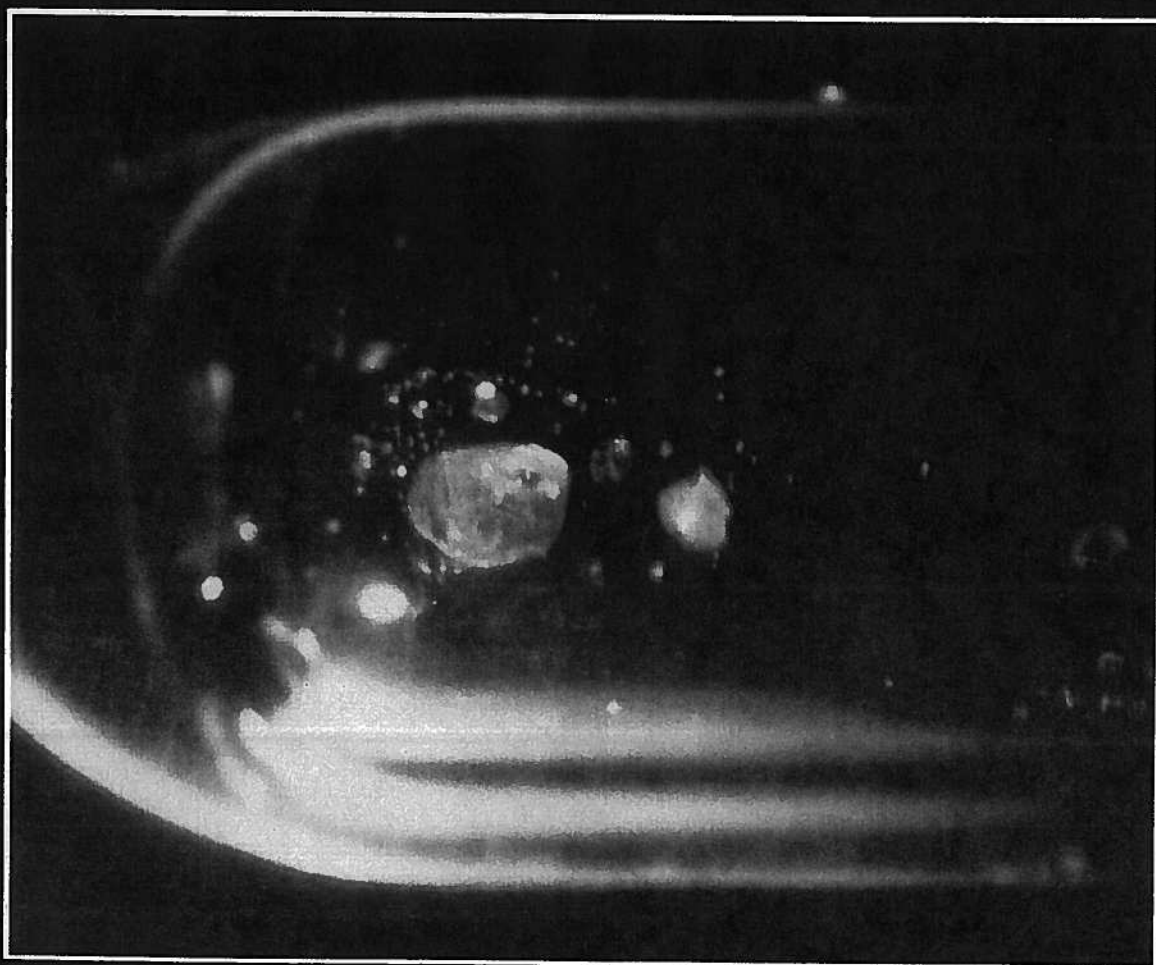# The Chemistry of the
Actinide Elements

SECOND EDITION

EDITED BY

J.J. Katz, G.T. Seaborg and L.R. Morss

Volume 2

THE CHEMISTRY OF THE
ACTINIDE ELEMENTS

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Volume 1

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7.8 PLUTONIUM IONS IN SOLUTION*

