

Uranium was the first actinoid to be discovered—by Klaproth in 1789.

warned him against publishing it, because they believed tampering with the established Periodic Table would destroy his professional reputation. As Seaborg later remarked, “I didn’t have any scientific reputation, so I published it anyway.” Now, of course, we assume that the elements 89 to 102 correspond to the filling of the $5f$ orbitals and do indeed fit in Seaborg’s proposed order.

23.1 Properties of the Rare Earth Elements

The first problem with the group of elements numbered 57 to 70 is the terminology. The elements lanthanum to ytterbium are known as the lanthanoids, and these elements correspond to the filling of the $4f$ orbital set. However, because of similarities with the lanthanoids in chemical behavior, the Group 3 elements (scandium, yttrium, and lutetium) are often considered as part of the same set. To refer collectively to the lanthanoid and Group 3 elements, the term *rare earth metals* can be used. However, the term “rare earth” is itself misleading, because many of these elements are quite common. For example, cerium is as abundant as copper.

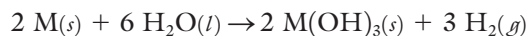
There is also dissension among chemists as to which group of elements actually constitutes the lanthanoids. Some claim cerium to lutetium, whereas others argue lanthanum to ytterbium. The problem becomes apparent when we look at the electron configurations (Table 23.1). Although most conventional designs of the Periodic Table show lutetium as a lanthanoid, its electron configuration as an element actually fits the pattern for the third transition series: $[\text{Xe}]6s^24f^{14}5d^n$ (where n is 1 in this case). However, because all 15 elements from lanthanum to lutetium share common chemical

Table 23.1 Ground-state electron configurations of elements 57 through 71

Element	Atom configuration	3+ ion configuration
Lanthanum	$[\text{Xe}] 6s^2 4f^0 5d^1$	$[\text{Xe}] 4f^0$
Cerium	$[\text{Xe}] 6s^2 4f^1 5d^1$	$[\text{Xe}] 4f^1$
Praseodymium	$[\text{Xe}] 6s^2 4f^3$	$[\text{Xe}] 4f^2$
Neodymium	$[\text{Xe}] 6s^2 4f^4$	$[\text{Xe}] 4f^3$
Promethium	$[\text{Xe}] 6s^2 4f^5$	$[\text{Xe}] 4f^4$
Samarium	$[\text{Xe}] 6s^2 4f^6$	$[\text{Xe}] 4f^5$
Europium	$[\text{Xe}] 6s^2 4f^7$	$[\text{Xe}] 4f^6$
Gadolinium	$[\text{Xe}] 6s^2 4f^7 5d^1$	$[\text{Xe}] 4f^7$
Terbium	$[\text{Xe}] 6s^2 4f^9$	$[\text{Xe}] 4f^8$
Dysprosium	$[\text{Xe}] 6s^2 4f^{10}$	$[\text{Xe}] 4f^9$
Holmium	$[\text{Xe}] 6s^2 4f^{11}$	$[\text{Xe}] 4f^{10}$
Erbium	$[\text{Xe}] 6s^2 4f^{12}$	$[\text{Xe}] 4f^{11}$
Thulium	$[\text{Xe}] 6s^2 4f^{13}$	$[\text{Xe}] 4f^{12}$
Ytterbium	$[\text{Xe}] 6s^2 4f^{14}$	$[\text{Xe}] 4f^{13}$
Lutetium	$[\text{Xe}] 6s^2 4f^{14} 5d^1$	$[\text{Xe}] 4f^{14}$

features, it makes more sense to consider them together. For example, the only common ion for each of these elements has the charge $3+$, and the electron configurations for this ion form a simple sequence of $4f$ orbital filling from 0 to 14.

The metals themselves are all soft and moderately dense (about $7 \text{ g}\cdot\text{cm}^{-3}$); they have melting points near 1000°C and boiling points near 3000°C . Chemically, the metals are about as reactive as the alkaline earths. For example, they all react with water to give the metal hydroxide and hydrogen gas:



The similarity among these elements comes in part from the lack of involvement of the $4f$ electrons in bonding. Thus, the progressive filling of these orbitals along the row has no effect on the chemistry of the elements. As mentioned earlier, the common oxidation state of all the elements is $+3$; for example, they all form oxides of the type M_2O_3 , where M is the metal ion.

The ionic radii of the $3+$ ions decrease smoothly from 117 pm for lanthanum to 100 pm for lutetium. Because the f orbitals do not shield the outer $5s$ and $5p$ electrons effectively, the increase in nuclear charge causes the ions to decrease in size. Such large ions have a high coordination number. For example, the hydrated lanthanum ion is a nonahydrate, $[\text{La}(\text{OH}_2)_9]^{3+}$.

