

Higher Oxidation States of Americium: Preparation, Characterization and Use for Separations

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1. INTRODUCTION

Today, there is a renewed worldwide interest in nuclear power, and this has initiated renewed research and development efforts for advanced nuclear fuel cycles. Responsible nuclear waste management and efficient use of uranium resources will almost certainly result in the recycling of used nuclear fuel. Current approaches

would partition americium to be transmuted to short-lived fission products in fast reactor fuel, rather than interring it in a high-level waste repository. Consequently, methods to separate americium from the lanthanides and higher actinides, a historically problematic separation, are being sought to be implemented on the process scale. There are two main approaches being investigated in those countries in Asia, Europe, and North America that are interested in reprocessing nuclear fuel. One approach is the use of soft-donor ligands that preferentially complex the actinides in favor of the lanthanides. The other approach is to utilize higher oxidation states of americium (i.e., IV, V, or VI) that exhibit solution chemistries quite different than that of the predominantly trivalent lanthanides and curium.

Isotopes of americium, element number 95, are produced in nuclear power reactors as a byproduct of the irradiation of uranium with neutrons. The amount of americium generated in the fuel depends greatly on the reactor type, the nature of the fuel irradiated, and the irradiation parameters for burn-up, the amount of americium formed in neutron-irradiated UO₂ fuel is generally small compared to the plutonium fraction. The main americium isotopes in used nuclear fuel are ²⁴¹Am (*t*_{1/2} = 423.7 years), ^{242m}Am (*t*_{1/2} = 141 years), and ²⁴³Am (*t*_{1/2} = 7380 years).¹ Croff calculated about 0.06 wt % americium isotopes to be present at discharge in neutron-irradiated UO₂ fuel.² With time the activity of most of the americium isotopes declines, however, ²⁴¹Am builds up because of the decay of ²⁴¹Pu.^{2,3} As an example, after 10 years of decay, Binney and co-workers calculated that used, but nonreprocessed nuclear fuel from pressurized water reactors contains 594 g of americium per metric ton uranium (503 g of ²⁴¹Am/MTU, 0.66 g of ^{242m}Am/MTU, and 90.6 g of ²⁴³Am/MTU).⁴ Americium isotopes are a part of the minor actinide fraction in used nuclear fuel that must be partitioned from the other actinides and fission products for transmutation or waste disposition.

Americium is located near the middle of the 5f-series of the actinide elements, and its redox chemistry is far less rich than that of the preceding actinides neptunium and plutonium. In general, the aqueous solution chemistry of americium is determined by its common +III oxidation state, which is in close analogy to its chemical lanthanide congener europium. The trivalent valence is normally encountered unless special efforts are made to oxidize the element to its higher oxidation states Am(IV), Am(V) and Am(VI), which were discovered in the 1950–1960s. By the end of the 1960s the descriptive chemistry of oxidized americium had been characterized, and the ions were known to exist as Am⁴⁺, AmO₂⁺, and AmO₂²⁺, analogous to the behavior of uranium,

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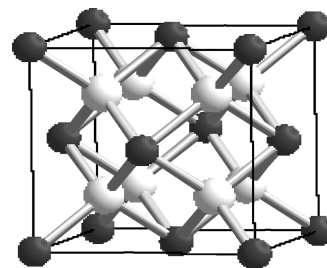
Table 1. Most Common Routes to Synthesize Am(IV), (V), and (VI)

oxidation state	conditions	starting material	ref
Am(IV)	0.6 M NaOCl in 0.2 M NaOH	Am(OH) ₃	6
	dissolution in 13 M NH ₄ F	Am(OH) ₄	7
	electrochemical (16 mA/2 V) in 10–15 M H ₃ PO ₄	Am(III)	8
	0.01 M Ag ₃ PO ₄ /0.05 M (NH ₄) ₂ S ₂ O ₈ in 12 M H ₃ PO ₄	Am(III)	9
	0.1 M K ₂ S ₂ O ₈ and excess K ₁₀ P ₂ W ₁₇ O ₆₁ at 98 °C	Am(III)	10
	10 ^{−4} M AgNO ₃ /0.03 M (NH ₄) ₂ S ₂ O ₈ and excess K ₁₀ P ₂ W ₁₇ O ₆₁ in 1 M HNO ₃	Am(III)	11
	0.5 M KBrO ₃ or 0.2 M K ₂ Cr ₂ O ₇ and excess K ₁₀ P ₂ W ₁₇ O ₆₁ in <6 M HNO ₃ or <3 M H ₂ SO ₄ or <1 M HClO ₄	Am(III)	12
	Np(VII) in 1.5 M KHCO ₃	Am(III)	13
	XeF ₂ at 0 °C in 1.5 M KHCO ₃	Am(III)	13
	dissolution in K ₂ CO ₃ /KOCi at 80 °C	Am(III)	14
	Radiolysis of ²⁴¹ Am in NaCl/Na ₂ CO ₃	Am(III)	15, 16
	Ozone in 2 M Na ₂ CO ₃ at 90 °C, precipitates as NaAmO ₂ CO ₃	Am(III)	17
	Ozone or S ₂ O ₈ ^{2−} in carbonate solution (followed by dissolution in 0.1 M HClO ₄)	Am(III)	18
Am(V)	NaBiO ₃ at 80 °C in HNO ₃	Am(III)	19
	ozone in 0.1 M NaHCO ₃ or 2 M Na ₂ CO ₃ at room temperature	Am(III,V)	17
Am(VI)	ozone in 0.1 M HClO ₄	Am(V)	18
	NaBiO ₃ at room temperature in HNO ₃	Am(III)	19
	excess (NH ₄) ₂ S ₂ O ₈ in 0.1 M HNO ₃ at 85 °C	Am(III)	20
	heating Na ₂ S ₂ O ₈ in 0.1 M NaHCO ₃	Am(III)	17
	0.01 M Na ₂ S ₂ O ₈ in 2 M Na ₂ CO ₃ at 90 °C	Am(III)	17
	~0.5% AgNO ₃ /2.5% (NH ₄) ₂ S ₂ O ₈ in 0.3 M HNO ₃	Am(III)	8
	electrochemical in 6 M HClO ₄	Am(III)	20
	0.013 M CsSO ₄ F/0.001 M Ag ⁺ in 0.9 M HNO ₃	Am(III)	21
	Na ₄ XeO ₆ /Ag ⁺ in 1 M HNO ₃	Am(III)	22

neptunium, and plutonium.⁵ Analytical-scale separations were designed to partition americium from the trivalent lanthanides and higher actinides (i.e., curium), usually by peroxydisulfate oxidation of Am(III) to Am(VI) and precipitation of the trivalent metals with fluoride. Except for their occasional use in analytical radiochemistry, the higher oxidation states of americium were largely forgotten, until recently. Given the renewed interest in closing the nuclear fuel cycle and the importance of the chemistry of high-valent americium for minor actinide partitioning, this paper reviews the preparation, characterization and solution chemistry of Am(IV), Am(V), and Am(VI), with special emphasis on their utility in separations.

2. PREPARATION OF HIGHER VALENCE STATES

Compounds with americium in four oxidation states, III, IV, V, and VI, have been reported as quite stable in many inorganic and organic environments. Evidence for the existence of Am(II) has been reported only for extremely reducing conditions, and thus is not the subject of this review. In general, americium can form five oxidation states (III, IV, V, VI, and VII) in alkaline solutions, while in acid only Am(III) and Am(V) and to some extent Am(VI) are stable. Table 1 summarizes the most common routes to prepare the higher oxidation states of americium. Tetravalent americium rapidly reduces, but has been stabilized successfully in the presence of complexing ligands such as phosphate, fluoride, polytungstate, or carbonate. In its IV oxidation state, americium forms hydrated or complexed highly charged Am⁴⁺ ions, while in the V

Figure 1. Unit cell of AmO₂.

and VI oxidation states the bare cations are unstable and hydrolyze to form the linear *trans*-dioxo americyl cations, AmO₂⁺ and AmO₂²⁺, respectively.

2.1. Americium(IV)

Tetravalent americium was first prepared in the solid state as the compounds AmO₂, AmF₄, and KAmF₅. Orange-pink crystals of orthorhombic Rb₂AmF₆ form in concentrated aqueous fluoride solutions with RbAmO₂F₂ or Am(OH)₄.²³ The Am(V) in the fluoride RbAmO₂F₂ is reported to be reduced overnight to Rb₂AmF₆ in acidic RbF solutions. In 1949, Zachariasen reported the dioxide, AmO₂ (Figure 1) as the first identified compound of americium.^{24,25} It can be prepared by heating americium hydroxide, carbonate, oxalate, or nitrate, in air or oxygen at temperatures of 600–800 °C.^{26–29} The monoclinic AmO₂ is isostructural with

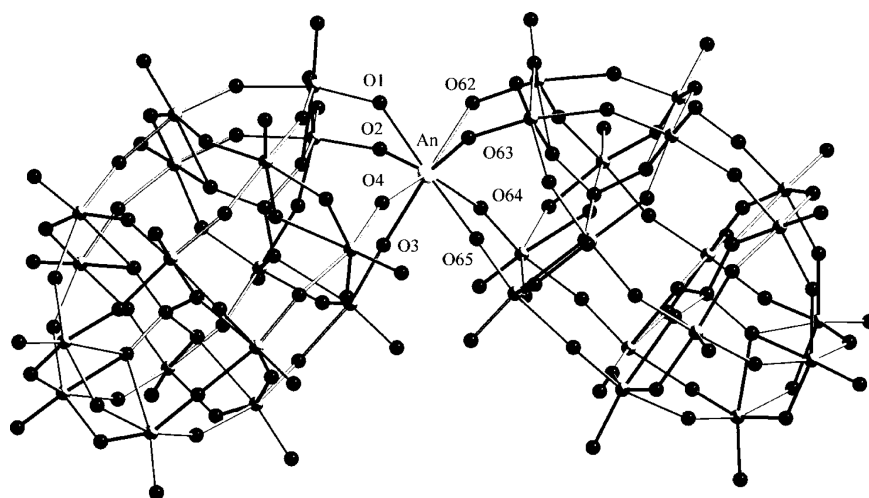


Figure 2. Butterfly like structure of the anion $\text{Am}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})_2^{16-}$.^{16–42}

the fluorite structure of PuO_2 with 8 Am—Am distances of 3.803 Å and a tetrahedral arrangement of four Am atoms around each oxygen atom (Am—O is 2.480 Å).³⁰ Despite the considerable evidence for the formation of Am(IV) during reduction and disproportionation reactions of Am(V) and Am(VI), tetravalent americium in solution was not characterized until the early 1960s. However, the characterization of Am(IV) in solution was complicated because it is reduced spontaneously to its more stable III oxidation state in noncomplexing media. In the early 1960s, Asprey and Penneman stabilized Am(IV) by dissolving $\text{Am}(\text{OH})_4$ in concentrated ammonium fluoride and reported the formation of $(\text{NH}_4)_4\text{AmF}_8$ upon exceeding the solubility at room temperature.^{6,7,31} On the basis of the resemblance of the solution absorption spectrum with that of solid AmF_4 , the authors concluded that the soluble Am(IV) was complexed with fluoride. Reduction and disproportionation of Am(IV) in this concentrated fluoride matrix was not observed.

Yanir and co-workers successfully prepared Am(IV) in concentrated phosphoric acid and pyrophosphate,³² while Myasoe-dov and co-workers reported its quantitative preparation in 8–15 M phosphoric acid by anodic oxidation.^{8,33,34} At lower phosphoric acid concentrations impurities of Am(VI) were formed, with nearly quantitative disproportionation of Am(IV) in approximately 3 M H_3PO_4 . The most stable conditions to minimize the reduction of 1.4×10^{-2} M $^{243}\text{Am}(\text{IV})$ were found in 8–12 M H_3PO_4 at 0 °C with a measured reduction rate of $0.6\% \text{ h}^{-1}$.³⁵ A similar stability of Am(IV) was reported in an oxidizing mixture of Ag_3PO_4 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$.^{9,34} A 15-fold excess of peroxydisulfate was required for the quantitative production of Am(IV), using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and Ag_3PO_4 in 9–12 M H_3PO_4 and 30 min oxidation times.^{9,36} The half-life of Am(IV) was determined to be 65–70 min. Erin and co-workers obtained Am(IV) in less concentrated phosphoric acid within 0.5 min at room temperature.³⁷ The yield of Am(IV) decreased with increasing peroxydisulfate concentration and was highest at phosphoric acid concentrations below 3 M. This behavior is caused by the decomposition of the oxidizing agent, peroxydisulfate, at high acidity resulting in the formation of reducing compounds.

