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MASTER

The Chemistry of AMERICIUM

Wallace W. Schulz

Technical Information Center, Energy Research and Development Administration

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Wallace W. Schulz
Atlantic Richfield Hanford Company

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FOREWORD

The two principal americium isotopes of interest (^{241}Am and ^{243}Am) are both by-products of the nuclear industry and are expected to be available in relatively large quantities in the future. Americium-241, which is formed by beta decay, has been in short supply since it was first offered for sale in March 1962 at $1500 per gram by the U. S. Atomic Energy Commission. The first material made available for sale came from the Atomic Energy Commission's Rocky Flats Plant. This source has been supplemented in recent years by the recovery of significant quantities of ^{241}Am at Richland and Savannah River reprocessing facilities.

Probably no actinide isotope has more uses than ^{241}Am, which is used in nuclear gauges for numerous applications, in location sensing devices, in ^{241}Am—Be neutron sources for oil well logging, etc., in static eliminators, in smoke detectors, and in many other applications. In addition, ^{241}Am has been used as a target material in nuclear reactors to produce ^{242}Am, which has a number of potential uses, including its decay to ^{238}Pu. Americium-243 is useful as a reactor target material for the production of ^{244}Am, ^{252}Cf, and other actinides.

In 1968, Richland demonstrated the recovery of americium from high-level wastes generated from the reprocessing of the Shippingport blanket. This americium was subsequently isolated and purified by chromatographic processes. Significant quantities of ^{243}Am were produced in Savannah River production reactors as early as the late 1950s as part of special irradiations to produce transplutonium isotopes for research uses and in the ^{252}Cf production programs. Thus the Savannah River Laboratory has played an important role in the americium chemistry development programs.

The long-range availability of americium looks attractive since increasing quantities of ^{241}Am and ^{243}Am could be expected from plutonium recycle either in light-water power reactors or fast breeder reactors. As greater quantities of these isotopes become available at reasonable prices, it can be expected that new and expanded uses will be found for them.

F. P. Baranowski
Director, Division of Nuclear Fuel Cycle and Production
Energy Research and Development Administration

PREFACE

This book has a straightforward purpose, that is, to collect and review in one place the essential features of the descriptive chemistry of americium as it is known in the mid-1970s. Highlights of this material are, of course, discussed in standard texts on the chemistry of the transuranium elements; but, because of space limitations, the coverage given americium is far from comprehensive. Other important aspects of americium chemistry are disclosed in widely scattered journal articles and in various governmental reports, both foreign and domestic, not always easily available to all the scientific community. These circumstances coupled with the great advances in our knowledge of americium chemistry during the past decade provide more than sufficient motivation for this review.

Americium chemistry is delineated here within the traditional "occurrence–properties–compounds–uses" framework. No attempt is made to compare americium chemistry with that of other actinide elements, this task being more properly in the scope of books that discuss the chemistry of all the transuranium elements. A chapter on the analytical chemistry of americium, provisionally included in the initial outline of this review, was omitted—partly to reduce the length of the manuscript but mainly because of the recent appearance of an excellent book* that treats the subject in great detail. Missing from this text also is any discussion of the behavior of americium in biological and ecological systems; this is a vast and important segment of americium chemistry which would more fittingly be reviewed by qualified life scientists.

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*B. F. Myasoedov, L. I. Guseva, I. A. Lebedev, M. S. Milyukova, and M. K. Chmutova, *Analytical Chemistry of Transplutonium Elements*, John Wiley & Sons, Inc., New York, 1974.

This book could not have been written without the cooperation and counsel of a great many talented scientists and engineers at various Energy Research and Development Administration (ERDA) laboratories and installations. Stimulating discussions of various facets of americium chemistry were held with R. A. Penneman and L. B. Asprey of the Los Alamos Scientific Laboratory; with W. H. Hale of the Savannah River Laboratory; with E. J. Wheelwright of the Battelle Pacific Northwest Laboratories; with R. E. Leuze of the Oak Ridge National Laboratory; and with J. B. Knighton, S. G. Proctor, and F. J. Minor at the Rocky Flats site. J. L. Ryan, Battelle Pacific Northwest Laboratories, a recognized authority on the chemistry of the transuranium elements, kindly reviewed the entire manuscript and made many helpful suggestions for its improvement. I am indebted also to T. D. Chikalla and R. P. Turcotte of the Battelle Pacific Northwest Laboratories for an expert critique of the chemistry of americium oxides.

The many drafts of the manuscript of the book were carefully typed (and retyped!) by Eleanore Earhart and Judy Foley, amanuenses of exceptional ability.

My special thanks go to my dear wife, Dorothy, and to R. F. Pigeon of ERDA's Office of Technical Information, for their encouragement and great patience while this book was being written.

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CONTENTS

1 DISCOVERY; ATOMIC AND NUCLEAR PROPERTIES; COLLATERAL READING

DISCOVERY

Americium, element 95, the third element past uranium, was actually the fourth transuranium element to be discovered—after curium. Working at the wartime Metallurgical Laboratory of the University of Chicago, Seaborg, Ghiorso, James, and Morgan in late 1944 and early 1945 identified ^{241}Am produced by the reactions

$$^{239}\mathrm{Pu}(n,\gamma)^{240}\mathrm{Pu}(n,\gamma)^{241}\mathrm{Pu} \xrightarrow[14.3\text{ years}]{\beta} {}^{241}\mathrm{Am}$$

Historical details surrounding discovery and identification of ^{241}Am, including the first (Nov. 11, 1945) announcement of its discovery on a national radio program, have been recounted by Seaborg and others.[1-8] By analogy with the naming of its rare-earth homolog, europium, after Europe, element 95 was named (in 1946) americium after the Americas. Less than a year after it was discovered, Cunningham[9,10] isolated americium in pure form as the compound $Am(OH)_3$ and made the first measurements of its absorption spectrum in aqueous solution.

The longest lived americium isotope, ^{243}Am ($t_{1/2} = 7400$ years), was identified in 1950 by Seaborg, Ghiorso, and Street[11] as the product resulting from two successive neutron captures by ^{241}Am. Now americium isotopes with all the mass numbers from 232 to 247 are known or at least have been tentatively identified.

