Plutonium Oxide Systems and Related Corrosion Products

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Introduction

Elemental plutonium is considered to be one of the most complex elements in the periodic table and, by some, one of the more toxic, given its moderate radioactivity and that it is a heavy metal. Essentially a manufactured element (only traces are found in nature), it was first discovered and produced some six decades ago. Amazingly, hundreds of tons of plutonium are presently in existence. Crystalline solids formed by plutonium and nonmetallic elements (e.g., hydrogen, oxygen, halides, etc.) were some of the first compounds investigated, and oxides and oxide-related materials have always been important compounds.

The determination of the chemical and physical properties of compounds and the elemental state was essential in the quest to prepare large quantities of the metal for military applications. Subsequently, information for plutonium oxides, carbides, nitrides, and so on became important for nuclear-reactor fuels. As a result of these different applications, plutonium has been studied extensively, despite the experimental difficulties involved.

Exploring and understanding the chemistry, physics, and materials science of nonmetallic plutonium solids remain important and relevant today, if for no other reason than the need to deal with the large worldwide inventory of this element and the different materials that contain it. According to the International Atomic Energy Agency,[1] this inventory exceeds 160 metric tons from civilian sources alone, in addition to military supplies. This inventory consists essentially of the fissionable ^{239}Pu isotope. Although the development and deployment of nuclear reactors is uncertain at the present time, both pure plutonium and uranium–plutonium mixtures (e.g., as mixed oxides, the so-called MOX fuels) can be considered as sources of energy. One concept for utilizing excess weapons-grade plutonium from stockpiles is to generate and use MOX reactor fuels for power generation. In this regard, ton quantities of plutonium have been placed in MOX-type fuels worldwide.

New scientific findings regarding plutonium continue to surface, which is a sign of the complexity of this element. A thorough understanding of the properties and corrosion reactions of plutonium and its compounds continues to be essential today. This is important given the storage and process operations involving this element that must be addressed and the potential for future accidental release or dispersion of these materials, as well as their limited presence in the environment.

There are other isotopes of plutonium, which are used for different applications. For example, ^{238}Pu is shorter-lived than ^{239}Pu (88 years versus 2.4×10^4 years, respectively) and has different nuclear properties. The ^{242}Pu and ^{244}Pu isotopes have low specific activities and are best for basic research studies. Amajor application for ^{238}Pu is in electric-power generators. These generators make use of the heat from radioactive decay to produce electricity by means of thermopiles.[2,3] Such devices often employ ^{238}Pu oxide in a special iridium container; they have been very useful as energy sources for space exploration (e.g., the Cassini mission to Saturn). At one time, they had even been considered as energy sources for heart pacemakers. Today, the U.S. Department of Energy has an active program to produce ^{238}Pu for such power generators, and this program itself will demand knowledge of plutonium chemistry and materials science.

If the existing fissile plutonium (mainly the ^{239}Pu isotope) is not used for nuclear-reactor fuels, it must be maintained in storage or disposed of in some safe fashion. One approach is to incorporate the plutonium in special glass or ceramic matrices and bury it in designated sites. This disposition has been considered for dealing with excess quantities of weapons-grade (mainly ^{239}Pu content) plutonium. Each concept for addressing these issues has proponents and objectors. Regardless of the approach or approaches taken, some form of storage and processing of plutonium materials will be required, and these different issues will drive the need for comprehensive science and technology. Certainly, plutonium oxides, oxide-related materials, and the different products formed during corrosion-type reactions involving plutonium metal are of central interest in this regard. This interest has led to new investigations, both fundamental and technological in nature, using state-of-the-art scientific tools and approaches that have generated new and unexpected findings regarding the chemistry of plutonium.

The volume of early work on plutonium and materials containing it, compared with that of the last two decades, shows that recent efforts have been more limited in number. The quantity of high-quality information about plutonium gathered in the past is impressive, given the hazardous nature of this element, its complex redox behavior (at least five oxidation states are known), and its relatively recent discovery. Much of the information known up to the mid-1980s is covered in several reviews; one of the more comprehensive is recommended.[4] Also recommended is a collection of extended abstracts from a conference dealing with recent plutonium investigations.[5]

The recent reduction in the number of studies on plutonium results in part from a perception that plutonium materials are thoroughly understood and additional investigations have limited value. Several of the latest advances in the basic science of plutonium have come as spin-offs of more applied investigations, where unexpected behaviors of plutonium were encountered, prompting basic investigations of these behaviors. Such has been the case with the extensive studies of plutonium-oxide systems, where it appears that the previous knowledge was not adequate to deal with and understand the complexities of these systems.

The electronic behavior of plutonium metal, which makes it the most complex metal in the periodic table, arises from a large number of electronic configurations of similar energy. The complexity is more subdued in plutonium's compounds, and in many instances their behavior can be linked to that observed in other 4*f* electron (lanthanide) and 5*f* electron (actinide) elements. This is especially true for the trivalent and tetravalent oxidation states of plutonium. There is a tendency toward decreased stability for plutonium's higher oxidation states in solid compounds; in general, it is more difficult to achieve oxidation states above four than for neptunium (plutonium's near neighbor) or uranium. Except for plutonium hexafluoride, higher halides of plutonium are conspicuously absent. There is also a reduced tendency for plutonium to form nonstoichiometric compounds. For many years, and after many controversies, it was accepted that the highest binary oxide of plutonium was the dioxide. Very recent work[6–8] challenges this concept, and it now appears that small amounts of binary oxides with a higher oxygen stoichiometry may indeed exist.

Many Pu(III) compounds are quite lanthanide-like in their behavior and properties. In several instances, their properties can be predicted on the basis of an ionic radius correlation. Examples of this are found in the phase behavior of plutonium sesquioxides and the chemistry of plutonium hydrides. This correlation can be carried over to the Pu(IV) state, but the comparison with lanthanide elements is limited, as cerium is the only lanthanide that readily exhibits this oxidation state.

