\text{Np}$	$^{239}\text{Np}$	$^{237}\text{Np}$	Planet Neptune
94	Plutonium	Pu	G. T. Seaborg, E. M. McMillan, J. W. Kennedy, A. Wahl (1940)	Bombardment of uranium with deuterons: $^{238}_{92}\text{U} + {}^2_1\text{H} \rightarrow$ $2{}_0^1n + {}^{238}_{93}\text{Np}$ $\xrightarrow[2.1\text{ days}]{-\beta^-} {}^{238}_{94}\text{Pu}$	$^{238}\text{Pu}$	$^{244}\text{Pu}$	Planet Pluto
95	Americium	Am	G. T. Seaborg, R. A. James, L. O. Morgan, A. Ghiorso (1944)	Bombardment of plutonium with neutrons: $^{239}_{94}\text{Pu} + 2{}_0^1n \rightarrow$ ${}^{241}_{94}\text{Pu} \xrightarrow[95]{-\beta^-} {}^{241}_{95}\text{Am}$	$^{241}\text{Am}$	$^{243}\text{Am}$	America
96	Curium	Cm	G. T. Seaborg, R. A. James, A. Ghiorso (1944)	Bombardment of plutonium with helium ions: $^{239}_{94}\text{Pu} + {}^4_2\text{He} \rightarrow$ ${}^{242}_{96}\text{Cm} + {}^1_0n$	$^{242}\text{Cm}$	$^{247}\text{Cm}$	Pierre and Marie Curie
97	Berkelium	Bk	S. G. Thompson, A. Ghiorso, G. T. Seaborg (1949)	Bombardment of americium with helium ions: ${}^{241}_{95}\text{Am} + {}^4_2\text{He} \rightarrow$ ${}^{243}_{97}\text{Bk} + 2{}_0^1n$	$^{243}\text{Bk}$	$^{247}\text{Bk}$	Berkeley, CA
98	Californium	Cf	S. G. Thompson, K. Street, A. Ghiorso, G. T. Seaborg (1950)	Bombardment of curium with helium ions: ${}^{242}_{96}\text{Cm} + {}^4_2\text{He} \rightarrow$ ${}^{245}_{98}\text{Cf} + {}^1_0n$	$^{245}\text{Cf}$	$^{251}\text{Cf}$	California
99	Einsteinium	Es	Workers at Berkeley, Argonne, and Los Alamos (1952)	Discovered in the fallout of the first thermonuclear explosion as a result of uranium bombardment with fast neutrons: $^{238}_{92}\text{U} + 15{}_0^1n \rightarrow$ ${}^{253}_{92}\text{U} \xrightarrow[99]{-7\beta^-} {}^{253}_{99}\text{Es}$	$^{253}\text{Es}$	$^{252}\text{Es}$	Albert Einstein

*Continues*

TABLE I (continued)

Atomic number	Element	Symbol	Investigators	Source or synthesis	Isotope first discovered	Most stable isotope	Source of name
100	Fermium	Fm	Workers at Berkeley, Argonne, and Los Alamos (1952)	Discovered in the fallout of the first thermonuclear explosion as a result of uranium bombardment with fast neutrons: ${}^{238}_{92}\text{U} + 17\frac{1}{0}n \rightarrow {}^{255}_{92}\text{U} \xrightarrow{-8\beta^-} {}^{255}_{100}\text{Fm}$	${}^{255}\text{Fm}$	${}^{257}\text{Fm}$	Enrico Fermi
101	Mendelevium	Md	A. Ghiorso, B. H. Harvey, G. R. Choppin, S. G. Thompson, G. T. Seaborg (1955)	Bombardment of einsteinium with helium ions: ${}^{253}_{99}\text{Es} + {}^4_2\text{He} \rightarrow {}^{256}_{101}\text{Md} + \frac{1}{0}n$	${}^{256}\text{Md}$	${}^{258}\text{Md}$	Dimitri Mendeleev
102	Nobelium	No	E. D. Donets, V. A. Shegolev, V. A. Ermakov (1966)	Bombardment of americium with nitrogen ions: ${}^{243}_{95}\text{Am} + {}^{15}_7\text{N} \rightarrow {}^{254}_{102}\text{No} + \frac{1}{0}n$	${}^{254}\text{No}$	${}^{259}\text{No}$	Alfred Nobel
103	Lawrencium	Lr	Workers at both Berkeley and Dubna (1961–1971)	Bombardments of actinide targets with heavy ions	( ${}^{258}\text{Lr}$ )	${}^{262}\text{Lr}$	Ernest Lawrence

### III. APPLICATIONS OF ACTINIDES

The practical importance of the actinide elements derives mainly from their nuclear properties. The principal application is in the production of nuclear energy. Controlled fission of fissile nuclides in nuclear reactors is used to provide heat to generate electricity. The fissile nuclides  ${}^{233}\text{U}$ ,  ${}^{235}\text{U}$ , and  ${}^{239}\text{Pu}$  constitute an enormous, practically inexhaustible, energy source.

Several actinide nuclides have found other applications. Heat sources made from kilogram amounts of  ${}^{238}\text{Pu}$  have been used to drive thermoelectric power units in space vehicles. In medicine,  ${}^{238}\text{Pu}$  was applied as a long-lived compact power unit to provide energy for cardiac pacemakers and artificial organs.  ${}^{241}\text{Am}$  has been used in neutron sources of various sizes on the basis of the  $(\alpha, n)$  reaction on beryllium. The monoenergetic 59-keV  $\gamma$  radiation of  ${}^{241}\text{Am}$  is used in a multitude of density and thickness determinations and in ionization smoke detectors.  ${}^{252}\text{Cf}$  decays by both  $\alpha$  emission and spontaneous fission. One gram of  ${}^{252}\text{Cf}$  emits  $2.4 \cdot 10^{12}$  neutrons per second.  ${}^{252}\text{Cf}$  thus provides an intense and compact neutron source. Neutron sources based on  ${}^{252}\text{Cf}$  are applied in nuclear reactor start-up operations and in neutron activation analysis.

Nuclear energy and the application of actinide elements in other fields may promise mankind a prosperous future; however, whether the promise becomes a reality depends on the solution of numerous technological, economic, so-

cial, and international problems. Technical problems are related to the safe operation of nuclear reactors, reprocessing, and waste disposal, to the prevention of environmental contamination with radioactive and toxic substances, and to the prevention of the diversion of plutonium for an uncontrolled manufacture of nuclear weapons. All these technical and technological problems are soluble, but the future of nuclear energy depends also on the solution of other problems of acute global concern.

### IV. ACTINIDE METALS

#### A. Preparation of Actinide Metals

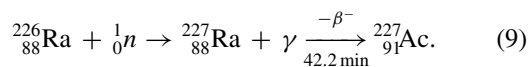
All of the actinide elements are metals with physical and chemical properties changing along the series from those typical of transition elements to those of the lanthanides. Several separation, purification, and preparation techniques have been developed considering the different properties of the actinide elements, their availability, and application. Powerful reducing agents are necessary to produce the metals from the actinide compounds. Actinide metals are produced by metallothermic reduction of halides, oxides, or carbides, followed by the evaporation in vacuum or the thermal dissociation of iodides to refine the metals.

The metallothermic reduction of halides was the first method to be successfully applied. Actinium metal can

TABLE II Important Isotopes of the Actinide Elements

Atomic number	Element	Isotope	Half-life	Mode of decay
89	Actinium	$^{227}\text{Ac}$	21.7 years	$\beta^-$ (0.986), $\alpha$ (0.014), $\gamma$
		$^{228}\text{Ac}$	6.15 h	$\beta^-$
90	Thorium	$^{232}\text{Th}$	$1.405 \cdot 10^{10}$ years	$\alpha$ ,
91	Protactinium	$^{231}\text{Pa}$	32760 years	$\alpha$ , $\gamma$
		$^{234}\text{Pa}$	6.70 h	$\beta^-$
92	Uranium	$^{235}\text{U}$	$7.038 \cdot 10^8$ years	$\alpha$
		$^{238}\text{U}$	$4.468 \cdot 10^9$ years	$\alpha$
93	Neptunium	$^{237}\text{Np}$	$2.144 \cdot 10^6$ years	$\alpha$
94	Plutonium	$^{238}\text{Pu}$	87.7 years	$\alpha$
		$^{239}\text{Pu}$	$2.411 \cdot 10^4$ years	$\alpha$
		$^{242}\text{Pu}$	$3.733 \cdot 10^5$ years	$\alpha$
		$^{244}\text{Pu}$	$8.08 \cdot 10^7$ years	$\alpha$ (0.999), sf(0.001)
95	Americium	$^{241}\text{Am}$	432.2 years	$\alpha$ , $\gamma$
		$^{243}\text{Am}$	7370 years	$\alpha$
96	Curium	$^{242}\text{Cm}$	162.8 days	$\alpha$
		$^{244}\text{Cm}$	18.10 years	$\alpha$
		$^{248}\text{Cm}$	$3.40 \cdot 10^5$ years	$\alpha$ (0.916), sf(0.084)
97	Berkelium	$^{247}\text{Bk}$	1380 years	$\alpha$ (<100%)
		$^{249}\text{Bk}$	320 days	$\beta^-$ (0.99999), $\alpha$ (0.00001)
98	Californium	$^{249}\text{Cf}$	351 years	$\alpha$
		$^{251}\text{Cf}$	898 years	$\alpha$
		$^{252}\text{Cf}$	2.645 year	$\alpha$ (0.969), sf(0.031)
99	Einsteinium	$^{252}\text{Es}$	471.7 days	$\alpha$ (0.76), $\varepsilon$ (0.24)
		$^{253}\text{Es}$	20.47 days	$\alpha$
		$^{254}\text{Es}$	275.7 days	$\alpha$
100	Fermium	$^{252}\text{Fm}$	25.39 h	$\alpha$ (0.99998), sf(0.00002)
		$^{255}\text{Fm}$	20.07 h	$\alpha$
		$^{256}\text{Fm}$	157.6 min	sf(0.919), $\alpha$ (0.081)
101	Mendelevium	$^{255}\text{Md}$	27 min	$\varepsilon$ (0.92), $\alpha$ (0.08)
		$^{256}\text{Md}$	78.1 min	$\varepsilon$ (0.907), $\alpha$ (0.093)
102	Nobelium	$^{259}\text{No}$	58 min	$\alpha$ (0.75), $\varepsilon$ (0.25)
103	Lawrencium	$^{260}\text{Lr}$	3.0 min	$\alpha$ (0.75), $\varepsilon$ (0.25)

be produced by reducing  $\text{AcF}_3$  with lithium at  $1200^\circ\text{C}$ . Small amounts of actinium can be obtained from residues of uranium processing. Gram amounts of  $^{227}\text{Ac}$  has been produced synthetically at Mol, Belgium, by neutron irradiation of  $^{226}\text{Ra}$  [Eq. (9)]:



Both thorium and uranium occur to a significant extent in nature, and industrial processes have been developed for the production of these elements.

Thorium is produced commercially from monazite sands. After mining, the monazite sands are concentrated magnetically and then treated with either hot, concentrated sulfuric acid or hot, concentrated sodium hydroxide. The

acid treatment dissolves the thorium phosphate present, while the basic process converts the phosphates to insoluble hydroxides. The separation of thorium from the uranium and rare-earth phosphates after the acid process can be carried out by selective precipitation of the thorium and rare earth phosphates and then by using a solvent extraction process to remove the thorium. When the alkali opening method is used, the insoluble hydroxides are dissolved in nitric acid and the thorium and uranium(VI) species are extracted, leaving the lanthanides in the aqueous phase. The thorium and uranium can then be separated by further solvent extraction.