ISOTOPES AND NUCLEAR PROPERTIES

Key data relative to the synthesis and radioactive decay properties of all the presently known isotopes of americium are compiled in Table 1.1. (Details of the

Table 1.1

AMERICIUM ISOTOPES AND PROPERTIES

Mass number^{a}	Half-life^{b}	Decay mode^{c}	Principal radiations, MeV	Principal synthesis reactions	Refs.
232	1.4 min	SF isomer		^{230}Th(^{10}B,8n)	13-15
234	3 3 ± 0.1 min	α	α 6.46	^{230}Th(^{10}B,6n)	13, 15
235^{md}				^{237}Np(^{4}He,6n)	16
236^{md}				^{237}Np(^{4}He,5n)	16
237	75 min	EC 99+% α 0 005%	α· 6.02	^{239}Pu(d,4n)	17-19
237^{m}	5 nsec	SF isomer		^{238}Pu(p,2n)	20
238	1 86 hr	EC, α 10 ^{4}%	γ 0 36, 0.58, 0.95, 0.98, 1.35, others	^{237}Np(α,3n) ^{239}Pu(d,3n)	21-24
238^{m}	60 μsec	SF isomer		^{239}Pu(p,2n)	25
239	12.1 hr	EC α 0 003-0.005%	γ 0.225, 0.275, others	^{239}Pu(d,2n) ^{237}Np(α,2n)	17, 21, 23 25-27
239^{m}	160 nsec	SF isomer		^{240}Pu(p,2n) ^{239}Np(d,2n)	28
240	51.0 hr	EC α 1 9 x 10^{-4}%	γ 0 90 (23%) 1.00 (77%) 1.40 (<10%)	^{240}Pu(d,n) ^{239}Pu(α,p2n) ^{237}Np(α,n)	11, 21, 26 29, 30
240^{m}	0.90 msec	SF isomer		^{240}Pu(d,2n) ^{241}Pu(p,2n)	31
241	432 9 years	α	α 5 49 (85%), 5.44 (13%) γ 0.060 (36%) Others see Fig. 1.1	^{241}Pu $\xrightarrow{\beta^-}$ ^{241}Am	26, 32-38
241$^{me\text{-}h}$	1.5 μsec	SF isomer		^{241}Pu(d,2n) ^{242}Pu(p,2n)	28
242	16.01 hr	β^{-} (82.8-84%) EC (17 2-16%)	β^{-} 0 67 max γ Pu X-rays e^{-} 0 021, 0.0037	^{241}Am(n,γ)	30, 39-44
242$^{m1e\text{-}h}$	152 years	IT 99+% α 0.48%	e 0 028, 0.044 α 5 21	^{241}Am(n,γ)	11, 26, 42, 45

242^{m2}	14.0 msec	SF isomer		^{243}Am(n,2n) ^{241}Am(d,p) ^{241}Am(n,γ) ^{238}U(^{11}B,α3n)	46-56
$243^{e\ h}$	7400 years	α	α 5.28 (87%), 5.23 (11.5%) Others see Fig. 1.2 γ 0.044 (5%), 0.075 (61%) Others see Fig. 1.2	^{243}Pu $\xrightarrow{\beta^-}$ ^{243}Am ^{243}Am(n,γ)	11, 30, 33 57, 58
243^{m}	6.5 μsec	SF isomer		^{243}Am(d,pn)	20
244	10.1 hr	β	β 0.387 max γ 0.746 (66%), 0.900 (28%)	^{243}Am(n,γ)	58, 59
244^{m1}	26 min	β^- (99+%) EC (0.039%)	β 1.50 max (80%), others γ 0.0429, others	^{243}Am(n,γ)	11, 59-61
244^{m2}	0.9 msec	SF isomer		^{243}Am(d,p)	47, 49, 50
245	2.04 hr	β^-	β^- 0.91 max, others γ (^{245}Cm) various	^{245}Pu $\xrightarrow{\beta^-}$ ^{245}Am	30, 50, 62, 63-66
245^{m}	640 ± 60 nsec	SF isomer		^{244}Pu(α,p2n)	67
246	25.0 min	β^-	β^- 2.10 max (7%), others γ (^{246}Cm) various	^{246}Pu $\xrightarrow{\beta}$ ^{246}Am	30, 65, 68
246^{m1}	39 min	β	β 1.12 (53%), 1.25 (13%) 1.80 (14%), 2.0 (20%) γ (^{246}Cm) various	^{244}Pu(α,d) ^{244}Pu(^{3}He,p) ^{244}Pu(α,pn)	58, 69, 70
246^{m2}	75 ± 10 μsec	SF isomer		^{244}Pu(α,pn)	67
247	22 min	β^-	γ (^{247}Cm) 0.226, 0.285	^{244}Pu(α,p)	58, 69, 70

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[a] Exact atomic masses are listed in Table 1.2, specific activities are given in Ref. 12.

[b] Accepted values are listed in *Nuclear Data Sheets*

[c] EC, electron capture, α, alpha decay, SF, spontaneous fission, β^-, negative beta decay, e^-, internal conversion electron

[d] Only tentatively identified.

[e] Spin ^{241}Am, 5/2 (Ref. 71), ^{242m1}Am, 1 (Ref. 71), ^{243}Am, 5/2 (Ref 71)

[f] $T_{1/2}$[SF] ^{241}Am, 1.15 x 10^{14} years (Ref 72), ^{242m1}Am, 9.50 x 10^{11} years (Ref 73), ^{243}Am, 2.00 x 10^{14} years (Ref. 74).

