Plutonium

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Plutonium is a transuranic radioactive chemical element with symbol **Pu** and atomic number 94. It is an actinide metal of silvery-gray appearance that tarnishes when exposed to air, and forms a dull coating when oxidized. The element normally exhibits six allotropes and four oxidation states. It reacts with carbon, halogens, nitrogen, silicon and hydrogen. When exposed to moist air, it forms oxides and hydrides that can expand the sample up to 70% in volume, which in turn flake off as a powder that is pyrophoric. It is radioactive and can accumulate in bones, which makes the handling of plutonium dangerous.

Plutonium was first produced and isolated on December 14, 1940 by Dr. Glenn T. Seaborg, Joseph W. Kennedy, Edwin M. McMillan, and Arthur C. Wahl by deuteron bombardment of uranium-238 in the 60-inch cyclotron at the University of California, Berkeley. They first synthesized neptunium-238 (half-life 2.1 days) which subsequently beta-decayed to form a new heavier element with atomic number 94 and atomic weight 238 (half-life 87.7 years). Uranium had been named after the planet Uranus and neptunium after the planet Neptune, and so element 94 was named after Pluto, which at the time was considered to be a planet as well. Wartime secrecy prevented them from announcing the discovery until 1948. Plutonium is the heaviest element to occur in nature as trace quantities arising similarly from the neutron capture of natural uranium-238. Plutonium is much more common on Earth since 1945 as a product of neutron capture and beta decay, where some of the neutrons released by the fission process convert uranium-238 nuclei into plutonium-239.

Both plutonium-239 and plutonium-241 are fissile, meaning that they can sustain a nuclear chain reaction, leading to applications in nuclear weapons and nuclear reactors. Plutonium-240 exhibits a high rate of spontaneous fission, raising the neutron flux of any sample containing it. The presence of plutonium-240 limits a plutonium sample's usability for weapons or its quality as reactor fuel, and the percentage of plutonium-240 determines its grade (weapons-grade, fuel-grade, or reactor-grade). Plutonium-238 has a half-life of 88 years and emits alpha particles. It is a heat source in radioisotope thermoelectric generators, which are used to power some spacecraft. Plutonium isotopes are expensive and inconvenient to separate, so particular isotopes are usually manufactured in specialized reactors.

Plutonium, $_{94}$Pu

General properties	
Name, symbol	plutonium, Pu
Appearance	silvery white, tarnishing to dark gray in air
Plutonium in the periodic table	
Atomic number (*Z*)	94
Group, block	group n/a, f-block
Period	period 7
Element category	actinide
Standard atomic weight (A_r)	(244)
Electron configuration	[Rn] $5f^6\ 7s^2$
per shell	2, 8, 18, 32, 24, 8, 2
Physical properties	
Phase	solid

Producing plutonium in useful quantities for the first time was a major part of the Manhattan Project during World War II that developed the first atomic bombs. The Fat Man bombs used in the Trinity nuclear test in July 1945, and in the bombing of Nagasaki in August 1945, had plutonium cores. Human radiation experiments studying plutonium were conducted without informed consent, and several criticality accidents, some lethal, occurred after the war. Disposal of plutonium waste from nuclear power plants and dismantled nuclear weapons built during the Cold War is a nuclear-proliferation and environmental concern. Other sources of plutonium in the environment are fallout from numerous above-ground nuclear tests, now banned.

Characteristics

Physical properties

Plutonium, like most metals, has a bright silvery appearance at first, much like nickel, but it oxidizes very quickly to a dull gray, although yellow and olive green are also reported.[2][3] At room temperature plutonium is in its α (*alpha*) form. This, the most common structural form of the element (allotrope), is about as hard and brittle as gray cast iron unless it is alloyed with other metals to make it soft and ductile. Unlike most metals, it is not a good conductor of heat or electricity. It has a low melting point (640 °C) and an unusually high boiling point (3,228 °C).[2]

Alpha decay, the release of a high-energy helium nucleus, is the most common form of radioactive decay for plutonium.[4] A 5 kg mass of ^{239}Pu contains about 12.5×10^{24} atoms. With a half-life of 24,100 years, about 11.5×10^{12} of its atoms decay each second by emitting a 5.157 MeV alpha particle. This amounts to 9.68 watts of power. Heat produced by the deceleration of these alpha particles makes it warm to the touch.[5][6]