Tripositive cations of many of the lanthanoids are colored, commonly green, pink, and yellow. These colors are the result of electron transitions among the f orbitals. Unlike the spectra of transition metal ions, the spectra of the lanthanoids do not show major variations for the different ligands. Furthermore, the absorptions are at very precise wavelengths, unlike the broad absorbance bands of the transition metal ions. The mixed oxides of neodymium and praseodymium absorb much of the yellow range, and this pinkish tan mixture is sometimes used as a filter in sunglasses, because the eye is most sensitive to the yellow part of the spectrum.

As mentioned earlier, scandium and yttrium are often included in discussions of the lanthanoids. Both these elements are soft, reactive metals that also exhibit the $+3$ oxidation state. Yttrium is found in the same ores that contain lanthanoids. The first discovery of a rare earth mineral was near the town of Ytterby in Sweden, as names of several of these elements testify: yttrium, terbium, erbium, and ytterbium. Both scandium and yttrium differ from their transition metal neighbors in that their only oxidation state is a d^0 electron configuration. Hence, they do not exhibit the range of oxidation states that is characteristic of the transition metals as a whole.

The rare earth metals have few uses, and their annual production amounts to about 20 000 tonnes. Most of the metals are used as additives in special-purpose steels. However, there is another use that places lanthanoid compounds in almost every household—the phosphors inside color television tubes. The impact of electrons on certain mixed lanthanoid compounds results in the emission of visible light over a small wavelength range. Thus, the inside surface of a television tube (and CRT computer color monitor) is coated with tiny patches of three different lanthanoid compositions to give the three colors that make up the color image. For example, a mixed oxide of europium and yttrium, $(\text{Eu},\text{Y})_2\text{O}_3$, releases an intense red color when bombarded by high-energy electrons.

23.2 Superconductivity

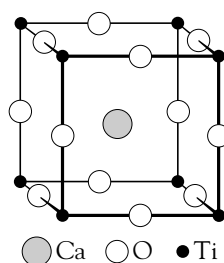


Figure 23.3 The structure of perovskite, CaTiO_3 .

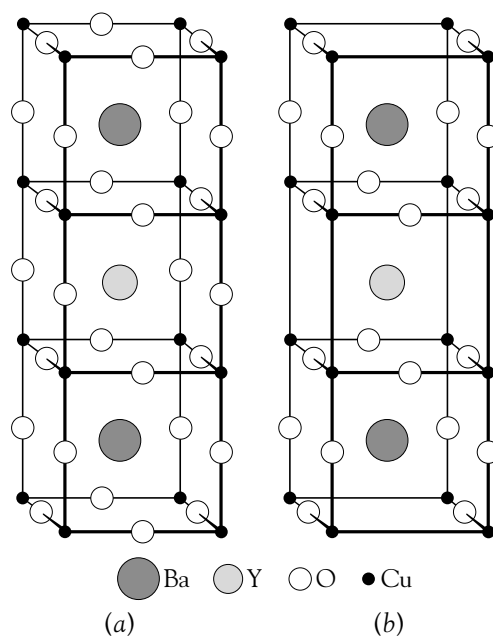


Figure 23.4 (a) The perovskite-like structure of the theoretical “ $\text{YBa}_2\text{Cu}_3\text{O}_9$.” (b) The related structure of the superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$.

In 1911, it was found that cooling certain metals to close to absolute zero caused them to lose all electrical resistance and become superconductors. Later it was found that many of the superconducting materials repelled a magnetic field—the *Meissner effect*. The first compounds to show superconductivity were discovered in the 1950s, but they had to be cooled to a temperature close to absolute zero before superconductivity was attained. The breakthrough came in Switzerland in 1985, when George Bedornz and Alex Müller prepared an oxide containing lanthanum, barium, and copper(II) ions. This compound becomes superconducting at 35 K, and Bedornz and Müller were awarded the Nobel Prize in physics for their work.

One year later, Paul Chu, at the University of Houston, and Maw-Kuen Wu, at the University of Alabama, Huntsville, synthesized a compound, $\text{YBa}_2\text{Cu}_3\text{O}_7$, that is superconducting above 77 K. Since then, other mixed metal oxides that are superconducting at a comparatively high temperature have been prepared.

