

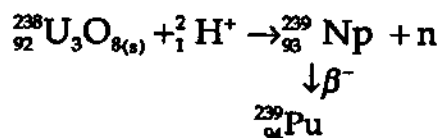
Plutonium - A Unique Element

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I History

- (i) Discovery: December, 1940 by G. T. Seaborg, A. C. Wahl, and J. W. Kennedy.



- (ii) Isolation 1st pure compound: August, 1942. (First visual observation of a synthetic element.)

Table 1. Some Physical Constants of Plutonium

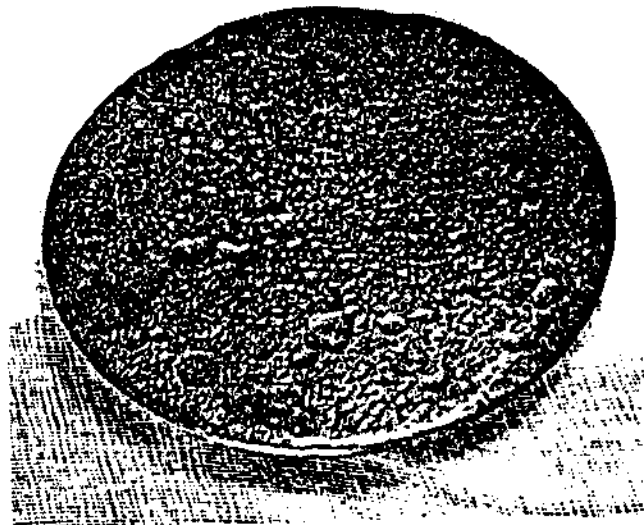
Atomic Number	94
Isotopic Mass, plutonium-239 (chemical scale)	239.06
Atomic Weight	239.11 [†]
Melting Point	640°C
Boiling Point	3327°C
Vapor Pressure (1120–1520°C)	$\text{Log}_{10} P_{\text{mm}} = -\frac{17,420}{t + 273.18} + 7.794$
Average heat of vaporization (1120–1520°C)	79.7 kcal/g-atom)

- (iii) Actinide Hypothesis: Seaborg (1944) proposed that Pu was member of 5f family, related to rare earths (4f-elements). Provided understanding of chemical properties and led to discovery of elements through Z=103.

II. Pu Metal

- (i) Highly reactive with O₂, CO, CO₂, N₂, H₂, etc.
(ii) Assembly (usually) of small crystals, quite brittle, hard as cast iron.

Figure 1. The product from the thermal reduction process is a solid chunk or "button" of plutonium metal. The button shown in the photograph weighed about 3/4 pound and was roughly 3 inches in diameter.



- (iii) Alloyed with 1% Al makes Pu soft as annealed copper.
- (iv) Exists in 6 allotropic forms (unique). Four allotropic phases expand on heating (normal behavior) while two contract!

Table 2. Plutonium Allotropes

Allotrope	Crystal Structure	Transformation Temperature (°C)	Density (g/cm ³)	Thermal Expansion (×10 ⁻⁶ /°C)
α	Simple monoclinic	115	19.9	+ 54
β	Body-centered monoclinic	185	17.7	+ 42
γ	Face-centered monoclinic	310	17.1	+ 35
δ	Face-centered cubic	452	15.9	- 8.6
δ ¹	Body-centered tetragonal	480	16.0	- 66
ξ	Body-centered cubic	640	16.5	+ 37

- (v) Densities are high; the α phase is denser than gold; all phases denser than lead.
- (vi) M.P. of metal is 640°C, very low for a metal (1535°C for iron).

B.P. of metal is 3327°C, quite high (3000°C for iron).

By contrast, for $U_{(m)}$, M.P. = 1132°C; B.P. = 3818°C.

- (vii) Thermal conductivity low; ca. 10% that of Ag and only 10 times that of fire clay (an insulator).
- (viii) High electrical resistivity; of metals, only Mg poorer electrical conductor.
- (ix) IN SUMMARY, Pu IS A POOR METAL.