In this brief article, an effort will be made to present some important facets of plutonium-oxide chemistry. It is hoped that from this overview, the reader will gain new perspectives and interest into the fascinating science of plutonium.

The focus of this article is on plutonium oxides, hydroxide materials, and products that accompany corrosion-type reactions of metallic plutonium. Also presented are some scientific findings regarding fundamental plutonium-oxide chemistry that have been acquired recently using advanced research tools. These include studies of gas-phase clusters of plutonium oxide or oxide–hydroxide, claims for the existence of PuO_3 and PuO_4 (a new formal oxidation state, VIII, for plutonium), the formation of PuO_{2+x} materials, establishing catalytic activity by Pu_2O_3, and the gas-phase oxidation of Pu and PuO ions by oxygen.

Plutonium Oxide Systems

Plutonium is known to exhibit oxidation states III through VII, and the III and IV states are well established in binary oxides.[4,9,10] Accordingly, there are multiple phases of the sesquioxide, the very stable dioxide, and intermediate phases between the sesquioxide and dioxide. Crystallographic data for these oxides are given in Table I.

The very stable dioxide has always dominated the oxide chemistry of plutonium. There have been some claims for the existence of solid PuO, especially in the form of films on metal surfaces, but it is unlikely that this material exists as a pure compound. There is a potential for the formation of solid solutions of the type Pu(O,N,C), which would have fcc-type structures and would be similar structurally to a monoxide. The monocarbide and mononitride are accepted compounds. However, the monoxide has been established as a high-temperature gas-phase product. Recently, evidence for binary materials having oxygen/plutonium ratios above 2.0 (PuO_{2+x}; PuO_3 and PuO_4) have been reported (see later discussion). Specialized publications[11–14] and an extensive array of literature augment these listed reviews. Several of the publications also cover special topics involving equilibrium, structure, thermodynamics, and magnetic properties.

The dissolution of oxygen in the different polymorphs of plutonium metal is small; the solubility limit for the ε form at 580°C is reported to represent an O/Pu ratio of 4×10^{-4}.[15] The oxygen content of molten plutonium metal may be higher.

The lowest-established stoichiometry in oxides is found in the hexagonal sesquioxide (La_2O_3 structure type; $a_0 = 0.3841$ and $c_0 = 0.5958$ nm), a phase often identified in the literature as the β-phase or the A-type oxide (lanthanide oxide designation), as well as by other terminology.[13] The situation with the sesquioxides can be confusing, as the $PuO_{1.52}$ phase, a bcc cubic (Mn_2O_3-type) oxide ($a_0 = 1.098$ nm), forms at an O/Pu ratio slightly above the ideal stoichiometry for Pu(III). It is designated as the α-phase, or the C-type sesquioxide. The phase behavior of plutonium oxides is discussed in detail in a later section.

Thermodynamic predictions[16] and results of numerous studies have indicated that plutonium dioxide is the highest composition binary phase in the Pu-O system.[4,9,10] This fcc (CaF_2-type) phase has a lattice parameter of $a_0 = 0.5397(1)$ nm at 25°C. The $PuO_{2.00}$ composition actually has a narrow substoichiometric (PuO_{2-x}) range at room temperature, where $a_0 = 0.5400$nm at the boundary of $PuO_{1.98}$.[17] Ordered removal of oxygen atoms from a fourth of the anion sites on a diagonal in the fcc PuO_2 structure yields the C-type structure of $PuO_{1.5}$. Its unit cell appears as a "double" unit cell of the dioxide cell; $a_0 = 2a_0$ of the fcc dioxide.[18,19]

As outlined in prior reviews,[4,9,10] PuO_2 is prepared by air oxidation of the metal or by calcination of plutonium precipitates (e.g., oxalate, peroxide, hydroxide, carbonate, etc.) at temperatures between 250°C and 1000°C. A significant variation in the oxide's particle size and surface area can be encountered when the material and/or calcining temperature are changed. These differences are essentially eliminated by heating the products at 1000°C or higher to form a high-fired oxide, which is difficult to dissolve in aqueous HNO_3 and other mineral acids.[4] Reaction of plutonium and oxygen in the stoichiometric ratio of the sesquioxide yields a 3:1 molar mixture of PuO_2 and elemental Pu. Hexagonal Pu_2O_3 is only obtained by reducing the

Table I: Crystallographic Data for Plutonium Oxides.[a]

Phase	Structure Type	Symmetry	Space Group	Unit Cell (nm)	Formula Units (per cell)	X-ray Density (g/cc)
$PuO_{1.50}$ (A-type)	La_2O_3	hexagonal	$P\bar{3}m1$	$a = 0.3841(6)$* $c = 0.5958(5)$	1	11.47
$PuO_{1.51}$ (C-type)	Mn_2O_3	bcc	$Ia3$	$a = 1.104(2)$	16	10.2
$PuO_{1.61}$ (C-type)	Fe_2O_3	bcc	$Ia3$	$a = 1.095–1.101$	…	…
PuO_2	CaF_2	fcc	$Fm3m$	$a = 0.53960(3)$	4	11.46
[PuO]**	NaCl	fcc	$Fm3m$	$a = 0.496$	4	13.9

[a] From Reference 4.

* Uncertainties of last digits are in parentheses.

** Probably a Pu(O,C)-type material—given only for comparison purposes.

dioxide with excess plutonium metal, under flowing dry H_2 or with excess C, in compacts at temperatures between 1500–2000°C. The latter process often leaves a carbon contamination in the product.