[g] Electric quadrupole moment, q(10^{24} cm^2) ^{241}Am, +4.9 (Ref. 75), ^{242m1}Am, −2.76 (Refs 75-77), ^{243}Am, +4.9 (Ref 78)

[h] Nuclear dipole moment, (nuclear magnetons) ^{241}Am, +1.58 (Refs 75, 79), ^{242m1}Am, +0.381 (Ref 79), ^{243}Am, +1.4 (Ref. 80).

various decay modes and associated energies of the long-lived ^{241}Am and ^{243}Am are shown in Figs. 1.1 and 1.2.) Table 1.1 is adapted from the listing recently prepared by Hyde.[81] Hyde's article[81] and the books by Hyde, Perlman, and Seaborg;[30] Lederer, Hollander, and Perlman;[82] and Dzhelepov and Peker[83] provide exhaustive treatment of the nuclear properties of the various americium isotopes. Mughabghab and Garber[84] have recently (1973) tabulated thermal cross sections and resonance properties of ^{241}Am, ^{242}Am, ^{242m}Am, ^{243}Am, ^{244}Am, and ^{243m}Am; cross-section data for ^{241}Am were listed earlier (1959) by Howerton.[85] Wapstra and Gove[86] have tabulated known nuclear systematics—masses and energetics—of the various americium isotopes of mass numbers 234 to 248; their data are given in Table 1.2. An earlier compilation of such data was given by Viola and Seaborg.[87]

ATOMIC PROPERTIES

Electron Configuration

The generally accepted[88-90] electron configuration of gaseous americium neutral atoms and cations, as determined from spectroscopic and atomic beam experiments,[91] is shown in Table 1.3. Americium is the sixth member of the actinide series of elements; the electron configurations of americium in both its ground and ionized states are completely analogous to those of its homolog, europium, the sixth member of the lanthanide series. Recognition in 1944 of the possibility that elements 95 and 96 might be members of an actinide series led directly, as Seaborg[3,92] has noted, to the identification of ^{242}Cm and ^{241}Am.

Atomic and Ionic Radii

Metallic, covalent crystal, and ionic radii of americium in various oxidation states were first calculated by Zachariasen.[93] His values (Table 1.4), even though 20 years old, are still cited.[88] The radius of americium metal [coordination number (CN)12] is 1.73 Å.[94,95] Peterson and Cunningham, as part of their studies of berkelium compounds, calculated the ionic radius (CN 6) of several trivalent actinides in various compounds. Their results for Am^{3+} are 0.962 Å in AmF_3 (Ref. 96), 1.006 Å in $AmCl_3$ (Ref. 97), and 0.985 Å in Am_2O_3 (Ref. 98). On the basis of a refined crystal structure for $AmCl_3$, Burns and Peterson[99] calculated the ionic radius (CN 6) of Am^{3+} in $AmCl_3$ to be 0.984 ± 0.003 Å.

Ionization Potentials

Carlson, Nestor, Wasserman, and McDowell[100] have calculated ionization potentials for americium (Table 1.5) based on a simple spherical shell model using eigenvalues and mean radii from Hartree–Fock solutions for neutral atoms.

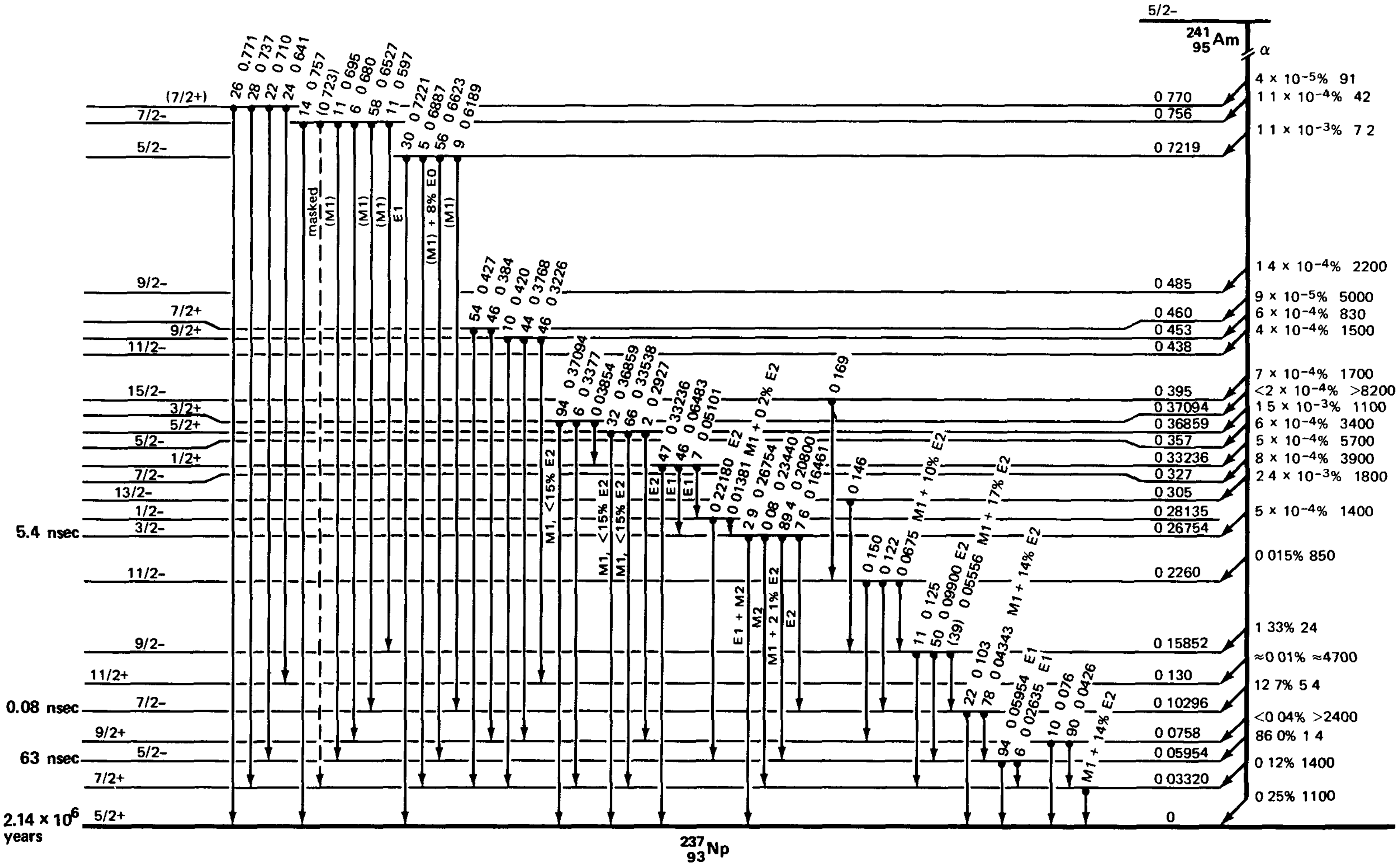

Fig. 1.1 Decay scheme for ^{241}Am. (From C. M. Lederer, J. M. Hollander, and I. Perlman, *Table of Isotopes,* 6th ed., p. 430, John Wiley & Sons, Inc., New York, 1967.)