Thorium metal can be produced in several ways. In the most common process, thorium oxide is reduced with calcium [Eq. (10)]:

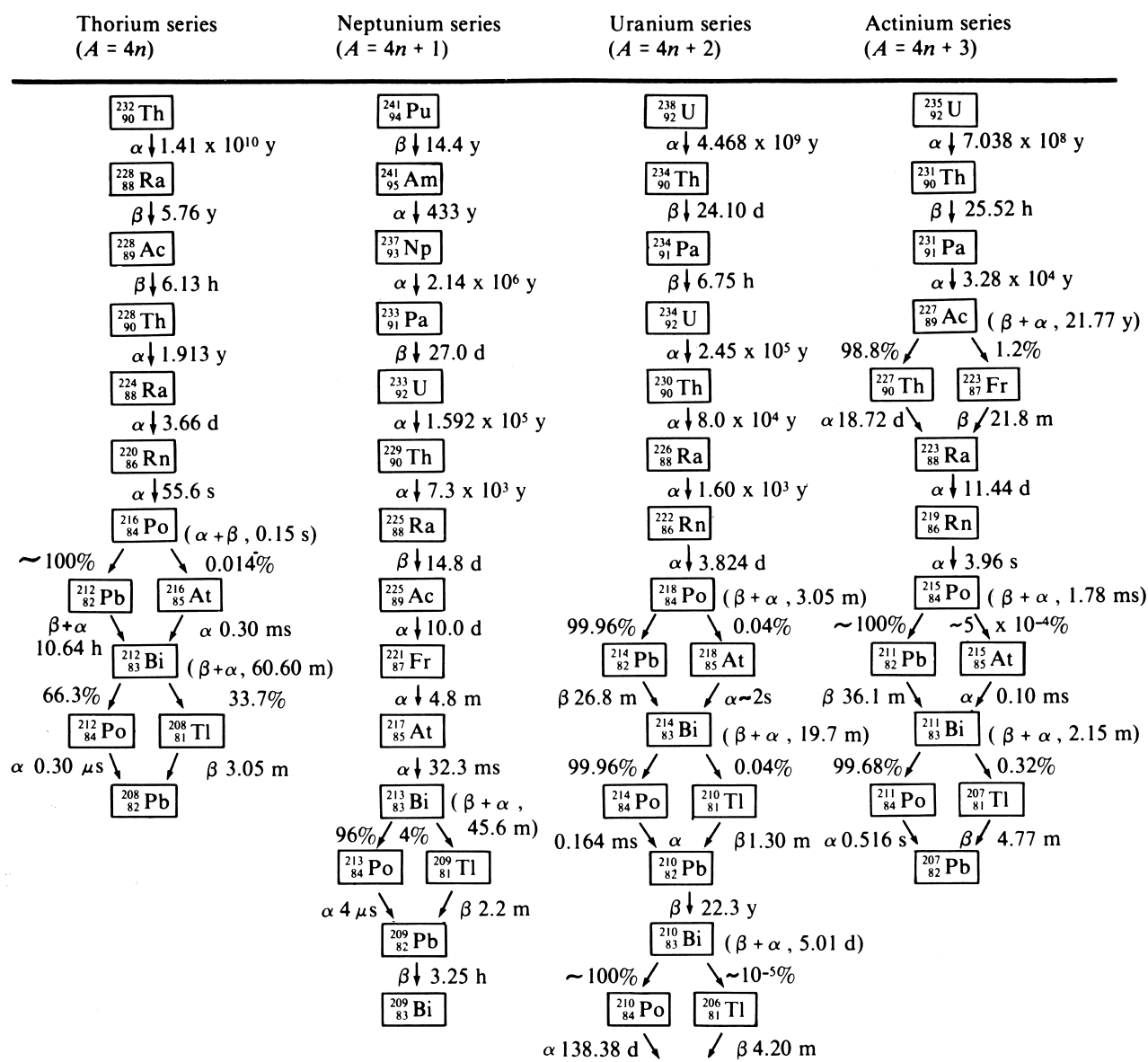
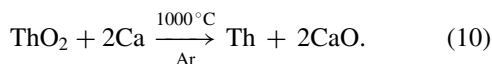


FIGURE 1



The reaction mass is leached with water and dilute acid, leaving thorium metal powder. Very pure thorium metal can be prepared by the van Arkel process involving the thermal decomposition of  $\text{ThI}_4$ .

To obtain significant quantities of protactinium, a separation procedure was developed for extracting protactinium from the sludge that was left after the ether extraction of uranium at the Springfield refinery. The process yielded 127 g of pure  $^{231}\text{Pa}$  from 60 tons of sludge. Protactinium metal can be obtained by reducing  $\text{PaF}_4$  with

barium vapor at  $1300^\circ\text{C}$ , followed by increasing the temperature to  $1600^\circ\text{C}$  to produce a bead of protactinium metal. Single-crystal protactinium metal is obtained by a modified van Arkel process starting from the carbide.

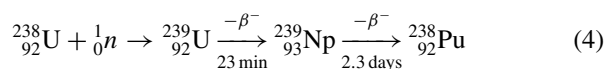
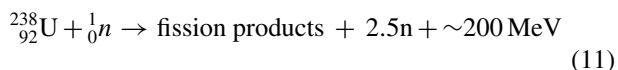
More than 150 minerals containing uranium are known. Typically, however, uranium ores contain only about 0.1% uranium. In the commercial production of uranium metal, the ore is crushed, concentrated, roasted, and in most cases leached with sulfuric acid in the presence of an oxidizing agent such as manganese dioxide or chlorate ions to convert all of the uranium to uranyl sulfate complexes. Carbonate leaching is used to extract uranium from ores containing minerals such as calcite. The recovery of uranium



from leach solutions can be affected by ion exchange, solvent extraction, and chemical precipitation. Most leach solutions are now treated by anion-exchange methods or solvent extraction or both for purification prior to precipitation. The two principal methods of precipitation are now neutralization with ammonia or the precipitation of uranium peroxide,  $\text{UO}_4 \cdot x\text{H}_2\text{O}$ , with hydrogen peroxide. The precipitates ("yellow cake") are dried and ignited to  $\text{U}_3\text{O}_8$  or  $\text{UO}_3$ , depending on temperature. To produce nuclear-grade material, these raw products are normally further refined by solvent extraction or fluoride volatility processes. The purified uranium is converted to  $\text{UO}_3$ , reduced with hydrogen to  $\text{UO}_2$ , and converted to  $\text{UF}_4$  with hydrogen fluoride. The  $\text{UF}_4$  can either be reduced to uranium metal or fluorinated to  $\text{UF}_6$  for isotope enrichment by gaseous diffusion.

The production of uranium metal usually involves the reduction of  $\text{UF}_4$  with magnesium at  $700^\circ\text{C}$ . The metal may be refined by molten-salt electrolysis followed by zone melting. Because of the low melting point of uranium, the van Arkel process is not as feasible as for thorium and protactinium.

The principal source of neptunium ( $^{237}\text{Np}$ ) is irradiated nuclear reactor fuel based on  $^{235}\text{U}$ . A slightly modified Purex (plutonium-uranium recovery by extraction) process can be used to separate neptunium from uranium, plutonium, and fission products during reprocessing of nuclear reactor fuel. Ion-exchange methods are used for the final purification and concentration. Neptunium metal is produced by reduction of  $\text{NpF}_4$  with calcium metal using iodine as a booster. Refining is accomplished by vacuum melting. Plutonium was the first synthetic actinide element to be produced on a large scale. It is produced in nuclear reactors by the so-called pile reactions [Eqs. (11) and (4)]:



The most widely employed method for plutonium reprocessing used today in almost all of the world's reprocessing plants is the Purex (plutonium-uranium reduction extraction) process. Tributylphosphate (TBP) is used as the extraction agent for the separation of plutonium from uranium and fission products. In effecting a separation, advantage is taken of differences in the extractability of the various oxidation states and in the thermodynamics and kinetics of oxidation reduction of uranium, plutonium, and impurities. Various methods are in use for the conversion of plutonium nitrate solution, the final product from fuel reprocessing plants, to the metal. The reduction of plutonium halides with calcium proved to be the best method

for metal production, and  $\text{PuF}_4$  is most commonly used as the starting material. The crude plutonium metal may be refined by electrolysis in molten salts.

Americium and curium can be obtained from the aqueous waste of the Purex process. This americium is a mixture of  $^{241}\text{Am}$  and  $^{243}\text{Am}$ . Isotopically pure  $^{241}\text{Am}$ , the decay product of  $^{241}\text{Pu}$ , can be obtained from aged plutonium. Solvent extraction and ion-exchange procedures are used to recover americium from waste streams. Americium metal is produced by lanthanum reduction of the oxide, followed by vacuum distillation of the americium at  $1400^\circ\text{C}$ .

$^{243}\text{Cm}$  and  $^{244}\text{Cm}$  are minor constituents of nuclear waste. Gram quantities of  $^{242}\text{Cm}$  and  $^{244}\text{Cm}$  were produced by neutron irradiations of  $^{241}\text{Am}$  and plutonium, respectively. The Trumex process based on the extraction with tertiary amines and high-pressure ion-exchange systems was developed for the recovery of curium. Curium metal is advantageously produced by thorium reduction of the oxide, followed by vacuum distillation of the metal at  $2000^\circ\text{C}$ .

Weighable quantities of the transcurium elements berkelium ( $^{249}\text{Bk}$ ), californium ( $^{252}\text{Cf}$ ), and einsteinium ( $^{253}\text{Es}$ ) for use in research are produced in the high-flux nuclear reactors HFIR at Oak Ridge and SM-2 at Dimitrovgrad, Russia.  $^{257}\text{Fm}$  in picogram quantities was produced only at Oak Ridge. Targets containing plutonium, americium, and curium are irradiated in the high-flux reactors and then processed. After target dissolution followed by impurity, rare-earth, and curium removal, the transcurium elements are separated by high-pressure cation exchange using ammonium  $\alpha$ -hydroxyisobutyrate as the eluent. Berkelium metal in microgram to milligram amounts is produced by reducing  $\text{BkF}_3$  or  $\text{BkF}_4$  with lithium metal, followed by the removal of lithium fluoride at  $1200^\circ\text{C}$  from the less volatile berkelium metal. The more volatile californium, einsteinium, and fermium metals can be prepared by reduction of the oxides with lanthanum metal, followed by a distillation of the actinide metals. To prepare the metals free of a supporting material at least a few milligrams of metal have to be distilled.

Californium is the heaviest actinide for which data like the enthalpy of sublimation have been determined directly with bulk quantities of about 2 mg of pure metal. Due to the limited availability of the heaviest actinides down to the "one-atom-at-a-time" scale, the preparation of the metals becomes an integral part of an experiment for studying the metals. Unusual experimental approaches like the measurement of partial pressures of the actinide under study over an alloy, studies of diffusion of actinide atoms in metals, and adsorption studies of actinide atoms onto metal surfaces by thermochromatography have been reported.

To obtain and stabilize the actinides under study in the elemental/metallic state, the reduction of actinide oxides with lanthanum metal and the desorption of actinide atoms from metals like tantalum, titanium, and zirconium have been applied successfully.

## B. Properties of Actinide Metals

### 1. Electronic Structure

The electronic ground state configurations of the gaseous actinide atoms consist of the closed-shell electronic structure of the noble gas radon, a partly filled  $5f$  shell, and two to four electrons in the  $6d$  and  $7s$  states. The electronic ground state configurations for the actinides and, for comparison, the lanthanides are given in Table III.

The filling of the  $f$  shell is a common feature of both lanthanides and actinides. However, there are remarkable differences in the properties of the  $4f$  and  $5f$  electrons. The  $4f$  orbitals of the lanthanides and the  $5f$  actinide orbitals have the same angular part of the wave function but differ in the radial part. The  $5f$  orbitals also have a radial node, while the  $4f$  orbitals do not. The major differences between actinide and lanthanide orbitals depend, then, on the relative energies and spatial distributions of these orbitals. The  $5f$  orbitals have a greater spatial extension relative to the  $7s$  and  $7p$  than the  $4f$  orbitals have relative to the  $6s$  and  $6p$ . This allows a small covalent contribution from the  $5f$  orbitals, whereas no compounds in which  $4f$  orbitals are used exist. In fact, the  $4f$  electrons are so highly localized that they do not participate in chemical bonding, whereas the  $5d$  and  $6s$  valence electrons over-

lap as for the transition elements. The energies of the  $5f$ ,  $6d$ ,  $7s$ , and  $7p$  orbitals are comparable over a range of atomic numbers, and since the orbitals overlap spatially, bonding can involve any or all of them. This is especially important in the first half of the actinide series. Oxidation states up to +7 are available, and the electronic structure of an actinide in any given oxidation state may vary from compound to compound and in solution, depending on the ligands, because the small differences in energy between the  $5f$ ,  $6d$ ,  $7s$ , and  $7p$  orbitals can be compensated within the range of chemical bonding energies.

With increasing atomic number, the  $5f$  electrons become increasingly localized as a consequence of insufficient screening. Beginning with americium, the  $5f$  electrons do not participate in bonding, similar to the  $4f$  electrons in the lanthanides. In the heaviest actinides, the  $5f$  electrons appear even more localized than the analogous  $4f$  electrons. This conclusion is supported by the tendency to form the divalent oxidation state well before the end of the actinide series.

In the region of the heaviest actinides, relativistic effects may become noticeable. Due to the relativistic mass increase of the electrons, which are strongly accelerated in the vicinity of a highly charged nucleus, the spherical  $7s$  and  $7p_{1/2}$  orbitals have high electron densities near the nucleus, whereas the  $6d$  and  $5f$  orbitals become destabilized. Thus, the ground state configuration for lawrencium was predicted to be  $[\text{Rn}]5f^{14}d^07s^2p^1$  instead of the  $[\text{Rn}]5f^{14}d^17s^2$  configuration, which might be expected by analogy with lutetium.

The  $5f$  electrons of the lighter actinide metals through plutonium have highly extended wave functions. Thus,

TABLE III Ground State Electronic Configurations of  $5f$  and  $4f$  Elements

Atomic number	Symbol	Element	Electronic structure [Rn] plus	Atomic number	Symbol	Element	Electronic structure [Xe] plus
89	Ac	Actinium	$6d7s^2$	57	La	Lanthanum	$5d6s^2$
90	Th	Thorium	$6d^27s^2$	58	Ce	Cerium	$4f5d6s^2$
91	Pa	Protactinium	$5f^26d7s^2$ or $5f6d^27s^2$	59	Pr	Praseodymium	$4f^36s^2$
92	U	Uranium	$5f^36d7s^2$	60	Nd	Neodymium	$4f^46s^2$
93	Np	Neptunium	$5f^57s^2$	61	Pm	Promethium	$4f^56s^2$
94	Pu	Plutonium	$5f^67s^2$	62	Sm	Samarium	$4f^66s^2$
95	Am	Americium	$5f^77s^2$	63	Eu	Europium	$4f^76s^2$
96	Cm	Curium	$5f^76d7s^2$	64	Gd	Gadolinium	$4f^75d6s^2$
97	Bk	Berkelium	$5f^86d7s^2$ or $5f^97s^2$	65	Tb	Terbium	$4f^96s^2$
98	Cf	Californium	$5f^{10}7s^2$	66	Dy	Dysprosium	$4f^{10}6s^2$
99	Es	Einsteinium	$5f^{11}7s^2$	67	Ho	Holmium	$4f^{11}6s^2$
100	Fm	Fermium	$5f^{12}7s^2$	68	Er	Erbium	$4f^{12}6s^2$
101	Md	Mendelevium	$5f^{13}7s^2$	69	Tm	Thulium	$4f^{13}6s^2$
102	No	Nobelium	$5f^{14}7s^2$	70	Yb	Ytterbium	$4f^{14}6s^2$
103	Lr	Lawrencium	$5f^{14}6d^07s^2p^1$ or $(5f^{14}6d^17s^2)$	71	Lu	Lutetium	$4f^{14}5d6s^2$

these delocalized or itinerant  $5f$  electrons are involved in the metallic bonding as a part of the conduction band formed together with the  $6d$  and  $7s$  electrons. The band character of the delocalized  $5f$  electrons is inhibitory to the development of magnetism. Within the framework of a simple model of the metallic bond, the metal is an array of ions held together by quasi-free conduction electrons, and a metallic valence can be defined as the contribution of outer electrons each atom gives to the “sea” of bonding conduction electrons. Conversely, the metallic valence is the charge left per atom when the bonding electrons have been stripped off. In this approach, the first five actinides after actinium, thorium up to plutonium, are considered as having metallic valences greater than three.