Confusion may develop when one examines the proposed preparation schemes for the sesquioxide materials. The silver-gray $PuO_{1.52}$ (α-Pu_2O_3) involves reduction of PuO_2 with carbon or dry hydrogen (often in the presence of titanium turnings) at 1520–1800°C.[4,9,10] However, the preparative conditions are indistinguishable from those for preparing β-Pu_2O_3. The reported preparation of C-type $PuO_{1.52}$ by heating PuO_2 in dynamic vacuum at 1650–1800°C is questionable, as the O/Pu ratio of congruently vaporizing PuO_{2-x} is 1.85–1.90 in this temperature region.[20] As suggested previously,[17] involvement of a Ta crucible, which serves as a reductant, is necessary to approach an oxide with an O/Pu ratio of 1.5. Incomplete reduction can yield products with O/Pu ratios greater than 1.52, and diphasic mixtures of $PuO_{1.52}$ and $PuO_{1.98}$ can form upon cooling to room temperature. Indeed, the oxide system between the sesquioxide and dioxide stoichiometries can be complex.

Although the preparation of pure α-Pu_2O_3 by high temperatures alone is difficult, the cubic oxide forms as a micrometer-thick surface layer when PuO_2-coated metal is heated at 150–200°C in vacuum.[21] Gram amounts of cubic $PuO_{1.46\pm0.04}$ powder can be obtained by reacting plutonium metal with water in a near-neutral salt solution at room temperature.[22,23]

The formation and the stability of PuO_2 have dominated plutonium oxide chemistry, and investigations have focused largely on the dioxide properties and behavior. The refractory dioxide has been identified as the terminal binary phase in the Pu-O system, and as the stable binary oxide in the environment.[24,25] The situation reflects an observation initially applied to corrosion chemistry of plutonium,[26] that investigators are inclined to concentrate their attention on plutonium dioxide and overlook other potential compounds that may contribute to the overall behavior of plutonium.

Plutonium hydroxides or hydrated dioxides have been discussed over many years. The most significant in the context discussed here is the so-called Pu(IV) polymer, which is best described as consisting of very small particles with a "PuO_2 backbone." These particles become a dispersed colloid when the surface atoms generate a charged particle that is counterbalanced by an anion layer.[27,28] When suspended, these colloids can appear as pseudo solutions, but in reality they consist of very small particles (e.g., 1–1000 nm in diameter) that may display special chemical/physical behavior. One form of plutonium colloid has been investigated by studies[29] using extended x-ray absorption fine structure (EXAFS) and XANES (x-ray absorption near edge structure), which confirmed that it consisted of tiny forms, smaller than those frequently reported by others. Studies of this "polymer" material are complicated by the wide variation of forms that may be encountered. One polymer form is crystalline, simulates a PuO_2 product with small crystallites, and yields a fluorite-type diffraction pattern. Other colloids are amorphous in nature.

A Pu(V) and Pu(VI) hydroxide material has been reported.[10,30] Hydroxides of Pu(III), which are very susceptible to oxidation to Pu(IV) by air,[4,14] and Pu(III)-oxide hydrides have also been reported.[22,23,31]

In a recent work[32] on the solubility of Pu(IV)-hydroxide materials, where the solid is identified as $Pu(OH)_4$, a log of the solubility product constant K_{sp} of -58.7 was given. This value generates a standard free energy of formation of -1446 kJ mol^{-1} for this compound. The difficulty in such K_{sp} assignments is the correct determination of the plutonium concentration—in this case, verifying that colloidal Pu-containing species were not present.

A wealth of high-quality information has been generated for the plutonium oxygen system, and the validity of these data and the understanding of plutonium's science have withstood the test of time. However, advances in scientific techniques and continued efforts have opened new aspects of plutonium science. Examples of new pursuits are investigations that employ EXAFS/XANES studies at synchrotrons, neutron-diffraction studies, and advanced gas-phase chemistry that often is employed in studies of transactinide work. Some of the recent efforts involve mass spectrometry, with and without the use of trapped-ion techniques. These new findings must now withstand the test of time as well as confirmatory studies.

One recent investigation examined several plutonium oxide and oxide–hydroxide clusters that can form in the gas phase.[33] These clusters and their chemical reactions can contribute to the general understanding of PuO_x chemistry, and they represent materials that bridge the gap between gaseous materials containing one plutonium atom and the condensed, solid phases that have large numbers of plutonium atoms. These plutonium clusters have been found to consist of 6–18 plutonium atoms. Other clusters with more plutonium atoms could very well exist, and this possibility will be investigated in future work.

In other gas-phase studies, using mass high-temperature spectrometry, Ronchi et al.[7] studied vapor species over plutonium dioxide and found evidence for volatile PuO_3 gas molecules, but only at a level of 0.02 ppm of the total plutonium content. Thermochromatography studies[6,34] indicate that both PuO_3 and PuO_4 exist as trace volatile species in a gas stream. The behavior of PuO_4 was reported to be similar to that of OsO_4 and RuO_4. Both of these oxide species are new—and surprising, based on the previous understanding of plutonium oxide chemistry. These species are also unexpected for high-temperature products, based on general entropy considerations,[19] which should favor lower oxidation states. The existence of these products must be confirmed and additional properties investigated.