Like many superconducting compounds, $\text{YBa}_2\text{Cu}_3\text{O}_7$ has a perovskite-derived structure. Figure 23.3 shows the structure of perovskite itself, CaTiO_3 ; it has the large calcium ion in the center and the small titanium(IV) ions at the unit cell corners. To construct the superconductor, we stack three perovskite unit cells and replace the titanium(IV) ions with copper(II) ions, the top and bottom calcium ions with barium ions, and the central barium ion with a yttrium ion (Figure 23.4(a)). This gives a formula of “ $\text{YBa}_2\text{Cu}_3\text{O}_9$,” which is erroneous, because there is an excess of anions. Thus, to arrive at the actual formula of $\text{YBa}_2\text{Cu}_3\text{O}_7$, eight edge-shared oxygen ions are removed (a total of two complete ions) to give the structure shown in Figure 23.4(b).

Most superconducting compounds have three common features: Their structures are related to the perovskite crystal lattice; they always contain slightly fewer oxygen atoms than the stoichiometry requires; they usually contain copper as one of the metal ions. Why is superconductivity of such interest? There are many ways in which high-temperature superconductors would change our lives. For example, a tremendous proportion of the generated electricity is lost in the transmission cables as a result of the resistance of the wires and the ensuing conversion of electrical energy to heat energy. Superconducting wires would economize our energy use.

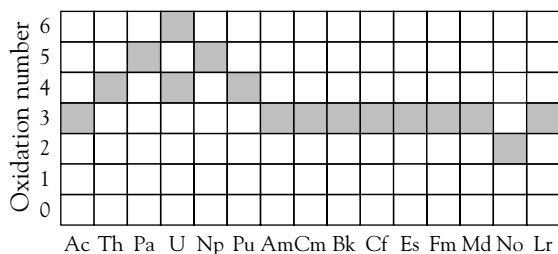
23.3 Properties of the Actinoids

Earlier we considered lanthanum as a member of the lanthanoid series. Similarly, we will consider actinium as an actinoid. Again, physical and chemical similarities provide the basis for this inclusion.

The actinoids are all radioactive. The half-lives of the isotopes of both thorium and uranium are long enough to allow appreciable quantities of these elements to exist in the rocks on Earth. The isotope half-lives of the longest lived isotopes of these elements are shown in Table 23.2. The values show that, with some irregularities, there is a dramatic reduction in an isotope’s half-life as atomic number increases.

Table 23.2 Half-lives of the longest lived isotope of each actinoid element

Element isotope	Half-life
Actinium-227	22 years
Thorium-232	1.4×10^{10} years
Protactinium-231	3.3×10^4 years
Uranium-238	4.5×10^9 years
Neptunium-237	2.2×10^6 years
Plutonium-244	8.2×10^7 years
Americium-243	7.4×10^3 years
Curium-247	1.6×10^7 years
Berkelium-247	1.4×10^3 years
Californium-251	9.0×10^2 years
Einsteinium-252	1.3 years
Fermium-257	100 days
Mendelevium-258	51.5 days
Nobelium-259	58 minutes
Lawrencium-257	3.6 hours

**Figure 23.5** The most common oxidation numbers of the actinoids.

It is obviously the long-lived elements that have been studied in the most detail (thorium, protactinium, uranium, neptunium, plutonium, and americium). These metals are dense (about 15 to $20 \text{ g}\cdot\text{cm}^{-3}$) and have high melting points (about 1000°C) and high boiling points (about 3000°C). The actinoids are not as reactive as the lanthanoids; for example, they react with hot, but not cold, water to give the hydroxide and hydrogen gas. They also differ from the lanthanoids in that they exhibit a range of oxidation numbers in their compounds. The most common oxidation numbers of the actinoids are shown in Figure 23.5.

The pattern of the highest common oxidation states of the early actinoids reflects the loss of all outer electrons, and it is more parallel to that of the transition metals than to that of the lanthanoids (Table 23.3). For example, uranium has the electron configuration of $[\text{Rn}]7s^25f^36d^1$. Thus, the formation of the common oxidation state of $+6$ corresponds to an electron configuration of $[\text{Rn}]$. Like the lanthanoids, formation of the $3+$ ion corresponds to the loss of the s and d electrons before those of the f orbitals.