Resistivity is a measure of how strongly a material opposes the flow of electric current. The resistivity of plutonium at room temperature is very high for a metal, and it gets even higher with lower temperatures, which is unusual for metals.[7] This trend continues down to 100 K, below which resistivity rapidly decreases for fresh

Melting point	912.5 K (639.4 °C, 1182.9 °F)
Boiling point	3505 K (3228 °C, 5842 °F)
Density near r.t.	19.816 g/cm^3
when liquid, at m.p.	16.63 g/cm^3
Heat of fusion	2.82 kJ/mol
Heat of vaporization	333.5 kJ/mol
Molar heat capacity	35.5 J/(mol·K)

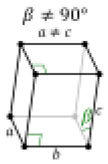
Vapor pressure

P (Pa)	**1**	**10**	**100**	**1 k**	**10 k**	**100 k**
at T (K)	1756	1953	2198	2511	2926	3499

Atomic properties

Oxidation states	8, 7, 6, 5, **4**, 3, 2, 1 (an amphoteric oxide)
Electronegativity	Pauling scale: 1.28
Ionization energies	1st: 584.7 kJ/mol
Atomic radius	empirical: 159 pm
Covalent radius	187±1 pm

Miscellanea

Crystal structure	monoclinic 
Speed of sound	2260 m/s
Thermal expansion	46.7 µm/(m·K) (at 25 °C)
Thermal conductivity	6.74 W/(m·K)

samples.[7] Resistivity then begins to increase with time at around 20 K due to radiation damage, with the rate dictated by the isotopic composition of the sample.[7]

Because of self-irradiation, a sample of plutonium fatigues throughout its crystal structure, meaning the ordered arrangement of its atoms becomes disrupted by radiation with time.[8] Self-irradiation can also lead to annealing which counteracts some of the fatigue effects as temperature increases above 100 K.[9]

Unlike most materials, plutonium *increases* in density when it melts, by 2.5%, but the liquid metal exhibits a linear decrease in density with temperature.[7] Near the melting point, the liquid plutonium has also very high viscosity and surface tension as compared to other metals.[8]

Allotropes

Plutonium normally has six allotropes and forms a seventh (zeta, ζ) at high temperature within a limited pressure range.[10] These allotropes, which are different structural modifications or forms of an element, have very similar internal energies but significantly varying densities and crystal structures. This makes plutonium very sensitive to changes in temperature, pressure, or chemistry, and allows for dramatic volume changes following phase transitions from one allotropic form to another.[8] The densities of the different allotropes vary from 16.00 g/cm^3 to 19.86 g/cm^3.[11]

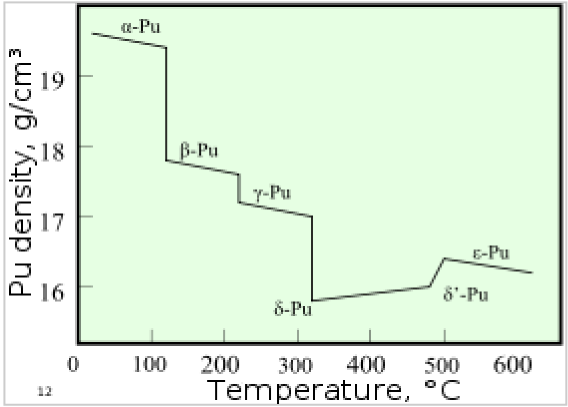
The presence of these many allotropes makes machining plutonium very difficult, as it changes state very readily. For example, the α form exists at room temperature in unalloyed plutonium. It has machining characteristics similar to cast iron but changes to the plastic and malleable β (*beta*) form at slightly higher temperatures.[12] The reasons for the complicated phase diagram are not entirely understood. The α form has a low-symmetry monoclinic structure, hence its brittleness, strength, compressibility, and poor thermal conductivity.[10]

Electrical resistivity	1.460 µΩ·m (at 0 °C)
Magnetic ordering	paramagnetic
Young's modulus	96 GPa
Shear modulus	43 GPa
Poisson ratio	0.21
CAS Number	7440-07-5
History	
Naming	after dwarf planet Pluto, itself named after classical god of the underworld Pluto
Discovery	Glenn T. Seaborg, Arthur Wahl, Joseph W. Kennedy, Edwin McMillan (1940–1)