As the atomic number increases, the radial extension and the bandwidth of the  $5f$  electrons decreases. From americium on the  $5f$  electrons are localized, nonbonding, and carry a magnetic moment. The actinide metals americium to californium and lawrencium are trivalent metals. Einsteinium to nobelium are divalent metals due to very high promotion energies needed to promote one  $f$  electron to the metallic bonding state as known from ytterbium in the lanthanide series. Thus, the actinide series displays more complex electronic structures than does the lanthanide series; not only in the first half of the series.

## 2. Crystal Structures

Actinide crystal structures are more complicated and diversified than the corresponding lanthanide metal structures. Information about the crystal structures of the actinide metals is given in Table IV.

Actinium and thorium have no  $f$  electrons and behave like transition metals with a body-centered cubic structure of thorium. Neptunium and plutonium have complex, low-symmetry, room-temperature crystal structures and exhibit multiple phase changes with increasing temperature due to their delocalized  $5f$  electrons. For plutonium metal, up to six crystalline modifications between room temperature and 915 K exist. The  $f$  electrons become localized for the heavier actinides. Americium, curium, berkelium, and californium all have room-temperature, double hexagonal, close-packed phases and high-temperature, face-centered cubic phases. Einsteinium, the heaviest actinide metal available in quantities sufficient for crystal structure studies on at least thin films, has a face-centered cubic structure as typical for a divalent metal.

## 3. Physical Properties

The radioactivity of the actinides along with their limited availability makes their experimental investigation in

most cases notoriously difficult. Therefore, data on physical properties of the actinide metals are very limited. Data on selected physical and thermodynamic properties are presented in Table V.

Proceeding along the  $5f$  series, the high melting points of Th and Pa reflect their transition metal character, Np and Pu have very low melting points due to  $f$ -orbital reflection, the melting points rise over Am to Cm, and they then again decrease. The maximum at Cm reflects both its half-filled  $5f$  shell and the presence of a  $d$ -type valence electron. The decreasing melting points of the transcurium elements reflect the onset of  $s$ -type bonding and the loss of  $d$  bonding in the divalent metals. The melting point of Lr is expected to be as high as that of Cm, assuming  $d$  bonding, but should be lower if it behaves like a  $p$  element due to relativistic effects.

Looking at transport and magnetic properties along the actinide series, superconductivity under atmospheric pressure (Th, Pa), superconductivity under high pressure (U), exchange reinforced Pauli paramagnetism without superconductivity (Np, Pu), superconductivity under atmospheric pressure (Am), and finally magnetic ordering and absence of superconductivity (Cm, Bk, Cf) are successively encountered. Measurements of electrical, magnetic, or electronic properties of the heaviest actinides beyond californium have been missing up to now.

## 4. Thermodynamic Properties

One of the fundamental properties of a metal is its enthalpy of sublimation. The enthalpy of sublimation of a metal, which is a measure of its cohesive energy, is related to the electronic structure in both the solid and its vapor. The enthalpies of sublimation of the actinide metals thorium through californium have been determined directly by vapor pressure measurements using the pure metals, those of einsteinium and fermium by measuring partial pressures over alloys. Estimates of the enthalpies of sublimation for the actinide metals californium through nobelium have also been made based on thermochromatographic measurements of the adsorption of actinide atoms on metals. The experimental enthalpies of sublimation clearly reflect the trends and changes in the electronic properties of the actinide metals when progressing across the series. Thus, there is further evidence for metallic divalency well before the end of the actinide series.

## 5. Alloying Behavior

Experimental studies of actinide alloys have been carried out with Np, Am, Cm, Bk, Es, and Fm, and far more extensive studies have been carried out with the actinide metals of technological importance, Th, U, and Pu. The

TABLE IV Crystal Structure of the Actinide Metals

Atomic number	Melting point (K)	Phase	Crystal symmetry <sup>a</sup>	Space group	Stability range (K)	Lattice parameters				Metallic valence	Temp. (K)	Density (g cm <sup>-3</sup> )	Metallic radii (Å)
						a (Å)	b (Å)	c (Å)	$\beta$ (deg)				
89	1320	Ac	fcc	Fm3m	<1320	5.314				3	293	10.06	1.88
90	2023	$\alpha$ -Th	fcc	Fm3m	<1633	5.180				4	293	11.72	1.798
		$\beta$ -Th	bcc	Im3m	1633–2023	4.11					1698		1.78
91	1845	$\alpha$ -Pa	bct	I4/mmm	<1200	3.921		3.235		$\geq 4$		15.43	1.631
		$\beta$ -Pa	fcc	Fm3m	1200–1845	5.018						12.31	1.777
92	1408	$\alpha$ -U	eco	Cmcm	<941	2.853	5.865	4.955		$\geq 4$	293	19.060	1.56
		$\beta$ -U	t	P4 <sub>2</sub> mm	941–1049	10.759	10.759	5.656			993	18.11	
		$\gamma$ -U	bcc	Im3m	1049–1408	3.525					1078	18.06	1.55
93	913	$\alpha$ -Np	o	Pnma	<553	6.663	4.723	4.887		$\geq 3$	293	20.45	1.55
		$\beta$ -Np	t	P4 <sub>1</sub> mm	553–849	4.897		3.388			586	19.36	
		$\gamma$ -Np	bcc	Im3m	849–913	3.52					873	18.00	1.54
94	913.2	$\alpha$ -Pu	m	P2 <sub>1</sub> Im	<398	6.183	4.822	10.963	101.79	$\geq 3$	294	19.86	1.58
		$\beta$ -Pu	bcm	12/m	398–488	9.284	10.463	7.859	92.13		463	17.70	1.59
		$\gamma$ -Pu	fco	Fddd	488–593	3.159	5.768	10.162			508	17.14	1.589
		$\delta$ -Pu	fcc	Fm3m	593–736	4.637					593	15.92	1.644
		$\delta'$ -Pu	bct	I4/mmm	736–756	3.34		4.44			738	6.00	1.644
		$\epsilon$ -Pu	bcc	Im3m	756–913.2	3.363					763	16.51	1.594
95	1449	$\alpha$ -Am	dhcp	P6 <sub>3</sub> /mmc	<1347	3.468		11.248		3	293	13.671	1.730
		$\beta$ -Am	fcc	Fm3m	1347–1449	4.894					295	13.65	1.730
96	1681	$\alpha$ -Cm	dhcp	P6 <sub>3</sub> /mmc	<1550	3.496		11.33		3	293	13.51	1.745
		$\beta$ -Cm	fcc	Fm3m	1550–1681	5.039							1.79
97	1323	$\alpha$ -Bk	dhcp	P6 <sub>3</sub> /mmc	<1250	3.416		11.068		3	293	14.79	1.704
		$\beta$ -Bk	fcc	Fm3m	1250–1323	4.999					293	13.24	1.764
98	1173	$\alpha$ -Cf	dhcp	P6 <sub>3</sub> /mmc	<863	3.39		11.01		3		15.1	1.69
		$\beta$ -Cf	fcc	Fm3m		4.94						13.7	1.75
		$\gamma$ -Cf	fcc	Fm3m		5.75						8.70	2.03
99	1130	( $\alpha$ -Es)	hcp	P6 <sub>3</sub> /mmc	<573	3.98		6.50		2			
		( $\beta$ -Es)	fcc	Fm3m		5.71							2.03
100		Fm	fcc							2			2.00
101		Md	fcc							2			1.985
102		No	fcc							2			1.97
103		Lr	bcc							3			1.66

<sup>a</sup> bcc, body-centered cubic; dhcp, double hexagonal close-packed; fcc, face-centered cubic; hcp, hexagonal close-packed; m, monoclinic; bcm, body-centered monoclinic; o, orthorhombic; eco, end-centered orthorhombic; fco, face-centered orthorhombic; t, tetragonal; bct, body-centered tetragonal.

complex and variable electronic properties of the actinides are reflected in their alloying behavior also. Varying the composition can result in properties ranging from superconductivity to magnetism. There is a huge number of possible intermetallic compounds because of the many possible valence states of the actinides itself. The itinerant *f*-electron metals protactinium through plutonium are mutually soluble. Uranium and plutonium form a number of isomorphous compounds due to their similarity in size. The trivalent actinide metals are expected to be mutually soluble in one another. The same should hold for the diva-

lent metals einsteinium through nobelium, but they should not alloy with the higher valent actinide metals.

A large number of intermetallic compounds of the actinide metals with transition metals and with elements of the aluminium and silicon groups are known. All have metallic properties. Compounds with AnX<sub>3</sub> stoichiometry have the AuCu<sub>3</sub>-, TiNi<sub>3</sub>-, MgCd<sub>3</sub>-, or PuAl<sub>3</sub>-type structure. At AnX<sub>2</sub>, stoichiometry Laves phases having the MgCu<sub>2</sub>-type or MgZn<sub>2</sub>-type structures are found very often, especially when the partner is an Fe- or Ni-group transition metal. At AnX the NaCl-type structure and at the

TABLE V Selected Physical and Thermodynamic Properties of Actinide Elements

Symbol	Boiling point (K, 1 atm)	Enthalpy of fusion, $\Delta H_{\text{fus}}$ (kJ mol <sup>-1</sup> )	Enthalpy of sublimation, $\Delta H_{298}^0$ (kJ mol <sup>-1</sup> )	Electrical resistivity ( $\mu\Omega$ cm, 295 K)
Ac	(3200)		(418)	
Th	(5000)	14	598	14
Pa	(4230)	16.7	570	18
U	3818	19.7	536	31
Np	(4174)	5.23	465	123
Pu	(3508)	2.82	342	138
Am	(2067)	14.4	284	67
Cm	(3383)	13.8	387	86
Bk	(2900)	7.91	310	
Cf	(1745)	7.51	196	
Es	(1269)	9.40	133(167) <sup>a</sup>	
Fm	(1350)		143(143) <sup>a</sup>	
Md			(136) <sup>a</sup>	
No			(134) <sup>a</sup>	

<sup>a</sup> Values in parentheses are estimates based on thermochromatographic measurements.

AnX<sub>5</sub> stoichiometry AuBe<sub>5</sub>-- and CaCu<sub>5</sub>-type structures are found.

V. ACTINIDE IONS

A. Oxidation States

The oxidation states of the actinide elements are listed in Table VI. Unlike the lanthanide elements, for which the dominant oxidation state is +3, the actinides exhibit a broad range of oxidation states, ranging from +2 to +7 in solution. The proximity of 5*f*, 6*d*, and 7*s* energy levels in the lighter actinides results in a variety of oxidation states up to +7. The stability of the higher oxidation states decreases with increasing atomic number. From americium

on, a more lanthanide-like behavior is exhibited. The most stable oxidation state of the heavier actinides with the exception of No is +3; however, in contrast to the analogous lanthanides, the divalent oxidation state appears well before the end of the actinide series. Thus, in comparison with the analogous 4*f* electrons, the 5*f* electrons in the latter part of the actinide series appear more tightly bound.

With the exception of thorium and protactinium, all of the actinide elements show a +3 oxidation state in aqueous solution. A stable +4 state is observed in the elements thorium through plutonium and in berkelium. The oxidation state +5 is well established for the elements protactinium through americium, and the +6 state is well established in the elements uranium through americium. The oxidation state +2 first appears at californium and becomes increasingly more stable in proceeding to nobelium.

For any oxidation state, the ionic radii decrease regularly with increasing atomic number as a consequence of the decreased shielding by *f* electrons of the outer valence electrons from the increasing effective nuclear charge. This actinide contraction is very similar to the corresponding lanthanide contraction. Table VII summarizes crystallographic ionic radii of lanthanide and actinide ions for coordination numbers 6 and 8.

B. Solution Chemistry

Although many solvents have been studied, the most widely used solvent is still water. Table VIII presents some data on the stability of various actinide ions in water. In aqueous solution the actinide ions present in the oxidation states +1 to +6 are M<sup>+</sup>, M<sup>2+</sup>, M<sup>3+</sup>, M<sup>4+</sup>, MO<sub>2</sub><sup>+</sup>, and MO<sub>2</sub><sup>2+</sup>. MO<sub>5</sub><sup>3-</sup> oxo anions are known for the oxidation state +7. The actinyl ions MO<sub>2</sub><sup>+</sup> and MO<sub>2</sub><sup>2+</sup> are remarkably stable. The oxygen atoms are linearly coordinated to the actinide metal with short metal-oxygen distances ranging from 1.6 to 2.0 Å for MO<sub>2</sub><sup>2+</sup>. The strength of the metal-oxygen bond decreases with increasing atomic number in the actinyl ions from uranium to americium.