Heteropolyanions, such as phosphotungstate, were shown by Erin and co-workers to significantly increase the stability of Am(IV) limiting the reduction of Am(IV) to Am(III) to solely radiolytic effects.^{10,11,38,39} Pink Am(III) solutions become yellow

upon complexation with phosphotungstate anions, but changing to orange-yellow upon oxidation to Am(IV), which was proposed to be caused by the anion $\text{Am}(\text{P}_2\text{W}_{17}\text{O}_{61})_2^{16-}$.^{16–12} Kosyakov and co-workers quantitatively prepared Am(IV) by heating a 0.1 M potassium peroxydisulfate solution of either ^{241}Am or ^{243}Am , in 4.3×10^{-3} M $\text{K}_{10}\text{P}_2\text{W}_{17}\text{O}_{61}$.¹⁰ The reduction of Am(IV) to Am(III) was zero-order with respect to the americium concentration, with a measured rate of $0.87\% \text{ h}^{-1}$ for ^{241}Am , and $0.08\% \text{ h}^{-1}$ for ^{243}Am . This difference in the rate suggests that the reduction of phosphotungstate-complexed Am(IV) resulted from the reaction of the complex with radiolysis products.

Within 2 h of reaction time, Shilov and co-workers prepared Am(IV) at 50 °C in a mixture of 0.1 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and 9×10^{-3} M $\text{K}_{10}\text{P}_2\text{W}_{17}\text{O}_{61}$.⁴⁰ Milyukova and co-workers reported the formation constants of $\beta = (2.8 \pm 1.3) \times 10^5$ for Am(III) and $(1 \pm 0.3) \times 10^9$ for the Am(IV) complex.¹¹ The 1:1 complex is reported to form depending on pH, reagent ratios, and temperature.⁴¹ Very recently, Sokolova and co-workers synthesized and reported the single crystal structure of $\text{K}_{10}\text{H}_6\text{Am}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})_2 \cdot 30.5\text{H}_2\text{O}$ after oxidizing Am(III) in the presence of $\text{K}_2\text{S}_2\text{O}_8$ at 90–95 °C.⁴² The 8-coordinate Am(IV) is chelated by two phosphotungstate anions through four oxygen atoms in a syn-configuration (Figure 2). The $[\text{AmO}_8]$ polyhedron is a distorted square antiprism.

In nitric acid, a large excess of decatungstate was required to oxidize Am(III) to Am(IV) using peroxydisulfate or ozone as the oxidizing agent.^{11,43} According to Milyukova and co-workers, the more acidic the solution the higher the excess of phosphotungstate required.^{11,44} These authors attributed the formation of Am(VI) to the disproportionation of not sufficiently complexed Am(IV). For example, in 0.1 M HNO_3 , a 4-fold excess was required, while a 40-fold excess in 3 M HNO_3 was insufficient to completely complex Am(IV), possibly because of the competing protonation of the polyoxometalate anion at high acidity. Litvina and co-workers demonstrated the use of KBrO_3 and $\text{K}_2\text{Cr}_2\text{O}_7$, as well as room temperature Ag-catalyzed peroxydisulfate to prepare Am(IV) in the presence of $\text{K}_{10}\text{P}_2\text{W}_{17}\text{O}_{61}$ in nitric, sulfuric, and perchloric acids.¹² The produced Am(IV) was most stable in nitric acid, with the highest oxidation rate being about 10 h^{-1} for 5×10^{-4} M $\text{K}_{10}\text{P}_2\text{W}_{17}\text{O}_{61}$ in 1 M acid with Ag-peroxydisulfate. Insufficient amounts of phosphotungstate resulted in the formation of Am(VI), which did not complex with the phosphotungstate

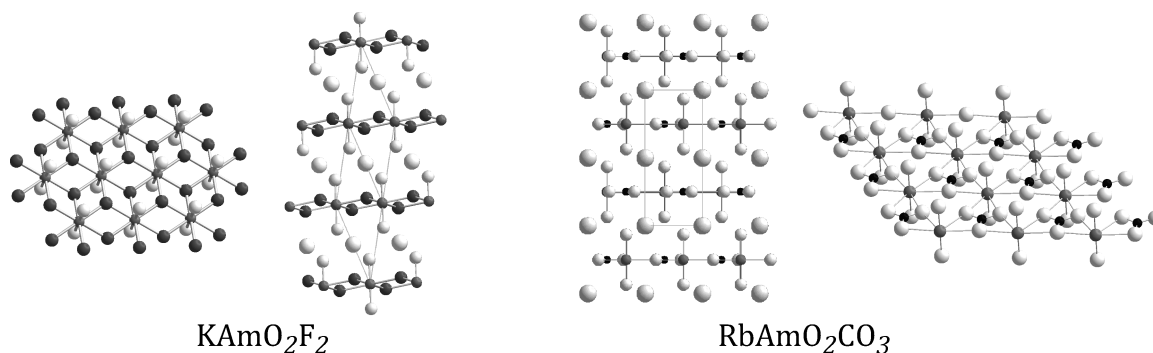


Figure 3. Layered structures of the Am(V) compounds KAmO_2F_2 ⁵² and $\text{RbAmO}_2\text{CO}_3$.⁵⁵

anion.^{11,45} This conclusion was based on very minor changes in the potential of the Am(V)/Am(VI) redox couple and the absence of any changes in the Am(VI) absorption spectrum. Both the decrease of the Am(IV)/Am(III) redox potential and the increase in the Am(VI)/Am(V) redox potential upon addition of phosphotungstate enhance the stability of Am(IV) and increase the disproportionation of Am(V).⁴⁵

Erin and co-workers reported that prolonged heating of a 1.3 mM Am(III) solution ($\text{pH} \leq 5$) containing 0.13 M peroxydisulfate and a 5-fold excess of phosphotungstate at 96 °C resulted in the quantitative production of Am(VI), rather than Am(IV).³⁸ Interestingly, all four americium oxidation states were recorded simultaneously as Am(VI) began to reduce over time in the phosphotungstate solution. However, at the lower temperature of 50 °C Shilov and co-workers prepared only Am(IV) using a 2 h oxidation with 0.1 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 9×10^{-3} M $\text{K}_{10}\text{P}_2\text{W}_{17}\text{O}_{61}$.⁴⁰

Hobart and co-workers found that electrolytic oxidation of $^{243}\text{Am(III)}$ in 2–5.5 M carbonate solutions at potentials above 1 V resulted in the formation of a golden-yellow Am(IV) carbonate species, which was slowly reduced to Am(III).⁴⁶ At potentials exceeding 1.1 V, Am(IV) was oxidized to Am(V) and Am(VI). However, in 10–15 M H_3PO_4 quantitative formation of Am(IV) was observed at a potential of 1.75 V.^{8,32} Transient Am(IV) has been observed in dilute perchloric acid using pulse radiolysis by Sullivan and co-workers.^{47,48} Tetravalent americium can also be prepared from Am(OH)_3 in the presence of excess $\text{K}_3\text{Fe(CN)}_6$ in 0.087 M NaOH or by mixing of Am(III) and Am(V) (or Am(VI)) in concentrated NaOH solutions.⁴⁹ Electrochemically produced Am(IV) in 6 mM potassium phosphotungstate over the pH range 0.5–5 reduced to Am(III).⁵⁰ A rate equation for this reduction contained two terms, one zero-order with respect to $[\text{Am(IV)}]$ because of radiolytic reduction, and one that was first-order with respect to $[\text{Am(IV)}]$, which was attributed to reaction with water. Frenkel and co-workers reported the reduction of Am(IV) by water in strongly complexing 10 M phosphoric acid solution, by measuring the production of oxygen gas over periods of 24 h.⁵¹ No oxygen was produced in Am(III) solutions.

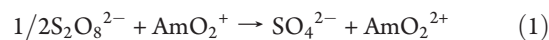
2.2. Americium(V)

Structural details on compounds of pentavalent americium remain rare and only a few structures are published. Reported structures of inorganic Am(V) compounds exhibit two-dimensional layered arrangements governed by the most prominent structural feature, the linear americyl trans-dioxo $\text{O}=\text{Am}=\text{O}^+$ moiety. The ternary Am(V) fluorides, KAmO_2F_2 , and RbAmO_2F_2 , precipitate from concentrated aqueous fluoride solutions of Am(V) and consist of AmO_2F_2^- connected by K^+ or Rb^+ cations,

respectively, as reported by Asprey and co-workers (Figure 3).⁵² Bagnall and co-workers showed that upon the addition of ethanol to Am(V) hydroxide and CsCl in 6 M HCl the chloride $\text{Cs}_3\text{AmO}_2\text{Cl}_4$ precipitates, which is isostructural with the analogous Np(V) compound.^{53,54} Six oxygen atoms from three bidentately bonded carbonate ligands in the equatorial plane and two axial americyl oxygens form the inner coordination sphere of Am(V) in $\text{RbAmO}_2\text{CO}_3$ (Figure 3).⁵⁵ Ellinger and Zachariassen calculated the $\text{Am}=\text{O}$ and $\text{Am}-\text{O}_{\text{eq}}$ bond distances from X-ray powder diffraction data to be 1.935 and 2.568 Å.⁵⁵

Pentavalent americium is predominantly prepared in near-neutral and alkaline solution. Oxidizing agents, such as ozone, peroxydisulfate, or hypochlorite have been used to oxidize Am(III) to Am(V) under these conditions.^{14,56,57} It can also be obtained by reducing Am(VI) with bromide.⁵⁸ In potassium carbonate solution Am(III) is oxidized to Am(V) at 95 °C, which precipitates in the form of KAmO_2CO_3 .^{14,17,59} At room temperature, Coleman showed that ozone oxidizes Am(III) in 2 M sodium carbonate to Am(VI), which can be reduced to Am(V) by heating to 90 °C.⁶⁰ However, in potassium carbonate solutions ozone does not oxidize Am(III) to Am(VI) and the oxidation does not proceed past Am(V).¹⁷ Coleman and co-workers attributed the instability of Am(VI) in potassium carbonate solutions to the low solubility of KAmO_2CO_3 . In sodium carbonate solutions, Runde and co-workers found that Am(V) forms anionic carbonate complexes $\text{AmO}_2(\text{CO}_3)_x^{1-x}$ where $x = 1-3$ and precipitates as $\text{NaAmO}_2\text{CO}_3$.¹⁶ With increasing carbonate concentration the solid $\text{NaAmO}_2\text{CO}_3$ can undergo a solid phase transformation to form $\text{Na}_3\text{AmO}_2(\text{CO}_3)_2$ in analogy to Np(V) (see also Figure 11).