Most stable isotopes of plutonium

iso	NA	half-life	DM	DE (MeV)	DP
^{238}Pu	trace	87.74 y	SF	204.66[1]	–
			α	5.5	^{234}U
^{239}Pu	trace	2.41×10^4 y	SF	207.06	–
			α	5.157	^{235}U
^{240}Pu	syn	6.5×10^3 y	SF	205.66	–
			α	5.256	^{236}U
^{241}Pu	syn	14 y	β$^-$	0.02078	^{241}Am
			SF	210.83	–
^{242}Pu	syn	3.73×10^5 y	SF	209.47	–
			α	4.984	^{238}U
^{244}Pu	syn	8.08×10^7 y	α	4.666	^{240}U
			SF		–

Plutonium in the δ (*delta*) form normally exists in the 310 °C to 452 °C range but is stable at room temperature when alloyed with a small percentage of gallium, aluminium, or cerium, enhancing workability and allowing it to be welded.[12] The δ form has more typical metallic character, and is roughly as strong and malleable as aluminium.[10] In fission weapons, the explosive shock waves used to compress a plutonium core will also cause a transition from the usual δ phase plutonium to the denser α form, significantly helping to achieve supercriticality.[13] The ε phase, the highest temperature solid allotrope, exhibits anomalously high atomic self-diffusion compared to other elements.[8]



Plutonium has six allotropes at ambient pressure: **alpha** (α), **beta** (β), **gamma** (γ), **delta** (δ), **delta prime** (δ'), & **epsilon** (ε)[10]

Nuclear fission

Plutonium is a radioactive actinide metal whose isotope, plutonium-239, is one of the three primary fissile isotopes (uranium-233 and uranium-235 are the other two); plutonium-241 is also highly fissile. To be considered fissile, an isotope's atomic nucleus must be able to break apart or fission when struck by a slow moving neutron and to release enough additional neutrons to sustain the nuclear chain reaction by splitting further nuclei.[14]

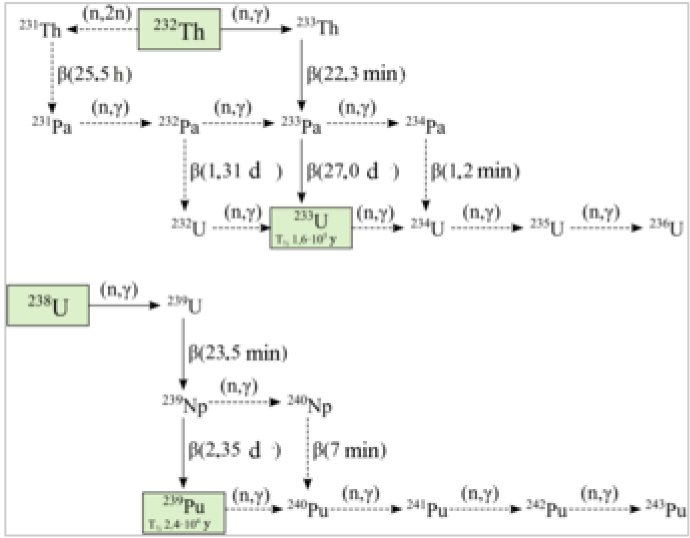
Pure plutonium-239 may have a multiplication factor (k_{eff}) larger than one, which means that if the metal is present in sufficient quantity and with an appropriate geometry (e.g., a sphere of sufficient size), it can form a critical mass.[15] During fission, a fraction of the nuclear binding energy, which holds a nucleus together, is released as a large amount of electromagnetic and kinetic energy (much of the latter being quickly converted to thermal energy). Fission of a kilogram of plutonium-239 can produce an explosion equivalent to 21,000 tons of TNT (88,000 GJ). It is this energy that makes plutonium-239 useful in nuclear weapons and reactors.[5]

A ring of weapons-grade 99.96% pure electrorefined plutonium, enough for one bomb core. The ring weighs 5.3 kg, is ca. 11 cm in diameter and its shape helps with criticality safety.

