PLUTONIUM AND PLUTONIUM COMPOUNDS

1. Introduction

Plutonium [7440-07-5], Pu, element number 94 in the Periodic Table, is a metal of the actinide series (see ACTINIDES AND TRANSACTINIDES). Isotopes of mass number 228–247 have been identified. All are radioactive. The most important isotope is plutonium-239 [15117-48-3], ^{239}Pu; also of importance are ^{238}Pu, ^{240}Pu, ^{242}Pu, and ^{244}Pu.

The large energy release that accompanies the nuclear fission reaction is the most significant property of plutonium. Upon fission, 1 g of plutonium-239 releases energy equivalent to that produced by combustion of 3 metric tons of coal. The energy can be applied in electric power generating reactors or military explosives. Large quantities of plutonium are produced in uranium-fueled nuclear power reactors (see NUCLEAR REACTOR TYPES). At the end of 2003, ~1855 metric tons of plutonium were estimated to exist worldwide. Most of this plutonium (1370 metric tons) was found within used fuel from nuclear power plants (1). About 225 metric tons of plutonium that had been separated and purified from used fuel of commercial power plants was stored in nonirradiated form. This plutonium will be used or is planned for use in mixed uranium–plutonium fuels to produce power in commercial nuclear reactor systems. About 260 metric tons of plutonium with high ^{239}Pu content had been separated for use in nuclear weapons programs, primarily in Russia and the United States. More than 100 tons of this weapons useable plutonium has been declared excess to military needs and is designated for use in mixed uranium–plutonium oxide fuels for power production. More detailed lists of the estimated plutonium stocks by country are found in Ref. (1). The rate of plutonium production in reactors operating worldwide at the end of 2003 was estimated at 70–75 metric tons/year. The inventory of plutonium will continue to grow for the foreseeable future, especially considering new nuclear power plant orders around the world. Thus large inventories of plutonium will need to be carefully managed as both a security concern and a potential energy source for many decades to come. The plutonium challenge is not only scientific, but also political and socioeconomic.

Plutonium was the first manmade element to be synthesized in weighable amounts (2). Since the discovery of plutonium in 1940, production has increased from submicrogram to metric ton quantities. Because of its great importance, more is known about plutonium and its chemistry than is known about many of the more common elements. The chemistry and metallurgy of plutonium are complex. Metallic plutonium exhibits seven allotropic modifications. Five different oxidation states are known to exist in compounds and in solution and the existence of a sixth oxidation state, formally Pu(VIII), has been claimed (3).

The discovery of plutonium-238, an α-emitter having a half-life, $t_{1/2}$, of 87.7 years, by Seaborg and co-workers in 1940 (4,5) was achieved by bombardment of uranium using deuterons, ^{2}H (eqs. 1 and 2):

$$^{238}_{92}\mathrm{U} + ^{2}_{1}\mathrm{H} \longrightarrow ^{238}_{93}\mathrm{Np} + 2^{1}_{0}\mathrm{n} \tag{1}$$

$$^{238}_{93}\mathrm{Np} \xrightarrow[2.1\ \mathrm{day}]{\beta-} ^{238}_{94}\mathrm{Pu}(t_{1/2} = 87.7\ \mathrm{years}) \tag{2}$$

In early 1941, 1 μg of ^{239}Pu was produced (eqs. 3 and 4) and subjected to neutron bombardment demonstrating that plutonium undergoes thermal neutron-induced fission with a cross section greater than that of ^{235}U (2). In 1942, a self-sustaining chain reaction was induced by fissioning ^{235}U in a large graphite natural uranium lattice. Some of the excess neutrons from the ^{235}U fission were captured in the abundant ^{238}U, thereby producing ^{239}Pu (eqs. 3 and 4). This is the basis for the large inventories of plutonium that have resulted from uranium-fueled reactors noted above.

$$^{238}_{92}\mathrm{U} + ^{1}_{0}\mathrm{n} \longrightarrow ^{239}_{92}\mathrm{U} + \gamma \tag{3}$$

$$^{239}_{92}\mathrm{U} \xrightarrow[23.5\ \mathrm{min}]{\beta-} ^{239}_{93}\mathrm{Np} \xrightarrow[2.36\ \mathrm{day}]{\beta-} ^{239}_{94}\mathrm{Pu}(t_{1/2} = 24,\ 110\ \mathrm{years}) \tag{4}$$

The first preparation, isolation, and weighing of a pure compound of plutonium, plutonium(IV) oxide [12059-95-5], PuO_2, was achieved in 1942 by ignition of hydrated $Pu(NO_3)_4$ [13823-27-3] (6). This 2.77-μg sample of PuO_2 was the first pure substance containing a synthetic element to be visible to the human eye. The first unequivocal preparation of metallic plutonium was in 1943 at the Metallurgical Laboratory of the University of Chicago by the reduction of plutonium tetrafluoride [13709-56-3] and barium metal in a sealed, evacuated reaction vessel at 1400°C (7). Fabricable amounts of metal were prepared in 1944 at Los Alamos, New Mexico as part of the Manhattan Project that produced the first fission explosive devices based on ^{235}U and ^{239}Pu (8).

Plutonium-239 is the most important isotope of plutonium. From the scientist's point of view, its half-life (24,100 years) is sufficiently long to permit the preparation of this isotope in large amounts, and to make it feasible to carry out conventional scientific studies. The ^{239}Pu isotope has a high cross-section for fission with slow neutrons, and is the isotope that serves as nuclear fuel for both nuclear reactors and nuclear weapons. By far the greatest portion of the knowledge of the chemical and physical properties of plutonium has been acquired by the use of ^{239}Pu. While its half-life is long enough to permit chemical studies, it is still short enough to provide considerable handling challenges. Safe handling methods for plutonium are discussed in more detail below.

The isotope plutonium-238 [13981-16-3], ^{238}Pu, is of technicological importance because of the high heat that accompanies its radioactive decay. For some time in the 1960s and 1970s, ^{238}Pu was considered to be the most promising power source for a potential radioisotope-powered artificial heart and for cardiovascular pacemakers. Usage of plutonium was discontinued because of advances in electronics and concerns about adequate elimination of penetrating radiation (9) (see PROSTHETIC AND BIOMEDICAL DEVICES). There are also some terrestrial applications for these power sources in remote locations.

The most prevalent application for ^{238}Pu is as an important fuel for heat and power sources for space exploration (10,11). For space exploration, heat source fuel is normally enriched to 83.5% in the ^{238}Pu isotope, and the oxygen atoms in $^{238}PuO_2$ are enriched in ^{16}O to reduce the neutron emission rate from α-n reactions to as low as 6000 n/s·g ^{238}Pu. In freshly prepared fuel the specific power is 0.4743 W/g Pu or 0.4181 W/g PuO_2. The ^{238}Pu isotope provides 99.9% of the thermal power in heat source fuel. Radioisotope thermoelectric generators (RTGs) have been used in the United States to provide electrical power for spacecraft since 1961 (12).

The current (2005) systems employ General Purpose Heat Source–Radioisotope Thermoelectric Generators (GPHS–RTGs) fueled by $^{238}PuO_2$ pellets. Each GPHS consists of a hot pressed 150 g pellet of $^{238}PuO_2$ encapsulated in an iridium alloy (iridium-0.3% tungsten) container (Fig. 1). Each iridium clad contains a sintered iridium powder frit vent designed to release the helium generated by the α-particle decay of the $^{238}PuO_2$. The heat sources are packed in a tightly woven pierced fabric graphite aeroshell assembly that protects the fuel from impact, fire, or atmospheric reentry. The RTG consists of 72 GPHS pellets and a thermoelectric converter. The GPHS–RTGs flown on the Galileo, Ulysses, and Cassini spacecraft (3 RTGs per spacecraft) had a mass of 54 kg of PuO_2 and supplied 285 W of electrical power at the beginning of

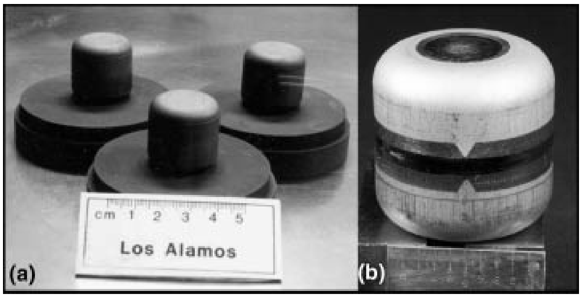


Fig. 1. A modern ^{238}Pu General Purpose Heat Source. Hot pressed 150-g pellets of $^{238}PuO_2$ (**a**) are encapsulated in an iridium-0.3% tungsten alloy container (**b**). Each iridium clad contains a sintered iridium powder frit vent designed to release the helium generated by the α-particle decay of the fuel. The iridium is compatible with plutonium dioxide at temperatures $> 1773\,K$, and melts at 2698 K. Each GPHS produces 62.5 thermal watts. (Photos courtesy of Los Alamos National Laboratory.)

the mission from 4300 W of ^{238}Pu decay heat (11). These plutonium power sources have enabled huge advances in our scientific understanding of the solar system. The Cassini-Huygens spacecraft arrived at Saturn on June 30, 2004 and will provide vast amounts of new scientific data on the Saturnian system in the years to come.

Smaller Light Weight Radioisotope Heater Units (LWRHUs) are also used to maintain spacecraft equipment within their normal operating temperature range (13). The LWRHUs are cylindrical fueled clads consisting of a hot-pressed, 2.67 g pellet of $^{238}PuO_2$ encapsulated in a Pt-30%Rh container with a sintered platinum powder frit vent to release helium. As in the GPHS, the capsules are contained in a pyrolytic graphite insulator and aeroshell assembly (11). These smaller heater units have been employed on the Pioneer 10 and 11, Galileo, Mars Pathfinder, Mars Exploration Rovers (Spirit and Opportunity), and Cassini spacecraft, and are planned for use in many future missions.

2. Isotopes

Numerous isotopes of plutonium have been synthesized, all of which are radioactive. The most important of these are listed in Table 1. The most recent isotope to be discovered is ^{231}Pu [15756-64-6], which was reported in 1999 (16). For data on nuclear masses the reader is referred to the compilation by Audi and Wapstra (17), and the update by Audi and co-workers (18). A more detailed description of the nuclear properties of the individual plutonium isotopes may be found in the book by Hyde, Perlman, and Seaborg (19), in the *Table of Isotopes* (14,20), and in *Nuclear Data Sheets* (15). The lighter isotopes decay mainly by K-electron capture, thereby forming neptunium isotopes. With the exception of mass numbers 237 [15411-93-5], 241 [14119-32-5], and 243 [15706-37-3], the intermediate isotopes, ie, 236–244, principally undergo α-decay to form uranium isotopes. The more neutron-rich heavy plutonium isotopes tend to undergo β-decay, thereby forming americium isotopes.

Table 1. **Radioactive Decay Properties of Selected Plutonium Isotopes**[a]

Mass number	Half-life	Mode of decay[a]	Main radiations, MeV	Method of production
238	87.7 year	α	α 5.499 (70.9%)	^{242}Cm daughter
	4.77×10^{10} year	SF 1.85×10^{-7}%	5.456 (29.0%)	^{238}Np daughter
239	2.411×10^{4} year	α	α 5.157 (70.77%)	^{239}Np daughter
	8×10^{15} year	SF 3.0×10^{-10}%	5.144 (17.11%)	
			5.106 (11.94%)	
			γ 0.129	
240	6.561×10^{3} year	α	α 5.168 (72.8%)	mult n capture
	1.15×10^{11} year	SF 5.75×10^{-6}%	5.124 (27.1%)	
241	14.35 year	β^- >99.99%	β^- 0.021	mult n capture
		α 2.45×10^{-3}%	α 4.896 (83.2%)	
			4.853 (12.2%)	
		SF 2.4×10^{-14}%	γ 0.149	
242	3.75×10^{5} year	α	α 4.902 (76.49%)	mult n capture
	6.77×10^{10} year	SF 5.54×10^{-4}%	4.856 (23.48%)	
243	4.956 h	β^-	β^- 0.582 (59%)	mult n capture
			γ 0.084 (23%)	
244	8.08×10^{7} year	α 99.88%	α 4.589 (81%)	mult n capture
	6.6×10^{10} year	SF 0.1214%	4.546 (19%)	

[a] See Refs. 14 and 15.

[b] SF = spontaneous fission.

3. Atomic Properties

Plutonium, like all of the heaviest elements, has a very complex electronic structure. The free atom and free ion spectra of plutonium are among the richest and most thoroughly studied of any chemical element. The complexity of the electronic structure is apparent in the spectral properties, such as X-ray absorption and emission spectra, and arc, spark, and discharge emission spectra. Early measurements were made with electrodeless discharge lamps and large grating spectrographs such as the 9.15 m Paschen-Runge spectrograph at Argonne National Laboratory (ANL). Very high resolution grating spectrographs have been replaced by Fourier transform (FT) spectrometers such as those at the Laboratoire Aimé Cotton (LAC) (built in 1970) and at the Kitt Peak National Solar Observatory. The plutonium free atom (Pu^0, denoted Pu I) has 94 electrons of which 86 electrons are in filled shells as found in the radon atom. It is customary in discussing the actinide series to only list the electrons in shells outside the radon core. The outermost electrons of the free actinide atoms and ions outside the radon core are found in the $7s$, $7p$, $6d$, and $5f$ shells. For example, the ground-state (lowest energy) configuration for Pu I is $5f^67s^2$. Identified excited configurations of Pu I within the first 3 eV ($\sim$24,000 cm^{-1}) of the ground-state include $5f^56d7s^2$, $5f^66d7s$, $5f^56d^27s$, $5f^67s7p$, $5f^57s^27p$, and $5f^56d7s7p$. In the free atoms and ions, many low lying configurations interact strongly with each other, giving rise to a large number of electronic states, and tens of thousands of spectral lines. A detailed discussion and review of the spectra of actinide free atoms and ions can be found in recent reviews (21,22).

3.1. Optical Emission Spectra. The emission spectrum of neutral (Pu I), singly ionized (Pu$^+$, or Pu II) [14700-74-4] or doubly ionized (Pu^{2+} or Pu III)

[17440-99-2] plutonium, which can be excited by arc, spark, hollow cathode, or inductively coupled plasmas, has been extensively studied. The first measurements of plutonium were conducted in 1943 by Rollefson and Dodgen (23–25) who measured the wavelengths and intensities of about 125 spectral lines. In the initial publications of plutonium spectra, only the wavelengths and intensities of unidentified transitions were reported. In 1959, McNally and Griffin reported the first energy level analysis for Pu II, where seven levels of the lowest terms of the $5f^6 7s$ (^{8}F and ^{6}F) electronic configuration were determined (26). In 1961, a collaboration was formed between scientists at ANL, LAC, and Lawrence Livermore National Laboratory (LLNL) to continue studies of the term analyses of Pu I and Pu II spectra. The first comprehensive description of Pu I and Pu II spectra became available in 1983 ANL when Blaise, Fred, and Gutmacher published wavelengths, wavenumbers, intensities, classifications, and isotope shift data (27). In 1992, Blaise and Wyart published all known energy levels of the actinide elements that had been analyzed up to that time and listed ionization stage, energies, intensities, *J* values, and level assignments of selected lines (21). The contents of that compilation are available on an updated database at LACs website (www.lac.u-psud.fr).