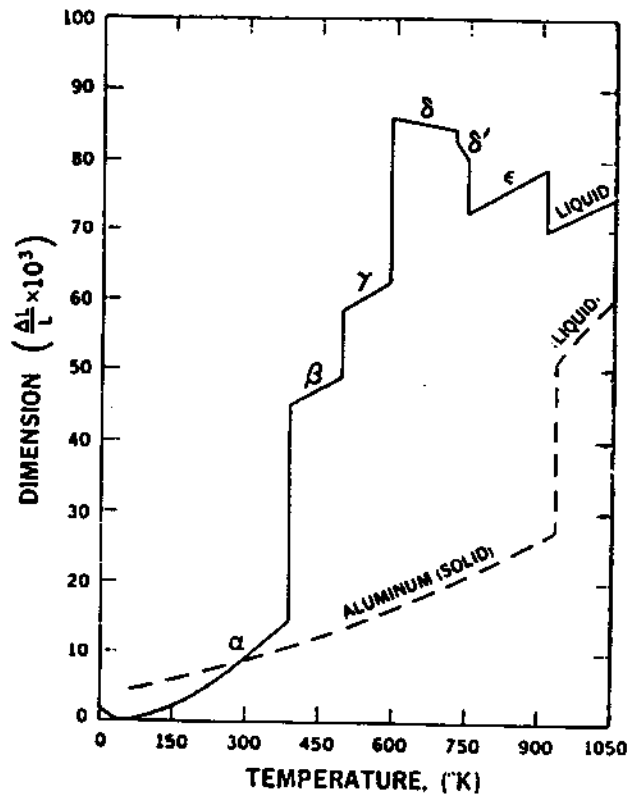


Figure 2. Expansion Behavior of Plutonium

Idealized version of the expansion behavior of plutonium, showing approximate temperature ranges in which the allotropes or phases of plutonium normally exist. The effect of temperature on the dimensions of a plutonium specimen is also shown.

When plutonium is heated from a temperature near absolute zero (0°K or -273°C), it is in the alpha phase and shrinks slightly until 50°K (-223°C) is reached, then expands with further heating to 388°K (115°C). At this temperature the specimen transforms to the beta phase undergoing marked expansion at constant temperature.

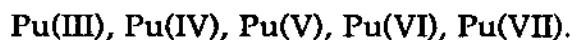
With heating to 583°K (310°C), the specimen expands in the beta phase, during beta-to-gamma transition, in the gamma phase, and during gamma-to-delta transition. In the delta phase, however, the specimen shrinks while being heated. It also shrinks as it transforms to the delta-prime phase at 725°K (425°C), as it is heated in the delta-prime phase, and as it transforms to the epsilon phase at 753°K (480°C).

Above that temperature the specimen is in the epsilon phase, and expands during heating until the melting point is reached at 913°K (640°C). The specimen shrinks as it changes from solid to liquid, then expands as it is heated in the liquid state.

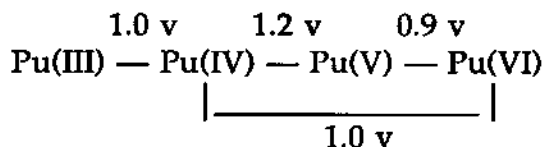
The dashed line represents the simpler, more normal expansion of aluminum.

III. Pu Solution Chemistry

(i) Exists in 5 different oxidation states in aqueous solution:



(ii) Redox potentials ca. 1 v. for III-VI in 1 M acid.



So can have 2, 3, and even all 4 simultaneously in solution in equilibrium. (Table 3)

TABLE 3. OXIDATION STATES STABILITIES

III.	U	Oxidizes spontaneously in aqueous solution
	Np	Stable to water, oxidized by air
	Pu	Stable to water and air but easily oxidized (by own α radiation)
IV.	U, Np	Stable to water, oxidized by air
	Pu	Stable in concentrated acid, disproportionates to III and VI at lower acidities.
V.	Np	Stable
	U, Pu	Disproportionates
VI.	U	Stable
	Np, Pu	Stable, reduces fairly easily (under own α radiation)

(iii) Colors due to $f \rightarrow f$ electronic transitions

a) Pu(III): purple Pu(V): pink
Pu(IV): brown Pu(VI): yellow
in HClO_4 solution.

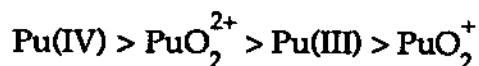
b) Pu(IV): reddish brown in HCl solution
Pu(IV): green in HNO_3 solution
Pu(IV): greenish yellow in colloidal system

(iv) Pu(V) and Pu(VI) present in aqueous solution as linear dioxo cations:

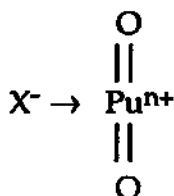


(v) Bonding is strongly ionic (hard acid cations) so interact best with "hard" (non-polarizable) anions such as oxygen, fluoride.