Fourier transform ion cyclotron mass spectrometer studies have also been employed recently to investigate plutonium in the gas phase. Among other reactions, the oxidation of $[PuO]^+$ molecular ions by oxygen was examined, which addressed reaction rates and sequential chemical reactions of ligated ions.[35]

Another area of recent research has concerned the existence and formation of plutonium oxides of the form PuO_{2+x},[8,36] where $x = 0.25$. This newly recognized material is described as a fluorite-related oxide, in which some of the Pu oxidation states are greater than IV and compositions reach and exceed $PuO_{2.25}$. Its behavior resembles that observed in uranium oxides, where oxides between UO_2 and $UO_{2.25}$ are known. A material assigned to be $PuO_3 \cdot 0.8H_2O$ has also been reported[30,37], but the latter compound may be a peroxide containing Pu(IV). Solid peroxides with a "high" oxygen content but containing Pu(IV) can be obtained by precipitation processes.[4] The observation and evidence for PuO_{2+x} came out of studies looking at the sorption of water on plutonium oxide surfaces, where chemical indications suggested that an oxide higher than the dioxide may have formed. The formation of a metastable $PuO(OH)_2$ surface by dissociative chemisorption of H_2O is believed to be the first step in a relatively slow process that forms the PuO_{2+x}. The reported formation of a higher oxide by reaction between the dioxide and water[8,36–39] contradicts previous theoretical and experiment results. Previously, it was accepted that the dioxide was the binary phase with the highest oxygen (O^{2-}) stoichiometry.

Support for this PuO_{2+x} material comes from x-ray diffraction analysis of the oxide formed on plutonium metal during corrosion by water vapor at 200–350°C. The data show a new fluorite-related phase ($PuO_{2.27}$) in addition to PuO_2 and α-Pu_2O_3.[38] X-ray photoelectron spectroscopy (XPS) analyses of oxide found at the interface show high-binding-energy peaks in the plutonium's $4f_{5/2}$ (441.9 eV) and $4f_{7/2}$ (429.0 eV) electronic levels, which are consistent with the presence of Pu(VI). The appearance of an O 1*s* band at 530.1 eV indicates the presence O^{2-}. Additional evidence for this $PuO_2 + H_2O$ reaction were obtained by a microbalance technique and by oxygen titration methods at constant water pressure (30 mbar) and temperatures of 25–350°C.[36,39,40] Isothermal measurements show that hydrogen is generated at linear temperature-dependent rates, and mass spectrometric analyses indicated that H_2 is the only gaseous product. Constant oxidation rates are described by a single $\ln(dH_2/dt)$ versus $1/T$ relationship, where the activation energy is 39 ± 3 kJ mol^{-1}. The lattice parameters of the products increased progressively with composition (O/Pu) from 2.016 to 2.265, suggesting the formation of a continuous oxide solid solution. Structural and XPS results indicate that this "higher oxide" of plutonium forms by the accommodation of hexavalent plutonium and interstitial oxygen in the fluorite PuO_2 structure, as found for the formation of UO_{2+x}.[36,40] Although this higher plutonium oxide is supported by experimental results, and its existence can account for unexplained experimental behavior, the findings are still controversial among scientists and will be a subject of future discussions and thermodynamic considerations.

There are also several mixed-oxide systems with plutonium, including MOX fuels (uranium–plutonium dioxides); ternary oxides of plutonium with transition elements, alkali metals, and the alkaline earths; and oxychalcogenide-type materials.[4] Oxides and silicate materials are formed when plutonium is placed in various glasses for waste forms. There are also important and complex ternary (or higher) oxide systems generated with transition metals, which have promise for ceramic waste forms. One compound ($Pu_2Zr_2O_7$), referred to as being a plutonium pyrochlore oxide (pyrochlore oxide refers to a crystal form of the mineral pyrochlore). This plutonium compound[41] is considered as one of several important waste forms. When prepared with neutron "poisons" (e.g., Gd and Hf, both of which absorb neutrons), a material of composition $(Pu, Gd)_2Hf_2O_7$ is obtained, which reduces nuclear criticality concerns regarding the plutonium. With regard to these potential waste forms, the reader is referred to a separate report (and the references therein) in the article by Muller and Weber in this issue. A discussion of these different plutonium waste materials is beyond the scope of this overview.

Thermodynamic Properties

Thermodynamics data are well defined for PuO_2 and to a lesser extent for hexagonal Pu_2O_3. Such data are limited for cubic $PuO_{1.52}$ and $PuO_{1.6}$ and are not available for other known intermediate oxides. The literature has been extensively reviewed.[13] Recommended thermodynamics values for plutonium oxides at 289 K[14] are given in Table II. However, a comparison of enthalpies and free energies of formation for hexagonal Pu_2O_3 and $PuO_{1.52}$ with those of an earlier assessment[1] show significant differences. The value of standard entropy, $S°$, for PuO_2, derived from the most recent heat-capacity measurements,[42] is 16 J K^{-1} mol^{-1} lower than reported by others.

Enthalpies of formation are also reported for gaseous oxides formed during vaporization of the PuO_{2-x}.[14] The enthalpies of formation of PuO(g) and PuO_2(g) are listed as -92 and -422 kJ mol^{-1} at 298 K, respectively. Free energies of formation for the hexagonal and cubic sesquioxides should help resolve the questions of phase relationship and their stability. However, comparison of $\Delta G_f°$ (standard free energy) for hexagonal Pu_2O_3 (-1580 kJ mol^{-1}) with the composition-adjusted enthalpy for bcc Pu_2O_3 (-1574 ± 22 kJ mol^{-1}) shows an uncertainty well in excess of the difference, emphasizing the need for significantly better thermodynamics data.

Phase Equilibria

The recently proposed plutonium–oxygen equilibrium phase diagram shown in part by Figure 1 is based on a reassessment of previous high-temperature data.[13] This region of the diagram is similar to that presented in prior reviews.[4,11] The three stable phases at room temperature are hexagonal Pu_2O_3 (identified as β-Pu_2O_3), $PuO_{1.52}$ (identified as α-Pu_2O_3) and PuO_{2-x}. Below 335°C, $PuO_{1.52}$ and PuO_{2-x} coexist; above that temperature, a fourth oxide, $PuO_{1.6\pm\delta}$, forms over a broad composition range. On the metal-rich side, this phase coexists with $PuO_{1.52}$ until it disproportionates peritectically above 450°C into β-Pu_2O_3 and $PuO_{1.6}$.