The ready loss of the $5f$ electrons by the early actinoids indicates that these electrons are much closer in energy to the $7s$ and $6d$ electrons than the $4f$ electrons are to the $6s$ and $5d$ electrons in the lanthanoids. An explanation for this difference can be found in terms of the relativistic effect that we discussed in the context of the so-called inert-pair effect. As a result of the relativistic increase in the mass of the $7s$ electrons, the $7s$ orbital undergoes a contraction. Because the electrons in the $5f$ and $6d$ orbitals are partially shielded from the nuclear attraction by the $7s$ electrons, these orbitals expand. As a result, all three orbital sets have very similar energies. In

Table 23.3 Ground-state electron configurations of elements 89 through 103

Element	Atom configuration	3+ ion configuration
Actinium	[Rn] $7s^2 5f^0 6d^1$	[Rn] $5f^0$
Thorium	[Rn] $7s^2 5f^0 6d^2$	[Rn] $5f^1$
Protactinium	[Rn] $7s^2 5f^2 6d^1$	[Rn] $5f^2$
Uranium	[Rn] $7s^2 5f^3 6d^1$	[Rn] $5f^3$
Neptunium	[Rn] $7s^2 5f^4 6d^1$	[Rn] $5f^4$
Plutonium	[Rn] $7s^2 5f^6$	[Rn] $5f^5$
Americium	[Rn] $7s^2 5f^7$	[Rn] $5f^6$
Curium	[Rn] $7s^2 5f^7 6d^1$	[Rn] $5f^7$
Berkelium	[Rn] $7s^2 5f^9$	[Rn] $5f^8$
Californium	[Rn] $7s^2 5f^{10}$	[Rn] $5f^9$
Einsteinium	[Rn] $7s^2 5f^{11}$	[Rn] $5f^{10}$
Fermium	[Rn] $7s^2 5f^{12}$	[Rn] $5f^{11}$
Mendelevium	[Rn] $7s^2 5f^{13}$	[Rn] $5f^{12}$
Nobelium	[Rn] $7s^2 5f^{14}$	[Rn] $5f^{13}$
Lawrencium	[Rn] $7s^2 5f^{14} 6d^1$	[Rn] $5f^{14}$

fact, even the middle actinoids very often exhibit the +4 oxidation state, in which a second 5*f* electron must have been lost.

Thorium chemistry is dominated by the +4 oxidation state, this oxidation state possessing the noble-gas core configuration. As a result, thorium shows a link in behavior to cerium, the corresponding member of the lanthanoids—another example of a periodic pattern (see Chapter 9, Section 9.10).

It is important to realize that the half-lives of the natural thorium and uranium isotopes are so long that the radiation from these elements and their compounds is quite negligible. Hence, we find these elements in everyday use. For example, thorium(IV) oxide, ThO₂, mixed with 1 percent cerium(IV) oxide converts heat energy from burning natural gas or propane to an intense light. Before the incandescent light bulb, a gauze (gas mantle) of this mixed oxide was placed around a gas flame to provide the major source of indoor lighting. Even today, there is a significant demand for these mantles in camping lights. Thorium(IV) oxide ceramic is also used for high-temperature reaction crucibles because it will withstand temperatures up to 3300°C.

The only actinoid element found in almost every home is americium-241. Because it has such a short half-life, americium-241 does not occur naturally, so it is obtained from nuclear reactor wastes. This isotope is at the heart of all common smoke detectors. It functions by ionizing the air in a sensing chamber, causing an electric current to flow. Smoke particles block the flow of ions, and the drop in current initiates the alarm. Of increasing concern is the disposal of defunct smoke detectors—particularly in areas where incineration is used for garbage disposal. It is preferable to contact the manufacturer to obtain an address to which the old unit can be shipped and the americium-241 recycled. Also, few people realize that smoke detectors

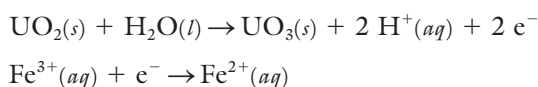
have a specific lifetime before the radiation level decays below that necessary for the detector functioning. This date is usually found on the inside of the unit in tiny print. Typically, the detector life is about 10 years.

To separate radioactive elements, chemists often use the concept of isomorphous substitution (Chapter 9, Section 9.6). For example, uranium ore contains very small quantities of radium. To separate the radium, we find an anion that forms an insoluble compound with the alkaline earth Ra^{2+} ion, but which forms soluble compounds with uranium and other actinoids. Sulfate is such an anion (recall that barium sulfate is highly insoluble). If we tried to precipitate the radium sulfate alone, there would be so little precipitate (even if there was enough to exceed the solubility product), it would be very difficult to collect. By mixing barium ion with the solution before attempting precipitation, the radium sulfate would be precipitated along with the barium sulfate as the two sulfates are isomorphous. This process is known as *co-precipitation*. With the radium now separated from the other radioactive elements, the barium/radium sulfate can be filtered and dried. The radium can then be separated from the small quantity of barium (compared to the original large volume of uranium ore).