The solution chemistry of plutonium is unique in many ways. The element displays five oxidation states in aqueous solution: $Pu(III)$, $Pu(IV)$, $Pu(V)$, $Pu(VI)$, and $Pu(VII)$. The lower four oxidation states coexist in dilute aqueous acids, and sometimes all four are present simultaneously in substantial quantities. In the laboratory and in manufacturing operations, it is more common to find one of $Pu(III)$, $Pu(IV)$, or $Pu(VI)$ predominating, however. The community of actinide chemists was treated to a surprise when, in 1967, Krot and Gel'man announced the identification of heptavalent plutonium in alkaline solutions [1169].

The lowest oxidation state of plutonium encountered in solution is the trivalent cation Pu^{3+}, a cation that imparts a blue color to its solutions and is similar to the rare earth neodymium in many of its hydrolysis, complexation, and compound-forming properties. Trivalent plutonium can be oxidized by a variety of oxidants to the tetravalent cation Pu^{4+}, a cation that usually imparts a brown color to dilute, non-complexing acids, but appears green in 7 M nitric acid due to the formation of nitrate complexes. Like other tetravalent cations, it hydrolyzes very easily, forming $PuOH^{3+}$ as the first hydrolysis product, and finally the insoluble green hydrous oxide, $Pu(OH)_4$ (or $PuO_2 \cdot nH_2O$). A polymeric colloidal form of this hydrous oxide is also known and is called 'plutonium polymer'. Oxidation of the tetravalent cation in aqueous solution produces hexavalent plutonium, PuO_2^{2+}, a cation that imparts a yellow or orange color to its solutions. Careful reduction of hexavalent plutonium in dilute acids produces pentavalent plutonium, PuO_2^{2+}, a cation that imparts a pink or light purple color to its solutions. This cation is not encountered as the predominant species in the acids customarily used for working plutonium because it disproportionates into a mixture of oxidation states in which it is generally the least abundant component. However, it is always present in dilute acids that contain more than one oxidation state of plutonium. It should be noted that reports of the colors of plutonium ions are not always in agreement. There are several reasons for this apparent discrepancy, including the complexes formed in various acids, normal variations in color perception, and the fact that no attempt seems to have been made to describe the colors of ions under standard conditions of illumination or to locate the ions in a chromaticity diagram. The ions are described in Table 7.95.

The discovery of heptavalent plutonium by Russian workers in 1967 resulted from the suspicion that the electrons present in the incomplete f shells of the cations NpO_2^{2+} and PuO_2^{2+} (not present in UO_2^{2+}) could be removed if sufficiently vigorous oxidizing conditions could be obtained. Success was realized in alkaline solutions of the hexavalent elements subjected to ozonization. The first

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* The introductory paragraphs to Section 7.8 and the text of sections 7.8.5 and 7.8.6 were written by G. L. Silver, Mound Facility, Monsanto Research Corporation, Miamisburg, Ohio, USA. Section 7.8.7 was edited by T. W. Newton, Los Alamos National Laboratory, Los Alamos, New Mexico, USA.

(b) Am(III)

The trivalent state of americium is the stable aqueous oxidation state. Although americium is the homolog of europium, the Am^{3+} radius (0.975 Å) is closer to that of Nd^{3+} (radius 0.983 Å) [76]. It is a convenient 'rule of thumb' that the radii of the light lanthanide ions are nearly identical to the radii of the corresponding actinides shifted three elements to the right in the periodic table, e.g. $r(La^{3+}) \simeq r(U^{3+})$. In some early purification schemes, fission-product promethium accompanied americium. Am(III) is precipitated by hydroxide, fluoride, phosphate, and oxalate ions from aqueous solution.