On the oxygen-rich side, $PuO_{1.6}$ coexists with PuO_{2-x} below 630°C, and with metal-rich PuO_{2+x} at higher temperatures, until it transforms congruently into PuO_{2-x} at 1180°C. The $PuO_{1.6}$ phase is either fcc ($a_0 = 0.5549 \pm 0.02$ nm) or bcc ($a_0 = 1.098 \pm 0.03$ nm). Hexagonal $Pu_2O_{3-\delta}$ coexists with oxygen-saturated metal and exhibits an increasing extent of nonstoichiometry until the congruent melting point at 2080°C is approached. A congruent melting point of 2425°C is recommended for PuO_2.[13]

The most recent diagram[13] is given in Figure 2 and differs from earlier proposals[4] in two important ways. In the earlier assessments, the $PuO_{1.6}$ phase is stable to a temperature in excess of 2350°C, instead of 1180°C, and the miscibility gap between Pu(s,l) closes below the 2080°C melting point of β-Pu_2O_3. In the more recent evaluation, the Pu + β-$Pu_2O_{3-\delta}$ two-phase region extends to temperatures in excess of 2500°C. This interpretation is consistent with experimental data indicating that liquid plutonium metal and molten plutonium oxide coexist at temperatures above 3230°C, the boiling point of the metal.[43,44] However, the time of coexistence (<0.5 s) may be too short for equilibration/equilibrium to have been reached.

The relationship between the cubic and hexagonal forms of Pu_2O_3 is complex and uncertain. The two oxides are described as distinct and separate equilibrium phases at low temperature, instead of dimorphic forms of the sesquioxide. As outlined in the most recent review,[13] reasons for recommending two phases are (1)the hexagonal Pu_2O_3 to cubic Pu_2O_3 transformation has not been observed; (2)the phases have been observed to coexist; and (3)their compositions do not overlap. With the lanthanide oxide, Nd_2O_3, the transformation of the hexagonal form to the cubic form is re-

Table II:Thermodynamic Properties of Plutonium Oxides at 298 K.[a]

Oxide Phase	$C_p°$ (J K^{-1} mol^{-1})	$S°$ (J K^{-1} mol^{-1})	$\Delta H_f°$ (kJ mol^{-1})	$\Delta G_f°$ (kJ mol^{-1})
Pu_2O_3 (hexagonal, β)	117.0(5)*	163.0(6)	−1656	−1580
$PuO_{1.52}$ (bcc, α)	…	57.7	−836(11)	−795
$PuO_{1.6}$ (cubic)	…	…	−884(17)	…
PuO_2 (fcc)	66.3(3)	66.1 (3)	−1056.2(7)	−998.0(7)

[a] From Reference14.

*Uncertainties of last digits are in parentheses.

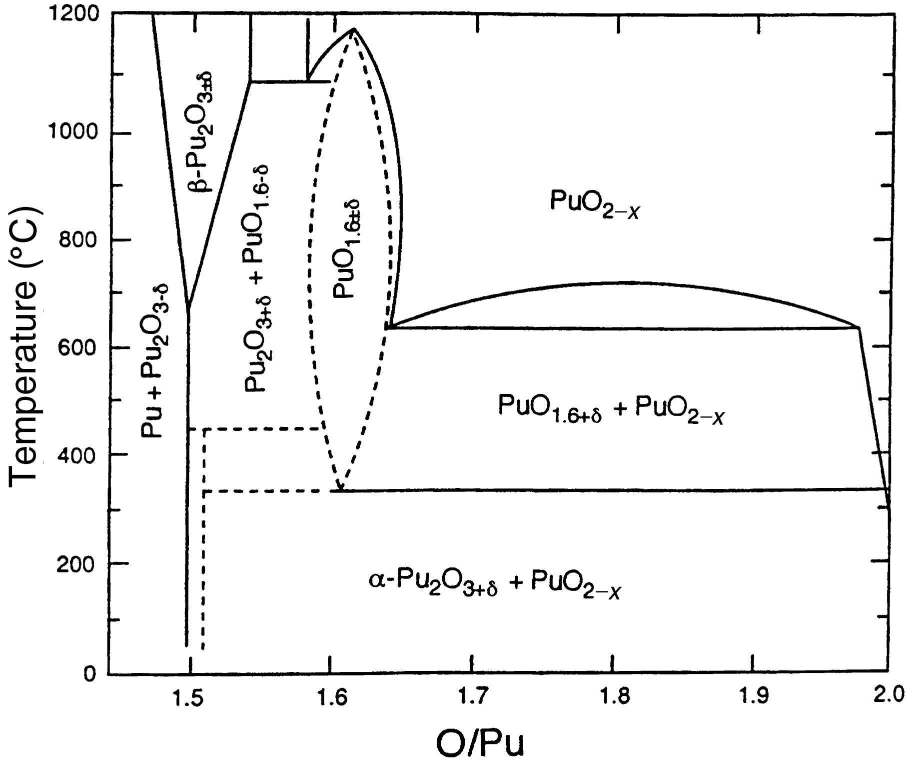

Figure 1. Phase diagram for the plutonium–oxygen system (based on the assessment by Wriedt[13]).