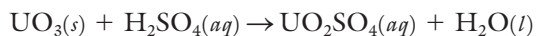
23.4 Extraction of Uranium

Uranium is the one actinoid in large demand—because of its use in nuclear reactors. Uranium is found in ore deposits around the world. Furthermore, seawater contains about 3 ppb, which does not appear to be much; but the total amount in all the oceans is about 5×10^9 tonnes. At present, the cheapest extraction method uses mined uranium(IV) oxide, UO_2 , commonly called pitchblende. The shafts of uranium mines must be ventilated with massive volumes of fresh air to prevent the levels of radon in the mine atmosphere, released by radioactive decay of the uranium, from exceeding safe values.

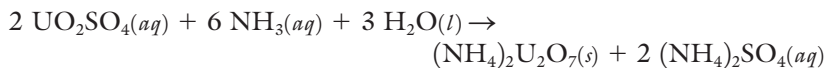
Like most metal extractions, a number of routes are used. The following method has the most interesting chemistry. The ore containing the uranium(IV) oxide is first treated with an oxidizing agent, such as the iron(III) ion, to produce uranium(VI) oxide, UO_3 :



Addition of sulfuric acid produces a solution of uranyl sulfate, which contains the uranyl cation, UO_2^{2+} :



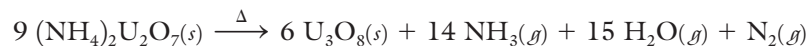
After removal of impurities, ammonia is added to the solution to give a bright yellow precipitate of ammonium diuranate, $(\text{NH}_4)_2\text{U}_2\text{O}_7$:



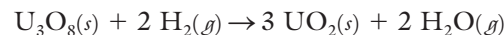
This precipitate, often called “yellow cake,” is the common marketable form of uranium.

For use in most types of nuclear reactors and for bomb manufacture, the two common isotopes of uranium, U-235 and U-238, must be separated. This is usually accomplished by allowing gaseous uranium(VI) fluoride to diffuse through a membrane; the lower mass molecules containing U-235

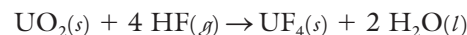
generally pass through more quickly. Again, there are several ways to manufacture this compound. One route is to heat the yellow cake to give the mixed oxide, uranium(IV) uranium(VI) oxide, U_3O_8 :



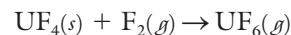
The mixed uranium oxide is then reduced with hydrogen to uranium(IV) oxide:



The uranium(IV) oxide is treated with hydrogen fluoride to give uranium(IV) fluoride, UF_4 :



Finally, the solid green uranium(IV) fluoride is oxidized to the required gaseous uranium(VI) fluoride, UF_6 , by using difluorine synthesized at the site:



The low boiling point of uranium(VI) fluoride is crucial to the purification of uranium and its isotopic separation. If we compare uranium(IV) fluoride and uranium(VI) fluoride, the contrast in physical properties becomes apparent. For example, uranium(IV) fluoride, UF_4 , melts at 960°C , whereas uranium(VI) fluoride, UF_6 , sublimates at 56°C . The difference can be interpreted in terms of charge densities—uranium(IV) ion, $140 \text{ C}\cdot\text{mm}^{-3}$, and uranium(VI) ion, $348 \text{ C}\cdot\text{mm}^{-3}$. Thus, the latter (theoretical) $6+$ ion would be sufficiently polarizing to cause covalent behavior.

23.5 Enriched and Depleted Uranium

Table 23.4 Naturally occurring isotopes of uranium

Isotope	Abundance (%)	Half-life (years)
U-234	0.0053	2×10^5
U-235	0.71	7×10^6
U-238	99.28	4×10^9

Natural uranium consists of the mixture of isotopes shown in Table 23.4. It is the isotopes U-234 and U-235 that are required for use in most nuclear reactors and in nuclear weapons. To separate the isotopes, one route is to pass gaseous uranium(VI) fluoride through a series of membranes. The gas molecules containing the lower mass uranium isotopes pass through the membrane very slightly faster (this is an application of the Law of Effusion). By cycling through a large number of membranes, a significant enrichment can be obtained. For most nuclear reactors, a concentration of about 0.03 percent U-234, 3.5 percent U-235, and 96.5 percent U-238 will suffice. This isotopic mixture is called *enriched uranium*.

Obviously, if uranium-234 and -235 is selectively concentrated in the enriched uranium, the remaining portion must be deficient in these two isotopes. This is known as *depleted uranium* (DU). In the United States alone, there is estimated to be over 500 000 tonnes of stockpiled depleted uranium.