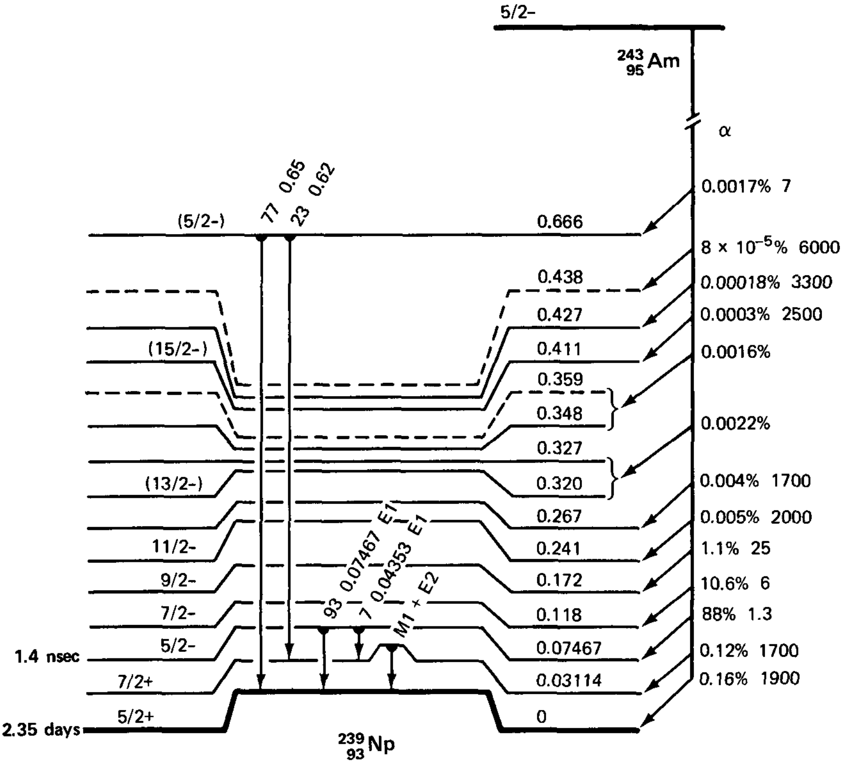

Fig. 1.2 Decay scheme for ^{243}Am. (From C. M. Lederer, J. M. Hollander, and I. Perlman, *Table of Isotopes*, 6th ed., p. 433, John Wiley & Sons, Inc., New York, 1967.)

Emission Spectra

Detailed studies of the arc and spark spectra of americium have been made by Tomkins and Fred,[91,101,102] Thorne,[103,104] and Oganov, Striganov, and Sobolev.[105] Such studies identified 1000 to 2000 Am I and Am II spectral lines. Table 1.6, compiled by Carnall,[106] lists term assignments relative to the $5f^7 7s^2 (^8S_{7/2})$ ground state made by Tomkins and Fred[102] for the identified even and odd parity levels of Am I. Carnall noted that the number of lines classified on the basis of the indicated terms constituted only about 10% of the Am I lines observed in the spectrum of ^{241}Am excited both in hollow cathode and electrodeless discharge sources. Term assignments for even and odd parity levels of Am II are also given in Ref. 106.

Corresponding to the absolute term value (48,767 cm^{-1}) of the ground state, the ionization potential of Am I is 6.0 eV. This value is in fair agreement with the value 5.655 eV shown in Table 1.5. The experimental isotope shift constant βC_{exp}

Table 1.2

NUCLEAR SYSTEMATICS OF AMERICIUM ISOTOPES*

A	Z	N	Atomic mass, μ	Mass excess, keV†	Binding energy, keV‡	Beta-decay energy, keV §
234	95	139	234.04770	44,430	1,770,010	−4,060
235	95	140	235.04796	44,670	1,777,840	
236	95	141	236.04942	46,030	1,784,550	−1,950
237	95	142	237.05008	46,650	1,792,010	−2,530
238	95	143	238.05205	48,490	1,798,240	−930
239	95	144	239.053039	49,406	1,805,394	−1,700
240	95	145	240.05533	51,540	1,811,330	−180
241	95	146	241.056844	52,951	1,817,992	−772
242	95	147	242.059575	55,494	1,823,520	667
243	95	148	243.061394	57,189	1,829,897	−7.1
244	95	149	244.064302	59,898	1,835,260	1,429
245	95	150	245.066475	61,922	1,841,307	901.6
246	95	151	246.06972	64,940	1,846,360	2,300
247	95	152	247.07209	67,160	1,852,220	1,600
248	95	153	248.07570	70,520	1,856,930	3,100

*From A. H. Wapstra and N. B. Gove, The 1971 Atomic Mass Evaluation in Five Parts, *Nuclear Data Tables*, 9: 265 (1971).

†M (in μ)−A.

‡Total binding energy [ZM(^{1}H) + NM(^{1}n)−M(A,Z)].

§M(A,Z)−M(A,Z + 1).

Table 1.3

OUTER ELECTRON CONFIGURATION OF NEUTRAL AND CHARGED AMERICIUM ATOMS

Ionization state	Electron configuration*	Term symbol
0	$5f^{7}7s^{2}$	$^{8}S_{7/2}$
1+	$5f^{7}7s$	$^{9}S_{4}$
2+	$5f^{7}$	$^{8}S_{7/2}$
3+	$5f^{6}$	$^{7}F_{0}$
4+	$5f^{5}$	$^{6}H_{5/2}$
5+	$5f^{4}$	$^{5}I_{4}$

*All with underlying radon core configuration.