In acidic solutions, the oxidation of Am(III) yields Am(VI) because Am(V) is more easily oxidized to Am(VI) than Am(III) is oxidized to Am(V).⁵ In nitric acid, the oxidation of Am(V) to Am(VI) by peroxydisulfate follows the reaction:⁶¹



Ermakov and co-workers reported the rate law in 0.09–0.6 M HNO_3 as $-\text{d}[\text{Am(V)}]/\text{dt} = (a' - b'[\text{H}^+])[\text{S}_2\text{O}_8^{2-}][\text{Am(V)}]_0$, where $a' = 15 \times 10^{-5} \text{ min}^{-1}$ and $b' = 2.7 \times 10^{-4} \text{ L mol}^{-1} \text{ min}^{-1}$ at 50.6 °C.^{62–64} In carbonate, peroxydisulfate oxidizes Am(III) to intermediate Am(V), with the oxidation rate being independent of the total Am and potassium carbonate concentrations, but proportional to the decomposition rate of $\text{S}_2\text{O}_8^{2-}$.^{62–64} The effective activation energy of the $\text{S}_2\text{O}_8^{2-}$ oxidation of Am(III) to Am(V) in potassium carbonate solutions is close to the activation energy (140 kJ mol^{−1}) of the thermal decomposition of $\text{S}_2\text{O}_8^{2-}$ ions.^{65,66}

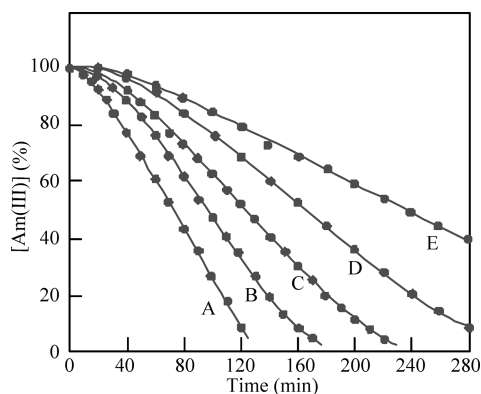


Figure 4. Kinetics of Am(III) oxidation by peroxydisulfate in nitric acid at 50.6 °C ($[S_2O_8^{2-}]_0 = 0.40$ M).^{62–64} HNO₃ concentrations: A, 0.09 M; B, 0.14 M; C, 0.19 M; D, 0.24 M; E, 0.28 M.

Recently, the quantitative production of Am(V) in acidic solution was demonstrated by Mincher and co-workers using sodium bismuthate as the oxidant.¹⁹ A 1 mM ²⁴³Am, 0.1 M HNO₃ solution at 80 °C was contacted with bismuthate powder for about 30 min, resulting in spectroscopically pure Am(V). At room temperature this procedure yields Am(VI).

Meyer and co-workers obtained pentavalent americium in solution by adding an alkaline solution of ferricyanide to a Am(III) hydroxide.⁶⁷ In the presence of larger amounts of americium the dissolution is followed by the precipitation of a reddish solid proposed to be the Am(V) hydroxide $Na_2AmO_2(OH)_3 \cdot 3H_2O$ based on spectroscopic and electrochemical investigations.

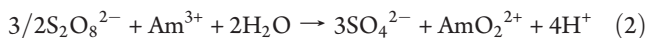
Pure AmO_2^+ solutions free of Am^{3+} can be also obtained by using selective solvent extraction from mixed valence solutions. Hara extracted Am(VI) in dilute nitric acid buffered with 1 M ammonium acetate at pH 3 into 0.1 M thenoyltrifluoroacetone (TTA)/isobutanol.⁶⁸ The loaded organic phase was selectively stripped of Am(V) using an aqueous, low-pH acetate or perchlorate solution. Sulfate solutions were less effective, probably because of the greater disproportionation rate of Am(V) in that solution. More exotic methods to prepare Am(V) in acidic solution include the dissolution of solid Li_3AmO_4 in dilute perchloric acid.⁶⁹

Americium(V) was reportedly generated electrochemically in 3 M KHCO₃/K₂CO₃ solution at pH > 13.5 and +1.25 V vs NHE and at +1.1 V in 2 M Na₂CO₃ solution by Hobart and co-workers and also by Myasoedov and co-workers.^{46,70} The electrochemical oxidation of Am(IV) in K₂CO₃ solution at +1.1 V provided for quantitative oxidation to Am(V) and resulted in the precipitation of Am(V) carbonate. Yanir and co-workers have also prepared pentavalent americium electrolytically in 2 M LiIO₃–0.7 M HIO₃ at pH 1.47.³²

2.3. Americium(VI)

Hexavalent americium can be prepared in dilute acids or in alkaline media. Powerful oxidants, such as peroxydisulfate or Ag(II), oxidize Am(III) and Am(V) in dilute, nonreducing acidic solution to Am(VI), while ozone does not oxidize Am(III) to Am(VI). At acidities above 0.5 M, peroxydisulfate will also not oxidize Am(III) completely to Am(VI) because of the interfering acid hydrolysis of $S_2O_8^{2-}$.⁷¹ It is established that the oxidizing agent is not the $S_2O_8^{2-}$ ion itself, but its thermal decomposition products (e.g., $SO_4^{\bullet-}$ or $HS_2O_8^-$). Newton proposed

the following reaction for the oxidation of Am(III) by peroxydisulfate⁶¹



The kinetics of the oxidation of Am(III) to Am(VI) by peroxydisulfate at various nitric acid concentrations are shown in Figure 4. The reaction between $S_2O_8^{2-}$ and Am(III) to form Am(VI) proceeds between 10^{-8} and 10^{-1} M Am(III) indicating a low-order rate dependence on Am(III) concentration.⁷² The oxidation reaction contains an induction period and a linear region of constant rate. Ermakov and co-workers used millimolar concentrations of ²⁴³Am(III) and claimed that the rate of oxidation of Am(III) in the linear portion of kinetic curves does not depend on the Am(III) concentration (in the absence of Ag⁺).^{62–64} However, the reaction rate is dependent on temperature and the concentration of HNO₃, $S_2O_8^{2-}$, and when present, Ag⁺.

In sodium carbonate and bicarbonate solutions, both Am(III) and Am(V) are oxidized by Na₂S₂O₈ to Am(VI). The oxidation of Am(III) to Am(VI) with peroxydisulfate proceeds through the formation of Am(V).^{62–64} However, the rate of Am(V) oxidation to Am(VI) is directly proportional to both the total americium and $S_2O_8^{2-}$ concentrations and is inversely proportional to the K₂CO₃ concentration.

Ce(IV) oxidizes Am(V) to Am(VI) but only partially oxidizes Am(III) to Am(VI).⁷¹ Cesium fluoroxysulfate (CsSO₄F) and a silver catalyst was used to oxidize Am(III) to Am(VI) in 0.4–1.0 M nitric acid by Appelman and co-workers.²¹ However, spectroscopic measurements demonstrated that no more than 30% of americium was oxidized in 2.6 M HNO₃. Fluoroxysulfate has the disadvantages of decomposing with a half-life of 35 min at 15 °C producing HF as a degradation product. Recently, Mincher and co-workers used sodium bismuthate to prepare spectroscopically pure Am(V) in 0.1 M HNO₃ at 80 °C, while the same oxidation at room temperature produced Am(VI) quantitatively.¹⁹ Solvent extraction experiments were used to show that Am(VI) was prepared in high yields even at nitric acid concentrations as high as 6 M.

In contrast to acidic solutions, Stephanou and co-workers reported that ozone oxidizes Am(III) and Am(V) in carbonate solution at 25 °C or below to yield Am(VI).¹⁸ However, at 90 °C oxidation does not proceed past Am(V). Coleman and co-workers used ozone to oxidize Am(V) to Am(VI), which was separated from lanthanides and other actinides by fluoride precipitation.⁷³ The Am(V) was prepared by oxidizing Am(III) in K₂CO₃ solution with K₂S₂O₈ at 90 °C for 30 min. Ozone does not oxidize Am(OH)₃ or KAmO₂CO₃ in 0.1–0.5 M KHCO₃ and K₂S₂O₈ does not oxidize Am(OH)₃ or NaAmO₂CO₃ in 0.1 M NaHCO₃.¹⁷ This difference is attributed to the lower solubility of KAmO₂CO₃ compared to NaAmO₂CO₃. In 0.1–0.5 M NaHCO₃, Am(VI) is stable at 90 °C to reduction by H₂O, Cl[–], or Br[–], but is easily reduced by I[–], N₂H₄, H₂O₂, NO₂[–], and NH₂OH. Very slow reduction of Am(VI) occurs in 2 M Na₂CO₃. Yellow-colored solutions of Am(VI) in any alkali hydroxide solution can be prepared by oxidation of solid Am(OH)₃ with ozone, according to Cohen.⁷⁴ Prolonged oxidation of Am(OH)₃ in bicarbonate reportedly results in an oscillatory reaction between Am(VI) and Am(V) with decreasing Am(VI) yield at higher americium concentrations.⁷⁵ Reducing agents that form upon the decomposition of ozone, such as the hydroperoxy radical or hydrogen peroxide, partially reduce the Am(VI).

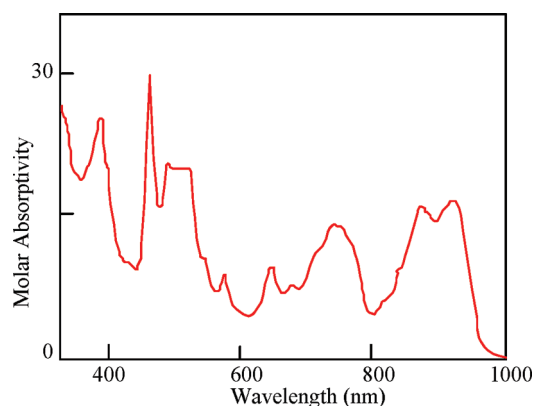


Figure 5. Absorption spectrum of Am(IV) in 13 M NH_4F .⁷

More exotic synthesis reactions involve noble gas compounds. Drobyshvskii and co-workers showed that the reaction of KrF_2 with AmF_3 in anhydrous HF yields a dark-brown solid of AmF_6 with a vapor pressure that is similar to that of UF_6 .⁷⁶ The Xe(VIII)-containing sodium perxenate, Na_4XeO_6 , has an oxidation potential of about 3 V and has been used to prepare Am(VI) in dilute nitric acid. Holcomb found that the addition of silver improved the yields most likely because of the capacity of silver ions to maintain Am(VI) after its oxidation by Xe(VIII).²² This effect was also observed by Hara when $(\text{NH}_3)_2\text{S}_2\text{O}_8$ and silver ion were used to oxidize americium to Am(VI) in dilute nitric acid.⁶⁸

Tsushima and co-workers oxidized americium photochemically in 0.02–0.2 M HNO_3 by using a deuterium lamp.⁷⁷ The oxidation rates were higher at elevated temperatures ($5\% \text{ h}^{-1}$ in 0.1 M HNO_3 at 65°C) and lower acidities. Earlier work by Friedman suggested that a wavelength $<240 \text{ nm}$ is required,⁷⁸ and thus, oxygen and hydrogen peroxide might also photolyze to interfere with americium oxidation.

Anodic oxidation to prepare Am(VI) was used successfully by Asprey and co-workers in 6 M HClO_4 , but at lower acidities the oxidation was unsuccessful.⁷² Myasoedov and co-workers found that electrolytic oxidation of Am(III) in 2 M H_3PO_4 and 6 M HClO_4 leads to Am(VI).^{8,34} The obtained Am(VI) was relatively stable with a reduction rate of about 50% in eight hours. At higher phosphoric acid concentrations, Am(VI) eventually became the main product, being produced quantitatively in 10–15 M H_3PO_4 . In aqueous 2 M carbonate solutions, Coleman and co-workers found that oxidation of Am(III), Am(IV), or Am(V) with ozone or with $\text{Na}_2\text{S}_2\text{O}_8$ yields an intensely colored red-brown carbonate complex of Am(VI).¹⁷ Hobart and co-workers also prepared this complex electrochemically at a potential of 1.3 V vs NHE in sodium carbonate solutions, or by dissolving sodium americyl(VI) acetate in sodium carbonate solutions.⁴⁶ Erin and colleagues prepared hexavalent americium electrochemically in potassium phosphotungstate solutions in the pH range 0–6.⁷⁹ Upon Am(VI) reduction, tetravalent americium formed, proportional to the decrease in Am(VI) concentration. Kamoshida and co-workers used a stoichiometrically deficient ammonium phosphotungstate solution to prepare Am(VI) with an order-of-magnitude lower concentration of peroxydisulfate than would otherwise be necessary.⁸⁰ Under these conditions, free Am^{4+} rapidly disproportionated to form Am(V), which was readily oxidized by Ag-catalyzed ammonium peroxydisulfate to Am(VI).