At the time of this writing (2005), 9500 isotope shifts have been measured, half of them in the IR region. More than 31,000 lines of the Pu I and Pu II spectra have been observed, of which 52% have been classified as transitions between pairs of levels (21,28,29). With the aid of Zeeman and isotope-shift data, a total of 606 even and 589 odd levels for Pu I, and 252 even and 746 odd levels for Pu II, have been identified. For all these levels the quantum number *J* has been assigned, and for many levels Landé *g* factors are given. To date, levels belonging to 14 different electronic configurations in Pu I, and 9 electronic configurations in Pu II have been identified. The lowest levels of these configurations are given in Table 2 (21,22,29).

Table 2. **The Lowest Energy Level of Each Electronic Configuration of Neutral Pu I and Monovalent Pu II with Their Corresponding Term Symbol and Energy**[a]

Pu I			Pu II		
Configuration	Term	Energy, cm^{-1}	Configuration	Term	Energy, cm^{-1}
$5f^6 7s^2$	$^7F_0$	0.000	$5f^6 7s$	$^8F_{1/2}$	0.000
$5f^5 6d 7s^2$	$^7K_4$	6,313.886	$5f^5 7s^2$	$^6H_{5/2}$	8,198.665
$5f^6 6d 7s$	$^9H_1$	13,528.246	$5f^5 6d 7s$	$^8K_{7/2}$	8,709.640
$5f^5 6d^2 7s$	$^9L_4$	14,912.011	$5f^6 6d$	$^8H_{3/2}$	12,007.520
$5f^6 7s 7p$	$^9G_0$	15,449.472	$5f^5 6d^2$	$^8L_{9/2}$	17,296.89
$5f^5 7s^2 7p$	$^7I_3$	17,897.119	$5f^6 7p$	$^8G_{1/2}$	22,038.970
$5f^5 6d 7s 7p$	$^9L_4$	20,828.477	$5f^5 7s 7p$	$^8I_{5/2}$	30,956.36
$5f^7 7s$	$^9S_4$	25,192.231	$5f^5 7s 7p$	$^8L_{9/2}$	33,793.30
$5f^6 7s 8s$	$^9F_1$	31,572.610	$5f^4 6d^2 7s$	$^8M_{11/2}$	37,640.78
$5f^6 6d^2$	$^9I_2$	31,710.912			
$5f^6 7s 7p$	$^9I_2$	33,070.58			
$5f^4 6d^2 7s^2$	$^7M_6$	36,050.562			
$5f^5 6d^2 7p$	$^9M_5$	37,415.524			
$5f^5 6d 7s 8s$	$^9K_3$	39,618.16			

[a] See Ref. 21.

The first ionization potential (IP) is a fundamental physical and chemical property of an element, and it is directly connected to the atomic spectra. Worden and co-workers measured the first IP of ^{239}Pu by laser resonance techniques. The photoionization threshold value for the ^{239}Pu I ionization potential was determined to be 48,582 (30) cm^{-1}, and the more accurate value from the Rydberg series measurements was 48,604 (1) cm^{-1} or 6.0262 (1) eV (30). In 1998, Erdmann and co-workers employed resonance ionization mass spectrometry (RIMS), from which the first IP was found to be 48,601 (2) cm^{-1} or 6.0258 (2) eV (31,32).

4. Sources

Traces of plutonium are found all over the world, predominantly from atmospheric nuclear weapons testing (33). In addition, two isotopes of plutonium (^{239}Pu and ^{244}Pu) can be found that are "natural" in origin. Natural ^{239}Pu is produced in nature by nuclear processes occurring in uranium ore bodies, and minute traces of ^{244}Pu exist in nature as remnants of primordial stellar nucleosynthesis. Plutonium occurs in natural ores in such small amounts that separation is impractical. The atomic ratio of plutonium to uranium in uranium ores is $< 1{:}10^{11}$. Traces of primordial ^{244}Pu have been isolated from the mineral bastnasite (34). One sample contained 1×10^{-18} g/g ore, corresponding to a plutonium-244 [14119-34-7], ^{244}Pu, terrestrial abundance of 7×10^{-27}–2.8×10^{-25} g/g of mineral and to <10 g of primordial ^{244}Pu on earth.

Commercial electric power generating reactors produce plutonium by neutron capture in uranium-238. A total average neutron exposure of 30,000–40,000 MW·day/t is common. The commercial trend is to move toward higher "burn-ups" of 50,000 MW·day/t or more. The plutonium in commercial used fuel contains a larger fraction of heavier plutonium isotopes, 240, 241, 242, than weapons-grade plutonium. The latter is separated from uranium irradiated for relatively short times to enhance the amount of plutonium-239 produced relative to the higher isotopes. The rate of production and the isotopic composition depends on the reactor type and method of operation, which depend on economics. In boiling water reactors (BWRs) and pressurized water reactors (PWRs), the rates of production average 270 and 360 g of plutonium per electrical megawatt-year of operation, respectively. The ORIGEN code has been used to calculate the growth of actinide and fission-product isotopes in a PWR operating at 30 thermal megawatts per metric ton of uranium (MTU) for 1100 days for a total burnup of 33,000 MW·day/t, at which time the ^{239}Pu content has reached a steady state of 5190 g/MTU (35). Natural uranium gas-cooled reactors, which are used for generating electricity in the United Kingdom and France, produce 500 g plutonium per electrical megawatt-year, whereas fully enriched uranium-fueled gas-cooled plants produce no plutonium. When a target with high ^{239}Pu content is irradiated for long periods with thermal neutrons to produce ^{243}Am and ^{244}Cm, the residual plutonium fraction, which is isolated after irradiation, consists almost entirely of plutonium-242 [13982-10-0], ^{242}Pu, and a small amount of ^{244}Pu [14119-34-7].

5. Separation and Purification from Irradiated Uranium

The build-up of plutonium and other transuranic isotopes in uranium reactor fuel is accompanied by the production of a great variety of fission product elements. The fission process leads mostly to two product nuclei (only 0.2–0.3% of the fission events yield three fragments) that have an asymmetric statistical mass distribution with peaks at mass numbers of 95 and 138 for ^{235}U thermal (low energy) neutron-induced fission. The fission product nuclei commonly have excess neutrons relative to stable nuclei with the same atomic number and thus most are radioactive. The fission products decay primarily by beta/gamma chains to more stable nuclei. The fission products and actinides produced from the irradiated uranium fuel are dispersed intimately in the uranium fuel matrix (36). The uranium matrix must be dissolved in a liquid phase or converted into a volatile compound to allow the fission product and transuranic element impurities to be separated from the uranium. The plutonium content in used fuels amounts to $\sim$1% of the mass of heavy metal content from a typical light-water reactor.

The large-scale separation and purification of plutonium has been primarily accomplished using the PUREX (Plutonium, Uranium, Reduction, EXtraction) liquid–liquid extraction process. This process was first developed for separating plutonium from metallic uranium fuels irradiated to produce plutonium for nuclear weapons applications, but has since been adapted to separate uranium and plutonium from many kinds of fuels and targets, including commercial power reactor fuels. While a variety of other processes have been used to separate and purify plutonium from irradiated fuels, many of these are now of only historical interest. For example, the bismuth phosphate process was the first production-scale method for plutonium separation used at the Hanford site, but was displaced by the more efficient continuous countercurrent solvent extraction methods. Very detailed information is available on these historical processes (37,38).

The PUREX process was first used in 1954 at the Savannah River site of the U.S. Atomic Energy Commission and then in 1956 at the Hanford site (39). With many variations in operational details, the process has since been used around the world as the principal method to separate plutonium and uranium from used reactor fuel and neutron-irradiated actinide materials (40). The key to this process is the selective extraction of U(VI) and Pu(IV) from a nitric acid solution of dissolved irradiated fuel into an aliphatic hydrocarbon solvent containing tri (*n*-butyl)phosphate (TBP) while leaving most of the fission products in the acid solution. The plutonium and then the uranium can be back-extracted separately from the loaded organic solvent into an aqueous strip phase. Additional solvent extraction stages with TBP can be used to further purify the uranium and plutonium or another method, such as ion exchange can be used. Most PUREX operations target very pure uranium and plutonium products with high decontamination factors from the fission products of $\sim 10^8$ and high recovery (typically $\sim$99.9%).

The following equilibrium equations represent the major separation steps of the PUREX process:

$$\mathrm{Pu}^{4+}_{(\mathrm{aq})} + 4\,\mathrm{NO}^{-}_{3\,(\mathrm{aq})} + 2\,\mathrm{TBP}_{(\mathrm{org})} \rightleftharpoons \mathrm{Pu(NO_3)_4(TBP)}_{2\,(\mathrm{org})} \tag{5}$$

$$UO^{2+}_{2\,(aq)} + 2\,NO^{-}_{3\,(aq)} + 2\,TBP_{(org)} \rightleftharpoons UO_2(NO_3)_2(TBP)_{2\,(org)} \tag{6}$$

$$HNO_{3\,(aq)} + TBP_{(org)} \rightleftharpoons TBP \cdot HNO_{3\,(org)} \tag{7}$$

The subscripts (aq) and (org) refer to species present in the aqueous and organic phases, respectively. The distribution coefficient (D) in liquid–liquid extraction is defined as the ratio of the concentration of the solute in the organic phase to that in aqueous phase under a particular set of conditions, eg, volume ratio of the aqueous to organic phase, temperature, extractant concentration, pH, metal ion concentration. Tetravalent and hexavalent actinide ions are selectively extracted under the PUREX conditions (typically 1–3 *M* nitric acid and 20–30 vol% TBP in an aliphatic hydrocarbon diluent), but the trivalent and pentavalent oxidation states of the actinides and most of the fission products are poorly extracted.

Adjusting the oxidation state of plutonium from Pu(IV) to Pu(III) is the most commonly used way of selectively stripping plutonium from the loaded organic phase. Various reducing agents have been used to strip plutonium from the TBP phase including Fe(II), hydroxylamine, and U(IV). The addition of ferrous sulfamate in the aqueous acid solution used to strip the plutonium has given some of the best results as indicated by the purity of the uranium and plutonium products that result (41). After the removal of the plutonium, the uranium can be stripped from the TBP phase with a dilute acid solution. The TBP solution can then be reused to extract more uranium and plutonium. The plutonium recovery section of a generalized PUREX process flow sheet is shown in Fig. 2.

The plutonium extracted by the PUREX process is produced as a concentrated nitrate solution that must be converted to other forms such as the metal or oxide for various applications. For metal production anhydrous PuF_3 [13842-83-6] or PuF_4 have often been used as intermediates. The nitrate solution is sufficiently pure for the processing to be conducted in gloveboxes without β- or γ-shielding (42). The plutonium is first precipitated as plutonium(IV) peroxide [12412-68-9], plutonium(III) oxalate [56609-10-0], plutonium(IV) oxalate [13278-81-4], or plutonium(III) fluoride. These precipitates are converted to anhydrous PuF_3 or PuF_4. The precipitation process used depends on numerous factors, eg, derived purity of product, safety considerations, ease of recovering wastes, and required process equipment. The peroxide precipitation yields the purest product and generally is the preferred route (43). The peroxide precipitate is converted to PuF_4 by $HF{-}O_2$ gas or to PuF_3 by $HF{-}H_2$ gas (44,45).

The ^{238}Pu isotope has been produced in multikilogram amounts by neutron bombardment of ^{237}Np. The ^{237}Np can be isolated from irradiated uranium fuels by modification of the PUREX process used to extract uranium and plutonium after the fuel is dissolved in nitric acid. The ^{238}Pu has been isolated from the neptunium target material by an ion exchange process (46). Conventional radioisotopic fuel contains ~80 wt% ^{238}Pu, 16.5 wt% ^{239}Pu, 2.5 wt% ^{240}Pu, 0.8 wt% ^{241}Pu, and 0.08 wt% ^{242}Pu. The specific power from α-decay of this isotopic mixture is 0.45 W/g [427 Btu $(g{\cdot}s)^{-1}$], compared to ~0.002 W/g [1.9 Btu $(g{\cdot}s)^{-1}$] for a weapons-grade plutonium isotopic mixture (47,48).

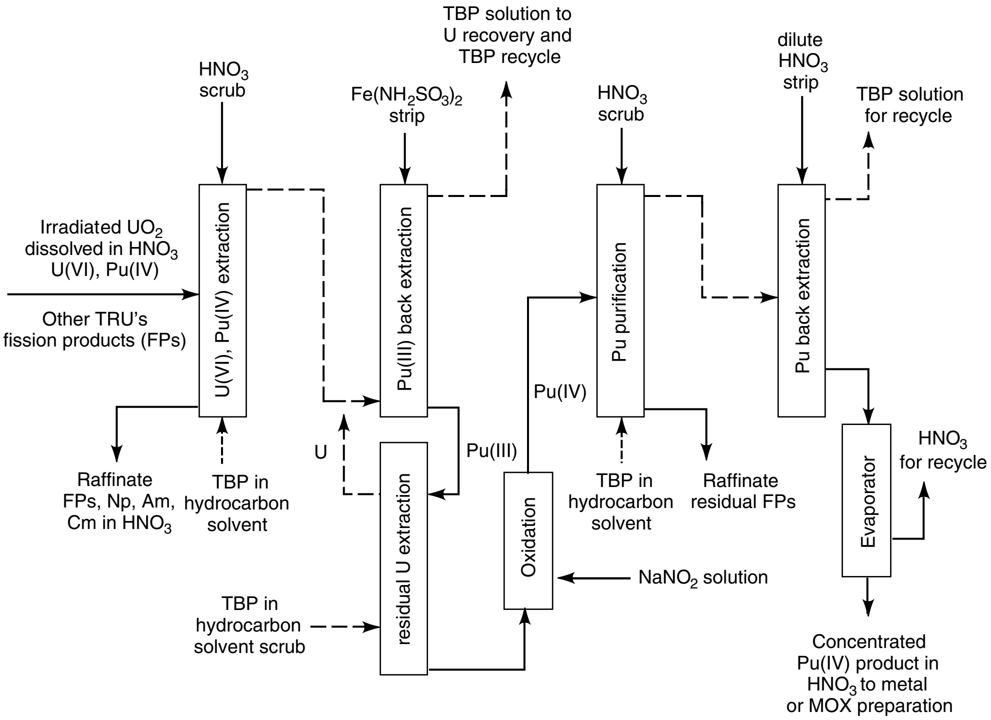


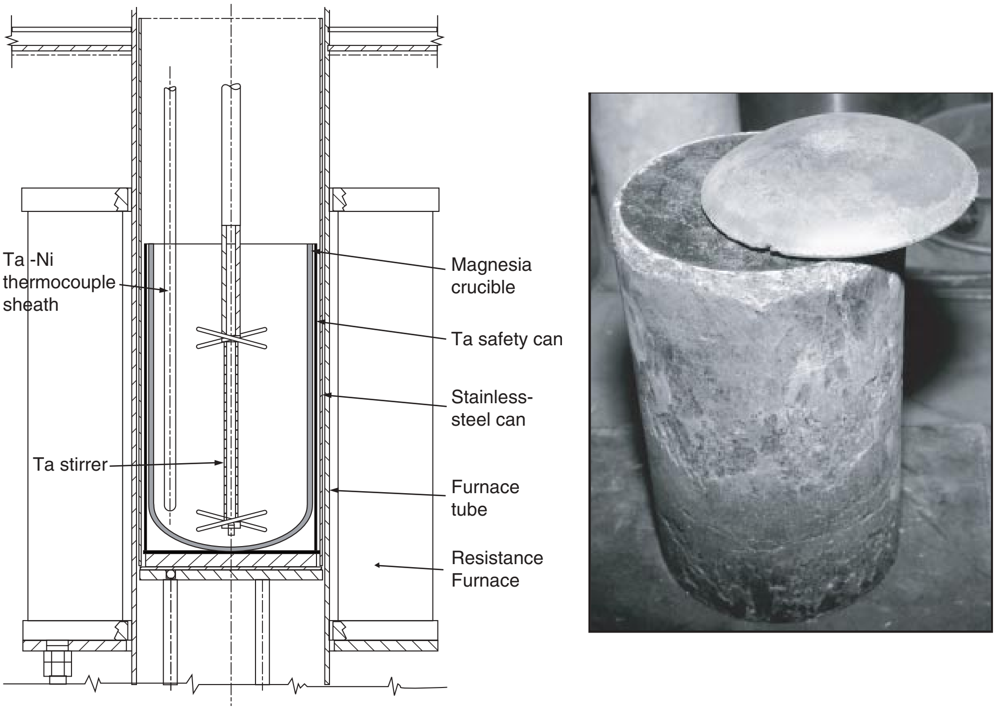
Fig. 2. A generalized PUREX flow sheet where the dashed line is the organic stream.