Table 1.4

CALCULATED RADII OF AMERICIUM ATOMS AND IONS*

Oxidation state	Radius, Å		
	Metallic†,‡	Ionic	Covalent crystal
+3	1.84	0.99	
+4	1.69	0.89	1.57
+5	1.58	0.86	1.47
+6	1.50	0.80	1.39

*Taken from W. H. Zachariasen, Crystal Chemistry of the 5f Elements, in *The Actinide Elements*, G. T. Seaborg and J. J. Katz (Eds.), p. 776, McGraw-Hill Book Company, Inc., New York, 1954.

†CN 12.

‡Radius expected if metal were trivalent, etc.

Table 1.5

CALCULATED IONIZATION POTENTIALS OF AMERICIUM

Atomic charge	Ionization potential, eV
Neutral	5 655
1+	12.15
2+	18.82
3+	36.15
4+	58.14
5+	80.12
6+	95.31
7+	110.4
8+	125.5
9+	140.6
10+	162.5

Table 1.6

ENERGY LEVELS OF Am I

Configuration	Term, J*	Level, cm^{-1}	Isotope shift,† 10^{-3} cm^{-1}	Hyperfine structure width, 10^{-3} cm^{-1}
Odd parity levels				
$5f^7 7s^2$	$a^8S_{7/2}$	0	(600)‡	0
$5f^7 6d7s$	$A_{9/2}$	15,135.94	302	1,062
	$A_{5/2}$	15,764.76	300	1,209
$5f^7 7s8s$	$e^{10}S_{9/2}$	30,884.73	455	1,860
	$e^8S_{7/2}$	31,795.77	450	1,424
	$e^6S_{5/2}$	33,728.27	430	−1,425
	$f^8S_{7/2}$	33,981.86	370	−684
$5f^7 7s7d$	$E_{7/2}$	35,092.24	400	509
		37,111.56	394	1,499
		37,156.73	429	
		37,165.32	472	
		37,995.11	440	
Even parity levels +				
$5f^7 7s7p$	$z^{10}P_{7/2}$	15,608.15	364	940
	$z^{10}P_{9/2}$	16,511.69	398	1,456
	(5/2)	17,858.18	763	−313
	5/2	18,429.09	577	−586
	7/2	18,504.40	447	−628
	7/2	18,701.44	821	0
	(7/2)	19,993.60	842	119
	(5/2)	20,031.33	649	201
	5/2	21,239.91	747	432
	7/2	21,354.01	543	917
	9/2	21,440.38	600	872
		21,845.97	854	200
		23,307.50	738	193
		23,437.04	756	118
	$(9/2^{2+})$	27,103.20	549	988
		27,217.06	523	217
		27,743.57	822	150
		28,009.78	527	0
	9/2	28,312.92	545	1,153
		28,480.85	606	0
		29,009.29	849	0
	7/2	29,446.55	512	1,311

*J-values in parentheses are uncertain.

†$^{241}Am-^{243}Am$.

‡Assumed.

Table 1.7

ANALYTICALLY USEFUL SPECTRAL LINES OF AMERICIUM

λ, Å	I*
2832 3	
2920 6	10
2969 4	
3162 1	
3510 1	>10
3569 2	10
3673 1	>10
3926 2	>10
4089 3	
4575 6	>10
4662 8	10
4681 6	10
5402 7	10
6054 9	10

*Relative intensity, Ref 92

$(^{241}\text{Am}-^{243}\text{Am}) = (890 \pm 50) \times 10^{3}$ cm^{1}, where $\beta \approx 1$ is the screening constant, is the average of three different calculations involving the ionization potential and experimentally observed shifts [107]

Spectral lines of americium useful for analytical purposes are listed in Table 1 7 [105,108]

X-Ray Spectra

The list of K and L X-ray energies and wavelengths for americium shown in Table 1 8 was compiled by Carnall[109] from data gathered by Nelson and associates[110,111] (K X-rays) and from the critical literature evaluation by Bearden[112] of the results of Merrill and DuMond[113] and Day [114] The K X-ray energies, all of which correspond to electric-dipole transitions, were measured with a Cauchois-type bent-crystal spectrometer [110,111] The absorption edge of Am(L_{III}) is 668 648 ± 0 028 X-units based on $\lambda(\text{MoK}_\alpha)$ [113] Atomic energy levels (binding energies) of americium have been calculated from experimental measurements of X-ray emission wavelengths, a listing of these values is given in the article by Carnall [109]

Luminescence Spectra of Am(III)

According to Carnall,[115] "The first observation of fluorescence in a transuranium element compound was made for LaCl_3 Am^{3+} self-excited by the intense α-activity of

Table 1.8

X-RAY ENERGIES OF AMERICIUM

		λ		
Line	Transition	X units	Å	Energy, keV
α_2	$K-L_{II}$	121.254	0.121506	102.041
α_1	$K-L_{III}$	116.194	0.116435	106.484
β_3	$K-M_{II}$	103.749	0.103964	119.258
β_1	$K-M_{III}$	102.834	0.103048	120.319
β_4	L_I-M_{II}	684.98	0.68640	18.0630
β_3	L_I-M_{III}	647.58	0.64892	19.1063
γ_2	L_I-N_{II}	553.3	0.5544	22.363
β_1	$L_{II}-M_{IV}$	656.305	0.657668	18.8523
γ_1	$L_{II}-N_{IV}$	560.733	0.561897	22.0655
α_1	$L_{III}-M_V$	846.446	0.848204	14.6174
λ	$L_{III}-M_I$	999.1	1.0012	12.383
α_2	$L_{III}-M_{IV}$	858.500	0.860283	14.4122
β_6	$L_{III}-N_I$	732.67	0.73419	16.8873

the ^{241}Am; 34 lines were detected.[116] More complete data were taken later and interpreted in terms of transitions in which the initial state was a component of $^5D_2$ or $^5L_6$ and the final state was a component of one of the terms of the ^7F ground multiplet.[117] No self-luminescence nor self-excited fluorescence was found for crystals of Am^{3+}-β diketone chelates."[118]*

Mössbauer Spectra

Israeli scientists[119] and various other workers[120-126] have found that ^{237}Np, formed by alpha decay of ^{241}Am, is a convenient nucleus for recoilless absorption (Mössbauer effect) measurements. Gal et al., using the Mössbauer effect, determined the charge states of neptunium ions in various ^{241}Am sources. Their results are shown in Table 1.9. (Additional Mössbauer-effect data for ^{241}Am sources are given in Chap. 4 and also in an article by Keller and Randl.[127]) The Israeli workers summarized their results by stating that the neptunium charge states were 3+ in all sources containing americium ions in frozen solutions and 4+ and 5+ in all oxide sources. In most other americium salts, neptunium attained the valence of the host lattice.