TABLE VI Oxidation States of the Actinide Elements

Atomic number Symbol	89 Ac	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
Oxidation states															
							(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?								

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

TABLE VII Crystallographic Ionic Radii of Lanthanide and Actinide Ions

Ion Symbol	Coordination number 6				Coordination number 8		
	M <sup>2+</sup>	M <sup>3+</sup>	M <sup>4+</sup>	MO <sub>2</sub> <sup>+</sup>	M <sup>3+</sup>	M <sup>4+</sup>	MO <sub>2</sub> <sup>2+</sup>
La	1.304	1.032			1.162		
Ce	1.278	1.010	0.863		1.138	0.967	
Pr	1.253	0.996	0.847		1.122	0.949	
Nd	1.225	0.983	0.836		1.107	0.936	
Pm	1.206	0.968	0.826		1.090	0.925	
Sm	1.183	0.958	0.815		1.079	0.912	
Eu	1.166	0.946	0.807		1.065	0.903	
Gd	1.140	0.937	0.799		1.055	0.894	
Tb	1.119	0.923	0.792		1.040	0.886	
Dy	1.096	0.912	0.782		1.027	0.874	
Ho	1.075	0.900	0.773		1.014	0.864	
Er	1.056	0.889	0.764		1.003	0.854	
Tm	1.038	0.879	0.756		0.993	0.844	
Yb	1.026	0.869	0.748		0.984	0.835	
Lu		0.863	0.741		0.979	0.827	
Ac	1.41	1.12			1.26		
Th	1.36	1.08	0.932		1.22	1.048	
Pa	1.30	1.05	0.906	0.78	1.20	1.016	
U	1.27	1.028	0.889	0.76	1.160	0.997	0.73
Np	1.24	1.011	0.874	0.75	1.141	0.980	0.72
Pu	1.21	0.995	0.859	0.74	1.123	0.962	0.71
Am	1.194	0.980	0.848		1.106	0.950	
Cm	1.164	0.970	0.841		1.094	0.942	
Bk	1.145	0.955	0.833		1.077	0.932	
Cf	1.125	0.945	0.827		1.066	0.925	
Es	1.102	0.934	0.818		1.053	0.914	
Fm	1.083	0.922	0.811		1.040	0.906	
Md	1.064	0.912	0.803		1.028	0.897	
No	1.052	0.902	0.796		1.017	0.889	
Lr		0.896	0.790		1.010	0.881	

The solution chemistry of the actinide elements can be affected by radiolysis. In principle, the chemistry of an actinide element is independent of its radioactivity. In practice, short-lived isotopes, decaying by  $\alpha$  emission or spontaneous fission, cause heating and solvent decomposition with the formation of hydrogen, hydroxide radicals, and hydrogen peroxide from water as well as decomposition products of acids. The decomposition products react with each other and with the actinide element under consideration so that the oxidation state gradually changes. To suppress radiolytic effects, chemical studies with actinide elements should be carried out preferably with long-lived nuclides or on a few-atom basis using radiochemical methods.

Reduction potentials for the actinide elements are given in Table IX. The M<sup>4+</sup>/M<sup>3+</sup> and the MO<sub>2</sub><sup>2+</sup>/MO<sub>2</sub><sup>+</sup> couples are reversible, while the formation and rupture of

bonds and the subsequent reorganization of the solvent shell results in nonreversibility of the couples MO<sub>2</sub><sup>2+</sup>/M<sup>3+</sup>, MO<sub>2</sub><sup>+</sup>/M<sup>4+</sup>, and MO<sub>2</sub><sup>2+</sup>/M<sup>4+</sup>. The redox reactions of UO<sub>2</sub><sup>+</sup>, Pu<sup>4+</sup>, PuO<sub>2</sub><sup>+</sup>, and AmO<sub>2</sub><sup>+</sup> are especially complex. In the special case of plutonium, all four ions Pu<sup>3+</sup>, Pu<sup>4+</sup>, PuO<sub>2</sub><sup>+</sup>, and PuO<sub>2</sub><sup>2+</sup> can coexist in solution. Pu<sup>4+</sup> or PuO<sub>2</sub><sup>+</sup> disproportionate into mixtures of all four oxidation states. An initially pure solution of Pu<sup>4+</sup> in 0.5M hydrochloric acid was reported to contain 26.3% Pu<sup>3+</sup>, 62.7% Pu<sup>4+</sup>, 0.5% PuO<sub>2</sub><sup>+</sup>, and 10.5% PuO<sub>2</sub><sup>2+</sup> after 200 h.

In aqueous solution the actinide cations interact with the solvent water. This hydration is a special case of complex ion formation with water as a nucleophilic ligand. The hydrated ions act as acids, splitting off protons from the water molecules of the hydration shell. Their acidity increases with the charge on the central atom. The divalent ions are weak acids. On account of their large radii, the

TABLE VIII Stability of Actinide Ions in Aqueous Solution

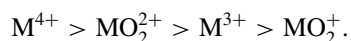
Ion	Preparation	Stability
Md <sup>2+</sup>		Slowly oxidized to Md <sup>3+</sup>
No <sup>2+</sup>		Stable
Ac <sup>3+</sup>		Stable
U <sup>3+</sup>	Electrolytic reduction (Zn or Na/Hg on UO)	Slowly oxidized by water; rapidly by air to U <sup>4+</sup>
Np <sup>3+</sup>	Electrolytic reduction (H <sub>2</sub> /Pt)	Stable to water; rapidly oxidized by air to Np <sup>4+</sup>
Pu <sup>3+</sup>	SO <sub>2</sub> , NH <sub>2</sub> OH, Zn, U <sup>4+</sup> , or H <sub>2</sub> (Pt) reduction	Stable to water and air; oxidized by its own $\alpha$ radiation to Pu <sup>4+</sup> (in case of <sup>239</sup> Pu)
Am <sup>3+</sup>	Iodide, SO <sub>2</sub> reduction	Stable; difficult to oxidize
Cm <sup>3+</sup>		Stable
Bk <sup>3+</sup>		Stable; can be oxidized to Bk <sup>4+</sup>
Cf <sup>3+</sup>		Stable
Es <sup>3+</sup>		Stable
Fm <sup>3+</sup>		Stable
Md <sup>3+</sup>		Stable; can be reduced to Md <sup>2+</sup>
No <sup>3+</sup>	Oxidation of No <sup>2+</sup> with Ce <sup>4+</sup>	Easily reduced to No <sup>2+</sup>
Lr <sup>3+</sup>		Stable
Th <sup>4+</sup>		Stable
Pa <sup>4+</sup>	Reduction of PaO <sup>2+</sup> in HCl (Zn/Hg, Cr <sup>2+</sup> , or Ti <sup>3+</sup> ); electrolytic reduction	Stable to water; rapidly oxidized by air to Pa(V)
U <sup>4+</sup>	Air oxidation of U <sup>3+</sup> ; reduction of UO <sup>2+</sup> (Zn or H <sub>2</sub> with Ni); electrolytic reduction of UO <sup>2+</sup>	Stable to water; slowly oxidized by air to UO <sup>2+</sup>
Np <sup>4+</sup>	Air oxidation of Np <sup>3+</sup> ; Fe <sup>2+</sup> , SO <sub>2</sub> , I <sup>-</sup> or H <sub>2</sub> (Pt) reduction	Stable to water; slowly oxidized by air to NpO <sub>2</sub> <sup>+</sup>
Pu <sup>4+</sup>	BrO <sub>3</sub> <sup>-</sup> , Ce <sup>4+</sup> , Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> , HIO <sub>3</sub> , or MnO <sub>4</sub> <sup>-</sup> oxidation in acid; HNO <sub>2</sub> , NH <sub>3</sub> OH <sup>+</sup> , I <sup>-</sup> , 3M HI, 3M HNO <sub>3</sub> , Fe <sup>2+</sup> , C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> , or HCOOH reduction in acid	Stable in 6M acids, disproportionates to Pu <sup>3+</sup> and PuO <sub>2</sub> <sup>+</sup> at lower acidities
Am <sup>4+</sup>	Electrolytic oxidation of Am <sup>3+</sup> in 12M H <sub>3</sub> PO <sub>4</sub>	Not stable in water; stable in 15M NH <sub>4</sub> F CmF <sub>6</sub> <sup>2-</sup> stable 1 h at 25°C
Cm <sup>4+</sup>	Dissolution of CmF <sub>4</sub> in 15M CsF	Reasonably stable in solution, easily reduced to Bk <sup>3+</sup>
Bk <sup>4+</sup>	Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> or BrO <sub>3</sub> <sup>-</sup> oxidation of Bk <sup>3+</sup>	Slowly reduced to Cf <sup>3+</sup>
Cf <sup>3+</sup>	Oxidation of Cf <sup>3+</sup> using potassium persulfate, stabilization with phosphotungstate	Stable; reduction difficult
PaO <sub>2</sub> <sup>+</sup>		Greatest stability at pH 2.5; disproportionates to U <sup>4+</sup> and UO <sub>2</sub> <sup>2+</sup>
UO <sub>2</sub> <sup>+</sup>	Electrolytic reduction of UO <sub>2</sub> <sup>2+</sup> ; UO <sub>2</sub> <sup>2+</sup> reduction by Zn/Hg or H <sub>2</sub> at pH 2.5	Stable; disproportionates only in strong acids
NpO <sub>2</sub> <sup>+</sup>	NH <sub>2</sub> NH <sub>2</sub> , NH <sub>2</sub> OH, HNO <sub>2</sub> , H <sub>2</sub> O <sub>2</sub> /HNO <sub>3</sub> , Sn <sup>2+</sup> , or SO <sub>2</sub> reduction of NpO <sub>2</sub> <sup>2+</sup>	Most stable at low acidity; disproportionates to Pu <sup>4+</sup> and PuO <sub>2</sub> <sup>2+</sup>
PuO <sub>2</sub> <sup>+</sup>	Reduction of PuO <sub>2</sub> <sup>2+</sup> by I <sup>-</sup> , Fe <sup>2+</sup> , V <sup>3+</sup> , SO <sub>2</sub> , or U <sup>4+</sup>	Disproportionates in strong acids to Am <sup>3+</sup> and AmO <sub>2</sub> <sup>2+</sup> , reduction to Am <sup>3+</sup> at low acidities by its own $\alpha$ radiation in case of <sup>241</sup> Am
AmO <sub>2</sub> <sup>+</sup>	Oxidation of Am <sup>3+</sup> with O <sub>3</sub> , S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> , OCl <sup>-</sup> , or by electrolysis	Stable; difficult to reduce
UO <sub>2</sub> <sup>2+</sup>		Stable in acidic or complexed solutions
NpO <sub>2</sub> <sup>2+</sup>	Oxidation of Np <sup>4+</sup> with Ce <sup>4+</sup> , MnO <sub>4</sub> <sup>-</sup> , Ag <sup>2+</sup> , Cl <sub>2</sub> , or BrO <sub>3</sub> <sup>-</sup>	Stable, fairly easy to reduce; slow reduction by its own $\alpha$ radiation
PuO <sub>2</sub> <sup>2+</sup>	Oxidation of Pu <sup>4+</sup> with BiO <sub>3</sub> <sup>-</sup> , Ce <sup>4+</sup> , Ag <sup>2+</sup> or a number of other reagents	Stable, rapid reduction by its own $\alpha$ radiation
AmO <sub>2</sub> <sup>2+</sup>	Oxidation of Am <sup>3+</sup> or AmO <sub>2</sub> <sup>+</sup> by S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> or Ag <sup>2+</sup>	Stable only in alkaline solution
NpO <sub>5</sub> <sup>3-</sup>	Oxidation of NpO <sub>2</sub> <sup>2+</sup> in alkaline solution by O <sub>3</sub> , S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> , ClO <sup>-</sup> , BrO <sup>-</sup> , or BiO <sub>3</sub> <sup>-</sup>	Stable only in alkaline solution, oxidizes water
PuO <sub>5</sub> <sup>3-</sup>	Oxidation of PuO <sub>2</sub> <sup>2+</sup> in alkaline solution by O <sub>3</sub> , S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> , ClO <sup>-</sup> , or BrO <sup>-</sup>	Stable only in alkaline solution
AmO <sub>5</sub> <sup>3-</sup>	Oxidation of AmO <sub>2</sub> <sup>2+</sup> in alkaline solution by O <sub>3</sub>	

TABLE IX Reduction Potentials of the Actinide Elements

Atomic number Symbol	89 Ac	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
Reduction															
$M^{2+} \rightarrow M$													-2.53	-2.6	
$M^{3+} \rightarrow M$				-1.66	-1.79	-2.00	-2.07	-2.06	-2.00	-1.91	-1.98	-2.07	-1.74	-1.26	-2.1
$M^{4+} \rightarrow M$		-1.83	-1.47	-1.38	-1.30	-1.25	-0.90								
$M^{3+} \rightarrow M^{2+}$													-0.15	+1.45	
$M^{4+} \rightarrow M^{3+}$				-0.55	+0.218	+1.051	+2.62	+3.1	+1.67						
$MO_2^+ \rightarrow M^{3+}$							+1.727								
$MO_2^{2+} \rightarrow M^{3+}$						+1.023									
$MO_2^+ \rightarrow M^{4+}$				+0.38	+0.606	+1.17	+0.84								
$MO_2^{2+} \rightarrow M^{4+}$				+0.267	+0.94	+1.04	+1.217								
$MO_2^{2+} \rightarrow M_2^+$				+0.088	+1.159	+0.936	+1.60								
$MO_3^+ \rightarrow M_2^{2+}$	-2.13				+0.04										

Note: Standard reduction potentials in acidic (pH 0) solutions are given in volts vs standard hydrogen electrode.

trivalent actinide ions are also weak acids. The tetravalent ions are the most acidic. The actinyl ions  $MO_2^+$  and  $MO_2^{2+}$  are formed with great speed whenever oxidation to the +5 and +6 states occurs in water. The actinyl ions are considerably less acidic than are the  $M^{4+}$  ions and, therefore, have a smaller tendency to undergo hydrolysis. Hydrolysis decreases in the order



Hydrolysis may result in the formation of polynuclear species. The  $M^{4+}$  ions, and among them especially  $Pu^{4+}$ , appear to be particularly prone to polymerization. Colloidal polymers of  $Pu^{4+}$  with molecular weights as high as  $10^{10}$  have been observed. Polymer formation and depolymerization are ill defined, and chemical studies may be rendered extremely difficult by the formation of intractable polymers. The formation of polymers can be suppressed by complexation with other ligands such as fluoride ions. Complex ion formation has proved to be extremely important for several fields of pure and applied chemistry of the actinide elements such as their solution chemistry, actinide and nuclear fuel processing and reprocessing using liquid-liquid extraction and ion-exchange methods, or their environmental and biological behavior.