6. Plutonium Metal

6.1. Preparation.

Pyrochemical processes carried out in centrifugal or stationary bombs dominate metal preparation methods due to a large cost reduction over aqueous chemical processes (49–52). For metal production processes, the chemical reactions must produce a dense, coherent mass of pure plutonium in high yield; generate sufficient heat to melt both the metal and the resulting slag; result in a slag that stays molten and nonviscous long enough to allow the plutonium to coalesce; and work on the scale desired. The general process for obtaining, preparing, and refining plutonium has evolved over time. Historically, plutonium was first produced in production reactors; extracted, concentrated, and converted to either an oxide or fluoride; and then reduced to metal. In modern times, the feed material for preparation and refining of metallic plutonium has evolved to recovery and recycle of residues and scrap material. The major pyrochemical processes that are currently employed in large facilities are bomb reduction of PuF_4, direct oxide reduction (DOR), molten salt extraction (MSE), anode casting, electrorefining (ER), and pyroredox.

In the DOR process, PuO_2 is reduced with calcium metal to produce plutonium metal and CaO (50,53,54). The reaction takes place in a molten $CaCl_2$ or $CaCl_2{-}CaF_2$ solvent, which dissolves the resulting CaO and allows the plutonium metal to coalesce in the bottom of the crucible to form a metal



(**a**) (**b**)

Fig. 3. (**a**) A general furnace assembly for direct oxide reduction (DOR), molten salt extraction of americium (MSE) and pyroredox operations (49). (**b**) A DOR metal button (top) and salt residues (bottom). (Photographs courtesy of Los Alamos National Laboratory.)

button. A typical DOR furnace assembly and reaction product is shown in Fig. 3.

$$PuO_2 + 2\,Ca^0 \longrightarrow Pu^0 + 2\,CaO \tag{8}$$

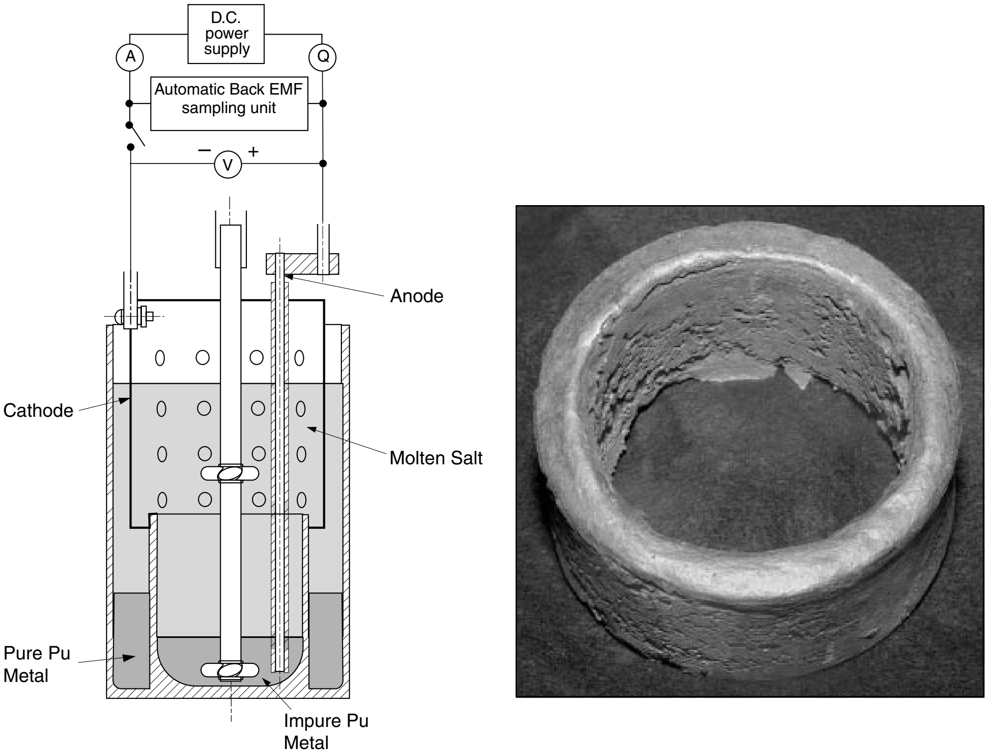
The DOR product is impure and needs to be refined. The MSE process primarily reduces the ^{241}Am content of plutonium metal (^{241}Am spontaneously grows into plutonium as a result of ^{241}Pu decay), but it also separates the more reactive elements, such as rare-earths, alkali-metals, and alkaline-earth metals (51). The reaction is conducted in a NaCl/KCl eutectic containing $MgCl_2$ as an oxidant to oxidize the americium to Am(III) which is extracted into the salt phase, leaving plutonium in the metallic phase (55,56).

$$2\,Am^0 + 3\,MgCl_2 \longrightarrow 2\,AmCl_3 + 3\,Mg^0 \tag{9}$$

$$2\,Pu^0 + 3\,MgCl_2 \longrightarrow 2\,PuCl_3 + 3\,Mg^0 \tag{10}$$

$$Am^0 + PuCl_3 \longrightarrow AmCl_3 + Pu^0 \tag{11}$$

Following the americium extraction, the plutonium metal must be cast into a cylindrical ingot that is compatible with the ER cell (57). In the ER process,



(**a**) (**b**)

Fig. 4. (**a**) A general schematic of an ER cell showing major features (49), and (**b**) a photograph of a plutonium product ring from ER. (Photographs courtesy of Los Alamos National Laboratory.)

liquid plutonium oxidizes from the anode ingot into a molten-salt electrolyte where the Pu(III) ion is transported through the salt to the cathode, where it is reduced back to metal (53,58). The liquid metal drips off the cathode and into the annular space to produce an annular metal casting, or ER ring. The process is carried out at 740°C in an equimolar mixture of NaCl/KCl containing a small amount of $MgCl_2$ as an oxidizing agent. A typical ER cell and metal product ring are shown in Fig. 4.

The pyroredox process recovers plutonium from impure scrap materials and has found application in recovering plutonium from the spent anode heels from the ER process (49,51,52,59). The process equipment is identical to that used in DOR (Fig. 3). The impure metal is oxidized to Pu(III) with $ZnCl_2$ dissolved in KCl at 750°C with stirring, and then heated to 850°C to promote phase separation to form a zinc button that is discarded. The salt containing $PuCl_3$ is then mixed with calcium and $CaCl_2$, and then reduced back to the metal with heating.

$$2\,\mathrm{Pu}^0 + 3\,\mathrm{ZnCl}_2 \longrightarrow 2\,\mathrm{PuCl}_3 + 3\,\mathrm{Zn}^0 \tag{12}$$

$$2\,\mathrm{PuCl}_3 + 3\,\mathrm{Ca}^0 \longrightarrow 2\,\mathrm{Pu}^0 + 3\,\mathrm{CaCl}_2 \tag{13}$$

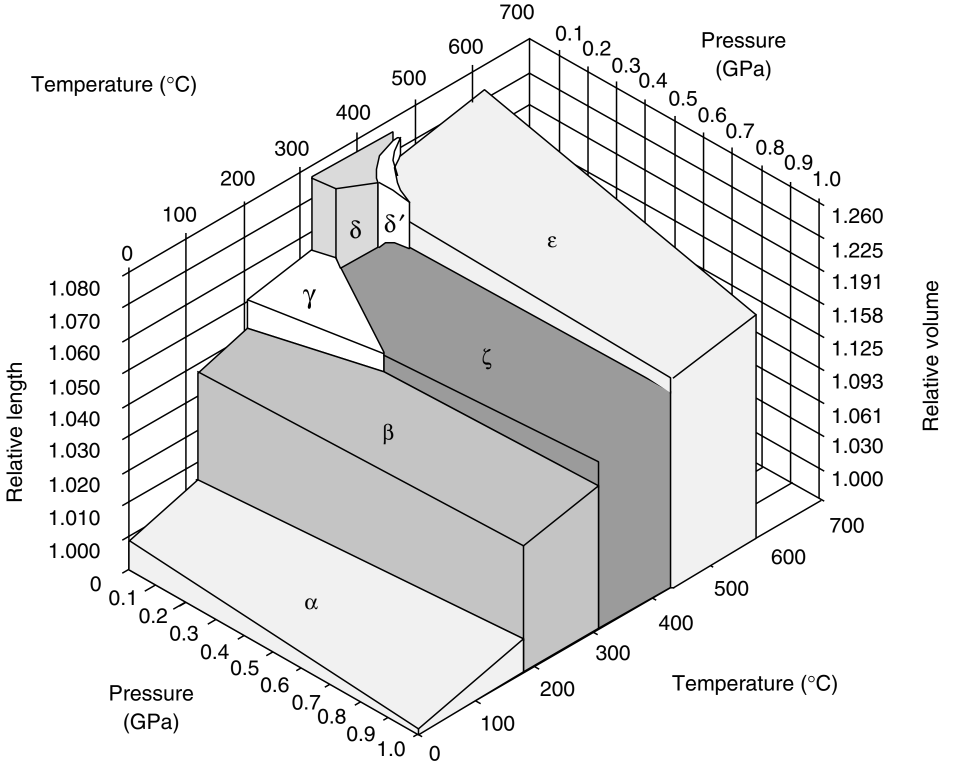


Fig. 5. Pressure–temperature phase diagram for Pu metal (60), showing the existence of a seventh phase, ς.

6.2. Physical Properties.

The pure element exists in six allotropic modifications under ordinary pressure, and there is a seventh phase that exists under high pressure (3,38,60,61) (Fig. 5). The stability ranges and crystal structure data for the individual allotropes are shown in Table 3, and solid-state structures of the six ambient pressure phases are shown in Figure 6. The temperatures and enthalpies of phase transitions are listed in Table 4.

The six solid allotropes at ambient pressure are the most of any element in the periodic table. Plutonium has an unusually low melting point of 640°C, and it contracts upon melting. The maximum density difference between the phases is a very large 20%. Moreover, the classical close-packed fcc phase is the least dense (less dense than the liquid). The two low temperature phases are low symmetry monoclinic structures, atypical of metals. The thermal expansion coefficients of these phases are very large and positive, whereas that of the fcc phase is negative.

Thermal Expansion. Thermal expansion of the unalloyed α, β, and γ phases of plutonium is large, positive and anisotropic because of their low symmetry crystal structures. The expansion of the high temperature δ and ε phases is isotropic. However, the δ and δ' phases exhibit negative thermal expansion. Thermal expansion of the δ' phase is also highly anisotropic. The peculiar thermal expansion behavior of δ-phase Pu alloys has been recently reviewed (64).

Table 3. **Crystal Structure Data for Elemental Plutonium**

Phase	Stability range, K	Crystal lattice and space group	Unit cell dimensions ( )	Atoms per unit cell	X-ray density, g/cm^3	Transformation temperature, K^b		
α	<397.6 ± 1.0 (397.6 ± 1)–(487.9 ± 1)	simple monoclinic $P2_1/m$	at 294 K $a = 6.183 \pm 0.001$ $b = 4.822 \pm 0.001$ $c = 10.963 \pm 0.001$ $\beta = 101.79^\circ \pm 0.01^\circ$	16	19.85			
β	(122 ± 4)–(207 ± 5) (487.9 ±1)–(593.1 ± 1)	body-centered monoclinic $I2/m^a$	at 463 K $a = 9.284 \pm 0.003$ $b = 10.463 \pm 0.004$ $c = 7.859 \pm 0.003$ $\beta = 93.13^\circ \pm 0.03^\circ$	34	17.71	α→β	122 ± 4	397.6 ± 1.0
γ	(207 ± 5)–(315 ± 3) (593.1 ± 1)–(736.0 ± 1)	face-centered orthorhombic $Fddd$	at 508 K $a = 3.159 \pm 0.001$ $b = 5.768 \pm 0.001$ $c = 10.162 \pm 0.002$	8	17.15	β→γ	207 ± 5	487.9 ± 1.0
δ	(315 ± 3)–(457 ± 2)	face-centered cubic (fcc) $Fm3m$	at 583 K $a = 4.6371 \pm 0.0004$	4	15.92	γ→δ	315 ± 3	593.1 ± 1.0
δ′	(457 ± 2)–(479 ± 4) (736.0 ± 1)–(755.7 ± 1)	body-centered tetragonal (bct) $I4/mmm$	at 738 K $a = 3.34 \pm 0.01$ $c = 4.44 \pm 0.04$	2	16.03	δ→δ′	457 ± 2	736 ± 1.0
εε	(479 ± 2)–(640 ± 2) (755.7 ± 1)–(913.0 ± 1)	body-centered cubic (bcc) $Im3m$	at 763 K $a = 3.6361 \pm 0.0004$	2	16.51	δ′→ε mp	479 ± 4 640 ± 2	755.7 ± 1.0 913.0 ± 1.0

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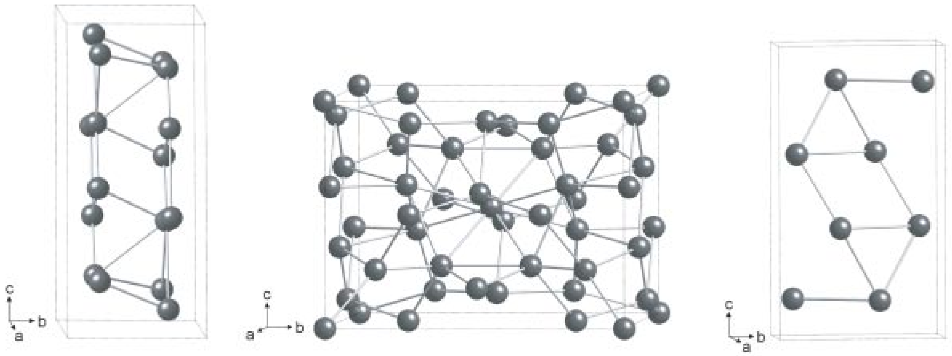
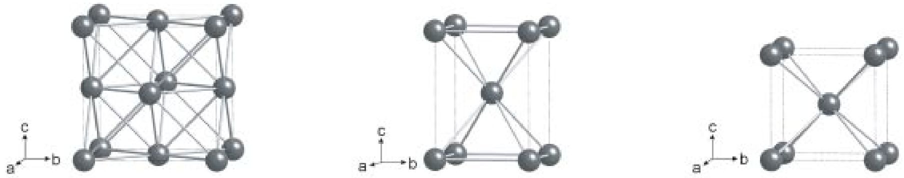
[a] Although space group $I2/m$ is not one of the standard space groups tabulated in the International Union of Crystallography, *International Tables for X-r Crystallography*, vol. 1, Kynoch Press, Birmingham, its notation is retained to obtain a β angle of approximately 90° (62).