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*References are those listed by Carnall but have been renumbered for purposes of this chapter.

Table 1.9

MOSSBAUER STUDIES WITH ^{241}Am SOURCES*

Am charge states	Sources	Isomer shift, mm sec ^{1}, Np charge states 3+	4+	5+	Temperature of source and absorber, °K
Solid compounds					
3+	Am_2O_3 (cubic)		1 8 ± 0 5	27 7 ± 0 5	77
3+	Am_2O_3 (hexagonal)		1 7 ± 0 5	28 0 ± 0 5	77
3+	AmF_3	44 6 ± 0 5			4 2
3+	$Am_2(C_2O_4)_3 \cdot 6H_2O$	–40 5 + 0 5			4 2
4+	AmO_2		1 1 ± 0 5	25 2 ± 0 5	77
4+	AmO_2		1 2 ± 0 5	25 1 + 0 5	4 2
4+	$Am(OH)_4 \cdot H_2O$ (precipitate)	40 9 ± 0 8			4 2
5+	$K_5[AmO_2(CO_3)_5]_3$			25 0 ± 2 0	4 2
Frozen solutions					
3+	Am(III) in HNO_3	42 6 ± 1 0			4 2
3+	Am(III) in 10*M* H_3PO_4	–42 6 ± 0 5			4 2
4+	Am(IV) in saturated NH_4F	–45 5 ± 0 8			4 2
4+	Am(IV) in 10*M* H_3PO_4	–42 6 ± 0 5			4 2
5+	$K_5[AmO_2(CO_3)_5]_3$ dissolved in HNO_3	–41 0 ± 1 0			4 2
6+	AmO_2^{2+} in H_3PO_4	–42 6 + 1 0			4 2
6+	AmO_2^{2+} in HNO_3	42 0 ± 1 0			4 2

*Adapted from J Gal, Z Hadari, E Yanir, E R Bauminger, and S Ofer, Charge States of Np Recoil Atoms Following α Decay, *Journal of Inorganic Nuclear Chemistry*, **32**: 2509 (1970)

Beta decay of ^{243}Pu ($t_{1/2}$ = 4 98 hr) to the 83 9-keV level of ^{243}Am occurs in 27 6% of the disintegrations [128] This excited nuclear state ($t_{1/2}$ = 2 34 nsec) of ^{243}Am is suitable for Mossbauer spectroscopy[129] as evidenced by the resonance spectra of $^{243}AmF_3$ and $^{243}AmO_2$ shown in Fig 1 3 These results were obtained at 4 2°K with a 50-mCi $^{243}PuO_2$ source The shift of the $^{243}AmF_3$ resonance line relative to the $^{243}AmO_2$ lines is 55 mm sec ^{1}, the greatest shift so far observed for two oxidation states differing by one unit

Critical Mass

Bierman and Clayton[130] have calculated the critical radii and mass of ^{241}Am and ^{242}Am metals (Table 1 10) In aqueous solution[131] the minimum critical mass of ^{242}Am is 23 g at a concentration of 5 g liter ^{1}

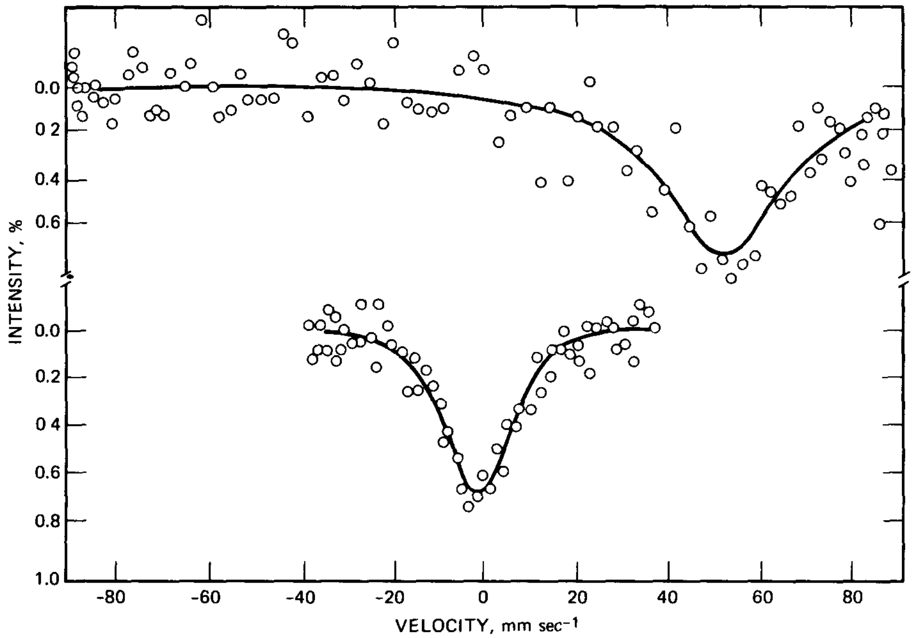

Fig. 1.3 Mossbauer spectrum of (a) $^{243}AmF_3$ and (b) $^{243}AmO_2$. [From G. M. Kalvius, S. L. Ruby, B. D. Dunlap, G. K. Shenoy, D. Cohen, and M. B. Brodsky, Mossbauer Isomer Shift in ^{243}Am, *Physics Letters, B,* 29: 489 (1969).]