The actinide ions are able to form complexes with various ligands. Complex formation involves an exchange of coordinated water, directly bonded to the central actinide ion, for ligands on the condition that the ligand has an affinity for the actinide ion strong enough to compete with that of the coordinated water. Such exchange results in the formation of inner-sphere complexes. Alternatively, ligands may be attached to coordinated water to form outer-sphere complexes. Strong complexes are mainly of the inner-sphere type. The stability sequences for a given

actinide ion seem to be  $F^- \gg \text{glycolate}^- > \text{acetate}^- > \text{SCN}^- > \text{NO}_3^- > \text{Cl}^- > \text{Br}^- > \text{I}^- > \text{ClO}_4^-$  for monovalent ligands and  $\text{CO}_3^{2-} > \text{EDTA}^{4-} > \text{HPO}_4^{2-} > \text{citrate}^{3-} > \text{tartrate}^{2-} > \text{oxalate}^{2-} > \text{SO}_4^{2-}$  for polyvalent ligands. For a given ligand the stability of the complexes follows the order of the effective charge on the central atom as typical for hard acceptors:  $M^{4+} > MO_2^{2+} \simeq M^{3+} > MO_2^+$ . The reversal in the order of  $MO_2^{2+}$  and  $M^{3+}$  ions is a result of the higher charge density of  $MO_2^{2+}$  because of imperfect shielding by the linear oxygen atoms. High stabilities of complexes formed by hard acceptors are not reflected in exothermic enthalpy changes, but rather in very positive entropy terms due to a large decrease of order as a result of complex formation.

The phosphate anion  $PO_4^{3-}$  and organic phosphates are powerful complexing agents for actinide ions, forming complexes that are insoluble in water but soluble in nonpolar aliphatic hydrocarbons. Complexes with such reagents have been used in the separation of the actinide elements by liquid-liquid extraction on a large scale. The actinides, in general, form more stable complexes than do the homologous lanthanide ions. Extraction with tertiary amines and *bis*-2-ethylhexyl hydrogen phosphate has been used to separate the trivalent transplutonium element ions from the lanthanides. Differences in complexation have also been used to separate lanthanides and actinides by ion-exchange techniques. The sorption of actinide ions on cation exchangers varies in the sequence  $MO_2^+ < M^{2+} < MO_2^{2+} < M^{3+} < M^{4+}$ . The sorption coefficients of ions of the same charge do not differ widely. Their separation coefficients can be much enhanced, however, by the use of selective, complex-forming eluting agents. Citrate, lactate, and especially  $\alpha$ -hydroxisobutyrate as eluting agents have been proved as



successful for the separation of trivalent lanthanide and actinide ions. A group separation of trivalent actinides and lanthanides may be accomplished also by anion exchange. The trivalent actinide ions form much more stable chloride complexes than do the trivalent lanthanide ions. They are therefore sorbed on anion-exchange resins from concentrated hydrochloric acid, while the lanthanides are not.

### C. Magnetic Properties

The actinides exhibit nearly all of the types of magnetism found in transition and lanthanide metals. Thorium behaves like a  $6d$  transition metal. The magnetic susceptibility is large, and the temperature dependence is low. The actinide metals protactinium to plutonium do not have ordered ground state moments. Hybridization of  $5f$  and  $6d$  levels broadens the  $f$  levels and suppresses the formation of localized moments. The temperature-independent paramagnetic susceptibilities indicate an itinerant character of the  $5f$  electrons. From americium on the  $5f$  electrons become localized and the heavy metals are localized magnets, similar to the lanthanide metals. For americium, the susceptibility is large with little temperature dependence. Curium has an antiferromagnetic transition at 65 K, but the face-centered cubic phase shows a ferrimagnetic transition near 200 K. Berkelium metal exhibits high-temperature magnetic behavior like its lanthanide homolog terbium. Californium metal exhibits either ferro- or ferrimagnetic behavior below 51 K and paramagnetic behavior above 160 K.

Actinide compounds and ions exhibit very different magnetic behavior arising from the spin and orbital angular moments of the unpaired electrons. Spin-orbit coupling is about twice that for the lanthanides, and the crystal field strengths for the actinides are an order of magnitude greater. There is a wealth of information about the magnetic properties of various actinide materials which has been reviewed elsewhere.

### D. Spectroscopic Properties

Actinide spectra reflect the characteristic features of the  $5f$  orbitals which can be considered as both containing the optically active electrons and belonging to the core of filled shells. The electronic transition spectra of actinide ions in solution are dominated by the structure of the  $f$  levels and transitions within the  $f$  shell. Free-atom spectra provide more information about the interactions between the  $5f$  and the valence electrons. The emission spectra of the free actinide atoms have an enormous number of lines. In the uranium spectrum, about 100,000 lines have been measured, from which about 2500 lines have been assigned.

In condensed phases, spectra are commonly measured in absorption. Three main types of transitions are observed in the absorption spectra of the actinide ions: (1) Laporte-forbidden  $f$  to  $f$  transitions, (2) orbitally allowed  $5f$  to  $6d$  transitions, and (3) metal to ligand charge transfer. Of these, study of internal  $f$  to  $f$  transitions has found wide use in the investigation of actinide chemistry. These bands usually in the visible and ultraviolet regions, can be easily identified because of their sharpness, and are sensitive to the metal environment. As discussed earlier, the  $5f$  orbitals of the actinide elements are more exposed than the lanthanide  $4f$  orbitals, and therefore, crystal field effects are larger in the  $5f$  series. The  $f$  to  $f$  transitions for actinide elements may be up to 10 times more intense and twice as broad as those observed for the lanthanides, due to the action of crystal fields. In addition, extra lines resulting from vibronic states coupled to  $f \rightarrow f$  states have been observed.

The  $5f$  to  $6d$  bands are orbitally allowed and therefore more intense than those of the  $f$  to  $f$  transitions. They are also usually broader and often observed in the ultraviolet region. The metal to ligand charge-transfer bands are also fully allowed transitions that are broad and occur commonly in the ultraviolet region. When these bands trail into the visible region, they produce the intense colors associated with many of the actinide compounds. Metal-ligand frequencies are also observed in the infrared and Raman spectra of actinide compounds.

Actinide spectra are used in different ways. First, because of their characteristic properties, actinide spectra can be used for the direct speciation of (complexed) actinide ions, the observation and quantification of reactions taking place in solution, or the identification of compounds. On the other hand, actinide spectra can be used to study electronic and physicochemical properties, including information on symmetry, coordination number, or stability constants.

Conventional optical absorption spectrometry has detection limits of between 0.01 and 1 mM for the actinides. Highly sensitive spectroscopic methods have been developed, based on powerful laser light sources. Time resolved laser fluorescence spectroscopy (TRLFS), based on the combined measurement of relaxation time and fluorescence wavelength, is capable of speciating Cm(III) down to  $10^{-12}$  mol/L but is restricted to fluorescent species like U(VI) and Cm(III). Spectroscopic methods based on the detection of nonradiative relaxation are the laser-induced photoacoustic spectroscopy (LPAS) and the laser-induced thermal lensing spectroscopy (LTLS). Like conventional absorption spectroscopic methods, these newly developed methods are capable of characterizing oxidation and complexation states of actinide ions but with higher sensitivity.

Methods of growing importance for speciation and complexation studies of actinides are the synchrotron-based X-ray absorption near-edge structure spectroscopy (XANES) and the extended X-ray absorption fine structure spectroscopy (EXAFS).

## VI. ACTINIDE COMPOUNDS AND COMPLEXES

### A. Binary Compounds

#### 1. Hydrides

Representative actinide hydride compounds are represented in Table X. Actinide metals react readily with hydrogen when heated. The temperature needed for reaction depends on the state of the metal, the amount of surface oxidation on the metal, and the purity and pressure of the hydrogen used. The actinide hydrides are not very thermally stable and are very air and moisture sensitive. The thermal instability of these compounds has been used to obtain finely divided metal via thermal decomposition of the corresponding hydride.

The physicochemical properties of the actinide hydrides are as varied as any in the entire periodic table. Thorium forms a “normal” dihydride like those of Zr and Hf, but also forms Th<sub>4</sub>H<sub>15</sub>, a unique superconductor. The hydrides of protactinium and uranium have cubic structures which have no counterparts in the periodic table. The transuranium element hydrides are more lanthanide like with wide cubic solid solution ranges. Hexagonal phases appear with regularity.

#### 2. Oxides

The actinide oxides have received intensive scrutiny because their refractory nature makes them suitable for use as ceramic fuel elements in nuclear reactors. UO<sub>2</sub> melts at 3150 K, and ThO<sub>2</sub> has the highest melting point of any oxide, about 3465 K. The actinide oxides are complicated by deviations from stoichiometry, polymorphism, and intermediate phases. The sesquioxides are basic, the dioxides are much less basic, and UO<sub>3</sub> is an acid in solid state reactions. The reactivity of these oxides depends greatly on their thermal history. If ignited, they are much more inert. Table XI contains some representative data on actinide oxides.

TABLE X Actinide Hydrides

Compound	Color	Symmetry <sup>a</sup>	Space group	Lattice parameters		M-H Bond length (Å)	Density (g cm <sup>-3</sup> )
				a (Å)	c (Å)		
AcH <sub>2</sub>	Black	fcc	<i>Fm3m</i>	5.670		2.46	8.35
ThH <sub>1.93</sub>	Black	bct		5.73	4.99	2.39	9.50
ThH <sub>2</sub>	Black	bct		4.10	5.03	2.39	9.20
Th <sub>4</sub> H <sub>15</sub>	Black	bcc	<i>I43d</i>	9.11		2.29, 2.46	8.29
α-PaH <sub>3</sub>	Black	Cubic	<i>Pm3n</i>	4.150			
β-PaH <sub>3</sub>	Black	Cubic	<i>Pm3n</i>	6.648		2.32	10.57
α-UH <sub>3</sub>	Black	Cubic	<i>Pm3n</i>	4.160		2.32	11.12
β-UH <sub>3</sub>	Black	Cubic	<i>Pm3n</i>	6.644			
NpH <sub>2</sub>	Black	fcc	<i>Fm3m</i>	5.348		2.32	10.41
NpH <sub>2.36</sub>	Black	fcc	<i>Fm3m</i>	5.346			
NpH <sub>2.42</sub>	Black	fcc	<i>Fm3m</i>	5.348			
NpH <sub>3</sub>	Black	Hexagonal	<i>P6<sub>3</sub>/mmc</i>	3.777	6.720		9.64
PuH <sub>2</sub>	Black	fcc	<i>Fm3m</i>	5.3594		2.32	10.40
PuH <sub>2.5</sub>	Black	fcc	<i>Fm3m</i>	5.34			
PuH <sub>3</sub>	Black	Hexagonal	<i>P6<sub>3</sub>/mmc</i>	3.779	6.771	2.18–2.41	9.61
AmH <sub>2</sub>	Black	fcc	<i>Fm3m</i>	5.348		2.316	10.6
AmH <sub>2.67</sub>	Black	fcc	<i>Fm3m</i>	5.338			
AmH <sub>3</sub>	Black	Hexagonal	<i>P6<sub>3</sub>/mmc</i>	3.764	6.763		9.76
CmH <sub>2(+x)</sub>	Black	fcc	<i>Fm3m</i>	5.322		2.314	10.7
CmH <sub>3</sub>	Black	Hexagonal		3.77	6.73		
BkH <sub>2(+x)</sub>	Black	fcc	<i>Fm3m</i>	5.25			
BkH <sub>3(-x)</sub>	Black	Trigonal		6.454	6.663		
CfH <sub>2+x</sub>	Black	Cubic		5.285			

<sup>a</sup> bct, body-centered tetragonal; fcc, face-centered cubic.