The presence of the isotope plutonium-240 in a sample limits its nuclear bomb potential, as plutonium-240 has a relatively high spontaneous fission rate (~440 fissions per second per gram—over 1,000 neutrons per second per gram),[16] raising the background neutron levels and thus increasing the risk of predetonation.[17] Plutonium is identified as either weapons-grade, fuel-grade, or reactor-grade based on the percentage of plutonium-240 that it contains. Weapons-grade plutonium contains less than 7% plutonium-240. Fuel-grade plutonium contains from 7% to less than 19%, and power reactor-grade contains 19% or more plutonium-240. Supergrade plutonium, with less than 4% of plutonium-240, is used in U.S. Navy weapons stored in proximity to ship and submarine crews, due to its lower radioactivity.[18] The isotope plutonium-238 is not fissile but can undergo nuclear fission easily with fast neutrons as well as alpha decay.[5]

Isotopes and synthesis

Twenty radioactive isotopes of plutonium have been characterized. The longest-lived are plutonium-244, with a half-life of 80.8 million years, plutonium-242, with a half-life of 373,300 years, and plutonium-239, with a half-life of 24,110 years. All of the remaining radioactive isotopes have half-lives that are less than 7,000 years. This element also has eight metastable states, though all have half-lives less than one second.[4]



Uranium-plutonium and thorium-uranium chains

The isotopes of plutonium range in mass number from 228 to 247. The primary decay modes of isotopes with mass numbers lower than the most stable isotope, plutonium-244, are spontaneous fission and alpha emission, mostly forming uranium (92 protons) and neptunium (93 protons) isotopes as decay products (neglecting the wide range of daughter nuclei created by fission processes). The primary decay mode for isotopes with mass numbers higher than plutonium-244 is beta emission, mostly forming americium (95 protons) isotopes as decay products. Plutonium-241 is the parent isotope of the neptunium decay series, decaying to americium-241 via beta or electron emission.[4][19]

Plutonium-238 and 239 are the most widely synthesized isotopes.[5] Plutonium-239 is synthesized via the following reaction using uranium (U) and neutrons (n) via beta decay (β^-) with neptunium (Np) as an intermediate:[20]

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{239}_{92}\mathrm{U} \xrightarrow[23.5\ \mathrm{min}]{\beta^-} {}^{239}_{93}\mathrm{Np} \xrightarrow[2.3565\ \mathrm{d}]{\beta^-} {}^{239}_{94}\mathrm{Pu}$$

Neutrons from the fission of uranium-235 are captured by uranium-238 nuclei to form uranium-239; a beta decay converts a neutron into a proton to form Np-239 (half-life 2.36 days) and another beta decay forms plutonium-239.[21] Egon Bretscher working on the British Tube Alloys project predicted this reaction theoretically in 1940.[22]

Plutonium-238 is synthesized by bombarding uranium-238 with deuterons (D, the nuclei of heavy hydrogen) in the following reaction:[23]

$$\begin{aligned}{}^{238}_{92}\mathrm{U} + {}^{2}_{1}\mathrm{D} &\longrightarrow {}^{238}_{93}\mathrm{Np} + 2\ {}^{1}_{0}\mathrm{n} \\ {}^{238}_{93}\mathrm{Np} &\xrightarrow[2.117\ \mathrm{d}]{\beta^-} {}^{238}_{94}\mathrm{Pu}\end{aligned}$$

In this process, a deuteron hitting uranium-238 produces two neutrons and neptunium-238, which spontaneously decays by emitting negative beta particles to form plutonium-238.[24]

Decay heat and fission properties

Plutonium isotopes undergo radioactive decay, which produces decay heat. Different isotopes produce different amounts of heat per mass. The decay heat is usually listed as watt/kilogram, or milliwatt/gram. In larger pieces of plutonium (e.g. a weapon pit) and inadequate heat removal the resulting self-heating may be significant. All isotopes produce weak gamma radiation on decay.

Compounds and chemistry

At room temperature, pure plutonium is silvery in color but gains a tarnish when oxidized.[26] The element displays four common ionic oxidation states in aqueous solution and one rare one:[11]

- Pu(III), as Pu^{3+} (blue lavender)
- Pu(IV), as Pu^{4+} (yellow brown)
- Pu(V), as PuO_2^+ (light pink)[note 1]
- Pu(VI), as PuO_2^{2+} (pink orange)
- Pu(VII), as PuO_5^{3-} (green)—the heptavalent ion is rare.