Table 1.10

CALCULATED CRITICAL RADII AND MASS OF AMERICIUM METAL*,†

	Isotope	
	^{241}Am	^{242}Am
Density, g cm^{-3}	11.7	11.7
Critical radius, cm		
Bare	13.23	5.55
Water-reflected‡	12.90	4.26
Critical mass, kg		
Bare	113.5	8.4
Water-reflected‡	105.2	3.8

*From S. R. Bierman and E. D. Clayton, Criticality of Transuranium Actinides: Unmoderated Systems, *Transactions of the American Nuclear Society,* 12: 887 (1969).

†Spherical geometry.

‡20-cm reflector.

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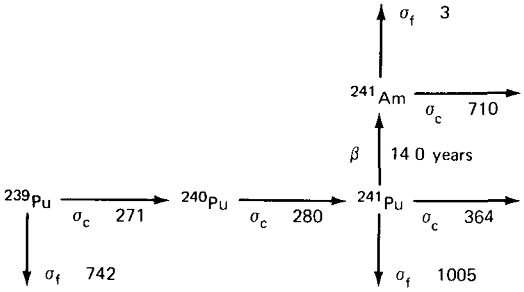
2 PRODUCTION AND USES

INTRODUCTION

Of the isotopes of americium, only three have half-lives greater than a few hours: ^{243}Am ($t_{1/2}$ = 7400 years); ^{241}Am ($t_{1/2}$ = 433 years); and ^{242m}Am ($t_{1/2}$ = 152 years). The latter isotope is formed by irradiation of ^{241}Am with thermal neutrons and can be separated from ^{241}Am only by electromagnetic means. For all practical purposes, therefore, the chemistry and uses of americium center around the production and availability of the isotopes with mass numbers 241 and 243. In this review the discussion of the availability of ^{241}Am and ^{243}Am is limited to their production by reactor irradiation; other sources, e.g., accelerators and nuclear explosions, do not contribute substantial amounts of these isotopes to the world's supply.

PRODUCTION OF ^{241}Am BY IRRADIATION OF ^{239}Pu

Neutron irradiation of ^{239}Pu produces ^{241}Pu, which beta decays with a half-life of 14.0 years ± 0.3 year to ^{241}Am; a 10-g sample of ^{241}Pu will yield about 4 g of ^{241}Am after about 10 years (Ref. 1). The nuclear transformations involved in the production of ^{241}Am by irradiation of ^{239}Pu are:



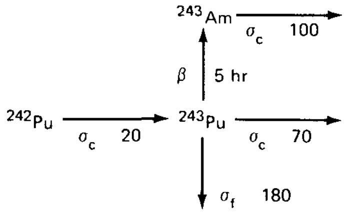
(2 1)

Currently at the various Energy Research and Development Administration (ERDA) sites in the United States, some 5 to 10 kg of ^{241}Am are recovered and purified each year as part of normal rework of aged plutonium inventories containing varying amounts of the ^{241}Pu isotope The bulk of this supply derives from the Rocky Flats site, annual availability of ^{241}Am from this site was estimated[2] at 4 to 5 kg in 1964 and may be higher now Additional ^{241}Am is recovered at the Hanford and Los Alamos sites in conjunction with operation of plutonium scrap-recovery facilities (Processes used to recover and purify ^{241}Am at the ERDA sites are discussed in Chap 5) The purified ^{241}Am is stockpiled at the Oak Ridge National Laboratory (ORNL), where it is marketed to various academic, governmental, and industrial customers, in 1973 alone, some 1 3 kg of ^{241}Am were sold to 13 different customers [3] The ERDA price for ^{241}Am in late 1970 was \$150 per gram,[4] down from \$1000 per gram[5] in 1969 and \$1500 per gram earlier

In addition to U S sources, various other countries also purify and market milligram to gram amounts of ^{241}Am recovered largely from aged plutonium For example, sealed solid ^{241}Am alpha and gamma sources are available from the Australian AEC,[6] the Radiochemical Centre, Amersham, England,[7] and the French Commissariat a l'Energie Atomique [8] Production statistics for the quantities of ^{241}Am recovered in these and other foreign countries have not been published

PRODUCTION OF ^{243}Am BY IRRADIATION OF ^{242}Pu

Nearly isotopically pure ^{243}Am results from irradiation of ^{242}Pu with thermal neutrons according to the reaction sequence



(2 2)

Over the last 10 years or so, Eq. 2.2 has been used in ERDA reactors to produce about 9 kg of ^{243}Am for use as target material in subsequent production of ^{252}Cf and for research purposes.[9-13] For production of ^{242}Pu for use in Eq. 2.2, most of the ^{239}Pu in Pu–Al alloy targets is first burned out during a preliminary irradiation in a production reactor at the ERDA Savannah River site at an average flux of about 10^{14} neutrons cm^{-2} sec^{-1}; the first irradiation is stopped at an exposure of 3×10^{21} neutrons cm^{-} (Fig. 2.1). After separation and purification (Fig. 2.2), ^{242}PuO$_2$ targets are irradiated either in high-flux (6×10^{15} neutrons cm^{-2} sec^{-1}) lattices at Savannah River[14-18] or in the High Flux Isotope Reactor (HFIR) at the ERDA Oak Ridge site at fluxes up to 3×10^{15} neutrons cm^{-2} sec^{-1}. Figure 2.3 and Table 2.1, from Baxter,[1] depict the production of ^{243}Am and other high mass nuclides from irradiation of