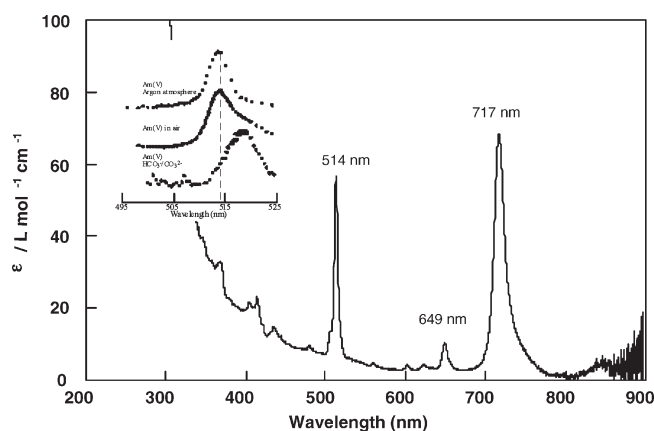


Figure 6. Electronic absorption spectra of AmO_2^+ in 1 M HClO_4 and in carbonate-containing solutions (inset).⁸⁹

3. CHARACTERIZATION

A variety of methods have been used to detect, quantify, and speciate americium in solution and solid-state compounds. Common radioanalytical procedures include alpha-spectrometry counting of the high-energy alpha particles emitted from both ^{241}Am and ^{243}Am , and high-sensitivity gamma-counting in a germanium multichannel detector primarily for probing the two main γ rays of ^{241}Am at 59.5 (36%) and 26.3 keV (2.4%) and the 44 (5%) and 75 keV (61%) γ rays of ^{243}Am . Scintillation counting is also commonly used when only one α -emitting isotope is in a sample.

Spectroscopic techniques have provided insight into americium oxidation state stability and the molecular coordination of americium. The most common methods used for americium speciation have been conventional vibrational and UV–vis–NIR absorption spectroscopies. More sophisticated X-ray absorption spectroscopy (XAS) has been increasingly used to obtain structural information on actinide compounds. However, XAS studies on americium compounds remain rare.

3.1. Absorption Spectroscopy

Oxidation states of americium can be easily identified using their characteristic fingerprints in their electronic absorption spectra. The spectrum of Am(IV) has been measured in concentrated salt solutions, that is, in 13 M NH_3F (Figure 5),^{7,31} 12 M KF ,⁸¹ 12 M H_3PO_4 ,³⁴ and in 2 M Na_2CO_3 .^{46,82} Am(IV) in acid media is characterized by one sharp, low intensity peak at 456 nm ($\epsilon = 25\text{--}30 \text{ L mol}^{-1} \text{ cm}^{-1}$) and broad absorption features at about 740, 873, and 923 nm. The spectrum of Am(IV) in concentrated fluoride solution (Figure 5) resembles very closely that of solid AmF_4 .³¹

The molar extinction coefficients reported in the literature differ significantly, most likely due to the difficulties in stabilizing Am(IV) and strong complexation even under acidic conditions, as is also known for the chemically analogous Np(IV) and Pu(IV). Shilov and co-workers reported ϵ_{500} for Am(IV) of about $1500 \text{ L mol}^{-1} \text{ cm}^{-1}$ at $50^\circ\text{--}70^\circ\text{C}$ and pH 1–4,⁴⁰ while the Myasoedov group reported $\epsilon_{333} = 1363 \pm 19$, $\epsilon_{357} = 1029 \pm 11$, $\epsilon_{384} = 701 \pm 10$, $\epsilon_{416} = 365 \pm 12$, and $\epsilon_{454} = 138 \pm 9 \text{ L mol}^{-1} \text{ cm}^{-1}$ in 12 M H_3PO_4 .³³ These data differ substantially from those reported by Lebedev and co-workers of $\epsilon_{333} = 1704$, $\epsilon_{384} = 885$, and $\epsilon_{416} = 450 \text{ L mol}^{-1} \text{ cm}^{-1}$.⁸³ In the presence of phosphotungstate the Am(IV) spectrum in acidic solution is characterized by strong absorbance in the 400–600 nm region,

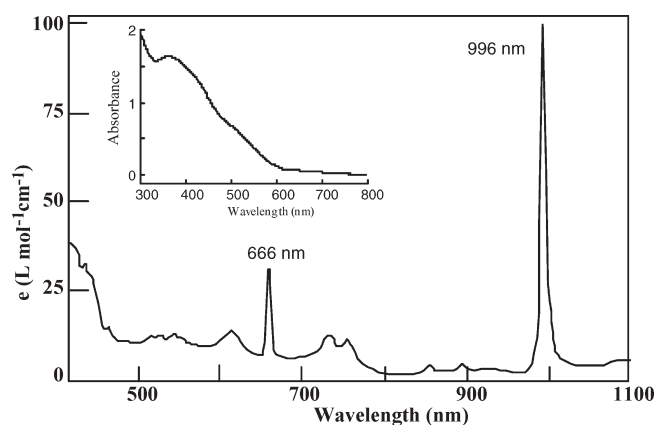


Figure 7. Absorption spectrum of Am(VI) in 1 M HClO₄ and in carbonate solution (inset).⁷¹

and two peaks at 756 and 940 nm, which can be used to analyze for Am(IV).^{84,85} Using the absorbance at 500 nm in 1 M HNO₃, an ϵ_{500} of 1227 ± 17 L mol⁻¹ cm⁻¹ was measured by the Myasoedov group, with adherence to Beer's Law over the range 8×10^{-9} – 9×10^{-7} M. Kulyako and co-workers also reported values of $\epsilon_{500} = 1106$ for Am(IV), $\epsilon_{996} = 96.3$ for Am(VI), and $\epsilon_{718} = 64.3$ L mol⁻¹ cm⁻¹ for Am(V) in 8.2×10^{-3} M phosphotungstate at ~pH 6.⁸⁶

The Am(V)-transitions $^5L_4 \rightarrow ^3G_5$ and $^5L_4 \rightarrow ^3I_7$ with their absorbance peaks at 514 nm ($\epsilon \approx 45$ L mol⁻¹ cm⁻¹) and 716 nm ($\epsilon \sim 60$ L mol⁻¹ cm⁻¹), respectively, are the main absorbances of the AmO₂⁺ ion in aqueous solutions (Figure 6). Absorbance spectra of Am(V) have been recorded in various media, such as H₂SO₄,⁵⁹ HCl,^{87–89} HClO₄,^{18,72} HNO₃,⁵⁷ NaCl,^{88,89} and in 2 M Na₂CO₃.^{46,82} For the peak at 514 nm, similar molar extinction coefficients of 48 L mol⁻¹ cm⁻¹ in 0.1 M H₂SO₄,⁵⁹ 45.6 L mol⁻¹ cm⁻¹,¹⁸ and 44.1 L mol⁻¹ cm⁻¹,⁹⁰ in 0.1 M HClO₄ have been reported. For the peak at about 716 nm, molar extinction values of 66 L mol⁻¹ cm⁻¹ in 0.1 M H₂SO₄,⁵⁹ and 59.3,¹⁸ and 59.6 L mol⁻¹ cm⁻¹,⁹⁰ in 0.1 M HClO₄ have been reported. Reports on the absorption of Am(V) coordinated in solution remain rare due to these low extinction coefficients.

The spectrum of americium(VI) in acid media is characterized by the most intense absorption band at about 996 nm and a less intense absorbance at 666 nm (Figure 7).²⁰ In 0.1 M HClO₄ the molar extinction coefficients of the prominent peaks at 666 and 995 nm have been reported to be $\epsilon = 24.6$ and $\epsilon = 63.8$ L mol⁻¹ cm⁻¹, respectively, by Yakovlev and Kosyakov.⁹⁰ Hall and Markin reported an $\epsilon_{996} = 63.8$ L mol⁻¹ cm⁻¹ in 0.1 M HClO₄ and 83.3 L mol⁻¹ cm⁻¹ in 1 M HClO₄.⁹¹ Mincher and colleagues reported $\epsilon = 24.6$ L mol⁻¹ cm⁻¹ at 666 nm in 0.1 M HNO₃.¹⁹ A shift of the prominent peaks to 673 and 1000 nm after the extraction of Am(VI) into 30% tributylphosphate solution from nitric acid was observed by Martin and Mincher (unpublished data). Bell has compared band positions of transuranium actinyl spectra, including those of AmO₂⁺ and AmO₂²⁺, with the spacings between positions of the UO₂²⁺ bands.⁹² His results indicate that a single molecular orbital model can represent any of the actinyl ions when the uranyl ion is assumed to have the bonding orbitals exactly filled; the transuranium actinyl ions are represented with the uranyl core and a progressive increase in electrons in the first two LUMOs (lowest unoccupied molecular orbital). Although Am(VI) absorbance appears when Am(V) disproportionates in

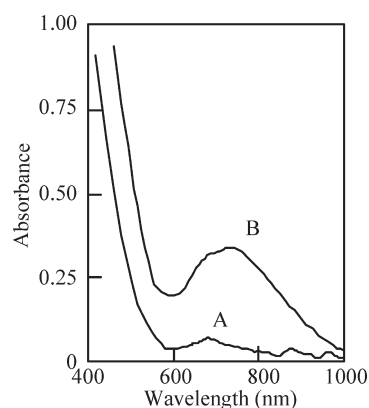


Figure 8. Absorption spectra of Am(VI) and Am(VII) in 3.5 M NaOH.⁹³ A: 0.0194 M Am(VI). B: 0.0194 M Am_{tot} with 50% Am(VI) and 50% Am(VII).

HClO₄, this absorbance is absent in HCl, potentially because of formation of chloride complexes of lower molar absorptivity or due to the instability of Am(VI) in acidic chloride media.

Green-colored solutions believed to be Am(VII) are prepared by oxidation of Am(VI) in 3–5 M NaOH at 0–7 °C with either ozone or the O^{•-} radical. The spectra of Am(VI) and Am(VII) were measured in 3.5 M NaOH solution by Krot and co-workers and exhibited a broad absorbance at 740 nm (Figure 8).⁹³ Heptavalent americium is unstable and reduces to Am(VI) within minutes. It can be easily reduced by hydrogen peroxide, hydrazine, hydroxylamine, sulfite, and ferrocyanide ions, and Np(VI) and Pu(VI).⁹⁴ The chemistry of heptavalent transplutonium elements has been reviewed by Mikheev and Myasoedov.⁹⁵

3.2. Vibrational Spectroscopy

There are few data on the IR spectra of americium compounds. Jones and Penneman studied the infrared absorption assigned to the O–An–O asymmetric stretch of actinyl(V) and (VI) ions, concluding that these ions were linear or very nearly so.^{96,97} For the solid NaAmO₂(CH₃COO)₂ the vibrational frequencies $\nu_1 = 749$ cm⁻¹ and $\nu_2 = 914$ cm⁻¹ were reported.⁹⁸ Tananaev reported the antisymmetric vibration frequency of the AmO₂⁺ group in CsAmO₂(OH)₂·*n*H₂O at 802 cm⁻¹.⁹⁹ Hobart and colleagues reported the Raman spectra of AmPO₄ and Am(PO₃)₃ with the most intense Raman frequencies for the symmetric stretching mode of PO₄³⁻ at 973 cm⁻¹ and of PO₃⁻ groups at 1195 cm⁻¹.¹⁰⁰ Data on Raman scattering of americyl(V) and (VI) ions have been reported in noncomplexing perchloric acid and complexing carbonate solutions by Basile and co-workers.¹⁰¹ The values for the polarized symmetric stretching frequencies (ν_1) of AmO₂⁺ and AmO₂²⁺ were found to be 730 and 796 cm⁻¹, respectively.¹⁰¹ The Raman scattering in carbonate solutions showed a shift of ν_1 to 747 cm⁻¹ for Am(V)¹⁰² and to 760 cm⁻¹ for Am(VI).¹⁰³ A study of the correlation of the Raman spectra of actinyl(V) and (VI) ions in perchlorate and carbonate solutions, as well as the spectra of solid actinide(V) double carbonate compounds, Na₃AnO₂(CO₃)₂·H₂O, was reported by Madic and co-workers.¹⁰²

3.3. X-ray Absorption Spectroscopy

Although X-ray absorption spectroscopy (XAS) has been increasingly used since 1990 to obtain structural information for actinide compounds, only a small number of XAS studies on americium compounds, and even fewer for high-valent americium, have

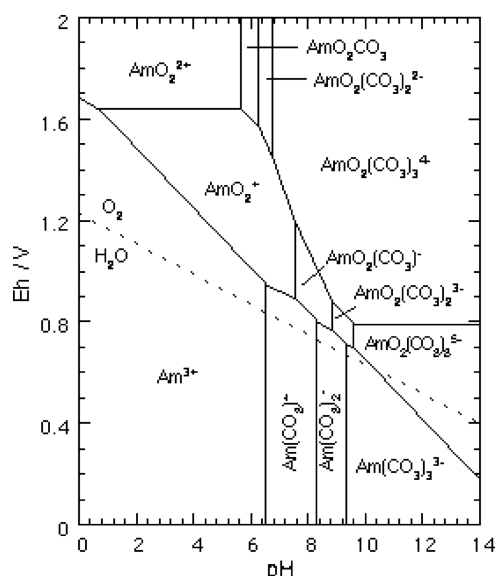


Figure 10. Pourbaix (Eh-pH) diagram for the aqueous species in the Am-H₂O-CO₂ system with a partial pressure of 0.01 atm CO₂.