[b] Data from Ref. 65. The reader is cautioned that the transformation temperatures vary between sources, and are sensitive to heating and cooling rates and metal impurity.



α - simple monoclinic β - body-centered monoclinic γ - face-centered orthorhombic



δ - face-centered cubic δ′ - body-centered tetragonal ε - body-centered cubic

Fig. 6. Crystal structures of all six solid phases of plutonium.

Thermodynamic Properties. The thermodynamic properties of elemental plutonium have been reviewed (3,38,65). Thermodynamic properties of solid and liquid plutonium, and of the transitions between the known phases are given in Table 4.

Magnetic and Electrical Behavior. A thorough review of experimental data for plutonium provides no evidence for localized magnetic moments (66). Neither temperature nor magnetic-field dependencies of measured susceptibilities show evidence for ordered or disordered moments.

The unusual electrical resistivity of unalloyed plutonium is shown in Fig. 7 (67). Unlike most normal metals that exhibit a linear decrease in resistivity at low temperatures, plutonium exhibits an increase and a maximum in resistivity at ~105 K. Since no magnetic ordering has been found in plutonium or its alloys, it has been suggested that the resistivity maximum is an indication of a Kondo effect in plutonium and its alloys (68,69). Boring and Smith make a convincing argument that the resistivity behavior along with other properties (eg, the enhanced low temperature specific heat) is an indication of strong electron–electron correlations involving spin and charge interactions (70).

Other Physical Properties. The thermal conductivity decreases smoothly from a value of 0.0155 cal/s·cm·K at 300 K to 0.0075 cal/s·cm·K at 80 K for the α phase. The thermoelectric power of plutonium at room temperature is large and positive, and it decreases after each allotropic transformation as the temperature is increased, except for the δ' to ε transformation, which shows an increase. The values for each allotrope have been tabulated (38). The melting point of plutonium is 913 ± 2 K. Liquid plutonium has many peculiarities, including a density greater than the last three solid allotropes, and its heat

Table 4. **Thermodynamic Properties and Transition Temperatures for Plutonium Metal**[a]

Property	Value
absolute entropy of α-Pu at 298 K, J/(mol·K)[b]	54.46 ± 0.80
heat capacity of α-Pu at 298 K, J/(mol·K)[b]	31.49 ± 0.40
heat capacity, C_p, J/(mol·K)	
α-Pu from 298 to 397.6 K	$18.126 + 0.04482\,T$
β-Pu from 397.6 to 487.9 K	$27.416 + 0.01306\,T$
γ-Pu from 487.9 to 593.1 K	$22.023 + 0.002959\,T$
δ-Pu from 593.1 to 736 K	$28.478 + 0.01081\,T$
δ'-Pu from 736 to 756 K	35.56
ε-Pu from 756 to 913 K	33.72
Pu (1), >913 K	42.248
enthalphy of transition, J/mol[b]	
$\alpha \rightarrow \beta$-Pu at 397.6 ± 1.0 K	3703 ± 4
$\beta \rightarrow \gamma$-Pu at 487.9 ± 1.0 K	477 ± 8
$\gamma \rightarrow \delta$-Pu at 593.1 ± 1.0 K	711 ± 13
$\delta \rightarrow \delta'$-Pu at 730 ± 2 K	84 ± 42
$\delta' \rightarrow \varepsilon'$-Pu at 752 ± 4 K	1840 ± 84
ε-Pu$\rightarrow$liquid at 913 ± 2 K	2825 ± 105
enthalpy of vaporization, kJ/mol[b]	
from 1200 to 1790 K	345.2 ± 4
from 1724 to 2219 K	342 ± 2
normal boiling point, K[c]	3573 ± 100
vapor pressure of liquid, $\log P$, in kPa[d,e]	$-(17{,}066 \pm 208)/T + 6.664 \pm 0.050$

[a] See Ref. 3.

[b] To convert J to cal, divide by 4.184.

[c] Value is extrapolated.

[d] See Ref. 63.

[e] To convert log P(kPa) to log P(atm), subtract 2.0056 from constant.

of fusion (2825 J/mol as shown in Table 4) is unusually small. The stability of liquid plutonium has been attributed to the nature of 5*f*-electron bonding (71,72). Its melting point decreases with increasing pressure up to 3 GPa (60,73) consistent with the volume contraction on melting. The viscosity of liquid plutonium follows the relation:

$$\log \eta = 672/\mathrm{T} + 0.037 \text{ (in centipoise)} \tag{14}$$

which yields a viscosity of 6 cP at the melting point (74). This is one of highest viscosities measured for metals. The accepted value for the surface tension of unalloyed liquid plutonium is 0.55 N/m (75). The vapor pressure of liquid plutonium can be described by the following equation with T in K and P in atm (76). This relationship extrapolates to a boiling point of 3573 ± 100 K.

$$\log P = (4.924 \pm 0.120) - (17{,}420 \pm 184)/T \tag{15}$$

6.3. Alloys and Phase Transformations. Binary-phase diagrams of plutonium have been compiled (38,77-79). Chemical additions (or alloying) significantly affect plutonium-phase stability with temperature and pressure. The dramatic effects of the addition of a few atomic percent gallium to plutonium

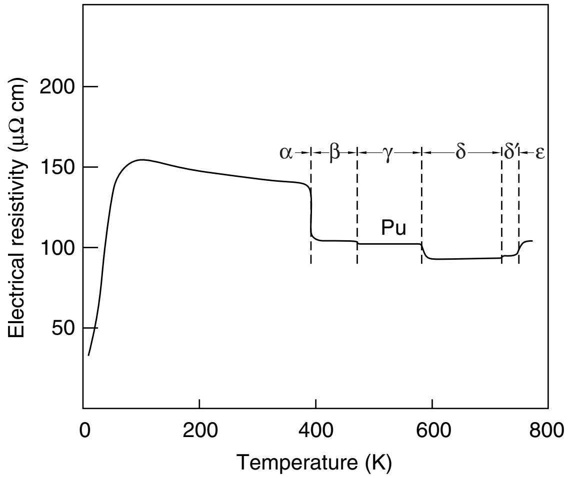


Fig. 7. Electrical resistivity of unalloyed plutonium (67).

on its thermal behavior are demonstrated in Fig. 8. The addition of gallium retains the attractive feature of expansion during solidification while avoiding all of the large volume perturbations during cooling because the addition of gallium retains the fcc δ phase to room temperature. The thermal expansion is essentially zero, or Invar-like (61), making Pu–Ga alloys much easier to cast. Moreover, the soft and ductile nature of the fcc δ phase makes these alloys much easier to shape than unalloyed plutonium. Consequently, most of the detailed work on properties of plutonium alloys has focused on systems that retain the δ phase. However, interest in metallic reactor fuels (80) has also

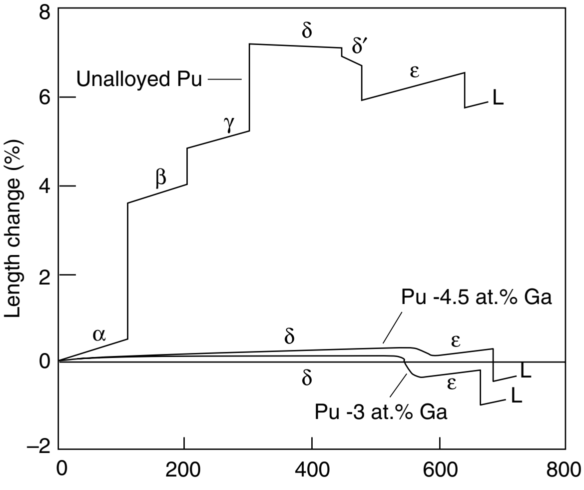


Fig. 8. Length changes for unalloyed plutonium compared to Pu–3.0 at.% Ga and Pu–4.5 at.% Ga alloys.

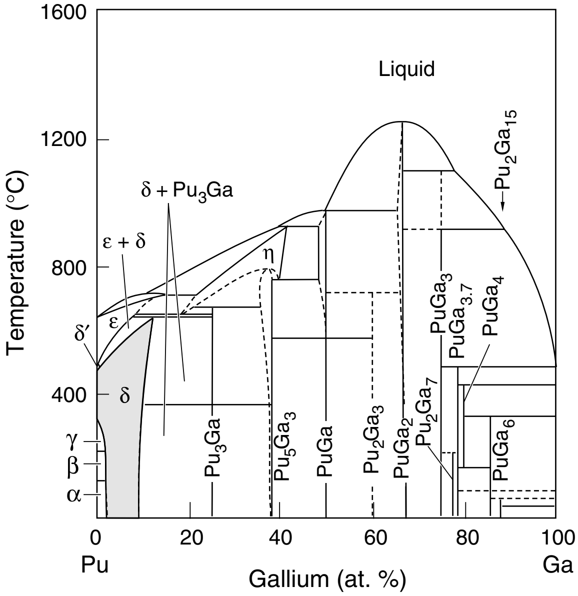


Fig. 9. The Pu−Ga phase diagram at ambient pressure (79).

resulted in work on β-phase retainers and on lean plutonium alloys involving uranium.

The complexity of chemical alloying is demonstrated in Fig. 9 for the Pu−Ga system. In addition to the six allotropes of plutonium, several new binary phases and 11 intermetallic compounds are formed. The fcc δ phase is retained to room temperature over a substantial range of gallium concentrations. Fundamental differences exist between the United States and Russian versions of the Pu−Ga phase diagram, and the question of whether the retained δ phase is stable or metastable was only recently resolved (81). A comparison of the two versions of this fundamental phase diagram is shown in Fig. 10. It is now believed that the Russian version (Fig. 10**b**), which shows an eutectoid point at 97°C and 7.9 at.% Ga, is the true equilibrium phase diagram. This diagram indicates that the δ phase should decompose <97°C into α-Pu + Pu$_3$Ga. Such decomposition has never been observed because the kinetics are too slow (82). Due to the exceedingly slow kinetics, the U.S. version (Fig. 10**a**), in which the δ phase is retained at least down to room temperature, represents an adequate working diagram.

6.4. Aging and Self-Irradiation Damage in Plutonium.

The effects of self-irradiation and aging of plutonium and its alloys has received increased attention due to interest in extending the lifetimes of plutonium components and in the long-term storage of excess weapons-grade plutonium (83−85). Radioactive decay can cause displacement damage in the crystal lattice changing lattice parameters, accumulating defects, and potentially void swelling. One of the decay products is helium, which can form bubbles if self-irradiation occurs at temperatures at which He is mobile. Schwartz and co-workers reviewed these effects and reported observation of nanometer-sized He bubbles using transmission electron microscopy (TEM) (86).

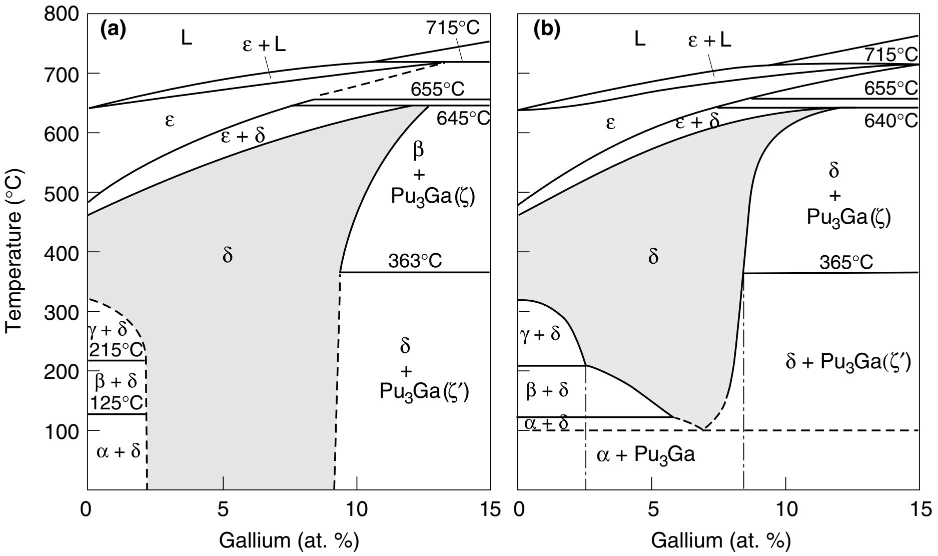


Fig. 10. Comparison of (**a**) United States and (**b**) Russian Pu–Ga phase diagrams from Ref. 81.

Because of radioactive decay, all plutonium isotopes generate heat. The self-heating of ^{239}Pu metal is 0.00193 W/g and for ^{238}Pu metal is 0.567 W/g (11). Under the appropriate conditions, self-heating is sufficient to heat a multigram ^{238}Pu metal or oxide sample to incandescence.

6.5. Storage and Handling. Plutonium metal can be stored safely in dry air. Because of self-heating, storage accompanied by heat removal is advisable. The metal can be machined in moisture-free air containing at least 70 vol % Ar or He. Casting and foundry operations that require melting of the metal must be carried out in vacuum or inert atmospheres and special containers.

6.6. Chemical Properties of Plutonium Metal. The metal dissolves readily in concentrated HCl, H_3PO_4, HI, or $HClO_4$. Nitric acid forms a protective oxide skin on the metal that can be removed by ~0.05 *M* HF. Dissolution of plutonium metal in HNO_3–HF mixtures is common practice in scrap-recovery plants. The metal does not dissolve readily in H_2SO_4 because passivation of the metal surface occurs. The reaction of water and plutonium metal is slow compared to that in HCl, HI, or $HClO_4$.