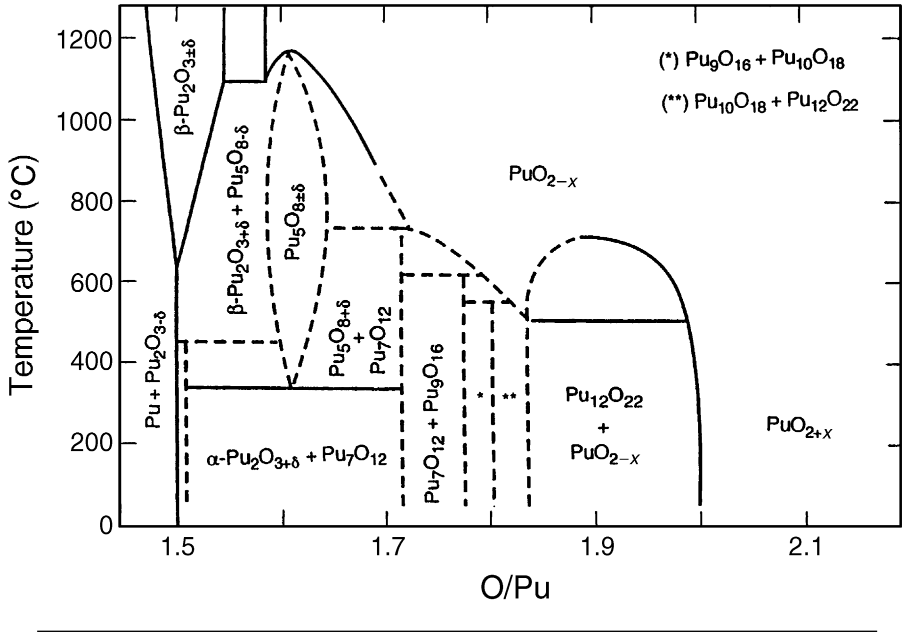

Figure 2. Revised phase diagram for the plutonium–oxygen system (combined information from high-temperature data and oxygen titration data between 25–350°C).

versible near 600°C.[18,19] However, a similar transformation process may be sluggish at lower temperatures (e.g., the transition of Pu_2O_3 phases), given the kinetic energy needed to rearrange metal atoms. Alternative interpretations are also possible. These include (1) the formation of a cubic sesquioxide during autoreduction of PuO_2 at 150–200°C; (2) the coexistence of this product with the metal;[21] (3) the formation of cubic $PuO_{1.46\pm0.04}$ at 23°C;[23] and (4) the formation of $PuO_{1.52}$ during cooling of structurally related $PuO_{1.6}$ and PuO_{2-x}.[17] Formation of the cubic sesquioxide seems to be kinetically favored, if the Pu sublattice of the parent phase has cubic (fcc) symmetry.

A cubic plutonium sesquioxide is formed at low temperatures by facile movement of anions in the preexisting fcc metal lattice; after formation, the phase cannot transform into β-Pu_2O_3 unless the temperature is above 450°C. Although the recent phase diagram for plutonium oxides may be correct, it is inconsistent with known relationships of isomorphous lanthanide oxides and with behavior indicating that cubic Pu_2O_3 is either stable or metastable at low temperatures. The cubic sesquioxide appears to catalyze reactions of plutonium with hydrogen to form hydride and with oxygen to form dioxide.[8,45] Intermediate oxides similar to those known for the cerium-, praseodymium- and terbium-oxygen systems[18,19] are not observed, as the formation of the dioxide is favored kinetically when the sesquioxide is exposed to oxygen.

Effects of kinetics factors in establishing the equilibrium diagram of Pu-O are also suggested by results of oxygen titration experiments, where H_2O was used for the controlled oxidation of plutonium metal to the dioxide at room temperature over a one-year period.[22,23] The quantity of hydrogen formed, and the time-dependence of the H_2/Pu ratio (which defines the O/Pu ratio in the solid product) were used to monitor the extent of reaction. The H_2/Pu ratio time data show a sequence of well-defined linear segments resulting from generation of H_2 at progressively slower constant rates, a behavior consistent with sequential free-energy-controlled reactions that must be completed before the next reaction begins. The reactions correspond to sequential formation of the PuOH and $Pu_7O_9H_3$ oxide-hydrides, Pu_2O_3, members of the Pu_nO_{2n-2} homologous series ($n = 7$, 9, 10, and 12), PuO_2, and the PuO_{2+x} phases. Absence of O_2 in the gaseous product shows that the pressure rise is not driven by the radiolysis of water. The terminal product obtained, $PuO_{2.265}$, had a fluorite structure with a lattice parameter $a_0 = 0.5404(1)$ nm; it decomposes upon heating to 500°C in vacuum to form PuO_2 [$a_0 = 0.5395(1)$ nm].

Results of these $PuO_2 + H_2O$ reactions[22,23] suggest that the equilibrium phase diagram is significantly more complex than indicated by Figure 1. Proposed phase relationships for O/Pu within the 1.5–2.0

range and at temperatures below 700°C in Figure 2 are derived by analogy to those of the praseodymium–oxygen system, in which the corresponding intermediate oxides are well known.[18,19] It should be emphasized that formation of the different phases in the plutonium–oxygen system can be strongly dependent on the experimental method used and the kinetic behavior of the materials involved.

Plutonium Corrosion

The corrosion chemistry and reactivity of plutonium during storage is an important aspect of plutonium technology with relevance to the safe handling and storage of plutonium metal and its alloys. It is also important with regard to mechanisms for the dispersal of plutonium into the environment.[26,44] Amassive form of oxide-free solid metal is essentially nondispersible and presents a lower risk than powdered (fine) materials, which have a greater probability of igniting and of becoming airborne. Mechanical pressures generated by the corrosion of plutonium metal are known to have ruptured sealed storage containers.[8] The hazard posed by plutonium oxides formed by corrosion depends on several factors. These include the corrosion rate that produces the oxide, the size distribution of particles formed, and the time interval for the corrosion (from periods of an hour or less for accidents, and up to decades for materials in storage).

The perplexing nature of plutonium corrosion is indicated by a discussion of factors associated with changes in the metal's reactivity.[26] Observations suggest that moisture can be a more important factor than temperature. Corrosion can be rapid in moist helium or argon, and moisture offers a greater potential for corrosion than dry oxygen. Kinetics data for pure, unalloyed plutonium metal in the presence of moisture show paralinear behavior, where an initial parabolic stage (consistent with diffusion control) of the reaction of the product layer is followed by a slow, constant-rate (linear) stage of reaction and then by a more rapid linear stage.