Désiré *et al.* [231] calculate for the first hydrolysis constant, $K_1 = [MOH^{2+}][H^+]/[M^{3+}] = 1.2 \times 10^{-6}$, and Shalinets and Stepanov [233] report $K_2 = [MOH^{2+}][H^+]/[M^{3+}]K_w = 5 \times 10^{10}$.

Contrary to such simple representations, Korotkin and others [234, 235] state that Am^{3+} hydrolysis is complicated, starting at pH values as low as 0.5–1.0 and dependent on the nature of other cations (e.g. Li^+, Na^+, and H^+) that may be present.

From diffusion measurements, Fourest *et al.* [361] have determined the hydration number of Am^{3+} to be 13 and the hydrated Am^{3+} radius to be 4.52 Å. They found that the hydrated Am^{3+} parallels its lanthanide homolog Eu^{3+}. (Hydrated radii increase as a function of atomic number in both the lanthanide and actinide series because increased covalency increases the number of water ligands.)

(c) Am(IV)

Tetravalent americium is unstable in non-complexing mineral acid solutions. Aqueous solutions of tetravalent americium were first prepared by Asprey and Penneman [140] by dissolution of $Am(OH)_4$ in concentrated solutions of ammonium fluoride. In 13 M NH_4F at 25°C the solubility of Am(IV) is 0.02 M, giving a rose-colored solution. Ozone oxidizes Am(IV) in 13 M NH_4F to Am(VI), whereas iodide reduces it to Am(III). Reduction of Am(IV) to Am(III) occurs spontaneously because of alpha-radiation effects. Yanir *et al.* [261] have demonstrated that Am(IV) is stable in phosphoric acid and pyrophosphate media. Myasoedov *et al.* [236] report that pure Am(IV) is obtained in 8–15 M phosphoric acid by anodic oxidation. In lower phosphoric acid concentrations some Am(VI) is formed. Similar results were obtained with an oxidizing mixture of Ag_3PO_4 and $(NH_4)_2S_2O_8$; with 94% ^{243}Am, the half-life for reduction is 20 h. Saprykin *et al.* [357] and Kosyakov and co-workers [317, 358] have stabilized Am(IV) by heteropolyanions and find that the reduction to Am(III) is caused solely by radiolytic effects. An approximate value of 10^9 for the formation constant β of $Am(P_2W_{17}O_{61})_2$ has been reported [230]. Produced by pulse radiolysis, the occurrence of transient Am(IV) has been observed [356]. Hobart *et al.* [362] report the stabilization of Am(IV) in alkali-metal carbonate media. Electrolytic

oxidation of Am(III) in 2–5.5 M carbonate solutions results in a dark red-brown Am(IV) carbonate complex which is stable to disproportionation.

(d) Am(v)

Oxidation of Am(III) yields only Am(VI) in acid solution but both Am(V) and Am(VI) in alkaline solution. Solutions of Am(V) are conventionally prepared by oxidation of Am(III) (which is soluble in alkali carbonate media) with ozone [112], peroxydisulfate [111], or hypochlorite ion [116], or by electrolysis [362]. Various insoluble carbonates containing Am(V) are precipitated [348]; these yield solutions of AmO_2^+ (usually containing several percent Am^{3+}) upon dissolution in dilute acid. Americium(V) solutions free of Am(III) can be prepared by intermediate preparation of Am(VI) in 2 M Na_2CO_3 solution [114]. After 5% ozone is bubbled through the solution for 1 h at room temperature to oxidize Am(III) to Am(VI), $NaAmO_2CO_3$ is precipitated by heating the solution for 30–60 min at 60°C and the precipitate is then dissolved in dilute acid.