The corrosion behavior of plutonium metal has been reviewed (87–89). α-Plutonium oxidizes very slowly in dry air, typically $<10^{-2}$ mm/year. The rate is accelerated by water vapor. Thus, a bright metal surface tarnishes rapidly in normal environments and a powdery surface soon forms. Eventually, olive green PuO_2 [12059-95-9] covers the surface. Plutonium is similar to uranium with respect to corrosion characteristics. The stabilization of δ-Pu confers substantial corrosion resistance to plutonium in the same way that stabilization of γ-U yields a more corrosion-resistant metal. The reaction of plutonium metal with liquid water produces both oxides and oxide-hydrides (90). The reaction with water vapor $>100°C$ also produces oxides and hydride (89).

7. Economic Aspects

7.1. Uses of Plutonium. The fissile isotope ^{239}Pu had its first use in fission weapons, beginning with the Trinity test at Alamogordo, New Mexico, on July 16, 1945, followed soon thereafter by the Fat Man bomb dropped on Nagasaki on August 9, 1945. Its weapons use was extended as triggers for thermonuclear weapons. The short-lived isotope ^{238}Pu has been used in radioisotope electrical generators and heater units in unmanned space satellites, lunar and interplanetary space missions, heart pacemakers, and neutron sources (as ^{238}Pu−Be alloy) (3,10,11). Approximately 40% of the power produced in LWRs results from fission of plutonium isotopes that are produced from neutron bombardment of uranium-238 in the fuel.

7.2. Cost and Value of Plutonium. Plutonium has no commercial (open-market) value because it is a carefully regulated substance under government control except for small quantities used in research laboratories. The economic value of reactor-grade plutonium as a fuel for electric power-producing reactors depends on a variety of factors that will vary with time and country, eg, the costs of capital, uranium fuel, reprocessing, MOX fuel fabrication, and spent fuel disposal. Some of these costs are very uncertain, such as the cost of disposal of spent fuel since no country has yet implemented such a system. Consequently, various economic estimates can obtain quite different conclusions on the value of reprocessing and reusing plutonium from power reactors. Reports from the OECD−NEA (91,92) and recent studies from MIT (93) and Harvard (94) provide a perspective on the uncertainties of the economics and the range of recommendations on the future of nuclear power that can result.

The reprocessing plants at La Hague in France and Sellafield in the United Kingdom have provided commercial reprocessing services to other countries in addition to processing domestic spent nuclear fuel. These contracts give some indication of the large investments involved in establishing these facilities. For example, the La Hague plant processed 3800 metric tons of spent fuel from Japan to produce >30 metric tons of plutonium for a cost of $4 billion.

More than 100 metric tons of plutonium has been declared as excess to military needs by the United States and Russia from weapons being retired or production residues. Both countries plan to use the bulk of this plutonium to make MOX fuel and use this fuel to generate electricity in commercial power reactors. The economic costs and benefits of this approach are also not well established at present since design of the facilities is still in progess, but this approach continues to be advocated (95) because the intense radioactivity of the fission products in the spent fuel provides a major barrier to diversion or theft.

The cost of building all U.S. nuclear weapons has been estimated as $378 billion in 1995 dollars (96). The fraction of this cost that could be assigned to plutonium production is difficult to estimate, but if one-half of this sum is attributed to U.S. plutonium production ($\sim$100 t), a cost of $1.9 million per kg results for weapons-grade plutonium. It should be noted that the 1995 estimates for the costs of nuclear weapons production in the United States do not include the final costs for waste disposal and decomissioning of facilities.

8. Plutonium Compounds

Plutonium forms compounds with many of the metallic elements and all of the nonmetallic elements, except the helium-group gases. The interactions of plutonium with metallic elements to form plutonium alloys and intermetallic compounds have been reviewed (3,8,38,97–102). Alloy phase diagrams, intermetallic crystal structures, and thermodynamics of plutonium binary alloys have been reviewed in detail (3,38,103). The chemistry of plutonium hydrides, oxides, halides, carbonates, sulfates, nitrates, phosphates, carbides, silicides, nitrides, phosphides, arsenides, sulfides, tellurides, and other compounds has been reviewed (3,38,97,98,104,105). Some physical properties of oxides and halides are given elsewhere in this *Encyclopedia* (see ACTINIDES AND TRANSACTINIDES). The physical and chemical properties of plutonium refractory compounds, ie, the oxides, carbides, nitrides, silicides, sulfides, hydrides, borides, and phosphides, have been thoroughly studied principally because these refractory compounds are of interest as potential fast-breeder reactor fuels. Thermodynamic properties of selected compounds are given in Table 5.

Table 5. **Thermodynamic Parameters for Selected Plutonium Species**[a]

Compound	$\Delta_f G^\circ_{298}$, kJ/mol	$\Delta_f H^\circ_{298}$, kJ/mol	S°_{298}, J/K·mol	$C^\circ_{p\,298}$, J/K·mol[b]
		Solids		
$PuC_{0.84}$ (cr)	−49.8 ± 8.0	−45.2 ± 8.0	74.8 ± 2.1	47.1 ± 1.0
Pu_2C_3 (cr)	−156.5 ± 16.7	−149.4 ± 16.7	150.0 ± 2.9	114.0 ± 0.4
$PuO_{1.61}$ (cr)	−834.8 ± 10.1	−875.5 ± 10.0	83.0 ± 5.0	61.2 ± 5.0
Pu_2O_3 (cr)	−1580.4 ± 10.0	−1656.0 ± 10.0	163.0 ± 0.6	117.0 ± 0.5
PuO_2 (cr)	−998.1 ± 1.0	−1055.8 ± 1.0	66.13 ± 0.26	66.25 ± 0.26
PuN (cr)	−273.7 ± 2.6	−299.2 ± 2.5	64.8 ± 1.5	49.6 ± 1.0
PuF_3 (cr)	−1517.4 ± 3.7	−1586.7 ± 3.7	126.1 ± 0.4	92.6 ± 0.3
PuF_4 (cr)	−1756.7 ± 20.0	−1850.0 ± 20.0	147.3 ± 0.4	116.2 ± 0.3
PuF_6 (cr)	−1729.9 ± 20.2	−1861.3 ± 20.2	221.8 ± 1.1	168.1 ± 2.0
$PuCl_3$ (cr)	−891.8 ± 2.0	−959.6 ± 1.8	161.7 ± 3.0	101.2 ± 4.0
$PuCl_4$ (cr)	−879.4 ± 5.8	−968.7 ± 5.0	201.0 ± 10.0	121.4 ± 4.0
Cs_2PuCl_6 (cr)	−1838.2 ± 6.7	−1982.0 ± 5.0	412.0 ± 15.0	
Cs_3PuCl_6 (cr)	−2208.0 ± 9.5	−2364.4 ± 9.0	545.9 ± 11.0	258.6 ± 10.0
$CsPu_2Cl_7$ (cr)	−2235.1 ± 5.3	−2399.4 ± 5.7	424.0 ± 7.3	254.9 ± 10.0
Cs_2PuBr_6 (cr)	−1636.3 ± 6.1	−1697.4 ± 4.2	470.0 ± 15.0	
$Cs_2NaPuCl_6$ (cr)	−2143.5 ± 5.2	−2294.2 ± 2.6	440.0 ± 15.0	
		Gases		
PuF_3 (g)	−1161.1 ± 4.8	−1167.8 ± 3.7	336.1 ± 10.0	72.2 ± 5.0
PuF_4 (g)	−1517.9 ± 22.2	−1548.0 ± 22.0	359.0 ± 10.0	92.4 ± 5.0
PuF_6 (g)	−1725.1 ± 20.1	−1812.7 ± 20.1	368.9 ± 1.0	129.3 ± 1.0
$PuCl_3$ (g)	−641.3 ± 3.6	−647.4 ± 2.0	368.6 ± 10.0	78.5 ± 5.0
$PuCl_4$ (g)	−764.7 ± 10.4	−792.0 ± 10.0	409.0 ± 10.0	103.4 ± 5.0

[a] See Ref. 65.

[b] Temperature coefficients of this function are tabulated by Lemire and co-workers (65) in their Table 4.3.

8.1. Oxides. Binary plutonium oxides, especially PuO_2, are of tremendous technological importance. They find widespread application as nuclear fuels, as long-term storage forms for both spent nuclear fuels and surplus weapons materials, and as heat and power generators (^{238}Pu) for interplanetary exploration. Their properties are also important because oxide particulates contribute to environmental actinide migration, participate in corrosion reactions in nuclear weapons, and exist chemical intermediates in the purification and preparation of other actinide compounds. A number of reviews on the plutonium−oxygen system have appeared (3,89,106–109). There are four fundamental equilibrium solid phases in the plutonium−oxygen system. There is a stoichiometric hexagonal sesquioxide β-Pu_2O_3 with an ideal stoichiometry of $PuO_{1.5}$, and a bcc sesquioxide (α-Pu_2O_3) of composition $PuO_{1.52}$. There is a bcc oxide of intermediate composition $PuO_{1.61}$, and a fcc dioxide PuO_2 with a wide composition range that runs from $PuO_{1.6}$ to PuO_2, and is sometimes referred to as substoichiometric PuO_2 or PuO_{2-x}. Only recently has there been enough new data to suggest the addition of a hyperstoichiometric fcc oxide, PuO_{2+x} with composition that runs from stoichiometric PuO_2 to $PuO_{2.27}$ between room temperature and 350°C (110).

The most important oxide is PuO_2. The high melting point (2425°C), chemical stability, radiation stability, and similarity to UO_2 characterize plutonium dioxide [12059-95-9], PuO_2, as an attractive reactor fuel. Plutonium dioxide is also an important intermediate in processing operations such as the preparation of plutonium metal by the DOR process. The ignition of plutonium or the sulfate, nitrate, chloride, fluoride, oxalate, carbonate, iodate, hydroxide, or many other Pu compounds in air results in the formation of PuO_2. However, for the preparation of pure crystalline PuO_2, ignition of Pu(III) or Pu(IV) oxalate or Pu(IV) peroxide to 1000°C is the preferred method. Dissolution of PuO_2 that has been calcined at high temperature, which is required in nuclear fuel reprocessing, is difficult and requires boiling with strong acid, such as HNO_3−HF under reflux, with other oxidants (111), reductants, or catalytic oxidative electrolysis (112,113). Dissolution of high temperature calcined PuO_2 has been effected by repetitive heating in concentrated hydrochloric acid containing HI and boiling to dryness in nitric acid; the completeness of dissolution was monitored by coulometry (114). The PuO_2 has the fluorite structure, a lattice parameter of 5.3960 Å, and is isomorphous with UO_2, which has a lattice parameter of 5.4862 Å. The uranium and plutonium dioxides form a continuous series of solid solutions, as does PuO_2 with other dioxides (ThO_2, CeO_2). The PuO_2 is stoichiometric as shown in Fig. 11. However, the observed O/Pu ratio is usually somewhat higher than 2.00 (3). While plutonium is capable of forming molecular compounds of oxidation state VI and VII, most specialists have concluded that the stoichiometric oxide $PuO_{2.0}$ in oxidation state IV represents the highest obtainable binary oxide. A number of recent reports on higher valent oxides such as the mixed-valent PuO_{2+x} in the solid state (110), and hexavalent PuO_3 (116,117) in the gas phase have challenged these traditional views. These recent reports strongly suggest that the established views on the oxidation behavior of plutonium are worth reconsideration, and that additional detailed study is appropriate.

Plutonium dioxide can be reduced to PuO_{2-x} by loss of oxygen at elevated temperatures in either an inert or reducing atmosphere or in vacuum. The best

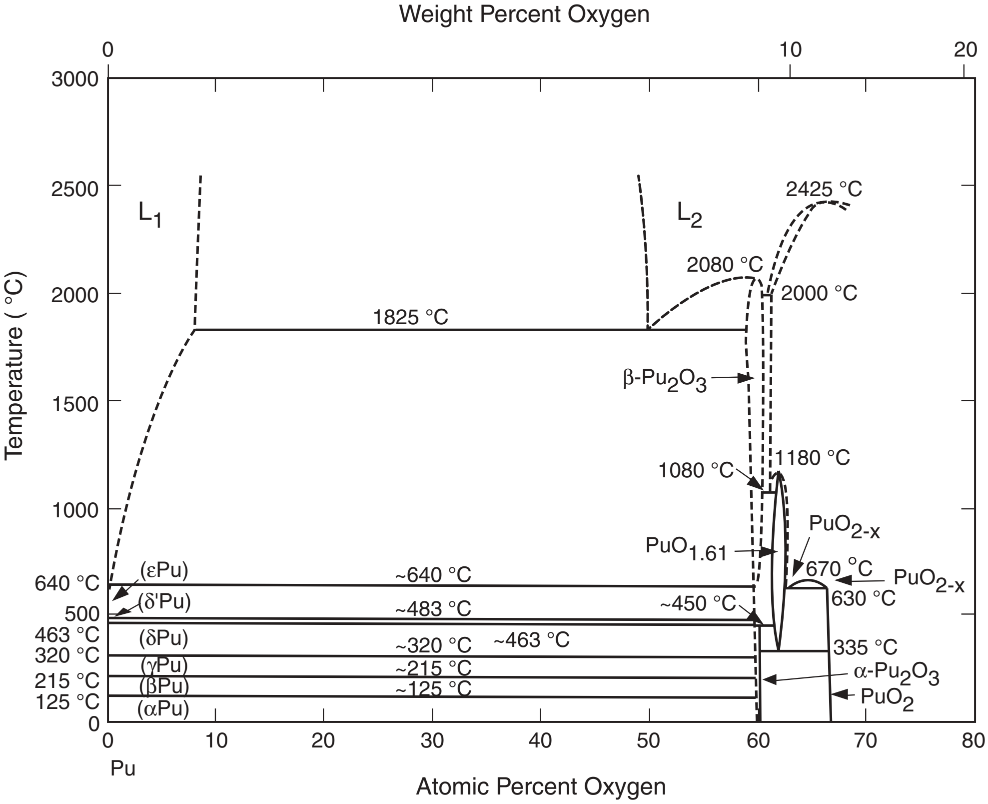


Fig. 11. The plutonium–oxygen phase diagram (108,109,115).

ways to prepare Pu(III) oxide Pu_2O_3 [12311-78-3] are to reduce PuO_2 using a stream of pure, dry H_2 (118), or with carbon or finely divided Pu metal in sealed vessels. The physical and chemical properties of Pu(III), Pu(IV), and mixed Pu(III,IV) oxides have been described (3,89) and discussions of the Pu–O and the U–Pu–O systems have been published (106–109).

There are numerous complex (ternary and quaternary) plutonium oxides. Their properties have been reviewed (3). Plutonium oxidizes readily to Pu(VI) from binary oxides to complex oxides such as Ba_3PuO_6. The best way to oxidize Pu to Pu(VII) is to prepare complex oxides such as Li_5PuO_6 from Li_2O and PuO_2 in flowing oxygen (119).