(vi) Complexing strength in order:



For the reaction of X^- with PuO_2^{2+}



X^- senses a charge of $\underline{n = +2.2}$ on the Pu in $\underline{\text{PuO}_2^+}$

and of $\underline{n = +3.3}$ on Pu in $\underline{\text{PuO}_2^{2+}}$.

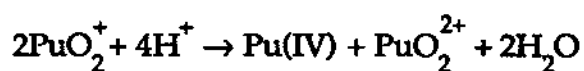
(vii) Pu(III) — stable in water but easily oxidized, hydrolyzes ca. pH 6.

Pu(IV) — stable in concentrated acid, hydrolyzes even at pH 1 and forms very insoluble Pu(OH)_4 at pH > 4.

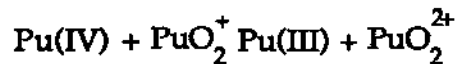
PuO_2^+ — stable form in neutral solutions (e.g., ocean) at trace concentrations, disproportionates above ca. 10^{-8} M.

PuO_2^{2+} — reduces readily in aqueous solution.

viii) Disproportionation:

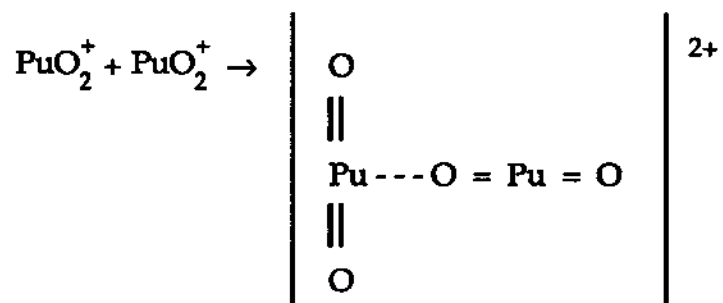


(ix) Redox

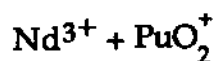
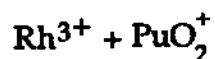
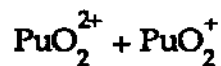


So frequently, have more than one oxidation state present.

(x) Cation-cation complexes:



Also,



but



(xi) Coordination numbers:

Pu(III) and Pu(IV), CN = 6 to 12 known; in solution $\text{Pu}(\text{H}_2\text{O})_9^{3+}$ and $\text{Pu}(\text{H}_2\text{O})_9^{4+}$.

PuO_2^+ and PuO_2^{2+} , CN = 4 to 6 most common; e.g., $\text{PuO}_2(\text{H}_2\text{O})_4^{2+}$.

IV. Environmental Behavior

(i) Oxidation state is dependent on redox potential (Eh) and on pH.

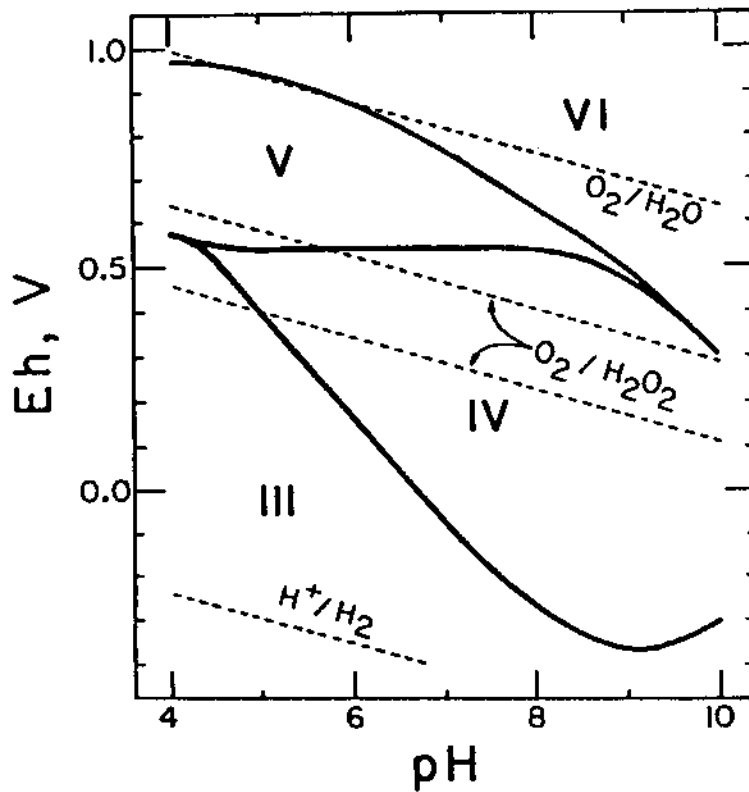


Figure 3.