TABLE XI Binary Actinide Oxides<sup>a</sup>

Compound	Color	Symmetry <sup>b</sup>	Lattice parameters					
			a (Å)	b (Å)	c (Å)	α (deg)	β (deg)	γ (deg)
<i>Ac</i> <sub>2</sub> <i>O</i> <sub>3</sub>	White	Hexagonal	4.07		6.29			
<i>Th</i> <i>O</i> <sub>2</sub>	White	Cubic	5.5971					
<i>Pa</i> <sub>2</sub> <i>O</i> <sub>5</sub>	White	fcc	5.446					
<i>Pa</i> <sub>2</sub> <i>O</i> <sub>5</sub>	White	Tetragonal	5.429		5.503			
<i>Pa</i> <sub>2</sub> <i>O</i> <sub>5</sub>	White	Hexagonal	3.817		13.220			
<i>Pa</i> <sub>2</sub> <i>O</i> <sub>5</sub>	White	Rhombohedral	5.424			89.76		
<i>Pa</i> <sub>2</sub> <i>O</i> <sub>5</sub>	White	Orthorhombic	6.92	4.02	4.18			
<i>PaO</i> <sub>2.42</sub> - <i>PaO</i> <sub>2.44</sub>	White	Rhombohedral	5.449			89.65		
<i>PaO</i> <sub>2.40</sub> - <i>PaO</i> <sub>2.42</sub>	White	Tetragonal	5.480		5.416			
<i>PaO</i> <sub>2.33</sub>	White	Tetragonal	5.425		5.568			
<i>PaO</i> <sub>2.18</sub> - <i>PaO</i> <sub>2.21</sub>	White	fcc	5.473					
<i>PaO</i> <sub>2</sub>	Black	fcc (CaF <sub>2</sub> )	5.509					
<i>α-U</i> <sub>3</sub> <i>O</i> <sub>8</sub>	Dark green	Orthorhombic	6.716	11.960	4.147			
<i>β-U</i> <sub>3</sub> <i>O</i> <sub>8</sub>	Dark green	Orthorhombic	7.069	11.445	8.303			
<i>α-U</i> <sub>2</sub> <i>O</i> <sub>5</sub>	Black	Monoclinic	12.40	5.074	6.75		99.2	
<i>β-U</i> <sub>2</sub> <i>O</i> <sub>5</sub>	Black	Hexagonal	3.813		13.18			
<i>γ-U</i> <sub>2</sub> <i>O</i> <sub>5</sub>	Black	Monoclinic	5.410	5.481	5.410		90.49	
<i>α-UO</i> <sub>3</sub>	Beige	Orthorhombic	6.84	43.45	4.157			
<i>β-UO</i> <sub>3</sub>	Orange	Monoclinic	10.34	14.33	3.910		99.03	
<i>γ-UO</i> <sub>3</sub>	Yellow	Orthorhombic	9.813	19.93	9.711			
<i>δ-UO</i> <sub>3</sub>	Deep red	Cubic	4.16					
<i>ε-UO</i> <sub>3</sub>	Brick red	Triclinic	4.002	3.841	4.165	98.10	90.20	120.17
<i>η-UO</i> <sub>3</sub>	Brown	Orthorhombic	7.511	5.466	5.224			
<i>UO</i> <sub>2</sub>	Dark brown	fcc	5.704					
<i>Np</i> <sub>2</sub> <i>O</i> <sub>5</sub>	Dark brown	Monoclinic	4.183	6.584	4.086		90.32	
<i>NpO</i> <sub>2</sub>	Brown-green	Cubic	5.425					
<i>α-Pu</i> <sub>2</sub> <i>O</i> <sub>3</sub>	Black	bcc	11.04					
<i>β-Pu</i> <sub>2</sub> <i>O</i> <sub>3</sub>	Black	Hexagonal	3.841		5.958			
<i>PuO</i> <sub>2</sub>	Yellow	fcc	5.3960					
<i>A-Am</i> <sub>2</sub> <i>O</i> <sub>3</sub>	Red-brown	Hexagonal	3.817		5.96			
<i>B-Am</i> <sub>2</sub> <i>O</i> <sub>3</sub>	Red-brown	Monoclinic	14.38	3.52	8.92		100.4	
<i>C-Am</i> <sub>2</sub> <i>O</i> <sub>3</sub>		Cubic	11.03					
<i>AmO</i> <sub>2</sub>	Dark brown	fcc	5.374					
<i>A-Cm</i> <sub>2</sub> <i>O</i> <sub>3</sub>	White	Hexagonal	3.792		5.985			
<i>B-Cm</i> <sub>2</sub> <i>O</i> <sub>3</sub>	White	Monoclinic	14.282	3.641	8.883		100.29	
<i>C-Cm</i> <sub>2</sub> <i>O</i> <sub>3</sub>	White	Cubic	11.002					
<i>CmO</i> <sub>2</sub>	Black	Cubic	5.3584					
<i>A-Bk</i> <sub>2</sub> <i>O</i> <sub>3</sub>	Yellow-green	Hexagonal	3.754		5.958			
<i>C-Bk</i> <sub>2</sub> <i>O</i> <sub>3</sub>	Yellow-green	bcc	10.887					
<i>BkO</i> <sub>2</sub>	Brown	fcc	5.3315					
<i>A-Cf</i> <sub>2</sub> <i>O</i> <sub>3</sub>	Pale green	Hexagonal	3.72		5.69			
<i>B-Cf</i> <sub>2</sub> <i>O</i> <sub>3</sub>	Pale green	Monoclinic	14.124	3.591	8.809			100.31
<i>C-Cf</i> <sub>2</sub> <i>O</i> <sub>3</sub>	Pale green	bcc	10.839					
<i>CfO</i> <sub>2</sub>	Black	fcc	5.310					
<i>Es</i> <sub>2</sub> <i>O</i> <sub>3</sub>	Black	bcc	10.766					
<i>Es</i> <sub>2</sub> <i>O</i> <sub>3</sub>		Monoclinic	14.1	3.59	8.80			100
<i>Es</i> <sub>2</sub> <i>O</i> <sub>3</sub>		Hexagonal	3.7		6.0			

<sup>a</sup> The most stable oxide of each element is italicized. Where more than one modification exists, the first listed is italicized.

<sup>b</sup> bcc, body-centered cubic; fcc, face-centered cubic.

The wide variety of oxidation states known for the actinides is reflected in the stoichiometry of their binary oxides; however, the highest attainable oxidation state may not be observed. The largest O/M ratio for an *f*-element binary oxide is achieved in  $\text{UO}_3$ .

All the solid actinide monoxides which have been reported are now believed to have been oxynitrides, oxycarbides, or hydrides. The highest potential for existence would have the monoxides for the divalent actinide metals einsteinium through nobelium. Only the gaseous monoxides are well-established species. All actinides are known or expected to form gaseous monoxides.

The sesquioxide is known for actinium and all the actinides from plutonium through einsteinium and is probably the highest binary oxide that could be formed for the heaviest actinides with nobelium as an exception, which may only form a solid monoxide. Oxides of the heaviest actinides beyond einsteinium have not been prepared or studied experimentally. The sesquioxides of Pu, Am, and Bk are readily oxidized to their dioxides, whereas those of Cm, Cf, and Es are resistant to air oxidation.

The dioxide is known for all the actinides from thorium through californium. Attempts to prepare einsteinium dioxide have not been successful. All the dioxides crystallize with the fluorite face-centered cubic structure. Actinides that form both a dioxide and a sesquioxide may form complex intermediate oxides, which have O/M ratios between 1.5 and 2.0.

Binary oxides with higher oxygen stoichiometries have been confirmed only for the elements Pa, U, and Np. Numerous phases in the composition range  $\text{UO}_2$  to  $\text{UO}_3$  have been observed. The reported formation of nonstoichiometric  $\text{PuO}_{2+x}$  has to be confirmed. Only  $\text{UO}_3$  is known for the anhydrous actinide trioxides and is prepared by decomposing uranyl nitrate or a hydrated uranyl hydroxide containing  $\text{NH}_4^+$  at  $350^\circ\text{C}$ . There are seven crystal modifications of  $\text{UO}_3$ . Many of these contain oxygen-bridged structures, with uranyl present.  $\delta\text{-UO}_3$  with its cubic  $\text{ReO}_3$  structure consists of linked  $\text{UO}_6$  octahedra.

Actinide sulfides, selenides, and tellurides are also known. The sulfides and selenides are generally isostructural, but not with the analogous tellurides. The thermal stability of these compounds decreases in the order sulfides > selenides > tellurides. These compounds are usually prepared via direct reaction of finely divided actinide metal powder with the chalcogen at about  $400\text{--}600^\circ\text{C}$ . Semimetallic behavior and nonstoichiometry are observed for these compounds.

### 3. Halides

A wealth of information has been accumulated on actinide halides. The known binary halides range from  $\text{AnX}_2$  to

$\text{AnX}_6$ , and some representative data for these are given in Table XII. The thermal stability of the halides toward reduction of higher oxidation state actinides decreases with increasing atomic number of the halogen.

Truly divalent actinide halides are known only for americium and californium.  $\text{AnX}_2$  species for Es have been identified by their absorption spectra. For Fm, Md, and No,  $\text{AnX}_2$  halides should be possible if sufficient amounts of these metals could be obtained.  $\text{ThI}_2$  is also known, but crystallographic studies of this compound reveal the true formulation to be  $\text{Th(IV)}$ ,  $2\text{I}^-$ , and  $2\text{e}^-$ . This compound has some metallic character, including its luster and electrical conductivity.

The actinide trihalides behave similarly to the lanthanide trihalides. The trifluorides through berkelium trifluoride crystallize at room temperature with the  $\text{LaF}_3$  hexagonal structure. Nine fluorine atoms are arranged around the actinide in a heptagonal bipyramid geometry.  $\text{CfF}_3$  and a second form of  $\text{BkF}_3$  have the orthorhombic  $\text{YF}_3$  structure, where nine fluorines form an approximate tricapped prism with one fluorine  $0.3\text{ \AA}$  farther from the metal. All of the trifluorides are high-melting solids, insoluble in water, and only slowly oxidized in air.

The actinide trichlorides are hygroscopic and water soluble and melt between  $1030$  and  $1110\text{ K}$ . They can be obtained by reaction of the metal hydride with  $\text{HCl}$  at elevated temperatures or by the reaction of  $\text{CCl}_4$  with  $\text{An(OH)}_3$ . With the larger actinide(III) ions, the crystal structures of the trichlorides show nine chlorine atoms arranged in a tricapped trigonal prismatic geometry. As the atomic number increases, the three actinide to face-capping-chlorine distances increase relative to the other six chlorines. At californium, a second form of  $\text{CfCl}_3$  has eight coordination.

$\text{AnBr}_3$  compounds can be prepared by reaction of  $\text{HBr}$  with the proper actinide hydride, hydroxide, oxalate hexahydrate, or oxide. Structures similar to the trichlorides are observed with the structural change from nine coordination to eight coordination occurring with  $\beta$ -neptunium tribromide. The triiodides to  $\alpha$ -americium triiodide have the same eight-coordinate structure found for the heavier bromides and chlorides. From  $\beta$ -americium triiodide on, the metals are six coordinate.  $\text{ThI}_3$  is best formulated as  $\text{Th(IV)}$ ,  $3\text{I}^-$ , and  $1\text{e}^-$ .

The best known actinide halides are the tetrahalides, the fluorides being known through californium. All of the  $\text{AnF}_4$  species are monoclinic, the metal being eight coordinate with antiprismatic geometry. These compounds, prepared by heating  $\text{HF}$  with the dioxides, are insoluble in water. The remaining tetrahalides can be prepared by heating the actinide dioxides in  $\text{CCl}_4$  ( $\text{ThCl}_4$  to  $\text{NpCl}_4$ ),  $\text{Cl}_2/\text{SOCl}_2$  ( $\text{BkCl}_4$ ), or from the elements ( $\text{ThBr}_4$  to  $\text{NpBr}_4$  and  $\text{ThI}_4$  to  $\text{U}_4$ ). The tetrachlorides are eight