Pronounced decreases in the corrosion rate of plutonium metal are found near 200°C (where the transition from the β-phase to the γ-phase occurs) and also near 400°C. The corrosion rate is also reduced by alloying and is markedly reduced for the fcc, δ-phase gallium alloys (containing a few percent of gallium) of plutonium compared to the monoclinic, α phase of the pure metal. Corrosion can occur by different reactions during storage of bulk plutonium in sealed containers; in such cases, the resulting plutonium metal (fines) often has a greater surface area and increased tendency to ignite spontaneously if exposed to air (see subsequent discussion).

Atmospheric corrosion of plutonium metal is dependent on the diffusion of oxygen through an adherent dioxide layer during reaction with dry air or oxygen, as demonstrated by the parabolic dependence of the corrosion rate on the reaction time.[12] The rate is found to be inversely proportional to the thickness of the product layer. Similarly, UO_{2+x} (with $x < 0.25$) is the only product obtained by the reactions of uranium metal with dry air and flowing water vapor, which prevents accumulation of hydrogen near the metal's surface. Plutonium chemistry may be similar in this regard. Data for kinetics studies of the corrosion of plutonium by air and water vapor show a paralinear time-dependence and have been examined on the basis of each allotropic form of the metal.[11] The nature of the linear stage of reaction is especially important, as only a thin (micrometers thick) oxide layer forms during the parabolic stage, and most corrosion occurs during a constant-rate process. The linear behavior of the rate is explained by formation of an intact inner oxide layer and a porous outer oxide layer.[46] Mechanisms proposed for rate enhancement by water include participation of a reactive PuH_2 intermediate and the rapid diffusion of OH^- ions through the oxide diffusion barrier.

The corrosion kinetics of plutonium metal and its alloys has been reviewed previously,[26] and an assessment of kinetics data and proposed mechanisms has been published.[45] In addition, studies of oxide properties and the kinetics of their formation have been described,[11,12] and the ignition/pyrophoric nature of plutonium metal has been discussed.[26,47]

Substantial progress toward understanding plutonium corrosion resulted from a series of careful kinetics studies.[47–52] Several observations reported in earlier work were addressed by measuring rates for unalloyed plutonium in dry air, moist O_2-N_2 mixtures, and moist N_2 at 90°C.[48] Tests were conducted with Pu samples that were prepared by rolling and casting techniques and that contained different levels of impurities due to radioactive decay. Results showed that PuO_2 was the only product; PuH_2 was not detected. Kinetics data suggest that the corrosion rate is not appreciably altered by impurities, radiation damage, or even differences induced by casting or rolling, although microcracks in the cast metal caused uneven corrosion (pitting). The corrosion rate is markedly enhanced by moisture, with oxidation being slightly faster in moist O_2-N_2 (or air) mixtures than in moist N_2 alone, not fully in accord with reports of rapid corrosion in moist inert atmospheres. Assessment of the chemical and kinetics data suggests that diffusion of reactive gases through an oxide layer of constant thickness is most likely responsible for the observed linear corrosion rate.[53]

Literature data for reactions of unalloyed metal with oxygen and water vapor at 25–400°C show that moisture-enhancement of the corrosion rate in air is confined to a rate-temperature envelope,[54] as suggested in Figure 3. The upper boundary of this envelope is defined by the Arrhenius equation for corrosion by the equilibrium vapor pressure of water vapor (e.g., pressure as a function of temperature) and at 0.2 bar pressure of O_2 (e.g., air). The lower boundary is fixed by the Arrhenius equation for reaction in dry (<0.5 ppm H_2O) air. This envelope is closed by intersection of these regions at −25°C and by a sharp decrease in the Pu + H_2O rate between 110°C and 200°C (attributed to a mechanism change that eliminates enhancement by moisture). Corrosion rates and activation energies within the envelope are independent of O_2 pressure, but vary systematically with the square root of the vapor pressure of water.

The chemistry of moisture-enhanced corrosion in air[55] corresponds closely with the formation of PuO_{2+x} by the water-catalyzed $PuO_2 + O_2$ reaction. Formation of PuO_{2+x} by that reaction at the gas–oxide interface increases the oxygen gradient and promotes diffusion of oxygen through the oxide layer to the oxide–metal interface. This interpretation is supported by identification of PuO_{2+x}, PuO_2, and α-Pu_2O_3 in succession between the gas–oxide and oxide–metal interfaces of a metal sample reacted with water vapor at 250°C.[38]

A mechanism for accelerated oxidation by water vapor or moist air has been proposed,[46] but its validity remains uncertain. Mechanisms that involve transport of hydrogen or hydroxide to the product–metal interface and the return of hydrogen to the gas–solid interface do not seem credible.[53] The hydride is stable, with an equilibrium hydrogen pressure of only 70 nanobar at 300°C,[54] and it must appear as the major product, if these mechanisms are correct. However, only small amounts of hydride are found in the interface at 250°C.[38]

A spallation-type process that maintains a constant thickness of an oxide layer has also been proposed, and an empirical relationship defining the thickness of such an adherent oxide infusion layer as a function of reaction temperature has been described.[56] The rate-limiting phase is probably a stoichiometric dioxide and not a bcc Pu_2O_3. Alikely enhancement mecha-