1.78 V in 10 M H₃PO₄,¹²⁴ respectively. The extrapolated standard thermodynamic values are $E^\circ = 2.50 \pm 0.06$ and 2.34 ± 0.22 V, respectively. A value of 2.6 ± 0.09 V was calculated by Morss and Fuger from enthalpy measurements²⁹ and has been confirmed by Hobart and colleagues with electrochemical data in carbonate solutions.⁴⁶ Stabilization by carbonate and phosphotungstate decreases the electrode potential to 0.92 V in 2 M Na₂CO₃^{46,82,125} and 1.52 V,¹⁰ respectively. The formal potential for the Am(III)/Am(IV) couple in phosphotungstate solution is reduced to -1.52 ± 0.01 V in 4.3×10^{-3} M K₁₀P₂W₁₇O₆₁ at 20 °C.¹⁰ Baranov and colleagues reported a minimum in this potential of about -1.45 V over the pH range 1–5 in phosphotungstate solutions acidified with nitric acid.¹²⁶

4.2. Am(V)/Am(III)

In the 1950s, a value of 1.74 V for the Am(V)/(III) couple in acidic solution was proposed by Gunn and accepted by Penneman and Asprey.^{71,120} Later, Gunn and Cunningham reported a value of 1.83 V based on heats of reaction with Fe²⁺ in 1 M HClO₄.¹²⁷ Schulz reviewed and reported the standard electrode potential for Am(III)/(V) as 1.74 V in 1 M HClO₄.⁵

4.3. Am(VI)/Am(III)

The electrode potential for the Am(VI)/Am(III) couple in 3.55 M H₃PO₄ was reported as 1.26 V.^{8,34} In acidic solution, original estimates based on the ability to oxidize americium to Am(VI) using peroxydisulfate or Ag²⁺, or partially oxidize using Ce⁴⁺, were in the range 1.8–2 V in perchloric acid.²⁰ Based on data reported by Gunn, Penneman and Asprey reported a best value of 1.70 V.^{71,120} Gunn and Cunningham later reported a value of 1.75 V based on heats of reaction with Fe²⁺ in 1 M HClO₄.¹²⁷

4.4. Am(VI)/V

Penneman and Asprey measured directly the electrode potential of the AmO₂²⁺/AmO₂⁺ couple to be 1.600 ± 0.0005 V in 1 M HClO₄ and 1.614 ± 0.001 V in 0.3 M HClO₄.¹²⁸ From studies of Am(VI) and Pu(VI) in NaOH, Nikolaevskii and co-workers estimated that the potential for the Am(VI)/Am(V) couple is about 0.65 V rather than 1.1 V.¹²⁹ The electrode potential

Table 3. Enthalpies of Formation, Gibbs Free Energies, and Standard Entropies for High-Valent Aquo Americium Ions and Solid Americium Oxides¹¹⁶

	$D_f H_m^\circ$ (298.15K) (J/mol)	$D_f G_m^\circ$ (298.15K) (J/mol)	S_m° (298.15K) (J/mol)
Am ⁴⁺ (aq)	-406 ± 6	-346 ± 9	-406 ± 21
AmO ₂ ⁺ (aq)	-804.3 ± 5.4	-739.8 ± 6.2	-21 ± 10
AmO ₂ ²⁺ (aq)	-650.8 ± 4.8	-585 ± 5.7	-88 ± 10
AmO ₂ (cr)	-932.2 ± 3.0	-874.5 ± 4.3	67 ± 10
SrAmO ₃ (cr)	-1539 ± 4		
BaAmO ₃ (cr)	-1545 ± 3		

was reported to be 1.43 V in dilute phosphoric acid and 1.32 V in 4.34 M H₃PO₄.^{122,130} In 2 M Na₂CO₃, the electrode potential for the Am(VI)/(V) couple was reported to be 0.975 V.^{46,82,125}

4.5. Am(VII)/(VI)

Shilov reported a value of 1.05 V for the Am(VII)/Am(VI) couple in 1 M NaOH,⁹⁴ while Peretrukhin reported 0.78 V for this couple in 10 M hydroxide.¹³¹

4.6. Thermodynamic data for Am(IV), Am(V), and Am(VI)

Table 3 presents the following enthalpies of formation, Gibbs free energies of formation, and standard entropies for the high-valent americium aquo ions that have been accepted by the NEA review.¹¹⁶

Experimental data and chemical thermodynamics for americium inorganic compounds were reviewed and published by the NEA in the 1990s and updated in 2003.^{116,117} The review indicated that very little work has been done on complexes with Am in higher oxidation states and thus only very limited thermodynamic data on complexation reactions of high-valent americium were recommended. The most studied system comprises the hydrolysis and carbonate complexation reactions of Am(V). For a detailed discussion and listing of reported experimental data and apparent formation constants of high-valent americium complexes, we refer to the published critical evaluations and compilations.^{1,5,116,117}

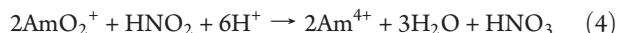
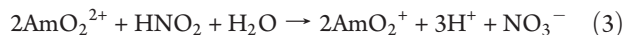
Both the hydrolysis reactions of Am(IV) and Am(VI) remain largely unexplored because of the difficulties to stabilize these oxidation states in the absence of strongly complexing ligands. The solid hydroxides of An(V) and An(VI) exhibit amphoteric character with increasing solubilities in alkaline solutions due to the formation of anionic hydroxo complexes. Slope analysis of the few Am(V) solubility data indicated the formation of only two americyl(V) hydrolysis products in solution, AmO₂(OH)_(aq) and AmO₂(OH)₂[−]. No thermodynamic data are available for Am(V) hydroxo complexes, but the reported apparent stability constants for AmO₂(OH)_(aq) and AmO₂(OH)₂[−] are close to those for the analogous Np(V) species.¹⁶ Tananaev suggested the formation of AmO₂(OH)₃^{2−} (with an absorption peak at 750 nm) and AmO₂(OH)₄^{3−} in highly alkaline media based on spectroscopic measurements of Am(V) in 0.001 to 1 M LiOH solutions.^{132,133}

In analogy to the Th(IV), U(IV), and Np(IV) carbonate systems, only one carbonate complex of Am(IV) is discussed in the literature. From combined spectroscopy and cyclic voltametry data in bicarbonate/carbonate solutions, it was concluded that Am(CO₃)₅^{6−} is the limiting carbonate complex of Am(IV) with a formation constant of $\log \beta_5^\circ = 39.3 \pm 2.1$.^{82,116} Giffaut and Vitorge studied the solubility of NaAmO₂CO₃ in carbonate-containing

4 M NaCl solution and claimed the formation of two Am(V) carbonate complexes, $\text{AmO}_2(\text{CO}_3)^-$ and $\text{AmO}_2(\text{CO}_3)_2^{3-}$.¹³⁴ Runde and co-workers reported identical solubility and speciation behavior of Am(V) and Np(V) in carbonated 3 and 5 M NaCl solutions.^{16,88} In analogy to the well-characterized Np(V) system in 5 M NaCl, the solubility data were interpreted with the formation of $\text{AmO}_2(\text{CO}_3)_n^{1-n}$ ($n = 1-3$) complexes in solution and $\text{NaAmO}_2\text{CO}_3 \cdot n\text{H}_2\text{O}$ as the solid equilibrium phase (Figure 11). The coordination of AmO_2^{2+} with carbonate ions is evidenced by the appearance of a burgundy-red color. On the basis of electrochemical measurements, it is assumed that the limiting complex is the $\text{AmO}_2(\text{CO}_3)_3^{4-}$ anion.^{82,116}

5. RADIOLYSIS EFFECTS ON AMERICIUM SPECIATION

There are numerous reports on the effect of the intense alpha-radiation of transuranium elements on their chemical behavior in acidic, basic, and highly concentrated chloride solutions. The most commonly used americium isotopes, ^{241}Am and ^{243}Am , decay primarily by emitting high-energy α -particles of about 5.4 and 5.2 MeV, respectively. In aqueous solution, the energy is released in dense tracks producing radicals, ions, and electrons, and thus impacting the stability of americium oxidation states. In acidic media, Am(III) is the most stable oxidation state and Am(V) and Am(VI) are rather rapidly reduced by the effects of their own alpha-radiation.^{136,137} The reduction rate is closely related to the dose rate and electrolyte concentration. Vladimirova suggested that Am(V) and Am(VI) reduction in nitric acid solutions cannot be explained by involving only radiolytically produced radicals but also require consideration of chemical reactions with radiolytically produced H_2O_2 and HNO_2 .^{137,138} These reduction reactions are shown in eqs 3–5.



In perchlorate solutions, α -radiolysis produces multiple species, such as Cl_2 , ClO_2 , or Cl^- , that are effective reductants for Am(VI).¹³⁶ Radiolytic oxidation of Am(III) to Am(V) and Am(VI) at high γ -doses is also observed in perchlorate solutions at pH 3–6 in the presence of excess of N_2O , $\text{S}_2\text{O}_8^{2-}$, or XeO_3 .¹³⁹ As expected, the stability of the higher oxidation states increases with pH. In carbonate solutions Am(III) is radiolytically oxidized to Am(V) under the exposure of intense α -radiation from ^{244}Cm (3–8 KCi/L).¹⁴⁰ The formation of oxidizing species in concentrated chloride solutions, that is, Cl_2 and ClO^- , leads to the autoradiolytic oxidation of Am(III) to Am(V).^{15,88} The radiolytic formation of hypochlorite in basic 5 M NaCl is directly correlated with the alpha-specific activity of ^{241}Am . Additional information concerning radiolytically induced redox reactions for americium is provided in the next section.