The only major uses of uranium in the commercial market are due to its high density, $19.3 \text{ g}\cdot\text{cm}^{-3}$, twice that of lead. For this reason, uranium is used in aircraft as counter-weights for the heavy doors. The metal is sometimes employed to shield γ -radiation. A very minor use is incorporation in some dental porcelain formulations for false teeth to simulate the fluorescence of natural teeth. Uranium salts are used in some glazes.

It is in munitions that uranium has found a major use. Cost is obviously an advantage, for governments are eager to find a use for all the stockpiled metal. More important, uranium has specific technical advantages over other metals. When an artillery shell is fired at an armored object, such as a tank,

the aim is to pierce the armor and penetrate the interior of the vehicle, destroying it. The penetrability depends in part on the density of the metal used for the shell: the greater the density, the greater the kinetic energy of the projectile. Tungsten has the same density as uranium and was formerly used in shells. However, each metal behaves differently when impacted on a surface at five times the speed of sound—the typical impact velocity of a shell. Steel shatters like glass while tungsten flows like putty. Uranium, hardened by alloying with titanium, will more easily penetrate a metal object virtually intact. Uranium has a second and equally important military advantage of being pyrophoric. A pyrophoric metal is one whose finely divided particles will burn in air. Small particles of iron will burn as can be seen in “sparklers” and when an iron object is ground or machined. Uranium is highly pyrophoric; thus, the hot uranium particles, some molten, as uranium has a comparatively low melting point of 1130°C , will burn intensely in the interior of the vehicle to give a dust of uranium oxides such as U_3O_8 .

DU shells were first used in combat in the Gulf War, about 14 000 large caliber shells being fired by ground vehicles and about 940 000 rounds of small caliber shells from aircraft. The total mass of uranium used was about 300 tonnes. It is believed that DU shells were also used in the Balkans and in Afghanistan. The U.S. Navy accidentally fired hundreds of rounds of DU ammunition on Vieques, Puerto Rico. A similar incident occurred in Japan. Both the United States and the United Kingdom deploy DU weapons while U.S. arms dealers sell DU to 16 countries around the world.

As many people are aware, there are concerns about the health risks of depleted uranium, particularly for those exposed to the uranium oxide dust produced in a battle environment. These individuals will be both combatants and civilians in the vicinity as the uranium oxide dust will remain in the environment, contaminating the soil. There are two potential hazards: radioactive and chemical. There is still much research to be done, but the general consensus is that the radioactive hazard is the lesser one. By depleting the uranium, the concentration of the more highly radioactive isotopes is decreased. In terms of gross body exposure, with an average half-life in billions of years, α -emitting uranium represents a negligible health risk. However, the dust will be absorbed on lung surfaces where there is the potential for it lodging and providing a long-term hazard.

Heavy metals are chemically toxic, and it is most likely that any health risks from exposure to uranium oxide particles comes from this mode of action. Upon ingestion, uranium is metabolized to the water-soluble uranyl ion, UO_2^{2+} . This ion can then be absorbed into the bloodstream. Though much of the ion—about 90%—is excreted through the urine, the uranyl ion can react with many biological molecules, such as the phosphate functions of phospholipids and nucleic acids, and the sulfhydryl ($-\text{SH}$) groups of cysteine in proteins. It would be through disruption of protein function that illness from uranium intake seems most likely to originate.

The next generation of weapons will provide another health risk. From “smart” weapons that can be guided to a target, technology is progressing to “brilliant” weapons that select their own target. These munitions fire a slug of molten tantalum at very high velocities into the target. The aerodynamic liquid drop, though less powerful than a DU shell, can penetrate the top of any current armored vehicle. As tantalum is a rarely studied element, little is known about its health risks, except that it is certainly toxic.

A Natural Fission Reactor

The atomic mass values that we use for elements assume that the isotope ratio is always constant. But this is not always true. For example, it was variations in the atomic mass values for lead—different values for lead from different sources—that first led Sir Frederick Soddy, a British chemist, to deduce the existence of isotopes. More recently, in a sample of uranium ore, only 0.296 percent of the uranium was found to be uranium-235, much less than the “normal” value of 0.720 percent.

This discrepancy might seem to be of little interest, but in 1972 it brought scientists from around the world to the mine site at Oklo in Gabon (in western Africa). We know that the U-235 isotope spontaneously fissions to give energy and various fission products. When nuclear chemists and physicists examined the chemical composition of the ore, they found 15 common fission products. In other words, at some time in the past, Oklo had been the site of a nuclear reaction.