Various oxidation states of plutonium in solution

The color shown by plutonium solutions depends on both the oxidation state and the nature of the acid anion.[28] It is the acid anion that influences the degree of complexing—how atoms connect to a central atom—of the plutonium species.

Metallic plutonium is produced by reacting plutonium tetrafluoride with barium, calcium or lithium at 1200 °C.[29] It is attacked by acids, oxygen, and steam but not by alkalis and dissolves easily in concentrated hydrochloric, hydroiodic and perchloric acids.[30] Molten metal must be kept in a vacuum or an inert atmosphere to avoid reaction with air.[12] At 135 °C the metal will ignite in air and will explode if placed in carbon tetrachloride.[31]

Plutonium pyrophoricity can cause it to look like a glowing ember under certain conditions.

Plutonium is a reactive metal. In moist air or moist argon, the metal oxidizes rapidly, producing a mixture of oxides and hydrides.[2] If the metal is exposed long enough to a limited amount of water vapor, a powdery surface coating of PuO_2 is formed.[2] Also formed is plutonium hydride but an excess of water vapor forms only PuO_2.[30]

Twenty micrograms of pure plutonium hydroxide

Plutonium shows enormous, and reversible, reaction rates with pure hydrogen, forming plutonium hydride.[8] It also reacts readily with oxygen, forming PuO and PuO_2 as well as intermediate oxides; plutonium oxide fills 40% more volume than plutonium metal. The metal reacts with the halogens, giving rise to compounds with the general formula PuX_3 where X can be F, Cl, Br or I and PuF_4 is also seen. The following oxyhalides are observed: PuOCl, PuOBr and PuOI. It will react with carbon to form PuC, nitrogen to form PuN and silicon to form $PuSi_2$.[11][31]

Powders of plutonium, its hydrides and certain oxides like Pu_2O_3 are pyrophoric, meaning they can ignite spontaneously at ambient temperature and are therefore handled in an inert, dry atmosphere of nitrogen or argon. Bulk plutonium ignites only when heated above 400 °C. Pu_2O_3 spontaneously heats up and transforms into PuO_2, which is stable in dry air, but reacts with water vapor when heated.[32]

Crucibles used to contain plutonium need to be able to withstand its strongly reducing properties. Refractory metals such as tantalum and tungsten along with the more stable oxides, borides, carbides, nitrides and silicides can tolerate this. Melting in an electric arc furnace can be used to produce small ingots of the metal without the need for a crucible.[12]

Cerium is used as a chemical simulant of plutonium for development of containment, extraction, and other technologies.[33]

Electronic structure

Plutonium is an element in which the 5f electrons are the transition border between delocalized and localized; it is therefore considered one of the most complex elements.[34] The anomalous behavior of plutonium is caused by its electronic structure. The energy difference between the 6d and 5f subshells is very low. The size of the 5f shell is just enough to allow the electrons to form bonds within the lattice, on the very boundary between localized and bonding behavior. The proximity of energy levels leads to multiple low-energy electron configurations with near equal energy levels. This leads to competing $5f^n7s^2$ and $5f^{n-1}6d^17s^2$ configurations, which causes the complexity of its chemical behavior. The highly directional nature of 5f orbitals is responsible for directional covalent bonds in molecules and complexes of plutonium.[8]

Alloys

Plutonium can form alloys and intermediate compounds with most other metals. Exceptions include lithium, sodium, potassium, rubidium and caesium of the alkali metals; and magnesium, calcium, strontium, and barium of the alkaline earth metals; and europium and ytterbium of the rare earth metals.[30] Partial exceptions include the refractory metals chromium, molybdenum, niobium, tantalum, and tungsten, which are soluble in liquid plutonium, but insoluble or only slightly soluble in solid plutonium.[30] Gallium, aluminium, americium, scandium and cerium can stabilize the δ phase of plutonium for room temperature. Silicon, indium, zinc and zirconium allow formation of metastable δ state when rapidly cooled. High amounts of hafnium, holmium and thallium also allows some retention of the δ phase at room temperature. Neptunium is the only element that can stabilize the α phase at higher temperatures.[8]