Hara [237] prepared perchlorate, sulfate, and acetate solutions containing AmO_2^+ free of Am^{3+} by first extracting AmO_2^+ from buffered 1 M acetate (pH ~ 3) solutions of Am(III) and Am(V) into 0.1 M thenoyltrifluoroacetone in isobutanol and back-extracting the Am(V) into an aqueous phase. More exotic methods for obtaining the AmO_2^+ ion in aqueous solution include dissolution of solid Li_3AmO_4 in dilute perchloric acid or the electrolytic oxidation of Am(III) in 2 M $LiIO_3$/0.7 M HIO_3 (pH 1.47) solution [3].

(e) Am(vi)

In dilute, non-reducing acid solutions, powerful chemical oxidants such as peroxydisulfate and Ag(II) oxidize both Am(III) and Am(V) to Am(VI); these oxidants were used in the discovery of Am(VI) [198]. Peroxydisulfate, however, will not oxidize Am(III) to Am(VI) completely at acidities above about 0.5 M, since acid hydrolysis of $S_2O_8^{2-}$ interferes [9]. In perchloric acid solution, Ce(IV) oxidizes Am(V) to Am(VI) but only partly oxidizes Am(III) to Am(VI) [9]. Similarly, ozone readily oxidizes Am(V) to Am(VI) in heated nitric or perchloric acid solution but will not oxidize Am(III) to Am(VI) in acid media. Electrolytic oxidation of Am(III) in 2 M H_3PO_4, in 6 M $HClO_4$ [236], or in 2 M Na_2CO_3 [362, 363] produces the AmO_2^{2+} ion [236], as does peroxydisulfate in dilute phosphotungstate solutions [317].

Ozone or peroxydisulfate oxidation of either Am(III) or Am(V) in aqueous sodium carbonate or bicarbonate yields an intensely colored red-brown solution thought to contain a carbonate complex of Am(VI) [114]. This same complex is also obtained by dissolution of solid sodium americyl acetate in sodium carbonate solutions. Nugent [238] speculates that an Am(VII)–carbonate complex may actually be present in such solutions. Americium(VI) in 0.1–0.5 M $NaHCO_3$

decomposition of these intermetallic compounds [43]. The dhcp form of curium has also been prepared by reducing the dioxide or sesquioxide with thorium metal, followed by volatilization and condensation of the curium metal vapor on a tantalum condenser [29, 30, 47].

9.5.3 Chemical properties of the metallic state

Metallic curium appears to be even more susceptible to corrosion than the earlier actinide elements, a property due at least in part to radioactive self-heating. The metal dissolves rapidly in dilute acid solutions and its enthalpy of solution has been measured in HCl (aq) [44, 164]. The metal reacts with hydrogen at 200–250°C to give fcc CmH_{2+x} ($a = 5.344$ Å) [45]. Recently hexagonal $CmH_{3-\delta}$ also has been reported [173]. The metal surface rapidly oxidizes in air to form a film, which may begin as CmO [27, 161, 162], progresses to Cm_2O_3 at room temperature, and further to CmO_2 at elevated temperatures. The metal is pyrophoric when finely divided.

The direct reactions of curium metal with non-metals such as P, As, Sb, S, and Se have been reported, and binary compounds with N, P, As, and Sb have been prepared by reactions using curium hydride (see next section) [31, 46, 47].

9.6 SIMPLE AND COMPLEX COMPOUNDS

9.6.1 General

Curium is the actinide element of highest atomic number (96) for which multigram quantities are available for chemical study. Even so, special micro-chemical techniques are necessarily applied to most studies with the 18 year α emitter [244]Cm and the 163 day α emitter [242]Cm. The 3.4×10^5 year isotope [248]Cm, only recently available in milligram quantities, greatly facilitates chemical progress with this element.

The most important chemical characteristic that distinguishes curium from the lighter actinides is the great stability of the 3 + state with respect to oxidation or reduction. The stability of Cm(III) has been attributed to the relative stability of a half-filled ($5f^7$) configuration, an observation which, in turn, has been used as a key argument in favor of the actinide hypothesis. The predominance of the 3 + state causes a chemical resemblance to lanthanides.