8.2. Halides and Oxyhalides.

The following binary plutonium halides have been characterized: PuF_6 [13693-06-6], PuF_4, PuF_3, $PuCl_3$ [13875-41-7], $PuBr_3$ [15752-46-2], and PuI_3 [13455-01-1] (3,120,121). The hexafluoride, a volatile and extremely reactive brown solid, is obtained by heating PuF_4 in flowing F_2 and immediately condensing the vapor on a cold surface. The hexafluoride has been studied extensively as part of the proposed fluoride volatility process for reprocessing nuclear fuel. Plutonium tetrafluoride, PuF_4, a pink solid, is made by passing a mixture of HF and O_2 gas over PuO_2 at ~600°C. Plutonium trifluoride, PuF_3, a blue-violet solid, is obtained from the reaction of PuO_2 and a mixture of HF and H_2 gas at ~600°C. In addition to the usual health hazards associated with plutonium, PuF_4 and PuF_3 radiate a high neutron flux from (α,n) reactions with fluorine. In the case of $^{238}PuF_4$, the neutron flux is so high as to require remote handling of the fluoride. In the presence of alkali fluorides, PuF_4 and PuF_3 form numerous complex compounds, which are important in molten salt reactor technology. Numerous efforts have failed to produce PuF_5, although a few complex Pu(V) fluorides such as $CsPuF_6$ are known and are relatively stable. Complex fluorides are also known for Pu(IV) and Pu(VI) (3).

Plutonium trichloride, $PuCl_3$, is the only known binary chloride of plutonium. No higher chloride in the solid state has been prepared so far. The trichloride is an emerald-green solid and can be prepared from the reaction of Pu metal or PuO_2 with HCl gas at elevated temperatures, and can be purified by sublimation and zone melting. The yellow complex chloride, Cs_2PuCl_6, is stoichiometric, stable, and can be used as a primary analytical standard for plutonium (122).

Plutonium tribromide [15752-46-2], $PuBr_3$, and plutonium triiodide [13455-01-1], PuI_3, both bright green solids, have no practical applications. Comprehensive reviews of the binary and ternary halides are available (3,120,121).

Only Pu(III) oxyhalides (PuOF, PuOCl, PuOBr, and PuOI) and Pu(VI) oxyhalides (PuO_2F_2, $PuOF_4$, and $PuO_2Cl_2{\cdot}6H_2O$) are known. Of these the most important are PuOCl, which is the stable product of hydrolysis of $PuCl_3$ (s) with H_2O (g) (123), and PuO_2F_2, which is the product of low temperature hydrolysis of PuF_6 and one of the products of room temperature hydrolysis of PuF_6 (124,125).

8.3. Hydrides. Recent interest in plutonium hydrides has emerged due to considerations of long-term storage and safe handling of plutonium metal and compounds (126) and the application of the plutonium–hydrogen reaction for pyrochemical processing of excess weapons plutonium (127,128). Several excellent reviews have appeared on the synthesis and kinetics (129), the thermodynamics (65,130), and the physicochemical characteristics of plutonium and other actinide hydrides (89,130–134). Plutonium hydrides can only be synthesized from the elements. These are important because they display unique involvement of the 5*f* electrons in bonding, thereby giving these compounds interesting magnetic and transport properties, and because they decompose to give pure and finely divided metal. The hydrides are pyrophoric and must be handled in inert atmospheres (He, Ar). The PuH_x phase relationships are remarkably complex. A broad range of nonstoichiometric phases is exhibited that extends from $PuH_{1.9}$ to near stoichiometric PuH_3. The PuH_x has the CaF_2 (fcc) structure over the composition $2.0 < x < 2.7$ and the hexagonal LaF_3 structure above $x = 2.9$. Syntheses, decomposition behavior, and reaction kinetics are discussed in detail (129). The phase diagram and thermodynamics of the Pu–H system have also been reviewed (133–135) (see HYDRIDES).

8.4. Carbides and Silicides. Plutonium carbides and silicides have received consideration as advanced reactor fuels (136–141). The plutonium–carbon system consists of four compounds that include Pu_3C_2, PuC_{1-x}, Pu_2C_3, and PuC_2, while the plutonium silicon system consists of Pu_5Si_3, Pu_3Si_2, PuSi, Pu_3Si_5, and $PuSi_2$. These compounds can be prepared from the elements. The carbides can also be produced by reaction of PuO_2 or PuH_x with graphite. Plutonium monocarbide PuC exists only as substoichiometric PuC_{1-x}, with a stoichiometry ranging from $PuC_{0.6}$ to $PuC_{0.92}$. At 1654°C, PuC_{1-x} decomposes into Pu_2C_3 plus liquid. It reacts with hot water to form hydroxide, hydrogen, and a mixture of hydrocarbons (142) (see CARBIDES). The PuSi can also be prepared by reacting PuF_3 with Si at 1300°C (143) and the other silicides can be prepared by reacting PuF_3 with $CaSi_2$ or PuO_2 with Si or SiC (137). The silicides are brittle and metallic but are pyrophoric and react with water at 90°C (137).

8.5. Pnictides. Plutonium pnictides are generally prepared by reaction of plutonium metal or hydride with the pnictogen in evacuated sealed quartz tubes that are heated to 400–750°C. The monopnictides can be prepared by thermal dissociation of a higher pnictide. Reviews of synthesis (144) and structural properties are available (145). Plutonium nitride, PuN [12033-54-4], has been studied as a possible fast-reactor fuel (146,147). It can be prepared by reaction of PuH_x with NH_3 at 600–650°C or $N_2 > 230$°C. The pnictides are also interesting for their solid-state magnetic and electrical properties (148).

8.6. Chalcogenides. With heavier chalcogen elements ($X = S$, Se, and Te), plutonium forms binary compounds in four basic families with the highest order composition being PuX_3 that is only found for tellurium. All the heavy chalcogen elements form the series of substoichiometric complexes PuX_{2-x}. For the sesquichalcogenides of formula Pu_2X_3, sulfur forms an α-phase, all the chalcogenides form a γ-phase, while selenium and tellurium form an η-phase. All the heavier chalcogenides form the simple binary PuX. All of the heavier chalcogenide compounds of plutonium can be prepared by gas–solid reaction between the appropriate stoichiometry of plutonium hydride (PuH_x) and chalcogen element in quartz tubes sealed under secondary vacuum (145,149–151). After a typical reaction time of 1 week at 350–750°C, the dichalcogenide, PuX_{2-x} is formed. Compounds with lower X/Pu ratio can be prepared by thermal decomposition of PuX_{2-x} in a sealed tube where one end is kept outside the furnace to allow for the deposition of the chalcogen element. The monochalcogenide, PuX requires much-higher temperature for formation. Typically the quartz tube is heated to 800°C, and the products are pressed into pellets and sintered at 1200–1600°C.

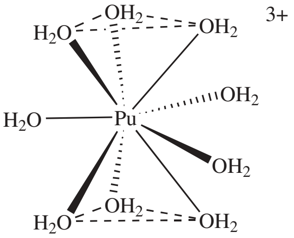
8.7. Oxalates. Stable oxalates of Pu(III), Pu(IV), and Pu(VI) are known. However, only the Pu(III) and Pu(IV) oxalates are technologically important (3,49). Brilliant green plutonium(III) oxalate [56609-10-0] precipitates from nitric acid solutions containing Pu(III) ions upon addition of oxalic acid or sodium oxalate. The composition of the precipitate is $Pu_2(C_2O_4)_3 \cdot 10H_2O$. A homogeneous oxalate precipitation by hydrolysis of diethyl oxalate at 75°C minimizes plutonium loss in the filtrate and decreases filtering time (105). Heating the compound to ~270°C in air or to 460°C in absence of air results in the formation of PuO_2. Yellow-green Pu(IV) oxalate [26588-74-9], $Pu(C_2O_4)_2 \cdot 6H_2O$, precipitates from acidic solutions of Pu(IV) upon addition of oxalic acid. The oxalate converts to PuO_2 upon heating in the presence or absence of air to ~500°C.

8.8. Other Compounds. Other compounds of technological interest include deep green plutonium(IV) nitrate pentahydrate [61204-24-8], $Pu(NO_3)_4 \cdot 5H_2O$; deep red plutonyl nitrate hexahydrate [19125-90-7], $PuO_2(NO_3)_2 \cdot 6H_2O$; coral red anhydrous plutonium(IV) sulfate [13692-89-2], $Pu(SO_4)_2$; pink or red $Pu(SO_4)_2 \cdot 4H_2O$; and pink-tan plutonyl carbonate [39292-10-9], PuO_2CO_3 (3).

9. Aqueous Solution Chemistry

The chemistry of plutonium in aqueous solution is unique and rich. It is also complicated, primarily due to the small energy separations between the various oxidation states and the extreme oxophilicity of plutonium cations. Five oxidation states, Pu(III), Pu(IV), Pu(V), Pu(VI), and Pu(VII), can be prepared and stabilized in aqueous solution under the appropriate conditions. The lower oxidation states, Pu(III) and Pu(IV), are generally more stable in acid solution; while the higher oxidation states, Pu(VI) and Pu(VII) are favored under alkaline conditions. Tetravalent plutonium is the most stable and consequently the most studied, followed by the trivalent and hexavalent states.

Under noncomplexing strongly acidic conditions, such as in perchloric or triflic acid solutions, both Pu(III) and Pu(IV) exist as the simple hydrated (or aqua) ions, Pu^{3+} and Pu^{4+}, retaining their overall formal charge. Pentavalent and hexavalent plutonium cations have such large positive charges that in aqueous solution they immediately hydrolyze to form a unique class of trans dioxo cations, $PuO_2{}^+$ and PuO_2^{2+}, which are commonly referred to as plutonyl ions. Under noncomplexing acid conditions (eg, perchloric or triflic acid), both ions exist as the simple hydrated (or aqua) ions. These plutonyl cations have estimated effective charges of 2.2 and 3.3, respectively (152). Recent X-ray absorption and vibrational spectroscopic studies reveal that under noncomplexing acid conditions, Pu(III), Pu(IV), Pu(V) and Pu(VI) are coordinated by water molecules, resulting in hydrated cations of general formula $[Pu(H_2O)_9]^{3+}$, $[Pu(H_2O)_8]^{4+}$, $[PuO_2(H_2O)_5]^+$, and $[PuO_2(H_2O)_5]^{2+}$, respectively (153,154). Heptavalent plutonium is not stable in acid solution. This oxidation state can only be prepared under highly alkaline (or basic) solution conditions where it forms a tetra-oxo species, PuO_4^-, which is always coordinated with hydroxide ions to give $[PuO_4(OH)_2]^{3-}$. Structural representations of the simple aquo ions of plutonium are given in **1**, **2**, **3**, and **4** (3).



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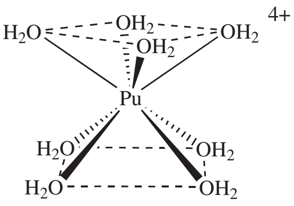

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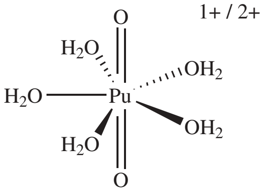

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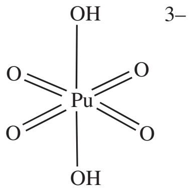

(**4**)

Table 6. **Selected Thermodynamic Values for Plutonium Aqua Ions**[a]

Ionic species	$\Delta_f G°$ kJ/mol	$\Delta_f H°$ kJ/mol	$S°$ J/mol·K
Pu^{3+}	$-(579.0 \pm 2.7)$	$-(591.8 \pm 2.0)$	$-(184.5 \pm 6.2)$
Pu^{4+}	$-(478.0 \pm 2.7)$	$-(539.9 \pm 3.1)$	$-(414.5 \pm 10.2)$
$PuO_2{}^{+}$	$-(852.6 \pm 2.9)$	$-(910.1 \pm 8.9)$	$-(1 \pm 30)$
$PuO_2{}^{2+}$	$-(762.4 \pm 2.8)$	$-(822.0 \pm 6.6)$	$-(71 \pm 22)$

[a] See Refs. 65, 157, 158.

Plutonium(III) in aqueous solution, Pu^{3+} (aq), is pale blue. Aqueous plutonium(IV) is tan or brown; the nitrate complex is green. Pu(V) is pale red-violet or pink in aqueous solution. The Pu(VI) ion is tan or orange in acid solution. In neutral or basic solution Pu(VI) is yellow; cationic and anionic hydrolysis complexes form. Pu(VII) in alkaline solution is best described as blue-black. The chemistry of plutonium ions in solution has been thoroughly studied and reviewed (3,105,155,156). Thermodynamic properties of aqueous ions of Pu are given in Table 6 (65,157,158).

The redox potentials that couple the four common oxidation states (III, IV, V, VI) of plutonium in acid solution are all of comparable magnitude and very close to 1 V. Moreover, the kinetics of the reactions that convert between oxidation states are such that finite amounts of multiple oxidation states can coexist in solution under the appropriate solution conditions (3). This situation is unique for plutonium among all the elements in the periodic table. The formal reduction potentials in aqueous solutions are listed in Table 7, and are shown in Fig. 12 for solutions of $1\,M$ $HClO_4$ at 25°C (65).

The electronic absorption spectra of Pu(III) [22541-70-4], Pu(IV) [22541-44-2], Pu(V) [22541-69-1], and Pu(VI) [22541-41-9] in mineral acids ($HClO_4$ and HNO_3) in aqueous solution show sharp bands in the wavelength region 400–1100 nm. The Pu(VII) [39611-88-61] spectrum, which can be measured only in strong alkali hydroxide solution, also has been reported (162). These aborption

Table 7. **Electrochemical Potentials for Redox Couples Relating Plutonium Ions in Aqueous Acidic, Neutral, and Basic Aqueous Solution versus the Standard Hydrogen Electrode (SHE)**

Couple	Acidic[a]	Neutral[b]	Basic[c]
Pu(IV)/Pu(III)	+0.982	−0.39	−0.96
Pu(V)/Pu(IV)	+1.170	+0.70	−0.67; +0.52[d]
Pu(VI)/Pu(V)	+0.913	+0.60	+0.12
Pu(VI)/Pu(IV)	+1.043	+0.65	+0.34
Pu(V)/Pu(III)		+1.076	
Pu(VII)/Pu(VI)			+0.85
Pu(V)/Pu(IV)	+1.17		

[a] Formal potential in $1\,M$ $HClO_4$ solution (63,105,159).

[b] pH 8 (160).

[c] Determined in $1\,M$ NaOH solution (161).

[d] Oxidation potential (160).

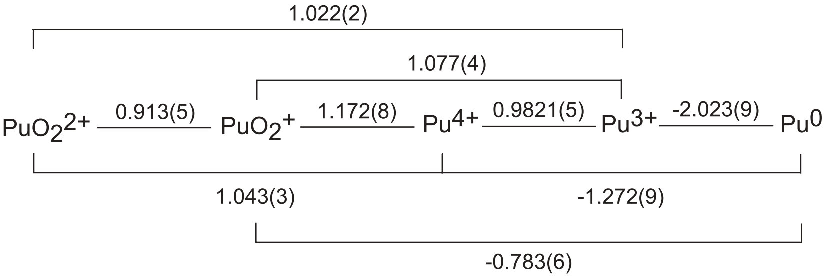

Fig. 12. Formal redox potentials for selected plutonium couples in 1 *M* $HClO_4$ solution at 25°C in V versus SHE (65).

features are characteristic for each oxidation state, and therefore frequently used for identification and quantitative analysis of the concentration of plutonium ions in solution (159). Representative electronic absorption spectra of plutonium ions of common oxidation states are given in Fig. 13 and molar absorptivities for distinctive bands are given in Table 8. Plutonium ions of all oxidation states have strong absorption in the ultraviolet (uv) region of the optical spectrum (163,165). Simlar to rare-earth ion spectra, the spectra of plutonium ions exhibit sharp lines, but have larger extinction coefficients than those of most lanthanide ions (see LANTHANIDES).