Plutonium alloys can be produced by adding a metal to molten plutonium. If the alloying metal is sufficiently reductive, plutonium can be added in the form of oxides or halides. The δ phase plutonium–gallium and plutonium–aluminium alloys are produced by adding plutonium(III) fluoride to molten gallium or aluminium, which has the advantage of avoiding dealing directly with the highly reactive plutonium metal.[35]

- Plutonium–gallium is used for stabilizing the δ phase of plutonium, avoiding the α-phase and α–δ related issues. Its main use is in pits of implosion nuclear weapons.[36]
- **Plutonium–aluminium** is an alternative to the Pu–Ga alloy. It was the original element considered for δ phase stabilization, but its tendency to react with the alpha particles and release neutrons reduces its usability for nuclear weapon pits. Plutonium–aluminium alloy can be also used as a component of nuclear fuel.[37]
- **Plutonium–gallium–cobalt** alloy ($PuCoGa_5$) is an unconventional superconductor, showing superconductivity below 18.5 K, an order of magnitude higher than the highest between heavy fermion systems, and has large critical current.[34][38]
- **Plutonium–zirconium** alloy can be used as nuclear fuel.[39]
- **Plutonium–cerium** and **plutonium–cerium–cobalt** alloys are used as nuclear fuels.[40]
- **Plutonium–uranium**, with about 15–30 mol.% plutonium, can be used as a nuclear fuel for fast breeder reactors. Its pyrophoric nature and high susceptibility to corrosion to the point of self-igniting or disintegrating after exposure to air require alloying with other components. Addition of aluminium, carbon or copper does not improve disintegration rates markedly, zirconium and iron alloys have better corrosion resistance but they disintegrate in several months in air as well. Addition of titanium and/or zirconium significantly increases the melting point of the alloy.[41]

- **Plutonium–uranium–titanium** and **plutonium–uranium–zirconium** were investigated for use as nuclear fuels. The addition of the third element increases corrosion resistance, reduces flammability, and improves ductility, fabricability, strength, and thermal expansion. **Plutonium–uranium–molybdenum** has the best corrosion resistance, forming a protective film of oxides, but titanium and zirconium are preferred for physics reasons.[41]
- **Thorium–uranium–plutonium** was investigated as a nuclear fuel for fast breeder reactors.[41]

Occurrence

Trace amounts of plutonium-238 and plutonium-239 can be found in nature. Small traces of plutonium-239, a few parts per trillion, and its decay products are naturally found in some concentrated ores of uranium,[42] such as the natural nuclear fission reactor in Oklo, Gabon.[43] The ratio of plutonium-239 to uranium at the Cigar Lake Mine uranium deposit ranges from 2.4×10^{-12} to 44×10^{-12}.[44] Due to its relatively long half-life of about 80 million years, it was suggested that plutonium-244 occurs naturally as a primordial nuclide, but early reports of its detection could not be confirmed.[45] These trace amounts of ^{239}Pu originate in the following fashion: on rare occasions, ^{238}U undergoes spontaneous fission, and in the process, the nucleus emits one or two free neutrons with some kinetic energy. When one of these neutrons strikes the nucleus of another ^{238}U atom, it is absorbed by the atom, which becomes ^{239}U. With a relatively short half-life, ^{239}U decays to ^{239}Np, which decays into ^{239}Pu.[46][47] Finally, exceedingly small amounts of plutonium-238, attributed to the extremely rare double beta decay of uranium-238, have been found in natural uranium samples.[48]

Minute traces of plutonium are usually found in the human body due to the 550 atmospheric and underwater nuclear tests that have been carried out, and to a small number of major nuclear accidents. Most atmospheric and underwater nuclear testing was stopped by the Limited Test Ban Treaty in 1963, which was signed and ratified by the United States, the United Kingdom, the Soviet Union, and other nations. Continued atmospheric nuclear weapons testing since 1963 by non-treaty nations included those by China (atomic bomb test above the Gobi Desert in 1964, hydrogen bomb test in 1967, and follow-on tests), and France (tests as recently as the 1990s). Because it is deliberately manufactured for nuclear weapons and nuclear reactors, plutonium-239 is the most abundant isotope of plutonium by far.[31]

Source

- "Wikipedia: Plutonium"