In contrast to americium, the oxidation of Cm(III) to Cm(IV) is achieved only with the strongest oxidizing agents and only one report [48] claims evidence for an oxidation state greater than IV. Transient divalent and tetravalent states have been observed in aqueous perchlorate media using pulse radiolysis techniques [49]. Attempts have been made to induce Cm(III)–Cm(IV) oxidation chemically (using ozone [50] and perxenate [51]) or electrochemically [52]. These early attempts have failed, an effect clearly not attributable solely to radiolytic reduction.

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Recently, however, formation of a red Cm(IV) complex in phosphotungstate solution was achieved by the use of peroxydisulfate as the oxidant [53]. Kosyakov *et al.* [54] demonstrated that in such solutions the Cm(IV) is reduced much faster than can be accounted for by radiolytic effects, while Am(IV) in such solutions is much more stable, being reduced at a rate attributable to radiolytic effects alone. No value for the $E°(Cm^{4+}/Cm^{3+})$ is known but from existing data it is substantially more positive than $E°(Am^{4+}/Am^{3+})$ and probably about as positive as $E°(Pr^{4+}/Pr^{3+})$. The recent success of generating soluble carbonate solutions of Pr(IV) suggests that similar soluble Cm(IV) species may be prepared [55]. All known Cm(IV) compounds are either fluorides or oxides, but a broader chemistry has been developed for Cm(III).

With the more common isotopes ^{242}Cm and ^{244}Cm, intense α self-irradiation and heating effects cause aqueous-solution instability (peroxide is always present) and solid-state instability (lattice changes and compound alteration). In some cases these effects are sufficiently large that certain compounds may be identified in bulk only with the more stable isotope, e.g. ^{244}CmF$_4$ and ^{248}Cm(π-C$_5$H$_5$)$_3$ [21, 57].

9.6.2 Halides

To date, the halides represent by far the most extensively characterized class of curium compounds (refer to Table 9.2). The complete CmX$_3$ series (X = F, Cl, Br, I), as well as CmF$_4$ and several complex Cm(IV) fluorides, have been prepared and studied. Several reviews deal specifically with actinide halides and for further information (especially for cross-comparisons of Cm with other actinide halides) the reader is referred to these articles [2, 3, 58, 59].

Curium trifluoride is a white, sparingly soluble (~ 10 mg l^{-1}) compound [60] with the LaF$_3$ structure, which precipitates when fluoride ion is added to weakly acidic Cm(III) solutions (or HF to Cm(OH)$_3$). The anhydrous trifluoride is obtained by desiccation over P$_2$O$_5$ or by treatment with hot HF(g). Lattice constants of $a = 7.019$, $c = 7.198$ Å and $a = 7.014$, $c = 7.194$ Å for trigonal CmF$_3$ have been reported using ^{244}Cm and ^{248}Cm, respectively [61]. The trifluoride metals at $1406 \pm 20°C$ and has an estimated standard entropy of 121 J K^{-1} mol^{-1} at 298 K [60, 63]. Curium has an irregular tricapped trigonal prismatic coordination in CmF$_3$ [2].

Magnetic susceptibilities of Cm(III) compounds have been reported by several authors. A recent determination gave an effective magnetic moment of 7.65 ± 0.1 μ_B for Cm^{3+} in CmF$_3$, CmOCl, and 5.6 mol % Cm^{3+} in LaF$_3$ [36, 64]. This value indicates a significant departure from Russell–Saunders coupling. Electron paramagnetic resonance experiments on several Cm^{3+} samples (doped into CaF$_2$ [65], ThO$_2$ and CeO$_2$ [66], and LaCl$_3$ and lanthanum ethylsulfate [67]) revealed a single-line spectrum and not a seven-line spectrum as earlier reported, which was apparently due to a Gd^{3+} impurity. Crystal field splittings for the nominally ^{8}S$_{7/2}$ Cm^{3+} ion are about 250 times larger than for Gd^{3+}, a