6. REDOX REACTIONS OF AM(IV), (V), AND (VI)

6.1. Reduction of Am(IV)

When Am(IV) is prepared in 10–15 M H_3PO_4 , it undergoes reduction without any evidence for disproportionation.^{8,32,33} The rate of reduction increases at both lower phosphoric acid concentration and higher α -activity. For example, Myasoedov and co-workers reported that in 5 M H_3PO_4 , and at an initial Am(IV)

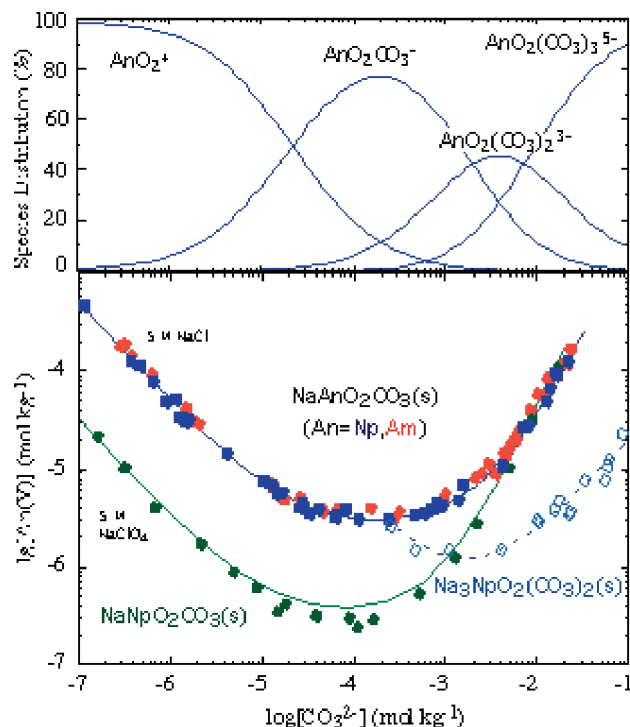
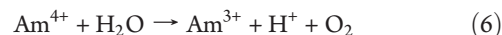


Figure 11. Species distribution (top) and solubility (bottom) of pentavalent actinides, Np(V) and Am(V), as a function of carbonate concentration.¹⁶ The solution speciation (top) is calculated from thermodynamic data recommended by Lemire and co-workers for pentavalent actinide ions.¹³⁵

concentration of 2.3×10^{-3} M twice as much Am(III) than Am(VI) was formed, while the average oxidation state remained $\sim\text{IV}$.³³ This indicates that tetravalent americium does indeed disproportionate at lower acid concentration. Higher reduction rates observed at higher α -activities suggest that Am(IV) reduction is also caused by the reaction with radiolysis products of the diluent. In contrast, Lebedev and co-workers measured a reduction half-life of 27 h in 12 M H_3PO_4 and 8×10^{-3} M americium (85% ^{243}Am).⁸³ These authors also reported that the rate of reduction was greater for lower americium concentrations, hence lower α -activity, with an activation energy of 65.3 kJ mol^{-1} , indicating that the reduction of Am(IV) was not caused by radiolysis, but by water as shown in eq 6



This may indicate that at low ^{243}Am concentrations, with the lower specific activity of this americium isotope, the water reduction mechanism becomes important.

The addition of highly radioactive curium increased the amount of radiolysis products and the rate of reduction. Self-reduction of Am(IV) to Am(III) in phosphoric acid solution follows first-order reaction kinetics. In 13 M NH_4F , $^{241}\text{Am(IV)}$ is autoreduced at a rate of about 4% per hour,⁷ increasing to 10% per hour in 3 M fluoride solution.³²

In bicarbonate/carbonate media Shilov found that Am(IV) is reduced at 54–70 °C, following a first-order rate law with respect to $[\text{Am(IV)}]$.¹⁴¹ The reduction rate increased with pH but decreased with an increase in carbonate concentration. In the absence of reliable evidence, the formation of an Am(IV) dimer was postulated at increased temperature, which dissociates into

Am(III) ions and peroxide. Interestingly, the reduction mechanisms of Am(VI) and Np(VII) are explained by the formation of a similar dimeric complex. Clearly, relatively little is known about the redox chemistry of Am(IV) and additional studies are needed.

6.2. Reduction of Am(V)

In weakly acidic solution, Am(V) can be reduced by radiolysis products generated upon its own decay or the decay of other alpha-emitting actinide isotopes. Early on, Asprey and Stephanou reported that the decrease in Am(V) absorbance at 514 nm and the increase in Am(III) absorbance at 503 nm for 8–33 mM americium in 0.035–1 M HClO₄ was linear with respect to time.¹⁴² However, no Am(IV) was detected. The linear decrease in [Am(V)] indicated a zero-order reduction with respect to the Am(V) concentration. When the total americium concentration was varied, the reduction was found to be first-order with respect to the total americium concentration, according to eq 7.

$$\begin{aligned} \frac{d[\text{AmV}]}{dt} &= \frac{d[\text{AmIII}]}{dt} \\ &= (0.023 \pm 0.002 \text{ h}^{-1}) \times [^{241}\text{Am}_{\text{tot}}] \quad (7) \end{aligned}$$

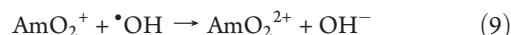
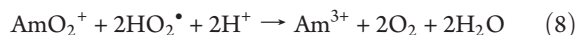
Hall and Markin obtained $k = 0.012 \pm 0.005 \text{ h}^{-1}$ for millimolar concentrations of americium in 0.2 M HClO₄,⁹¹ while Gunn and Cunningham found 0.020 h^{-1} in 0.2 M HClO₄.¹²⁷ Rates measured by Gunn varied from 0.016 – 0.022 h^{-1} .¹²⁰ Reduction rates for different solution conditions were compiled about 20 years ago.^{5,61}

The first-order dependence on the total americium concentration was attributed to the alpha-induced radiolytic reduction of americium. Any factor that changes the concentration of radiolytically produced reducing agents, such as total americium concentration, impurities in the acid solution, or the half-life of the americium isotope used in the study, affects the reduction rate. For example, radiolysis products may react with impurities first before initiating the reduction of Am(V) causing an induction period in the reduction of ²⁴¹Am(V) and subsequent ingrowth of ²⁴¹Am(III).⁸⁷ Zaitsev and co-workers confirmed the initial zero-order kinetics of ²⁴¹Am(V) in HClO₄ and H₂SO₄.¹⁴³ However, with time the Am(V) concentration apparently became the limiting parameter, resulting in a reduction rate dependence on the Am(V) concentration.

The autoreduction of Am(V) has been attributed to radiolytically produced H₂O₂ in aqueous solutions. Gunn and Cunningham reported that the rate of Am(V) reduction was first-order with respect to H₂O₂ concentration in 1 M HClO₄.¹²⁷ Gunn reported that “an amount of H₂O₂ sufficient to reduce one-fourth of the remaining AmO₂⁺” resulted in the reduction of americium in first order fashion, while the addition of Zr(ClO₄)₄ to scavenge H₂O₂ suppressed this reduction.¹²⁰ Zaitsev and colleagues reported H₂O₂ yields of $0.12 \mu\text{mol J}^{-1}$ for 0.1 M, and $0.07 \mu\text{mol J}^{-1}$ for 1 M H₂SO₄ solutions of americium.¹⁴³ The presence of H₂O₂ in 0.1 M HClO₄ solutions of ²⁴¹Am(III) was observed as an increase in background absorbance below about 340 nm.¹⁸ This absorbance was not found in solutions of the higher americium oxidation states, and its absence was attributed to its reaction with oxidized americium.

The hydrogen atom ([•]H) is another potential reducing agent created during the alpha-radiolysis of water. The rate constant of $2.00 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ was reported for the reaction with AmO₂⁺ to form Am(IV) at pH 0 by the Pikaev group.^{144,145} However, in aerated solution [•]H reacts with oxygen to create the hydroperoxy radical, [•]HO₂.¹⁴⁶ Although the reaction of HO₂[•] with Am(V) has

not been measured, Zaitsev and colleagues reported that the bimolecular rate constant for the reaction of H₂O₂ and Am(V) of only $21.6 \pm 2.2 \text{ M}^{-1} \text{ h}^{-1}$ at 30 °C, in 0.1 M HClO₄ was too slow to account for Am(V) reduction.¹⁴³ They therefore attributed Am(V) reduction to HO₂[•] rather than H₂O₂, in competition with its oxidation by the hydroxyl radical, [•]OH, according to eqs 8 and 9.¹⁴⁷



The reported autoreduction rates vary with the nature and the concentration of the acid, which then determine the type and concentration of radiolysis products. As an example, in 12 M HClO₄, autoreduction of Am(V), and even Am(VI), was not observed within 300 h, which was attributed to the radiolytic generation of oxidizing agents such as Cl₂ and ClO₂.¹⁴⁸ Further, the oxidation of Am(III) by the chloride radical, [•]Cl₂[−] has been reported in pulse radiolysis experiments,¹⁴⁹ and the addition of chlorine to Am(V) solutions slowed the reduction rate.⁷¹

The reduction of Am(V) in nitric acid is slow, with the rates reported by Zaitsev and co-workers as 1% h^{-1} in 0.5 M and 0.8% h^{-1} in 3 M HNO₃.¹⁵⁰ The slow reduction kinetics may be caused by the absence of detectable amounts of H₂O₂,¹⁴⁸ probably because of its reaction with radiolytically produced nitrous acid, as expressed in eq 10.¹⁵¹ Nitrous acid may also scavenge the hydroperoxyl radical (eq 11), although this reaction has not yet been verified.



Added nitrite¹⁴⁸ or H₂O₂¹⁵² did not accelerate the reduction of Am(V) in dilute nitric acid solution, possibly because the reactions in eqs 10 and 11. In contrast, Frolov and co-workers reported that the radiolytically induced reduction of Am(V) increased with increasing nitric acid or lithium nitrate concentration, which they attributed to the reduction by the radiolytically produced nitrite ion.¹⁵³ In this case, concentrations of NO₃[−] up to 9 M were used, possibly explaining the failure of radiolytically produced hydrogen peroxide to scavenge the nitrite ion.

6.3. Reduction of Am(VI)

Similarly to pentavalent americium, Am(VI) is subject to reduction by reaction with its own radiolysis products. As with Am(V), Hall and Markin reported that the autoreduction of ²⁴¹Am(VI) in 0.2 M perchloric acid was zero-order with respect to [Am(VI)] with the reduction rate being proportional to the total americium concentration.⁹¹ The rate law was reported to be $d[\text{Am(VI)}]/dt = 0.030 \text{ h}^{-1} [\text{Am}_T]$. However, the reported rate constant does not account for the production of Am(VI) via Am(V) disproportionation or a proposed reaction of Am(VI) with Am(IV) to produce Am(V). When considering these reactions, the authors calculated an actual rate constant for the reduction of Am(VI) of $0.019 \pm 0.002 \text{ h}^{-1}$. The produced Am(V) reduced linearly to Am(III) after the disappearance of the Am(VI). Disproportionation of Am(V) to replenish Am(VI) was insignificant at the low acidity used in these experiments. Gunn and Cunningham reported a rate constant of 0.02 h^{-1} for the reduction of ²⁴¹Am(VI) in 1 M HClO₄, and observed that Am(VI) was reduced within 5 min upon the addition of H₂O₂.¹²⁷

A table of rate constants for the Am(VI) autoreduction under various conditions was provided by Newton.⁶¹

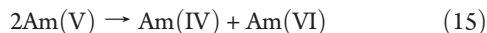
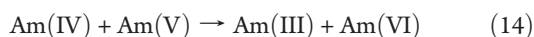
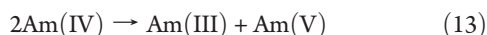
Zaitsev and co-workers attributed the Am(VI) reduction to radiolysis products, that is, H₂O₂ and the [•]H atom, in irradiated solutions of nitric, sulfuric, and perchloric acids.¹⁴⁷ However, in 12 M HClO₄, almost no reduction was found. This was attributed to the accumulation of Cl₂ and ClO₂ in irradiated HClO₄, which acted as oxidants to stabilize hexavalent americium. However, when the reduction of Am(VI) in concentrated HClO₄ was examined by Kornilov and co-workers using ²⁴⁴Cm as a high dose-rate α-radiation source, they found that these radiolysis products were actually reducing agents for Am(VI).¹⁵⁴ To explain the stability of Am(VI) in those solutions, the authors speculated that the qualitative composition of HClO₄ radiolysis products changed at very high HClO₄ concentrations. The addition of oxidizing agents such as S₂O₈²⁻ decreased the rate of autoreduction of Am(VI) in highly α-active solutions, probably by scavenging radiolytically produced reducing agents.^{62,155} Woods and colleagues used ²⁴³Am in LiClO₄–HClO₄ and found the reduction of Am(VI) by H₂O₂ to be first order in both Am(VI) and H₂O₂ concentrations.¹⁵⁶ The reduction of Am(VI) by H₂O₂ is shown in eq 12.



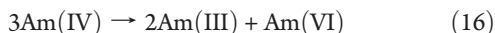
Kinetic analysis revealed that over the range 0.01–1.0 M H₂O₂ there was very little dependence on [H⁺] resulting in a rate law $d[\text{Am(VI)}]/dt = k[\text{Am(VI)}][\text{H}_2\text{O}_2]$.¹⁵⁶ The value of k in perchlorate media was reported to be $(3.83 \pm 0.52) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C and $I = 1.00$, [H⁺] = 0.98 M.