TABLE XII Binary Actinide Halides

Compound	Color	Symmetry	Lattice parameters					
			a (Å)	b (Å)	c (Å)	$\alpha$ (deg)	$\beta$ (deg)	$\gamma$ (deg)
$\beta$ -ThI <sub>2</sub>	Gold	Hexagonal	3.97		31.75			
AmI <sub>2</sub>	Black	Monoclinic	7.677	8.311	7.925		98.5	
$\alpha$ -CfI <sub>2</sub>	Violet	Hexagonal	4.557		6.992			
$\beta$ -CfI <sub>2</sub>	Violet	Rhombohedral	7.434			35.8		
AmBr <sub>2</sub>	Black	Trigonal	11.59		7.121			
CfBr <sub>2</sub>	Amber	Trigonal	11.000		7.109			
AmCl <sub>2</sub>	Black	Orthorhombic	8.963	7.573	4.532			
PaI <sub>3</sub>	Black	Orthorhombic	4.33	14.00	10.02			
UI <sub>3</sub>	Black	Orthorhombic	4.328	13.996	9.984			
NpI <sub>3</sub>	Purple	Orthorhombic	4.3	14.03	9.95			
PuI <sub>3</sub>	Green	Orthorhombic	4.33	13.95	9.96			
$\alpha$ -AmI <sub>3</sub>	Yellow	Orthorhombic	4.31	14.03	9.92			
$\beta$ -AmI <sub>3</sub>	Yellow	Hexagonal	7.42		20.55			
CmI <sub>3</sub>	White	Hexagonal	7.44		20.4			
BkI <sub>3</sub>	Yellow	Hexagonal	7.84		20.87			
CfI <sub>3</sub>	Yellow	Hexagonal	7.587		20.814			
EsI <sub>3</sub>	Red	Hexagonal	7.53		20.84			
AcBr <sub>3</sub>		Hexagonal	8.06		4.68			
UBr <sub>3</sub>	Red	Hexagonal	7.936		4.438			
$\alpha$ -NpBr <sub>3</sub>	Green	Hexagonal	7.919		4.392			
$\beta$ -NpBr <sub>3</sub>	Green	Orthorhombic	12.618	4.109	9.153			
PuBr <sub>3</sub>	Green	Orthorhombic	12.65	4.10	9.15			
AmBr <sub>3</sub>	White	Orthorhombic	12.66	4.064	9.144			
CmBr <sub>3</sub>	White	Orthorhombic	12.70	4.041	9.135			
BkBr <sub>3</sub>	Yellow-green	Monoclinic	7.23	12.53	6.83		110.6	
$\alpha$ -CfBr <sub>3</sub>	Pale green	Monoclinic	7.215	12.423	6.825		110.7	
$\beta$ -CfBr <sub>3</sub>	Pale green	Rhombohedral	7.58			56.2		
EsBr <sub>3</sub>	Straw	Monoclinic	7.27	12.59	6.81		110.8	
AcCl <sub>3</sub>	White	Hexagonal	7.62		4.55			
UCl <sub>3</sub>	Green	Hexagonal	7.442		4.320			
NpCl <sub>3</sub>	Green	Hexagonal	7.413		4.282			
PuCl <sub>3</sub>	Green	Hexagonal	7.395		4.246			
AmCl <sub>3</sub>	Pink	Hexagonal	7.382		4.214			
CmCl <sub>3</sub>	White	Hexagonal	7.374		4.185			
BkCl <sub>3</sub>	Green	Hexagonal	7.382		4.127			
$\beta$ -CfCl <sub>3</sub>	Green	Hexagonal	7.379		4.090			
$\alpha$ -CfCl <sub>3</sub>	Green	Orthorhombic	3.859	11.748	8.561			
EsCl <sub>3</sub>		Hexagonal	7.40		4.07			
AcF <sub>3</sub>	White	Trigonal	7.41		7.53			
UF <sub>3</sub>	Black	Trigonal	7.181		7.348			
NpF <sub>3</sub>	Purple	Trigonal	7.129		7.288			
PuF <sub>3</sub>	Violet	Trigonal	7.092		7.254			
AmF <sub>3</sub>	Pink	Hexagonal	7.044		7.225			
CmF <sub>3</sub>	White	Trigonal	7.019		7.198			
$\beta$ -BkF <sub>3</sub>	Yellow-green	Trigonal	6.97		7.14			
$\alpha$ -BkF <sub>3</sub>	Yellow-green	Orthorhombic	6.70	7.09	4.41			
$\alpha$ -CfF <sub>3</sub>	Light green	Orthorhombic	6.653	7.039	4.393			
$\beta$ -CfF <sub>3</sub>	Light green	Trigonal	6.945		7.101			

Continues

TABLE XII (continued)

Compound	Color	Symmetry	Lattice parameters					
			a (Å)	b (Å)	c (Å)	$\alpha$ (deg)	$\beta$ (deg)	$\gamma$ (deg)
ThI <sub>4</sub>	White	Monoclinic	13.216	8.069	7.766		98.68	
$\alpha$ -ThBr <sub>4</sub>	White	Tetragonal	6.737		13.601			
$\beta$ -ThBr <sub>4</sub>	White	Tetragonal	8.932		7.963			
PaBr <sub>4</sub>	Brown	Tetragonal	8.824		7.957			
UBr <sub>4</sub>	Brown	Monoclinic	10.92	8.69	7.05		93.15	
NpBr <sub>4</sub>	Dark red	Monoclinic	10.89	8.74	7.05		94.19	
$\alpha$ -ThCl <sub>4</sub>	White	Orthorhombic	11.18	5.93	9.09			
$\beta$ -ThCl <sub>4</sub>	White	Tetragonal	8.473		7.468			
PaCl <sub>4</sub>	Green-yellow	Tetragonal	8.377		7.482			
UCl <sub>4</sub>	Green	Tetragonal	8.296		7.481			
NpCl <sub>4</sub>	Red-brown	Tetragonal	8.266		7.475			
ThF <sub>4</sub>	White	Monoclinic	12.90	10.93	8.58		126.4	
PaF <sub>4</sub>	Brown	Monoclinic	12.86	10.88	8.54		126.3	
UF <sub>4</sub>	Green	Monoclinic	12.803	10.792	8.372		126.3	
NpF <sub>4</sub>	Green	Monoclinic	12.68	10.66	8.34		126.3	
PuF <sub>4</sub>	Pale brown	Monoclinic	12.599	10.573	8.84		126.25	
AmF <sub>4</sub>	Tan	Monoclinic	12.538	10.516	8.204		126.8	
CmF <sub>4</sub>	Brown	Monoclinic	12.51	10.61	8.20	125.8		
BkF <sub>4</sub>		Monoclinic	12.40	10.47	8.12		126.3	
CfF <sub>4</sub>	Green	Monoclinic	12.42	10.468	8.126		126.0	
Pa <sub>2</sub> F <sub>9</sub>	Black	Cubic	8.507					
U <sub>2</sub> F <sub>9</sub>	Black	Cubic	8.471					
PaI <sub>5</sub>	Black	Orthorhombic	7.22	21.20	6.85			
$\alpha$ -PaBr <sub>5</sub>		Monoclinic	12.69	12.82	9.92		108	
$\beta$ -PaBr <sub>5</sub>	Dark red	Monoclinic	8.385	11.205	8.950		91.1	
UBr <sub>5</sub>	Brown	Triclinic	7.449	10.127	6.686	89.25	117.56	108.87
PaCl <sub>5</sub>	Yellow	Monoclinic	8.00	11.42	8.43		106.38	
$\alpha$ -UCl <sub>5</sub>	Brown	Monoclinic	7.99	10.69	8.48		91.5	
$\beta$ -UCl <sub>5</sub>	Brown	Triclinic	7.09	9.66	6.36	88.5	117.6	108.5
PaF <sub>5</sub>	White	Tetragonal	11.525		5.218			
$\alpha$ -UF <sub>5</sub>	Pale blue	Tetragonal	6.512		4.463			
$\beta$ -UF <sub>5</sub>	Pale blue	Tetragonal	11.450		5.207			
NpF <sub>5</sub>	Bluish-white	Tetragonal	6.53		4.45			
UCl <sub>6</sub>	Dark green	Hexagonal	10.90		6.03			
UF <sub>6</sub>	White	Orthorhombic	9.900	8.962	5.207			
NpF <sub>6</sub>	Orange	Orthorhombic	9.909	8.997	5.202			
PuF <sub>6</sub>	Brown	Orthorhombic	9.95	9.020	5.260			

coordinate with dodecahedral geometry. UBr<sub>4</sub> and NpBr<sub>4</sub> are seven coordinate, and UI<sub>4</sub> is octahedral. UCl<sub>4</sub> and ThCl<sub>4</sub> are well-known starting materials for the synthesis of organometallic compounds.

Pentahalides are known only to neptunium. All of these compounds are very water sensitive. The pentafluorides and PaCl<sub>5</sub> are polymeric seven-coordinate compounds. The geometry is that of a distorted pentagonal bipyramid with double bridging occurring through four of the equa-

torial atoms. UCl<sub>5</sub> and PaBr<sub>5</sub> consist of halogenbridged dimeric An<sub>2</sub>X<sub>10</sub> units.

AnX<sub>6</sub> species are known for fluorides of uranium, neptunium, and plutonium and for UCl<sub>6</sub>. The hexafluorides are volatile compounds obtained by fluorinating AnF<sub>4</sub>. The highly volatile UF<sub>6</sub> is the compound used for the large-scale isotope separation of <sup>235</sup>U from <sup>238</sup>U. UCl<sub>6</sub> can be made by the reaction of AlCl<sub>3</sub> and UF<sub>6</sub>. The hexahalides have octahedral geometry.

Oxyhalides of the actinides are known mainly for the types  $\text{AnO}_2\text{X}_2$ ,  $\text{AnO}_2\text{X}$ ,  $\text{AnOX}_2$ , and  $\text{AnOX}$ . They can be prepared by low-temperature hydrolysis or by oxygenating the corresponding halide with oxygen or  $\text{Sb}_2\text{O}_3$ . The hydrolysis of the trihalides results in  $\text{AnOX}$  species. The higher oxidation states found for  $\text{AnO}_2\text{X}_2$  compounds confine these to uranium.

#### 4. Compounds with Other Elements

Compounds of actinides with nitrogen, phosphorus, arsenic, antimony, and bismuth have been studied as a result of their refractory nature and possible uses as nuclear fuel materials. Many of these compounds can be prepared by heating a finely divided actinide metal or a hydride of the metal in a sealed tube with the Group 15 element. Borides, carbides, and silicides are also known.

Monocarbides, mononitrides, and other actinide compounds with the general formulation  $\text{AnX}$  ( $\text{X}$  = Group 15 and 16 elements) have the face-centered cubic  $\text{NaCl}$  structure. These compounds are mainly ionic with a partially filled conduction band and, thus, are good conductors of heat and electricity.

Tetragonal compounds of the  $\text{UX}_2$  and  $\text{UXY}$  type, again with  $\text{X}$  and  $\text{Y}$  being elements of Group 15 or 16, are also good conductors. Metallic  $\text{An}_3\text{X}_4$  compounds have body-centered cubic structures.

Table XIII presents some data on these compounds.

#### B. Oxo Acid Salts

Much of the information on actinide oxo acid salt compounds is provided from studies of the analytical separation chemistry of the actinides, solvent extraction, ion exchange, and precipitation technologies. Little structural information is available on these species. Isolated examples of borates, silicates, nitrites, phosphites, hypophosphites, arsenates, thiosulfates, selenates, selenides, tellurates, and tellurites are known but not well characterized. A much broader chemistry is known for complexes with nitrates, carbonates, phosphates, sulfates, halides, and carboxylates, reflecting the importance of these ions in separation techniques.

The chloride, bromide, bromate, nitrate, and perchlorate anions form water-soluble salts with the actinide  $\text{M}^{3+}$  ions, which can be isolated by evaporation. Precipitates are formed with hydroxide, fluoride, carbonate, oxalate, and phosphate anions. The actinide  $\text{M}^{4+}$  ions form insoluble fluorides, iodates, arsenates, and oxalates; the nitrates, sulfates, perchlorates, and sulfides are all water soluble. The  $\text{MO}_2^+$  ions can be precipitated from concentrated carbonate solutions as potassium salts.  $\text{Na}_2\text{U}_2\text{O}_7$  can be precipitated from alkaline solutions of the uranyl,  $\text{UO}_2^{2+}$ , ion.

TABLE XIII Other Early Actinide Compounds

Compound	Symmetry <sup>a</sup>	Space group	Lattice parameters	
			a (Å)	b (Å)
UAs	fcc	<i>Fm3m</i>	5.7788	
UBi	fcc	<i>Fm3m</i>	6.364	
UC	fcc	<i>Fm3m</i>	4.961	
UN	fcc	<i>Fm3m</i>	4.889	
UP	fcc	<i>Fm3m</i>	5.589	
US	Cubic	<i>Pm3m</i>	5.4903	
USb	fcc	<i>Fm3m</i>	6.203	
USE	fcc	<i>Fm3m</i>	5.7399	
UTe	fcc	<i>Fm3m</i>	6.150	
NpAs	fcc	<i>Fm3m</i>	5.835	
NpC	fcc	<i>Fm3m</i>	4.992	
NpN	fcc	<i>Fm3m</i>	4.898	
NpP	fcc	<i>Fm3m</i>	5.610	
NpS	fcc	<i>Fm3m</i>	5.527	
NpSb	fcc	<i>Fm3m</i>	6.249	
PuAs	fcc	<i>Fm3m</i>	5.855	
PuC	fcc	<i>Fm3m</i>	4.974	
PuN	fcc	<i>Fm3m</i>	4.9055	
PuP	fcc	<i>Fm3m</i>	5.664	
PuS	fcc	<i>Fm3m</i>	5.537	
PuSb	fcc	<i>Fm3m</i>	6.241	
UP <sub>2</sub>	Tetragonal	<i>P4/nmm</i>	3.808	7.780
UAs <sub>2</sub>	Tetragonal	<i>P4/nmm</i>	3.954	8.116
USb <sub>2</sub>	Tetragonal	<i>P4/nmm</i>	4.272	8.759
UBi <sub>2</sub>	Tetragonal	<i>P4/nmm</i>	4.445	8.908
$\alpha$ -US <sub>2</sub>	Tetragonal	<i>I1/mcm</i>	10.27	6.32
$\alpha$ -USE <sub>2</sub>	Tetragonal	<i>I4/mcm</i>	10.772	6.668
UOSe	Tetragonal	<i>P4/nmm</i>	3.9035	6.9823
UOTe	Tetragonal	<i>P4/nmm</i>	4.004	7.491
UOS	Tetragonal	<i>P4/nmm</i>	3.483	6.697
UAsS	Tetragonal	<i>P4/nmm</i>	3.884	8.176
UAsSe	Tetragonal	<i>P4/nmm</i>	3.962	8.422
UAsTe	Body-centered tetragonal	<i>I4/mcm</i>	4.1483	17.2538
UNSe	Tetragonal	<i>P4/nmm</i>		
UNTe	Tetragonal	<i>P4/nmm</i>		
U <sub>3</sub> P <sub>4</sub>	bcc	<i>I43d</i>	8.207	
U <sub>3</sub> As <sub>4</sub>	bcc	<i>I43d</i>	8.507	
U <sub>3</sub> Sb <sub>4</sub>	bcc	<i>I43d</i>	9.113	
U <sub>3</sub> Bi <sub>4</sub>	bcc	<i>I43d</i>	9.350	
U <sub>3</sub> Se <sub>4</sub>	bcc	<i>I43d</i>	8.760	
U <sub>3</sub> Te <sub>4</sub>	bcc	<i>I43d</i>	9.398	

<sup>a</sup> bcc, body-centered cubic; fcc, face-centered cubic.