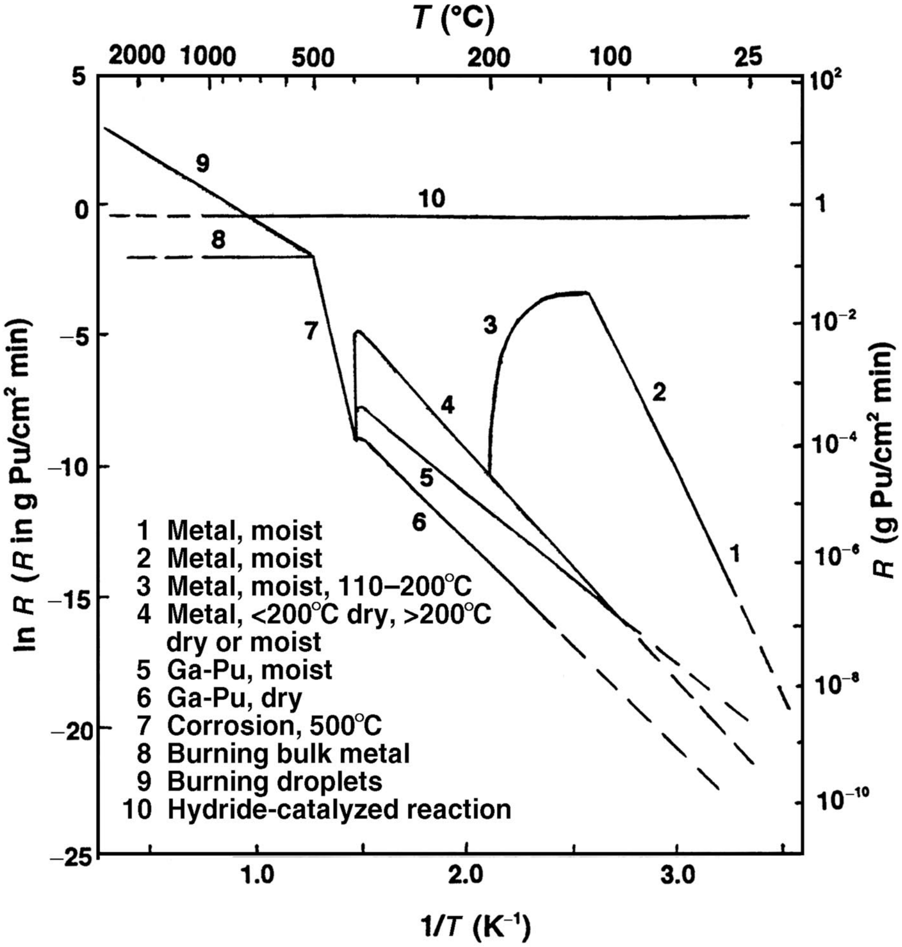

Figure 3. Arrhenius-type plot for the corrosion rate R *of both pure and alloyed plutonium metal in dry (<0.5 ppm water) and moist (0.2 bar water vapor) air atmospheres (from Reference 45). Curve 1, metal in air with moisture at the equilibrium pressure fixed by temperature; Curve 2, metal with moist air; Curve 3, metal at 110–200°C with moist air; Curve 4, metal <200°C with dry air and >200°C with either dry or moist air; Curve 5, Ga-Pu alloy with moist air; Curve 6, Ga-Pu alloy with dry air; Curve 7, corrosion at 500°C (independent of moisture or alloying); Curve 8 is for burning bulk metal in static air (temperature-independent); Curve 9 is for burning, free-falling droplets of metal in air; and Curve 10 represents the temperature-independence of the rate in air when a hydride-catalyzed reaction is involved.*

nism suggested by the occurrence of the water-catalyzed reaction is that water increases the rate by increasing the oxygen gradient across a constant thickness of oxide by forming PuO_{2+x} at the gas–solid interface.[8,53]

The increased chemical reactivity of metal stored in sealed containers is consistent with the emerging chemistry of plutonium with oxygen and water.[8,36,44,53] If moisture and air are present, the pressure in the container first decreases as oxygen reacts via the water-catalyzed cycle, then increases at the identical rate as hydrogen is formed by the metal-plus-water reaction, and then decreases as the hydrogen reacts to form a hydride.[57] An autoreduction process transforms the dioxide layer on metal to α-Pu_2O_3 during extended storage. Upon exposure to air or oxygen at a pressure of 1 bar, surface layers of the sesquioxide and $PuH_{2\pm x}$ catalyze the reaction of plutonium with nitrogen and oxygen (~air) at a rate of ~6 cm/h; with oxygen, oxidation is intense at ~0.3 meters/h.[45] These reactions may be sufficient to ignite chips or fines of the plutonium metal, which have very high surface areas.

Although plutonium metal reacts slowly with distilled water,[10] formation of a plutonium monoxide monohydride is accelerated in salt solutions containing Cl^-, NO_3^- ,SO_4^{2-} or other anionic species.[22,23,53] The rate is accelerated by the presence of cations that hydrolyze to form H^+ and is slowed by increasing the pH above 7. Kinetics data for 25–100°C give an activation energy of 29 ± 4 kJ mol^{-1} for the metal-plus-water reaction.

Concluding Comments

Understanding the chemistry and acquisition of scientific data for plutonium oxides and related products remains as important today as it has been in past decades. Although the focus and the specific knowledge sought regarding these materials may have shifted since the discovery of this element, new scientific data and knowledge continue to be essential. Large amounts of plutonium exist, and it is critical that its existence be addressed. Plutonium is a valuable material, certainly in the sense of being a potential source of energy, but even its disposition as a waste will require careful consideration.

It is essential that the critical parameters be well defined and understood for safely handling, storing, disposing of, and using this element. The migration behavior of plutonium presently in the environment, or plutonium that might be released accidentally into the environment, are additional important issues that will require study. The data from studies involving plutonium are also important for developing rational models to consider various potential scenarios that may be encountered with plutonium materials. Clearly, additional studies are needed to be able to understand and control the complex chemistry of plutonium and to establish fully its fundamental science and technological applications.

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