In oceans (Eh ~0.6-0.7 v and pH ~8) have Pu(V). In deep reducing underground waters (Eh ~-3-4 v and pH 6-8).

- (ii) Pu(IV) has $K_{sp} \sim 10^{-56}$ for $Pu(OH)_4$ formation. It irreversibly ages to form oxo bridges:

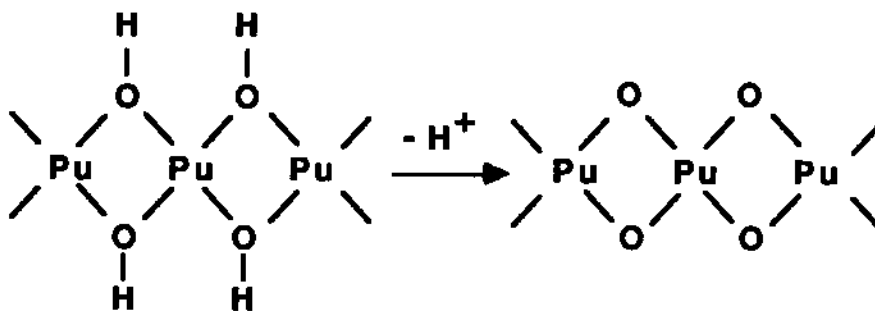


Figure 4.

Very difficult to dissolve old $Pu(OH)_4$.

- (iii) With $K_{sp} = 10^{-56}$, in ocean (pH ~8) have $[Pu^{4+}] \sim 10^{-32}$ M or much less than 1 cation per liter! However, in sea water, soluble Pu is PuO and concentration in surface sea water is $\sim 10^{-15}$ M.

- iv) In environment have:
- complexation (by OH^- , CO_3^{2-} , humic acids, etc.)
 - precipitation (of hydroxides, carbonates, phosphates, etc.)
 - Colloid formation
 - sorption (to rocks, colloids, organisms, etc.)

See figure for possible reactions

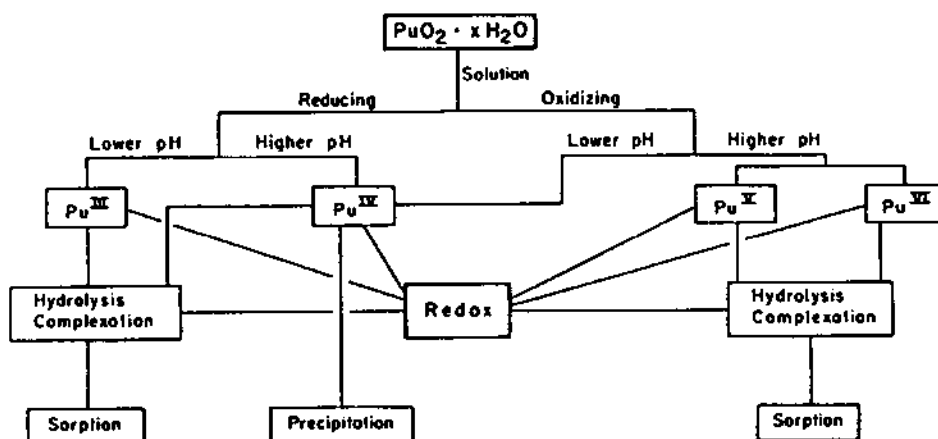


Figure 5.

SUMMARY:

PERHAPS NO OTHER ELEMENT DISPLAYS THE RANGE OF INTERESTING PROPERTIES THAT PU DOES. IT CAN BE USED TO TEACH REDOX EQUILIBRIUM, COMPLEXATION AS A FUNCTION OF CATION CHARGE DENSITY, UNUSUAL METALLIC PROPERTIES, AND THE BROAD RANGE OF ENVIRONMENTAL PROPERTIES (TO NAME ONLY A FEW AREAS). AND, TO ADD TO THE FASCINATION OF THIS COMPLEX BEHAVIOR IS THE PERTURBATION OF THESE PROPERTIES BY THE RADIOACTIVITY WHEN SOLUTIONS ARE CONCENTRATED (10^{-6} M) OR SOLID COMPOUNDS ARE STUDIED.