The existence of this buried nuclear reaction was not a sign of some visitors from outer space nor of some previous civilization. Instead, it was a result of the early uranium composition on this planet. Uranium-235 has a much shorter half-life than U-238; hence, the proportion of U-235 is steadily decreasing. About 2 billion years ago, when the Oklo nuclear reaction occurred (an event that lasted between 2×10^5 and 1×10^6 years), there was about 3 percent U-235 in the Oklo rocks. Rainwater is believed to have leached the uranium salts into pockets, where the uranium was concentrated enough to initiate the fission chain reaction. Equally important, the water acted as a moderator, slowing the emitted neutrons so that they could fission a neighboring nucleus and continue the chain reaction. The discovery of the ancient reaction was an interesting event for scientists, even if it did not have tabloid newspaper appeal.

23.6 *The Postactinoid Elements*

The elements beyond the actinoid series are known as the *postactinoid elements*. Even though the postactinoid elements definitively known so far are all transition metals, it is more instructive to consider them in this chapter because they can only be synthesized in nuclear reactions, like most of the actinoid elements. In fact, the short-lived elements with atomic numbers greater than 100—the later actinoids and the postactinoids—are sometimes called the *transfermium elements*. Up to now, nine postactinoid elements have been definitely synthesized.

A major controversy arose over the naming of these elements. The choice of an element name belongs to its discoverer. In the case of the postactinoids, three nuclear facilities have competed for the first synthesis of each of these elements: Berkeley, California; Dubna, Russia; and Darmstadt, Germany. Unfortunately, it was sometimes difficult to identify which country had the most valid claim. For example, the first discovery of element 104 was claimed by both the Berkeley and Dubna groups, the former naming the

Table 23.5 Proposed and agreed names for newly discovered elements

Element	Proposed names	Accepted name
104	Kurchatovium (Ku), dubnium (Db)	Rutherfordium (Rf)
105	Nielsbohrium (Ns), hahnium (Ha), joliotium (Jl)	Dubnium (Db)
106	Rutherfordium (Rf)	Seaborgium (Sg)
107	Nielsbohrium (Ns)	Bohrium (Bh)
108	Hahnium (Hn)	Hassium (Hs)
109	—	Meitnerium (Mt)

Table 23.6 The hybrid Latin–Greek prefixes for the temporary names of newly discovered elements

0	nil	5	pent
1	un	6	hex
2	bi	7	sept
3	tri	8	oct
4	quad	9	enn

element rutherfordium; and the latter, kurchatovium. Confusion continued as each of the vying groups for priority gave their own names to the elements (Table 23.5). There was a separate disagreement over the name for element 106, the U.S. proposal of seaborgium being initially rejected on the grounds that traditionally no element was named after a still-living scientist. This principle has now been overthrown, and the name seaborgium has been adopted.

While the conflicting claims were being settled, the International Union of Pure and Applied Chemistry (IUPAC) devised a hybrid Latin–Greek numerical method of providing provisional names and symbols for all newly discovered elements. To name an element, the atomic number is broken down into its individual digits; thus element 116 would be broken down to 1-1-6. The numbers are then replaced by hybrid Latin–Greek prefixes (Table 23.6), thus un-un-hex. The ending -ium is then added, giving ununhexium. The symbol will be the first letter of the parts comprising the name; thus, the symbol of element 116 would be Uuh.

The short half-lives of the postactinoid elements have made it very difficult to study their chemistry. Indeed, the only known isotope of element 112 has a half-life of 2.8×10^{-4} seconds (Table 23.7).

As relativistic effects become more important as the nuclear charge becomes larger and the size of the atom increases, chemists are very keen to discover whether the fourth transition metal series has chemical behavior

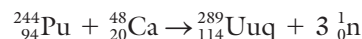
Table 23.7 Half-lives of the longest lived isotope of each postactinoid element

Element isotope	Half-life
Rutherfordium-263	10 minutes
Dubnium-262	30 seconds
Seaborgium-266	20 seconds
Bohrium-264	0.44 seconds
Hassium-269	9.3 seconds
Meitnerium-268	0.70 seconds
Ununilium-272	0.0086 seconds
Unununium-272	0.0015 seconds
Ununbium-285	0.00028 seconds

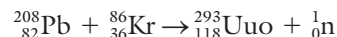
like the corresponding second and third rows. So far, the parallels seem to hold. For example, rutherfordium forms a chloride, RfCl_4 , which seems to be similar to the chlorides of the Group 4 elements, zirconium and hafnium, in their +4 oxidation state. Dubnium chemistry, however, shows resemblance to that of both Group 5 transition metals, niobium(V), and the actinoid, protactinium(V).