Radiolysis of bulk water creates active species such as H, OH, HO_2, and H_2O_2 (166,167) that can oxidize or reduce plutonium ions. Self-radiolysis of Pu solutions has in general been found to decrease the plutonium oxidation state (155), but radiolysis of HCl or NaCl solutions can generate Cl_2, HClO, or ClO, counteracting the processes that reduce Pu, such that neither Pu(IV) nor Pu(VI) appear to be reduced in 1 *M* HCl. With high chloride concentrations Pu(IV) can be oxidized to Pu(V) or Pu(VI) (168).

9.1. Coordination Complexes. The coordination chemistry of plutonium ions is generally characteristic of exceptionally hard Lewis acids, those that show preference for complexation by hard (ie, first row donor atom) ligands. Weak Lewis bases, eg, HS^- form weak complexes with plutonium. Strong Lewis bases, eg, CO_3^{2-}, F^-, and PO_4^{3-} form very stable complexes. For a given plutonium ion the order of complexation strength for common oxoanions is $ClO_4^- < IO_3^- < NO_3^- < SO_4^{2-} \ll CO_3^{2-} < PO_4^{3-}$. Perchlorate is often referred to as a non-interacting counter ion, but it does coordinate to plutonium at very high concentrations. Nitrate complexes are much more stable than analogous perchlorate species, and slightly more stable than chloride complexes of the same stoichiometry. Phosphate is an exceptionally strong ligand for plutonium. Plutonium ions have relatively large ionic radii and therefore form complexes with high coordination numbers (8–14). For a given ligand the strength of complexation (the stability of the solution Pu–ligand complex) and the tendency of ions to hydrolyze decrease following the effective charges:

$$\mathrm{Pu(IV)} > \mathrm{Pu(VI)} \approx \mathrm{Pu(III)} > \mathrm{Pu(V)}$$

Overall, the bonding in plutonium complexes is best viewed as being intermediate between the strongly ionic bonding observed in lanthanide elements,

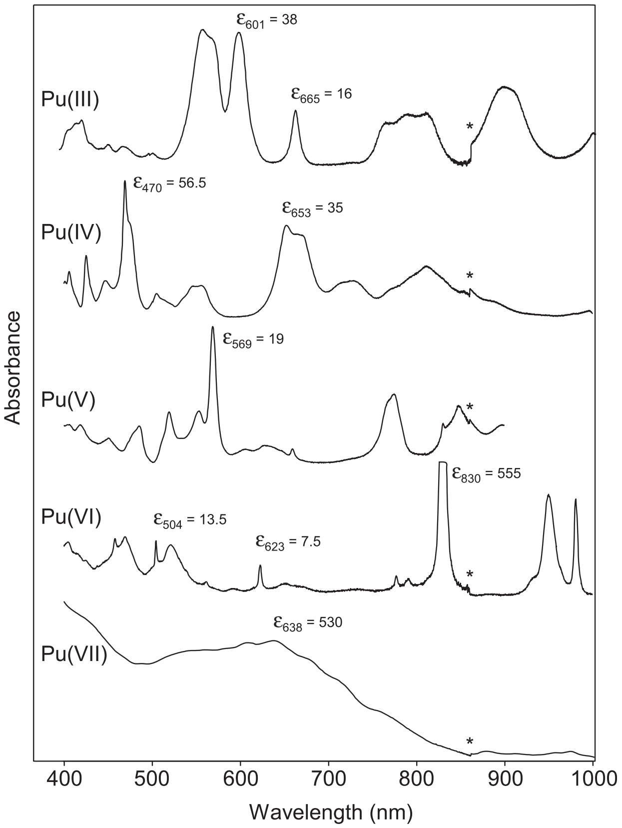

Fig. 13. Electronic absorption spectra of major plutonium aqua ions recorded at 25°C. The asterisk marks a spectrophotometer grating change. Plutonium(III) recorded on 1.89 m*M* solution in 1 *M* $HClO_4$ using 1-cm cell. Plutonium(IV) recorded on 2.91 m*M* solution in 1 *M* $HClO_4$ using 1-cm cell. Plutonium(V) recorded on 10.2 m*M* solution in 1 *M* (Na,H)ClO_4 solution at pH 3.14 using a 1-cm cell. Plutonium(VI) recorded on 0.89 m*M* solution in 1 *M* $HClO_4$ using 1-cm cell. Plutonium(VII) recorded on 20 m*M* solution in 2.5 *M* NaOH using 1-cm cell. (Spectra courtesy of Phillip D. Palmer of Los Alamos.)

and the more covalent bonding observed in *d*-block transition elements. Many plutonium-ligand bonds are nondirectional, and determined largely by electrostatic attraction to the metal, electrostatic repulsion between ligands, and steric demands around the metal center. These metal–ligand bonds are relatively weak, and kinetically labile in solution. There are also examples of metal–ligand bonds (ie, Pu–O bonds in PuO_2^{2+}) that are incredibly strong, show a stereochemical orientation, and are kinetically inert. The former situation is often taken as evidence for ionic behavior, while the latter is clearly consistent with covalent interactions. In plutonium complexes, the dominant metal–ligand bonding takes place through ligand interactions with the 6*d* orbitals. The 6*d* orbitals are strongly split by the presence of a ligand field (as in transition element complexes), but the more contracted 5*f* orbitals show only weak splitting. The ground-state electron configurations are therefore generally governed by the occupation of these closely spaced 5*f* orbitals, which leads to many open shell states (169–173).

Table 8. **Characteristic Optical Absorption Bands of Plutonium Aqua Ions in 1 *M* (H,Na)ClO$_4$ at 25°C Unless Noted Otherwise** [a]

Species	Peak Max, nm	Full-width at half maximum (fwhm), nm[b]	Molar absorp., ε, L/mol/cm
Pu^{3+}	244	broad	1500
	561	broad	38
	601	21.7	38
	665	10.9	16
Pu^{4+}	470	13.6 (shoulder)	56.5
	653	42.7 (shoulder)	35
$\mathrm{PuO_2}^{+}$[c]	569	8.6	19
	1131	32	22
$\mathrm{PuO_2}^{2+}$	504	3.0	13.5
	623	3.8	7.5
	830	2.5	555
$\mathrm{PuO_4(OH)_4}^{3-}$[d]	638	broad	530

[a] See Ref. 163.

[b] The fwhm estimated from Ref. 163.

[c] 10°C, 0.2*M* HClO.

[d] Pu(VII) spectrum from Ref. 164.

In the text that follows, K will be used for the consecutive or stepwise formation constant, and β for the cumulative or overall formation constant (65). In cases (like hydrolysis) where complex formation involves deprotonation of a ligand, the equilibrium constant (K) or formation constant (β) will be denoted by an asterisk as indicated below.

$$\mathrm{PuL}_{n-1} + \mathrm{L} \rightleftharpoons \mathrm{PuL}_n \quad K_n = \frac{[\mathrm{PuL}_n]}{[\mathrm{PuL}_{n-1}][\mathrm{L}]} \tag{16}$$

$$\mathrm{PuL}_{n-1} + \mathrm{HL} \rightleftharpoons \mathrm{PuL}_n + \mathrm{H}^+ \quad {}^{*}\mathrm{K}_n = \frac{[\mathrm{PuL}_n][\mathrm{H}^+]}{[\mathrm{PuL}_{n-1}][\mathrm{HL}]} \tag{17}$$

$$\mathrm{Pu} + n\mathrm{L} \rightleftharpoons \mathrm{PuL}_n \quad \beta_n = \frac{[\mathrm{PuL}_n]}{[\mathrm{Pu}][\mathrm{L}]^n} \tag{18}$$

$$\mathrm{Pu} + n\mathrm{HL} \rightleftharpoons \mathrm{PuL}_n + n\mathrm{H}^+ \quad {}^{*}\beta_n = \frac{[\mathrm{PuL}_n][\mathrm{H}^+]^n}{[\mathrm{Pu}][\mathrm{HL}]^n} \tag{19}$$

Selected formation constants and equilibrium constants will be defined and conditions specified in summary tables. For a more comprehensive discussion of stability constant determinations and analysis done to compute thermodynamic constants under standard conditions the reader is referred to specialized critical reviews (65,174,175). Selected formation and equilibrium constants for plutonium complexes are given in Table 9.

Hydrolysis. The hydrolytic behavior of Pu ions has been the subject of much study. Hydrolyis leads to the formation of ionic species or precipitates by the action of water as illustrated in equation 20 for trivalent plutonium. While hydrolysis reactions are often written as in equation 20, hydrolysis is actually

Table 9. **Selected Formation Constants for Plutonium Complexes**[a]

Reaction stoichiometry	$\log_{10}\beta_n^\circ$	Reaction stoichiometry	$\log_{10}\beta_n^\circ$
Carbonate		*Sulfate*	
$Pu^{4+} + 4CO_3^{2-} \rightleftharpoons [Pu(CO_3)_4]^{4-}$	37.0 ± 1.1	$Pu^{3+} + HSO_4^- \rightleftharpoons [PuSO_4]^+ + H^+$	1.93 ± 0.61
$Pu^{4+} + 5CO_3^{2-} \rightleftharpoons [Pu(CO_3)_5]^{6-}$	36.65 ± 1.13	$Pu^{3+} + 2HSO_4^- \rightleftharpoons [Pu(SO_4)_2]^- + 2H^+$	1.74 ± 0.76
$PuO_2^+ + CO_3^{2-} \rightleftharpoons PuO_2CO_3^-$	5.12 ± 0.14	$Pu^{4+} + HSO_4^- \rightleftharpoons [PuSO_4]^{2+} + H^+$	4.91 ± 0.22
$PuO_2^+ + 3CO_3^{2-} \rightleftharpoons [PuO_2(CO_3)_3]^{5-}$	5.025 ± 0.92	$Pu^{4+} + 2HSO_4^- \rightleftharpoons Pu(SO_4)_4 + 2H^+$	7.18 ± 0.32
$PuO_2^{2+} + CO_3^{2-} \rightleftharpoons PuO_2CO_3$	9.5 ± 0.5	$PuO_2^{2+} + SO_4^{2-} \rightleftharpoons PuO_2SO_4$	3.38 ± 0.20
$PuO_2^{2+} + 2CO_3^{2-} \rightleftharpoons [PuO_2(CO_3)_2]^{2-}$	14.7 ± 0.5	$PuO_2^{2+} + 2SO_4^{2-} \rightleftharpoons [PuO_2(SO_4)_2]^{2-}$	4.4 ± 0.2
$PuO_2^+ + 3CO_3^{2-} \rightleftharpoons [PuO_2(CO_3)_3]^{4-}$	18.0 ± 0.5		
		Halide	
Nitrate		$Pu^{4+} + F^- \rightleftharpoons PuF^{3+}$	8.84 ± 0.1
$Pu^{4+} + NO_3^- \rightleftharpoons Pu(NO_3)^{3+}$	1.95 ± 0.15	$Pu^{4+} + 2F^- \rightleftharpoons PuF_2^{2+}$	15.7 ± 0.2
		$PuO_2^{2+} + F^- \rightleftharpoons PuO_2F^+$	4.56 ± 0.2
Phosphate		$PuO_2^{2+} + 2F^- \rightleftharpoons PuO_2F_2(aq)$	7.25 ± 0.45
$Pu^{4+} + H_3PO_4 \rightleftharpoons [PuH_3PO_4]^{4+}$	2.4 ± 0.30	$Pu^{3+} + Cl^- \rightleftharpoons PuCl^{2+}$	1.2 ± 0.2
		$Pu^{4+} + Cl^- \rightleftharpoons PuCl^{3+}$	1.8 ± 0.3
		$PuO_2^{2+} + Cl^- \rightleftharpoons PuO_2Cl^+$	0.23 ± 0.03
		$PuO_2^{2+} + 2Cl^- \rightleftharpoons PuO_2Cl_2(aq)$	-1.15 ± 0.3
		$Pu^{4+} + Br^- \rightleftharpoons PuBr^{3+}$	1.60 ± 0.3
		$Pu^{3+} + I^- \rightleftharpoons PuI^{2+}$	1.1 ± 0.4

[a] Ref. 175 unless otherwise noted.

a complexation reaction with the hydroxide ion. Therefore, it is also common to express hydrolysis as a complex formation as indicated in equation 21. The hydrolysis constant $^*\beta_1$ (eq. 20) is related to the formation constant β_1 (eq. 21) by the ion product of water, K_w.

$$Pu^{3+} + H_2O \rightleftharpoons Pu(OH)^{2+} + H^+ \tag{20}$$

$$Pu^{3+} + OH^- \rightleftharpoons Pu(OH)^{2+} \tag{21}$$

Characterization of the hydrolysis behavior of plutonium is the cornerstone of understanding its aqueous coordination chemistry, particularly the thermodynamic stability of complexes. The tendency to undergo hydrolysis increases with the charge/size ratio of the ion. Therefore hydrolysis is most pronounced for Pu^{4+}, and the least pronounced for $PuO_2{}^+$. The tendency for hydrolysis follows the general order

$$Pu^{4+} > PuO_2^{2+} > Pu^{3+} > PuO_2^+$$

Plutonium ions hydrolyze readily and thereby limit both the stability fields of individual aquo ions and the overall solubility of plutonium ions in aqueous solution. At the extreme end of the spectrum, Pu(IV) hydrolyzes even in pH 1 solutions and can form complicated polymeric (or colloidal) hydroxides and precipitates (65,176,177), making even the first hydrolysis product of Pu(IV) difficult to characterize. Each of the other common oxidation states forms more soluble and discrete hydroxide species, although Pu(VI) also forms both monomeric and polymeric hydroxide species. The coordination numbers and structures of all of the pure hydroxides can be inferred from the hydration numbers, the stoichiometry of the hydroxo species, and X-ray structures of corresponding solids. X-ray absorption spectroscopy has been used to determine the bond lengths and coordination numbers more directly. Selected hydrolysis constants for plutonium ions are given in Table 10 and follow the conventional hydrolysis equilibrium expression and associated hydrolysis constant, $^*\beta$ (65).

A complete review of hydrolysis products and the solubility of plutonium hydroxides is available in the NEA compilation of the chemical thermodynamics of neptunium and plutonium (65) and its most recent update (175).

Hydrolysis is very extensive in Pu(IV) solutions, less so in Pu(III) and Pu(VI), and least in Pu(V). The chemical properties of Pu(IV) are somewhat similar to those of Ce(IV) and U(IV) (see CERIUM AND CERIUM COMPOUNDS). An interesting but troublesome characteristic of Pu(IV) is the irreversible formation of Pu(IV) polymers. The bright green polymer (185) forms rapidly at low acidities or can form when an acidic Pu(IV) solution is diluted with water. Depolymerization requires strong acid, high temperature, complexants, and/or oxidants (111). The polymer is of high molecular weight and can be identified from optical absorption and X-ray absorption fine structure (XAFS) spectra (177). Its role in the sol–gel process for preparation of PuO_2 ceramics has been described (185) (see SOL–GEL TECHNOLOGY).