6.4. Disproportionation of Am(IV)

Lebedev and colleagues found that while in concentrated phosphoric acid Am(IV) undergoes reduction, at lower phosphoric acid concentrations Am(IV) disproportionates as evidenced by the appearance of Am(VI).⁸³ Equations 13–15 have been postulated for the disproportionation of Am(IV)



with the overall Am(IV) disproportionation reaction being



The disproportionation of Am(IV) adds a second-order component to the kinetics of Am(IV) reduction, for which the rate becomes faster as the acidity decreases. Second-order rate constants of 1.2×10^3 and $1.3 \times 10^5 \text{ M}^{-1} \text{ h}^{-1}$ were reported for 6 and 2 M H₃PO₄, respectively. These authors derived eq 17 for the disproportionation of Am(IV) in phosphoric acid⁸³

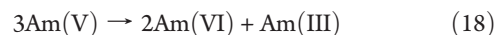
$$-d[\text{Am(IV)}]dt = 2k_1[\text{Am(IV)}]^2 + (k_2 + k')[\text{Am(IV)}] + k'' \quad (17)$$

where k_1 is the rate constant for Am(IV) disproportionation, k_2 is the rate constant for the reaction of Am(IV) with Am(V), k' is a summary rate constant for both the oxidation and reduction of Am(IV) by radiolysis products and k'' is the rate constant of Am(IV) reduction by water. Americium(IV) disproportionation in sulfuric acid apparently proceeds by the same stoichiometry.^{150,157} Zaitsev and colleagues also found that dissolution of AmO₂ in

varying concentrations of sulfuric acid resulted in predominantly Am(III), smaller amounts of Am(VI) and traces of Am(V).^{145,150} Since Am(V) was not expected to disproportionate in 1–2 M H₂SO₄ and yet Am(VI) appeared in those solutions, this was taken as evidence of the Am(IV)/Am(V) reaction in eq 14. Similarly, Penneman and colleagues concluded that the reaction in eq 14 is promoted with the presence of sulfate.⁶ In weaker complexing acids, such as perchloric or nitric acids, the reaction is not observed, and only trace amounts of Am(VI) are found.

6.5. Disproportionation of Am(V)

While Am(V) undergoes autoreduction in dilute acids, it disproportionates in strongly acidic solutions because of a strong dependence of the reaction on the [H⁺] concentration. Low-specific activity ²⁴³Am was first used by Coleman to investigate Am(V) disproportionation in 6 M HClO₄ without autoreduction effects.⁶⁰ As expected for the disproportionation of Am(V), the amount of Am(V) decreased while Am(III) and Am(VI) concentrations increased leaving the average oxidation state for all americium species unchanged. The stoichiometry of the disproportionation reaction in perchloric, nitric, and sulfuric acids was reported by Gunn and Cunningham and Zaitsev and co-workers as^{127,157}

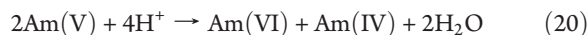


In all solutions studied, the disproportionation rate was proportional to the square of the Am(V) concentration, shown in eq 19

$$d[\text{Am(V)}]/dt = 3k[\text{Am(V)}]^2 \quad (19)$$

Coleman proposed that eq 15 was the rate-determining step.⁶⁰ Since Am(IV) was never measured, it was suggested that it rapidly disproportionated or reacted with Am(V) to form Am(III) and Am(VI), as was shown in eqs 13 and 14. The sum of eqs 14 and 15 results in the overall reaction given in eq 18.⁶⁰ The formation and subsequent reduction of hexavalent americium can be monitored spectroscopically in HClO₄, while in HCl Am(VI) is not detected spectroscopically (Figure 12).⁸⁸

While the dependence of the Am(V) disproportionation on the Am(V) concentration is well established, the dependence of the reaction on the acidity is less agreed upon, especially in nitric acid. Early studies reported reaction dependences of [H⁺]^{2.5} in 1–2 M HClO₄ and [H⁺]⁵ in 3–8 M HClO₄.⁶⁰ In contrast, several authors reported the fourth power dependence in HClO₄, as expressed in eq 20^{148,157,158}



For this reaction, Yakovlev and Kosyakov determined a rate constant of $k = (1.45 \pm 0.10) \times 10^{-2} \text{ M}^{-1} \text{ h}^{-1}$ in 1 M HClO₄ at 25 °C.¹⁴⁸ In sulfuric acid, the rate of disproportionation was found to be higher with a proposed dependence on [H⁺]^{4.6, 60, 87, 157}. The higher reaction rate was explained by the complexation of Am(VI) and the formation of americium anionic sulfate complexes.

Zaitsev and co-workers reported that the relationship between [H⁺] and the rate of disproportionation was nonlinear in nitric acid.¹⁵⁷ These authors reported $k = 10.3 \pm 1.2$, 140 ± 15 , and $4.1 \times 10^3 \text{ M}^{-1} \text{ h}^{-1}$ for nitric acid concentrations of 6.0, 9.1, and 14.3 M, respectively. Hall and Herniman also recognized that the hydrogen ion dependence in nitric acid was “not straightforward.”⁸⁷ Frolov and co-workers reported a seventh power acid dependency for the Am(V) disproportionation in 6 M nitric acid, but only a 1.5th-order dependence at <3 M HNO₃.¹⁵³ In the absence of

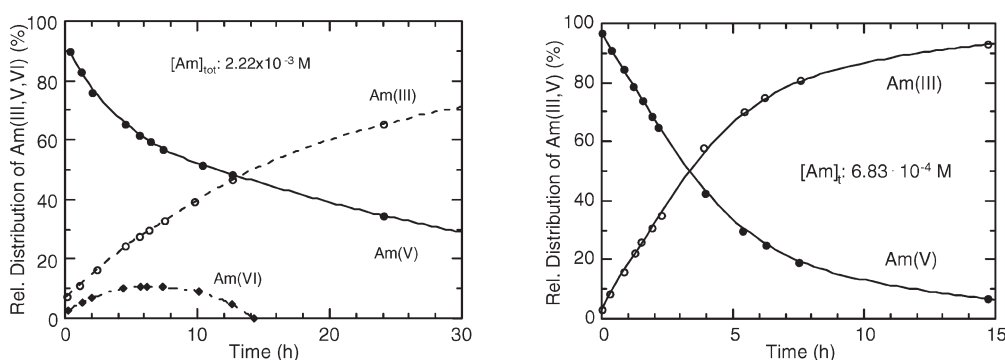
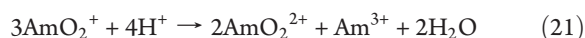


Figure 12. Spectroscopically monitored disproportionation of Am(V) in 5 M HClO₄ (left) and 5 M HCl (right).⁸⁸

supporting data, Erin and co-workers proposed the Am(V) disproportionation in nitric acid in the presence of the complexing agent potassium phosphotungstate (K₁₀P₂W₁₇O₆₁) to be:¹⁵⁹



The presence of phosphotungstate is known to complex and stabilize Am(IV) in solution and thus strengthens the disproportionation reaction and decreases the stability of Am(V) toward disproportionation. Interestingly, Erin and co-workers reported a first-order, rather than second-order dependence on Am(V) concentration for this reaction.¹⁵⁹

7. HIGH-VALENT AMERICIUM IN SEPARATIONS

Most of the standard methods for both aqueous and nonaqueous separation and purification of americium from a variety of sources and materials were developed in the 1950s, 1960s, and 1970s. In the 1980s and 1990s, research efforts focused largely on the development and testing of new and improved solvent extraction processes for americium separation from the lanthanides and curium. The various separations technologies applied to americium were compiled recently^{1,160} and actinide partitioning technologies were previously reviewed.^{161–163} In general, the behavior of the various metal ions in solution can be predicted, to a first approximation by their valence state. The higher oxidation states of americium, for example, behave much like the corresponding oxidation states of plutonium or neptunium in separations. Early separations relied on the precipitation of insoluble americium compounds or coprecipitation of americium(III) with insoluble lanthanide(III) compounds. These techniques afford facile separation of the trivalent f-series metals from the lighter actinides, which favor higher, nonprecipitable oxidation states. With advancements in nuclear fuel technologies, new, improved separation methods to partition the minor actinides regained importance and are currently being developed for the separation of americium from other trivalent ions such as the lanthanides.

Americium is relatively easily separated from earlier actinides, such as uranium, neptunium, and plutonium, utilizing their different thermodynamic properties and oxidation state stabilities. The lighter actinides favor higher oxidation states, with their trivalent ions requiring careful preparation. However, the separation of americium from curium and from the lanthanides poses a greater challenge because americium, curium, and most of the lanthanides have similar ionic radii and very comparable chemical properties with the trivalent oxidation state being most stable.

For the development of effective separations of the trivalent lanthanides from the trivalent actinides the differences in the covalency of 4f- and 5f-element compounds have been explored using soft-donor ligands to preferentially complex and extract the actinides.^{164–166} Other concepts take advantage of the ability of americium to exist in multiple oxidation states, as has been discussed above. Oxidized americium has been used for the successful separation of milligram amounts of americium^{17,167} and curium.^{168,169} Early studies included the separation of americium from curium based on the retention of Am(VI) on chromatographic columns prepared from di(2-ethylhexyl)phosphoric acid,¹⁷⁰ the high solubility of Am(VI) in lanthanum fluoride¹⁷¹ or calcium fluoride.¹⁷² Americium(VI) is soluble in fluoride solutions and passes through a column of calcium fluoride, while trivalent actinides and lanthanides are retained. In this work, we concentrate on summarizing methods that utilize the properties of higher-valent americium for its separation from its 4f and 5f analogs.

7.1. Separation by Precipitation

Initially, the methods to separate and purify americium from other actinides and lanthanides encompassed only precipitation processes. Soon after the discovery that peroxydisulfate oxidizes Am(III) to Am(VI), analytical chemists began using higher americium oxidation states to separate it from the lanthanides and curium.^{171–174} In these methods, precipitation of the trivalent elements was used to separate them from soluble Am(VI), as had been done previously for hexavalent uranium, neptunium, and plutonium. Similar precipitation methods have been used to distinguish between the valence states to study the oxidation kinetics of americium.¹⁷⁵ In general, compounds of Am(III) exhibit low solubilities and can be scavenged in lanthanide precipitates. The higher oxidation states, Am(V) and Am(VI), in analogy with the corresponding oxidation states for uranium, neptunium, and plutonium, have higher solubility and have been utilized to retain americium in solution while precipitating the remaining heavier trivalent actinides or lanthanides. Because of their thermodynamic properties, precipitation of compounds, such as AmF₃, K₈Am₂(SO₄)₇, Am₂(C₂O₄)₃, or K₃AmO₂(CO₃)₂, have been routinely used to separate americium.¹

Carbonates and oxalates are of special interest because both are convenient starting materials for the preparation of AmO₂ and because oxalate ions prevent precipitable, nonoxalate impurities from accompanying americium in the precipitate. The insoluble Am(V) carbonate complex has been particularly useful

for the large-scale separation of americium from curium.^{176,177} In some cases even the trivalent metals have been separated from each other by precipitation. For example, Hermann demonstrated the separation of americium(III) from lanthanum(III) by fractional precipitation of their oxalates, generated by slow hydrolysis of dimethyl oxalate.¹⁷⁸ The oxalate precipitate is greatly enriched in americium, and about 50% of the lanthanum can be rejected at each stage containing only about 4% of the americium. More commonly, oxidation of americium is employed.

Stephanou and co-workers separated Cm(III) from americium by oxidizing the latter to Am(VI) with potassium peroxydisulfate and precipitating the curium as CmF₃; Am(VI) is soluble under these conditions.¹⁶⁸ In analogy to Pu(IV) peroxide, Proctor and Connor precipitated Ce(IV) peroxide to separate gram quantities of americium(III) from cerium.¹⁷⁹ Proctor also used trifluoride precipitates to separate Am(VI) from large quantities of rare earths.^{179,180} Similarly, Holcomb oxidized an americium solution containing lanthanum nitrate carrier by using silver-catalyzed ammonium peroxydisulfate at 85 °C, then cooled the treated solution in an ice bath and loaded it onto a column of calcium fluoride.¹⁷² Americium eluted while the trivalent elements were retained. Bhanushali and his co-workers have proposed an oxalate precipitation for industrial separation of americium(III).¹⁸¹ On the basis of some experimental data, these workers suggest that traces of americium and plutonium remaining in the aqueous waste generated during plant-scale precipitation of plutonium oxalate can be effectively removed by simple coprecipitation with thorium oxalate.