Efforts are continuing to synthesize new elements. This is accomplished by bombarding a target of one element with the nuclei of another element. The projectile nuclei are the lower mass ones so that they can be accelerated to a higher velocity giving a greater kinetic energy. This is enough to overcome the repulsion between the two positively charged nuclei. Among the many collisions causing nuclear fragmentation, physicists hope that some nuclei will combine to form the super-heavy nuclei for which they are searching.

To stabilize nuclei with large numbers of protons, a very high neutron-to-proton ratio is necessary. The lighter elements that are used for bombardment usually do not have enough. One of the chosen routes is to make use of the “magic number” concept of the shell model of the nucleus that we discussed in Chapter 2, Section 2.3. One stable isotope of calcium has an abnormally high neutron-to-proton ratio, the “doubly magic” calcium-48. Ions of this isotope are then used to bombard the plutonium-244 isotope, and there is evidence—not yet verified—that a few atoms of element 114 were obtained.



In 1999, ions of “magic” krypton-86 were used to bombard the “doubly magic” lead-208 isotope with its high nuclear stability. There was great excitement when it was believed that three atoms of element 118 had been created by this means:



And it was claimed that element 118 decayed to 116 and then to 114. Unfortunately, the evidence now suggests that elements 118 and 116 have not yet been synthesized.

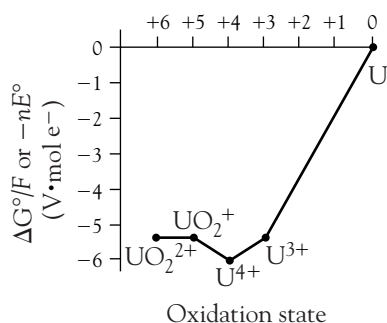
For the latest information on the discovery of new elements, see www.webelements.com/index.html.

- 23.1** Write balanced equations for the following chemical reactions:
 (a) europium with water
 (b) uranium(VI) oxide with sulfuric acid
- 23.2** Although +3 is the common oxidation state of the rare earth elements, europium and ytterbium can form an ion with a +2 charge. Suggest an explanation for this. What other oxidation state might terbium adopt?
- 23.3** The europium 2+ ion is almost identical in size to the strontium ion. Which simple europium salts would you expect to be water soluble and which insoluble?
- 23.4** Discuss the reasons for and against including scandium and yttrium with the lanthanoids.
- 23.5** A solution of cerium(IV) ion is acidic. Write a chemical equation to account for this.
- 23.6** Calculate the enthalpy change for the reaction:
 $\text{UX}_6(s) \rightarrow \text{UX}_4(s) + \text{X}_2(g)$, where $\text{X} = \text{F}$ or Cl
 given $\Delta H_f^\circ(\text{UF}_6(s)) = -2197 \text{ kJ}\cdot\text{mol}^{-1}$;
 $\Delta H_f^\circ(\text{UF}_4(s)) = -1509 \text{ kJ}\cdot\text{mol}^{-1}$; $\Delta H_f^\circ(\text{UCl}_6(s)) = -1092 \text{ kJ}\cdot\text{mol}^{-1}$; and $\Delta H_f^\circ(\text{UCl}_4(s)) = -1019 \text{ kJ}\cdot\text{mol}^{-1}$. Explain the difference in your two calculated values.

- 23.7 Suggest a reason why the longest lived isotopes of actinium and protactinium have much shorter half-lives than those of thorium and uranium.
- 23.8 Suggest a reason why nobelium is the only actinoid for which the +2 oxidation number is most common.
- 23.9 There were convincing chemical reasons why the early actinoids seemed to fit with the transition metals. Suggest one of the most important reasons and, in particular, mention the diuranate ion in your discussion.

BEYOND THE BASICS

- 23.10 Lanthanum only forms a trifluoride, whereas cerium forms both a trifluoride and a tetrafluoride. Identify the reason for the difference on the basis of Born–Haber cycle calculations for each of the four possibilities (LaF_3 , LaF_4 , CeF_3 , and CeF_4). Assume the MX_3 lattice energy to be $-5000 \text{ kJ}\cdot\text{mol}^{-1}$ and the MX_4 lattice energy to be $-8400 \text{ kJ}\cdot\text{mol}^{-1}$. Obtain the other necessary values from data tables.
- 23.11 Using the following Frost diagram, comment on the redox chemistry of uranium.



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