The hydroxides or hydrous oxides of any of the actinide ions in all oxidation states are insoluble in water.

Complexes of the actinyl ions with sulfate, nitrate, and carboxylate ions have octahedral, pentagonal

bipyramidal, and hexagonal bipyramidal geometries. The actinyl group is linear with further coordination occurring in the equatorial plane. The oxoanions are often bidentate. The anionic complexes  $[\text{An}(\text{NO}_3)_6]^{2-}$  are also known, having bidentate nitrate ions forming a distorted icosahedron.

Several carboxylates have been prepared, either during separations of  $\text{An}^{4+}$  ions or for thermal decomposition as a route to the dioxides. Most of the actinide carboxylates can be prepared as hydrates by dissolving the appropriate oxide and hydroxide in carboxylic acid. Formates, acetates, oxalates, xanthates, and carbamates are also known.

### C. Organometallic Compounds

A rich and diversified organometallic chemistry of the actinide elements has come into existence in the last three decades of the previous century. High reactivities, unusual reaction paths, catalysis, high coordination numbers, and unique structures continue to reward those working in this area.

The first organoactinide compound was  $(\eta^5 - \text{C}_5\text{H}_5)_3\text{UCl}$ , synthesized by L. T. Reynolds and G. Wilkinson in 1956. The triscyclopentadienyl alkyl and aryl actinide compounds, with a formal coordination number of 10, contain the most stable actinide carbon  $\sigma$  bonds. Later on, compounds containing indenyl and cyclooctatetraenyl groups as the  $\pi$  donor ligands were synthesized. The chemical bonds in these organometallic compounds range from covalent  $\sigma$  bonds to ionic and, thus, provide excellent samples for the study of chemical bonding of the  $5f$  elements.

$\text{An}(\text{C}_5\text{H}_5)_4$  and  $\text{An}(\text{C}_5\text{H}_5)_3\text{X}$  compounds can be prepared via the reaction of  $\text{AnCl}_4$  with  $\text{K}(\text{C}_5\text{H}_5)$ . The tetracyclopentadienyl derivatives (thorium through neptunium) contain four  $\pi$ -bonded aromatic rings. This is in contrast to the (two  $\pi$ -, two  $\sigma$ -) bonded cyclopentadienyl rings observed in the structure of tetracyclopentadienyl hafnium and the three  $\pi$ /one  $\sigma$  arrangement found for the corresponding zirconium analogue and is presumably the result of the larger size of the actinide ions. The  $\text{An}(\text{C}_5\text{H}_5)_3\text{X}$  compounds have a similar structure to that observed for  $(\eta^5 - \text{C}_5\text{H}_5)_4\text{U}$ . The centroids of the three  $\pi$ -bonded aromatic rings occupy three vertices of a tetrahedron, with the fourth occupied by the halogen.

Cyclopentadienyl derivatives of the actinides have received a great deal of attention in the search for alkoxy, alkyl, aryl, allyl, borohydride, amide, and other actinide compounds. The cyclopentadienyl and pentamethylcyclopentadienyl ligands significantly increase the solubility of the actinide in organic solvents, thus allowing their chemistries to be developed. In addition, the reactivity of

TABLE XIV Organometallic Actinide Compounds

Type	Compound <sup>a</sup>	Color
$(\eta^5 - \text{C}_5\text{H}_5)_4\text{An}$	$\text{Cp}_4\text{Th}$	Colorless
	$\text{Cp}_4\text{Pa}$	Orange
	$\text{Cp}_4\text{U}$	Red
	$\text{Cp}_4\text{Np}$	Brown
$(\eta^5 - \text{C}_5\text{H}_5)_3\text{An}$	$\text{Cp}_3\text{U}$	Bronze
	$\text{Cp}_3\text{Pu}$	Moss green
	$\text{Cp}_3\text{Am}$	Rose
	$\text{Cp}_3\text{Cm}$	Colorless
	$\text{Cp}_3\text{Bk}$	Amber
	$\text{Cp}_3\text{Cf}$	Red
	$\text{Cp}_3\text{ThF}$	Yellow
$(\eta^5 - \text{C}_5\text{H}_5)_3\text{AnX}$	$\text{Cp}_3\text{ThCl}$	Colorless
	$\text{Cp}_3\text{ThBr}$	Yellow
	$\text{Cp}_3\text{ThI}$	Yellow
	$\text{Cp}_3\text{UF}$	Green
	$\text{Cp}_3\text{UCI}$	Brown
	$\text{Cp}_3\text{UBr}$	Dark brown
	$\text{Cp}_3\text{UI}$	Brown
	$\text{Cp}_3\text{NpF}$	Green
	$\text{Cp}_3\text{NpCl}$	Dark brown
	$\text{Cp}_3\text{U}(\text{CH}_3)$	
	$\text{Cp}_3\text{U}(i\text{-C}_3\text{H}_7)$	
	$\text{Cp}_3\text{U}(n\text{-C}_4\text{H}_9)$	Dark red
	$\text{Cp}_3\text{U}(t\text{-C}_4\text{H}_9)$	
	$\text{Cp}_3\text{U}(\text{neopentyl})$	Dark red
	$\text{Cp}_3\text{U}(\text{ferrocenyl})$	Brown
	$\text{Cp}_3\text{U}(\text{allyl})$	Dark brown
	$\text{Cp}_3\text{U}(2\text{-methylallyl})$	
	$\text{Cp}_3\text{U}(\text{vinyl})$	
	$\text{Cp}_3\text{U}(\text{C}_6\text{H}_5)$	Greenish
	$\text{Cp}_3\text{U}(\text{C}_6\text{F}_5)$	Dark brown
	$\text{Cp}_3\text{U}(p\text{-C}_6\text{H}_4\text{UCp}_3)$	Red-orange
	$\text{Cp}_3\text{U}(\text{C}_2\text{H})$	Yellow-green
	$\text{Cp}_3\text{U}(\text{C}_2\text{C}_6\text{H}_5)$	Yellow-green
	$\text{Cp}_3\text{U}(p\text{-methylbenzyl})$	Dark violet
	$\text{Cp}_3\text{U}(\text{benzyl})$	Dark violet
	$\text{Cp}_3\text{U}(2\text{-cis-2-butenyl})$	
	$\text{Cp}_3\text{U}(2\text{-trans-2-butenyl})$	
	$(\text{C}_5\text{H}_4)_2\text{Fe}[\text{UCp}_3]_2$	Green
	$\text{Cp}_3\text{Th}(\text{neopentyl})$	White
	$\text{Cp}_3\text{Th}(\text{allyl})$	White
	$\text{Cp}_3\text{Th}(i\text{-C}_3\text{H}_7)$	White
	$\text{Cp}_3\text{Th}(2\text{-cis-2-butenyl})$	White
	$\text{Cp}_3\text{Th}(2\text{-trans-2-butenyl})$	White
	$\text{Cp}_3\text{Th}(n\text{-C}_4\text{H}_9)$	White
$(\eta^5 - \text{C}_9\text{H}_7)_3\text{AnR}$	$(\text{C}_9\text{H}_7)_3\text{U}(\text{CH}_3)$	Red-brown
	$(\text{C}_9\text{H}_7)_3\text{Th}(\text{CH}_3)$	Yellow
	$(\text{C}_9\text{H}_7)_3\text{Th}(n\text{-C}_4\text{H}_9)$	Yellow

Continues



**TABLE XIV** (continued)

Type	Compound <sup>a</sup>	Color
$(\eta^5 - \text{C}_5\text{Me}_5)_2\text{AnR}_2$	$\text{Cp}_2^*\text{U}(\text{CH}_3)_2$	Orange
	$\text{Cp}_2^*\text{Th}(\text{CH}_3)_2$	White
	$\text{Cp}_2^*\text{U}(\text{CH}_3)\text{Cl}$	Red-orange
	$\text{Cp}_2^*\text{Th}(\text{CH}_3)\text{Cl}$	White
	$\text{Cp}_2^*\text{U}[\text{CH}_2\text{Si}(\text{CH}_3)_3]_2$	Orange
	$\text{Cp}_2^*\text{Th}[\text{CH}_2\text{Si}(\text{CH}_3)_3]_2$	White
	$\text{Cp}_2^*\text{U}[\text{CH}_2\text{Si}(\text{CH}_3)_3]\text{Cl}$	Red
	$\text{Cp}_2^*\text{Th}[\text{CH}_2\text{Si}(\text{CH}_3)_3]\text{Cl}$	White
	$\text{Cp}_2^*\text{U}[\text{CH}_2\text{C}(\text{CH}_3)_3]_2$	Brown
	$\text{Cp}_2^*\text{Th}[\text{CH}_2\text{C}(\text{CH}_3)_3]_2$	White
	$\text{Cp}_2^*\text{U}(\text{CH}_2\text{C}_6\text{H}_5)_2$	Black
	$\text{Cp}_2^*\text{U}(\text{CH}_2\text{C}_6\text{H}_5)\text{Cl}$	Black
	$\text{Cp}_2^*\text{Th}(\text{CH}_2\text{C}_6\text{H}_5)_2$	White
	$\text{Cp}_2^*\text{Th}(\text{CH}_2\text{C}_6\text{H}_5)\text{Cl}$	White
	$\text{Cp}_2^*\text{U}(\text{C}_6\text{H}_5)_2$	Orange-brown
	$\text{Cp}_2^*\text{Th}(\text{C}_6\text{H}_5)_2$	White
	$\text{Cp}_2^*\text{Th}(\text{C}_6\text{H}_5)\text{Cl}$	White
	$\text{Cp}_2^*\text{U}[\text{C}_4(\text{C}_6\text{H}_5)_4]$	Brown
	$\text{Cp}_2^*\text{Th}(\text{CH}_2\text{CH}_3)_2$	White
$(\eta^8 - \text{C}_8\text{H}_8)_2\text{An}$	$\text{COT}_2\text{Th}$	Yellow
	$\text{COT}_2\text{U}$	Green
	$\text{COT}_2\text{Np}$	Yellow-red
	$\text{COT}_2\text{Pu}$	Red

<sup>a</sup> Cp, cyclopentadienyl; Cp\*, pentamethylcyclopentadienyl; COT, cyclooctatetraenyl.

actinide compounds has been found to be a sensitive function of the metal's coligands, and these compounds react readily with alkylolithium and Grignard reagents to give  $\sigma$ -bonded carbon compounds. The resulting alkyl compounds are highly reactive and extremely air and moisture sensitive. Hydrogenolysis yields organoactinide hydrides. The dihydrocarbyls react with carbon monoxide to form metal–oxygen and carbon–carbon double bonds, reactions which are of interest in catalysis.

Some representative organoactinide compounds are given in Table XIV.  $(\eta^5 - \text{C}_5\text{H}_5)_2\text{AnCl}_2$  compounds are unstable. These compounds disproportionate to  $(\eta^5 - \text{C}_5\text{H}_5)_3\text{AnCl}$  and  $(\eta^5 - \text{C}_5\text{H}_5)\text{AnCl}_3$ . Compounds of the type  $(\eta^5 - \text{C}_5\text{H}_5)_2\text{AnX}_2$  have been prepared either by placing the cyclopentadienyl ligands on the metal last or by using charged multidentate acetyl acetate, dihydrobis(pyrazolyl) borate, or hydrotris(pyrazolyl) borate ligands to stabilize the  $(\eta^5 - \text{C}_5\text{H}_5)_2\text{AnX}_2$  configuration. Trivalent triscyclopentadienyl compounds of the actinides can be prepared starting from  $\text{AnCl}_3$ . These compounds readily form adducts, and a large number

of  $(\eta^5 - \text{C}_5\text{H}_5)_3\text{AnL}$  complexes have been structurally characterized.  $(\eta^5 - \text{C}_5\text{H}_5)_3\text{UCl}$  and other organometallic compounds of the 5f elements show a greater degree of covalency than their lanthanide analogues.

The reaction of actinide tetrachlorides (thorium through plutonium) with the potassium salt of cyclo-octatetraene (COT) results in the formation of “actocene” complexes,  $(\eta^8 - \text{C}_8\text{H}_8)_2\text{An}$ , named by analogy with ferrocene. All these compounds have a sandwich structure in which two planar COT rings enclose a metal atom.

In the search for catalytically active species, heterobi- and polynuclear molecules containing both U(III) and a transition metal (palladium, platinum, rhodium, or ruthenium) strongly bonded in close proximity but without a direct metal–metal bond were synthesized. Difunctional bridging ligands like cyclopentadienylphosphido ligands were used to form such complexes.

Only recently were the actinide containing metallofullerenes  $\text{Am}@\text{C}_{82}$ ,  $\text{Np}@\text{C}_{82}$ , and  $\text{U}@\text{C}_{82}$ , which consist of actinide atoms being encapsulated into the carbon cage of fullerene compounds, prepared and characterized.

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