7.2. Separation by Extraction

Solvent extraction technology exhibits many advantages for process-scale separations, not the least of which is its compatibility with existing fuel recycling processes. Typically, the extraction of the actinides into the organic phase increases in efficiency with the charge density of the extracted ion. The usual order is $An^{4+} > AnO_2^{2+} > Am^{3+} > AnO_2^+$. Thus, valence control is important to successful separations. Only a few reports describe the use and extraction of higher-valent americium. As one of the rare examples, solutions of HDEHP have been used to selectively extract Am(VI) from Cm(III) by Musikas and colleagues.¹⁸² However, in such systems rapid reduction of Am(VI) to lower oxidation states posed a significant problem. This is common for other solvent systems as well and has been exploited in separations.⁵ Given that Am(VI) reduction in the organic phase may be rapid, a number of procedures have relied on this process to generate Am(V), which, in analogy with NpO_2^+ , is not extractable in most solvent extraction procedures.

Americium(VI)-loaded 0.1 M thenoyltrifluoroacetone (TTA)/butanol was stripped of Am(V) using acetate or perchlorate solution by Hara.⁶⁸ Myasoedov and his colleagues used 0.05 M 1-phenyl-3-methyl-4-benzoylpyrazolone-5 (PMBP)/0.025 M trioctylphosphine oxide (TOPO) in cyclohexane to partition americium from Ce, U, Np, Pu, Bk, and Cf.^{183,184} The americium was oxidized to Am(VI) using peroxydisulfate, with or without Ag, which would also oxidize Ce(III) to Ce(IV), and neptunium and plutonium to Np(VI) and Pu(VI). Upon solvent contact Am(VI) reduced to Am(V), which remained in the aqueous phase. Americium(V) was extractable at pH 4–6 by PMBP/TOPO from polar-oxygen containing diluents, such as alcohols or ketones, but not in nonpolar diluents.

The use of tri-*n*-butyl phosphate (TBP), the most important ligand in nuclear solvent extraction, has been explored to separate

Am(VI) from lanthanides. Kamoshida and co-workers investigated the TBP extraction of Am(VI) from used nuclear reactor fuel reprocessing solutions.^{80,185} In these studies, oxidation of Am(III) with silver-catalyzed peroxydisulfate generated Am(VI) both in the presence and absence of stoichiometrically deficient $(NH_4)_{10}P_2W_{17}O_{61}$, added to stabilize americium in the tetravalent oxidation state. Under these conditions, free Am^{4+} rapidly disproportionated to give Am(V), which was readily oxidized by Ag-catalyzed ammonium peroxydisulfate to Am(VI). By use of neat TBP to extract Am(VI) from 1 M HNO₃, an americium distribution ratio of about 4 was obtained and the separation factor from Nd(III) reached 87. On the other hand, Am(IV) complexed by phosphotungstate was not extractable. The amount of peroxydisulfate not only controlled the americium valency but also determined the separation efficiency affected by the formation of Am(VI) sulfate complexes. However, for process application, this method suffers the disadvantage of requiring an initial denitration to reduce the nitric acid concentration, followed by the addition of more nitric acid after the oxidation. This is necessary because the decomposition of peroxydisulfate under acidic conditions produces reducing agents. A high concentration of 1.6 M $(NH_4)_2S_2O_8$ and 0.01 M AgNO₃ was used to achieve successful oxidation to ~85% Am(VI) in actual nuclear fuel dissolution, following a 66% dilution to reduce the acidity to 1 M HNO₃. Quantitative Am(VI) was produced in actual fuel dissolution that was first twice extracted with 30% TBP/*n*-dodecane to reduce the uranium and oxidizable plutonium concentrations. The principal disadvantage of this method is the generation of large amounts of waste due to the high concentration of peroxydisulfate required.

The oxidation reagent sodium bismuthate has the advantage that, unlike peroxydisulfate, it will oxidize americium in strongly acidic solution. It was used by Hara and Suzuki to demonstrate quantitative oxidation of Am(III) to Am(VI) in nitric acid acidities as high as 4 M.¹⁸⁶ The oxidation is performed at room temperature, simply by mixing the solid bismuthate powder with the Am-spiked nitric acid solution and vigorous stirring. Recently, Mincher and co-workers used sodium bismuthate to demonstrate 30% TBP/dodecane solvent coextraction of UO_2^{2+} , NpO_2^{2+} , PuO_2^{2+} , and AmO_2^{2+} across a range of nitric acid concentrations up to 6 M (Figure 13).¹⁹ In strong nitric acid, uranium is naturally hexavalent, plutonium is tetravalent, and neptunium may be present as a mixture of mainly penta-, and hexavalent ions. All these actinides remained in the hexavalent oxidation state in the presence of sodium bismuthate. The Am(VI) was slowly reduced upon contact with 30% TBP solution, but was successfully extracted in short contact times as shown in Figure 13. It can also be seen that the extraction efficiency of the actinyl ions decreases with increasing Z-number. Although the metal charge density actually increases with Z-number because of the actinide contraction, for the actinyl (AnO_2^{2+}) ions the decreased extraction efficiency is attributed to the electron density provided to the metal center by the axial oxygens. This results in a weaker bond to the TBP ligand.¹⁸⁷

Recently, these authors found that dibutylbutylphosphonate provided a factor of 5 increase in extraction efficiency over TBP.¹⁸⁸ The higher basicity of dibutylbutylphosphonate significantly improved the extraction efficiency of Am(VI) from nitric acid solution. Am(VI) was generated by oxidizing Am(III) with sodium bismuthate at room temperature, while oxidation at 80 °C produced Am(V).¹⁹

The addition of ammonium dihydrogenphosphate in 3 M HNO₃ increased the separation of americium from Nd(III) with

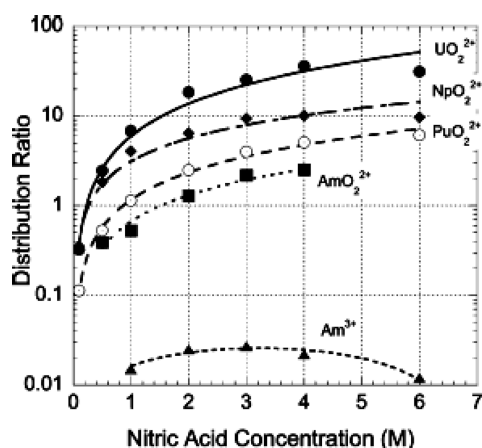


Figure 13. Solvent extraction of UO_2^{2+} , NpO_2^{2+} , PuO_2^{2+} , and AmO_2^{2+} from nitric acid using 30% TBP in dodecane after sodium bismuthate oxidation.¹⁹

TBP to a factor of 120, although the extraction efficiency was reduced.¹⁸⁹ It was suggested that the phosphate anion formed an Am(VI) complex, which lowered the distribution ratio. In contrast, CMPO and TOA reduce Am(VI).¹⁸⁹

The proposed French SESAME (selective extraction and separation of americium by means of electrolysis) process aimed to partition americium from the lanthanides by selectively extracting Am(VI).^{190,191} The main steps in this process include the electrochemical oxidation of Am(III) to Am(IV) in nitric acid in the presence of phosphotungstate or silicotungstate. Complexation of Am(IV) lowers the potential for the Am(IV)/Am(III) redox couple. Subsequent oxidation of Am(IV) to Am(VI) via an Am(V) intermediate was achieved by Ag^{2+} and extraction of Am(VI) by 50% TBP. In 1 M HNO_3 , an americium yield higher than 99% was obtained with americium purity close to 99%. However, the process was abandoned when americium recoveries of only 80% were achieved in a hot test. These disappointing results were thought to be due to incomplete americium oxidation.¹⁹²

As was mentioned above, solvent extraction of the more stable Am(V) has been used successfully. Hara prepared Am(V) solutions free of Am^{3+} by first extracting AmO_2^+ from buffered 1 M acetate (pH 3) solutions into 0.1 M TTA in isobutanol and back-extraction into an aqueous phase.⁶⁸ Fardy and Buchanan suggested that Am(V) remains in the aqueous phase when contacted with a mixture of TTA and TOPO in cyclohexane.¹⁹³ Trace amounts of americium were oxidized in 0.05 M nitric acid preheated with 0.05 M ammonium peroxydisulphate. However, incomplete oxidation to Am(V) prior to the extraction step caused inconsistent extraction results, since Am(III) was readily extracted. It was not possible to obtain quantitative extraction of hexavalent americium by this solvent mixture or the organophosphorus reagent, di-(2-ethylhexyl) phosphoric acid in cyclohexane. Similarly, Stokely and Moore showed that Am(V) remains in the aqueous phase when contacted with a 0.5 M solution of 2-theynoyltrifluoroacetone in xylene to extract actinide (III, IV, VI).¹⁹⁴ The Am(III) was oxidized to Am(VI) using ammonium peroxydisulfate and silver ions as catalysts and Am(VI) was reduced to Am(V) by buffering the solution with acetate to pH 4.8–5.2.

7.3. Ion Exchange Chromatography

Few developments have been reported using ion exchange for the separation of oxidized americium from curium and the

lanthanides. Hulet describes a separation of Am(VI) from Cm(III) on HDEHP-silica columns in the presence of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ where Cm(III) is washed from the column using 0.1 M HNO_3 and americium is eluted with 1 M HNO_3 .¹⁷⁰ Curium was decontaminated from americium by a factor of 10–14, whereas the decontamination factor for curium in americium is 1000.

8. CONCLUDING REMARKS

The higher oxidation states of americium have been known for five or six decades, although interest in their chemistry had waned. Renewed interest in the separation of americium from the lanthanides and higher actinides for fuel cycle purposes has resulted in renewed research in this area in recent years. In general, few reagents are available for the oxidation of Am(III), and once produced, high-valent americium is easily reduced.^{1,5,160} It is especially difficult to work with Am(IV), which must be complexed to prevent its disproportionation, and thus far few separations have been proposed using this oxidation state. The rapid reduction of especially Am(VI) produces solutions of mixed oxidation states with Am(V) and Am(III), which also makes separations difficult. Maintaining americium in the form of Am(VI) for process separations has proven problematic in practice, as the studies by French scientists have shown. However, continued work to develop advanced separations technology and the utilization of basic extractants and short contact times may yet yield viable solvent extraction methods.

A less developed opportunity for separating americium from the lanthanides and curium is the oxidation to more soluble, poorly complexed Am(V). The investigation of the higher oxidation states of americium is an area of actinide chemistry, which still has great opportunities for new discoveries and development of advanced separation technologies.

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Wolfgang H. Runde received a Ph.D. in inorganic chemistry in 1993 from the Technical University of Munich, Germany. Before joining Los Alamos National Laboratory in 1996, Runde was a project leader at the Institute of Radiochemistry of the Technical University of Munich (1993–1995) and a postdoctoral associate with the G.T. Seaborg Institute at Lawrence Livermore and Lawrence Berkeley Laboratories (1995–1996).

Wolfgang Runde is currently the Associate Director of the National Isotope Development Center and the Associate Director of the Seaborg Institute at Los Alamos National Laboratory. He has more than 25 years of experience and an established record in the chemistry of *f*-elements, including the light actinide elements uranium, neptunium, plutonium, americium, and curium, with extended knowledge in thermodynamics, spectroscopy and characterization, radiolysis effects, radio- and radioanalytical chemistry. Runde has had an active research career in actinide chemistry, leading projects related to repository science (Gorleben, YMP, WIPP), weapons material disposition, separation, environmental research, and basic actinide chemistry. He has published over 50 papers in peer-reviewed journals and coauthored several book chapters on the chemistry and behavior of actinides, including chapters on “Americium” and “Actinides in the Geosphere” for the 3rd edition of the *Chemistry of the Actinide Elements*. He has received several awards for outstanding contributions, including a Distinguished Performance Award for his efforts of student mentoring.



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