Table 10. **Hydrolysis Constants for Plutonium Ions**

Reaction stoichiometry	IM	$\log_{10}{}^*\beta_{mn}$	$\log_{10}{}^*\beta^0{}_{mn}$	References
$Pu^{3+} + H_2O \rightleftharpoons Pu(OH)^{2+} + H^+$	0.1	−6.9	-6.9 ± 0.3	65,178
$Pu^{3+} + 2H_2O \rightleftharpoons [Pu(OH)_2]^+ + 2H^+$		−15.0		179
$Pu^{4+} + H_2O \rightleftharpoons Pu(OH)^{3+} + H^+$	1.0	−0.45	0.6 ± 0.2	175,180
$Pu^{4+} + 2H_2O \rightleftharpoons [Pu(OH)_2]^{2+} + 2H^+$	1.0	−0.75	0.6 ± 0.3	175,180
$Pu^{4+} + 3H_2O \rightleftharpoons [Pu(OH)_3]^+ + 3H^+$	1.0	−0.33	-2.3 ± 0.4	175,180
$Pu^{4+} + 4H_2O \rightleftharpoons [Pu(OH)_{4(aq)}] + 4H^+$	1.0	−0.63	-8.5 ± 0.5	175,180
$PuO_2^+ + H_2O \rightleftharpoons PuO_2(OH)_{(aq)} + H^+$	0.1	−9.73	$\leq -11.3 \pm 1.5$	65,181
$PuO_2^{2+} + H_2O \rightleftharpoons PuO_2(OH)^+ + H^+$	0		-5.5 ± 0.5^a	175
$PuO_2^+ + 2H_2O \rightleftharpoons PuO_2(OH)_{2(aq)} + 2H^+$	0		-13.2 ± 0.5^a	175
$2PuO_2^{2+} + 2H_2O \rightleftharpoons [(PuO_2)_2(OH)_2]^{2+} + 2H^+$	0.1	−7.8	-7.5 ± 0.5^a	175,182–184
$2PuO_2^{2+} + 4H_2O \rightleftharpoons (PuO_2)_2(OH)_4 + 4H^+$	0.1	−19.3		182,183

[a] Asymmetric uncertainties (+0.5, −1.5).

10. Analytical Chemistry

The analytical chemistry of plutonium has been reviewed (33,185–191). It is possible to analyze a plutonium-containing sample gravimetrically by precipitating it as oxalate, calcining to PuO_2, and weighing. The sample must contain no other metal (rare-earths, barium, or other transuranics) that precipitates as an oxalate. Plutonium can be reduced to Pu^{3+} using Ti^{3+} and then titrated with Ce^{4+}. Potentiometric (oxidation–reduction) titration of plutonium in solution is usually faster, more versatile, and potentially as accurate (as good as ±0.06%).

Only slightly less accurate (±0.3–0.5%) and more versatile in scale are other titration techniques. Plutonium may be oxidized in aqueous solution to PuO_2^{2+} using AgO, and then reduced to Pu^{4+} by a known excess of Fe^{2+}, which is back-titrated with Ce^{4+}. The Pu^{4+} ion may be titrated complexometrically with ethylenediaminetetraacetic acid (EDTA) and a colorimetric indicator, such as Arsenazo(I), even in the presence of a large excess of UO_2^{2+}. Solution spectrophotometry (Fig. 13) can be utilized if the plutonium oxidation state is known or controlled. The spectrophotometric method is very sensitive if a colored dye complex such as Arsenazo(III) is used. Analytically useful absorption maxima and molar absorption coefficients (ε) are given in Table 8. Laser photoacoustic spectroscopy has been developed for both elemental analysis and speciation (oxidation state) at concentrations of 10^{-4}–$10^{-5}M$ (192). Chemical extraction can also be used as a method to separate oxidation states prior to spectrophotometric analysis.

The standard elemental analysis techniques, X-ray fluorescence, mass spectroscopy, emission spectrography, and ion-conductive plasma–atomic emission spectroscopy (icp–aes) are also used in specialized laboratories equipped for handling radioisotopes with these instruments.

A large number of radiometric techniques have been developed for plutonium analysis on tracer, biochemical, and environmental samples (193–196). In general, the α-particles of most Pu isotopes are detected by surface-barrier or scintillation detectors. When the level of ^{239}Pu is lower than 10^{-12} g/g sample, radiometric techniques must be enhanced by preliminary extraction of the plutonium to concentrate the plutonium and separate it from other radioisotopes (197,198). Alternatively, fission–fragment track detection can detect ^{239}Pu at a level of 10^{-13} g/g sample or better (199,200). Chemical concentration of plutonium from urine, neutron irradiation in a research reactor, followed by fission track detection, can achieve a sensitivity for plutonium of >1 mBq/L (4×10^{-19} g/g sample) (201).

11. Storage, Usage, and Disposal of Excess Weapons Plutonium

Beginning with the signing of arms reduction treaties in the late 1980s, and accelerating in the post-Cold War era of the 1990s, the production of plutonium for nuclear weapons in the United States and Russia has ended. A large amount, approximately 50 metric tons in each country, has been declared as excess for military purposes in weapons (202,203). The plutonium, mainly as metal and oxide is being stored in militarily secure facilities. Options and criteria for long-term storage have been published (204,205).

Long-term disposition of excess weapons plutonium can be achieved by using it as a reactor fuel for electricity generation as UO_2–PuO_2, mixed-oxide (MOX) fuel, or as a specially fabricated new fuel; by transmuting it in very large-scale accelerators; or by mixing it with high level nuclear waste and vitrifying it into glass logs which would be stored in a geologically inert repository (202). Each of these options represents an enormous commitment of secure and reliable facilities that do not exist as of this writing (2005), but that are planned or under construction. The U.S. National Academy of Sciences has recommended fabrication and use as nuclear fuel without reprocessing or vitrification. Other options that have been considered are subseabed burial, dispersal into the oceans, or space launch. Although these latter options are feasible from an engineering viewpoint and may be environmentally appropriate, these options violate international agreements and are not being pursued (202).

12. Plutonium in the Environment

The behavior of plutonium in the environment has been reviewed (33,206–208). It has been estimated that 1.3×10^{16} Bq of $^{239+240}$Pu has been released to the environment from atmospheric detonation of nuclear weapons along with fission products and other actinides. It has been estimated that 7.9×10^{14} Bq of ^{238}Pu has been released, mostly from burn-up of the nuclear powered satellite SNAP-9a; and that 3.7×10^{13} Bq of $^{239+240}$Pu was released by the Chernobyl accident (209–211). Many studies have been performed to determine the cumulative fallout on soils, plants, bodies of water, animals, and humans.

13. Health and Safety Factors

The principal hazards of plutonium are those posed by its radioactivity, nuclear criticality potential, and chemical reactivity in the metallic state. The ^{239}Pu is primarily an α-emitter. Thus, protection of a worker from its radiation is relatively straightforward. Shielding is generally not required unless very large (kilogram) quantities are handled or unless other isotopes are present. Guides for radiological safety have been published (212).

13.1. Protection against Penetrating Radiation. The external dose at the surface of 1 kg of pure plutonium (nearly pure ^{239}Pu) obtained from uranium irradiated at 3000 MW·d/t is ~0.025 Gy/h (2.5 rad/h) (190). Thus, for the direct handling of kilogram quantities of plutonium, lead-lined gloves (Rad-Bar) are recommended. Isotopes other than ^{239}Pu, which are present in normal plutonium, emit weak γ- and X-rays; for large amounts of these isotopes lead shielding is necessary. In plutonium compounds with light elements, especially fluorides, the (α,n) reaction produces significant neutron doses that require shielding to slow the neutrons to thermal energies and absorb them.

13.2. Protection against Internal Radiation. The extreme health hazard of plutonium comes from two causes. First, when plutonium enters the body, it may not be excreted immediately. Once absorbed or lodged in the body its biological half-life is months or longer. In soluble form it can be metabolized and accumulates in the blood-forming tissues of the bones and in the liver (213-216). Insoluble particles of PuO_2 can lodge in the alveolae of the lung. Second, the α-particles deposit energy locally, breaking many bonds and causing much tissue damage.

Elaborate precautions must be taken to prevent the entrance of Pu into the worker's body by ingestion, inhalation, or entry through the skin, because all common Pu isotopes except for ^{241}Pu are α-emitters. The ^{241}Pu is a β-emitter; but it decays to ^{241}Am, which emits both α- and γ-radiation. Acute intake of plutonium, from ingestion or a wound, thus mandates prompt and aggressive medical intervention to remove as much plutonium as possible before it deposits in the body. Subcutaneous deposition of plutonium from a puncture wound has been effectively controlled by prompt surgical excision followed by prolonged intravenous chelation therapy with diethylenetriaminepentaacetate (Ca^{2+}-DTPA) (217).

Plutonium can enter the body by the gastrointestinal tract (ingestion), by absorption through the skin, from a wound, or by inhalation. Of these possibilities, inhalation is the most likely source of entry and poses the greatest risk (218,219). Inhalation may result in insoluble particles of PuO_2 lodging in the respiratory tract or soluble species migrating to bone or liver. PuO_2 is assigned to inhalation class Y (biological clearance time $\geq$100 day) with fractional absorption $f_1 = 10^{-5}$ (fraction reaching body fluids following transfer to the gastrointestinal tract). Other plutonium compounds are assigned to inhalation class W (biological clearance time 10–100 day) with $f_1 = 10^{-4}$ for nitrates and $f_1 = 10^{-3}$ for other compounds or mixtures. Although these f_1 values are small, ~45% of the transferred plutonium deposits in the liver with a retention half-time of 20 years and 45% deposits in bone with a retention half-time of 50 years (218).

The International Commission on Radiation Protection has established 20 mSv/year (2 rads/year) as the recommended occupational dose limit from the sum of external exposure to ionizing radiation and the 50-year committed dose from intakes of radionuclides. The annual limit of intake (ALI) is 300 Bq

(0.0081 μCi) for ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{242}Pu by inhalation. For ingestion the ALI of these isotopes is 3×10^5 Bq (8 μCi) for PuO_2 and 4×10^4 Bq (1.3 μCi) for other plutonium compounds (220). Because the inhalation ALI is so low (300 Bq represents only 0.13 μg of ^{239}Pu) most plutonium laboratories are required to monitor workplace air. The maximum derived air concentration (DAC) of ^{239}Pu for radiation workers in the United States is 2×10^{-12} μCi/mL (0.074 Bq/m^3). A worker who breathes this air for fifty 40-h weeks can receive a maximum annual intake of 148 Bq (0.004 μCi = 0.064 μg) of ^{239}Pu.

13.3. Protection against Nuclear and Chemical Hazards. Safe handling of plutonium metal, its compounds, and its aqueous solutions in chemical, metallurgical, and engineering operations has been the subject of several comprehensive reports (221-223). In a laboratory where plutonium is processed and workers are present, a ventilation rate of 8–10 air changes per hour has been recommended (224). The design and operation of hoods, gloveboxes, and laboratories for work with plutonium are specialties that have been highly developed as a result of years of experience.

Plutonium solutions that have a low activity [$\leq 3.7 \times 10^7$ Bq (1 mCi) or 10 mg of ^{239}Pu] and that do not produce aerosols can be handled safely by a trained radiochemist in a laboratory fume hood with face velocity 125–150 linear feet per minute (38–45 m/min). Larger amounts of solutions, solutions that may produce aerosols, and plutonium compounds that are not air-sensitive are handled in gloveboxes that are maintained at a slight negative pressure, ~0.1 kPa (0.001 atm, more precisely measured as 1.0–1.2 cm (0.35–0.50 in.) differential pressure on a water column) with respect to the surrounding laboratory pressure (222,225). This air is exhausted through high efficiency particulate air (HEPA) filters.

Plutonium metal and air-sensitive plutonium compounds, eg, hydride, must be isolated for chemical as well as radiological safety. They are handled in airtight gloveboxes containing an inert atmosphere (nitrogen, helium, or argon), which are maintained at a slight negative pressure, ~0.1 kPa (0.001 atm, ie, 1-cm differential pressure on a water column) (222,225). These conditions are especially demanding for operations, such as powder metallurgy, grinding, and machining. Plutonium-inert atmosphere boxes require extensive gas repurification because most inert atmosphere gloveboxes for inorganic and organometallic chemistry are airtight, but at slight positive pressure [0.1 kPa (0.001 atm)].

Although massive pieces of plutonium and its alloys are safe to handle in air, a few plutonium compounds and finely powdered plutonium metal are pyrophoric. The ignition and pyrophoricity of plutonium metal and alloys have been thoroughly reviewed (87,226). Plutonium metal burns in a nitrogen atmosphere containing only 5% oxygen (227,228). Fire extinguishing must contain the Pu and should not create a nuclear criticality potential (229,230). The preferred method of extinguishing a plutonium fire is by excluding oxygen, either by making the glovebox atmosphere inert or by smothering the plutonium with a powder, such as graphite, magnesia, or sodium carbonate (231). Such powders are available in class D fire extinguishers (Met-L-X, Na-X, etc) used in most chemical laboratories. Controlled burning of plutonium metal also has been recommended as a way to convert it to an inert oxide.

13.4. Criticality Precautions. The presence of a critical mass of plutonium in a container can result in a fission chain reaction. Lethal amounts of gamma and neutron radiation are emitted, and a large amount of heat is produced. The assembly can simmer near critical or can make repeated critical excursions. The generation of heat results eventually in an explosion which destroys the assembly. The quantity of ^{239}Pu required for a critical mass depends on several factors: the form and concentration of the plutonium, the geometry of the system, the presence of moderators (water, hydrogen-rich compounds such as polyethylene, cadmium, etc), the proximity of neutron reflectors, the presence of nuclear poisons, and the potential interaction with neighboring fissile systems (232). As little as 509 g of $^{239}Pu(NO_3)_4$ solution at a plutonium concentration of 33 g/L in a spherical container, reflected by an infinite amount of water, is a critical mass (233). Evaluation of criticality controls is available (221,233).

13.5. Special Precautions for ^{238}Pu. Because of its high specific activity, ^{238}Pu samples emit a great deal of heat. Large samples may have to be handled with tongs or heat-resistant gloves drawn over the standard glovebox gloves. The gloves may be penetrated by ^{238}Pu unless Hypalon-coated gloves are used. Because the α,n-reaction from contact of ^{238}Pu with light elements emits large numbers of neutrons on gloveboxes with 10-cm Lucite front windows and for operations with compounds, eg, $^{238}PuF_4$, remote-control equipment is recommended (234). Inhalation of ^{238}Pu aerosols yield a higher liver and bone surface dose, but a lower lung dose, than ^{239}Pu aerosols because $^{238}PuO_2$ appears to be more soluble *in vivo* than $^{239}PuO_2$ (235).

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