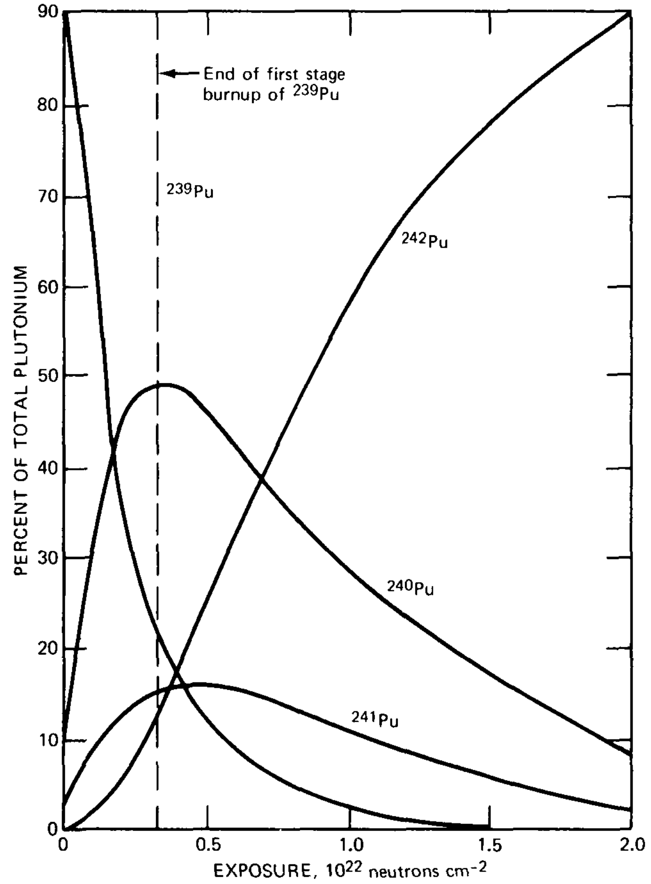


Fig. 2.1 Yield of plutonium isotopes from irradiation of ^{239}Pu.

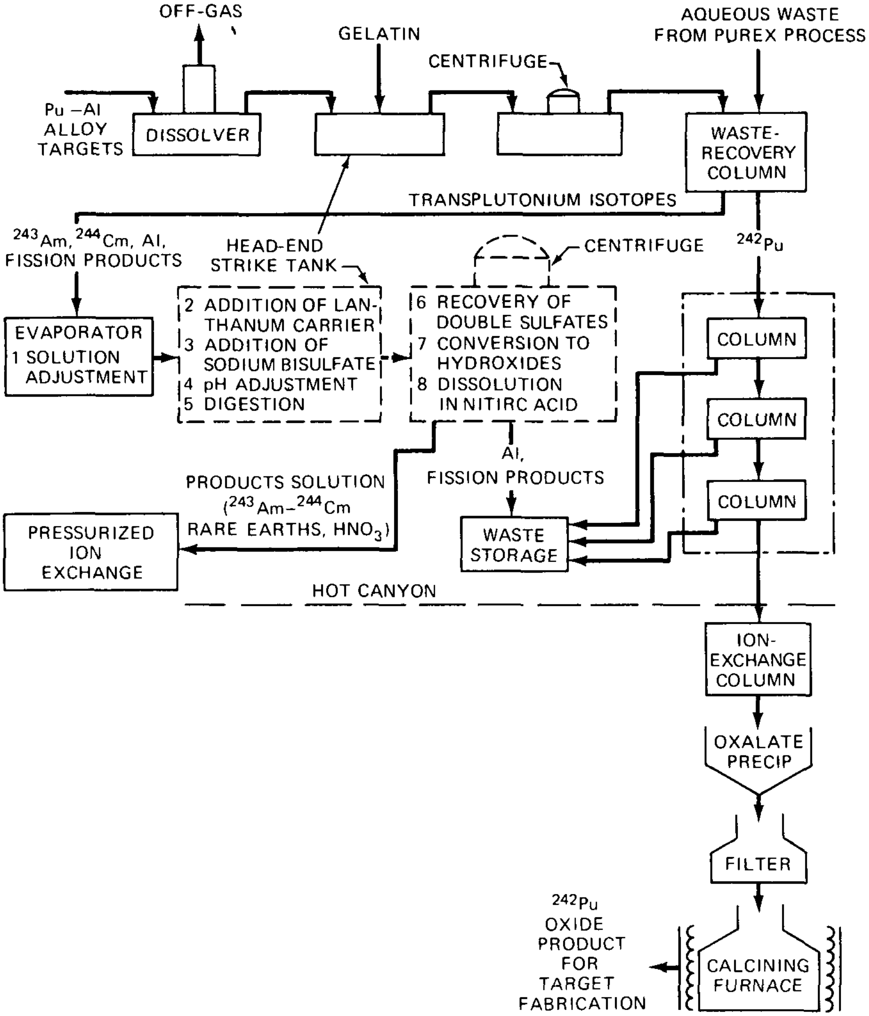


Fig. 2.2 Flow sheet of Savannah River Plant transplutonium process.

^{242}Pu. Chemical procedures used to recover and purify ^{243}Am from irradiated ^{242}PuO$_2$ targets are discussed in Chap. 5, and use of ^{243}Am for production of ^{244}Cm is outlined on pages 33 to 36. Several authors[1,10-12,19,20] have reviewed construction and operation of the HFIR and overall objectives of the ERDA Transplutonium Element Program.

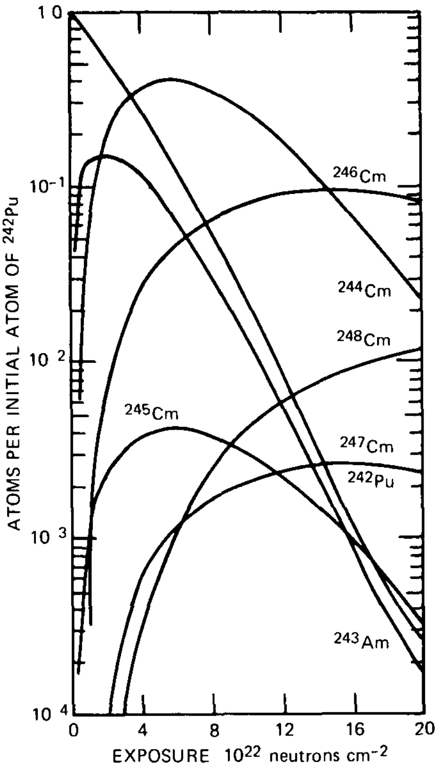


Fig. 2.3 Production of americium and curium from irradiation of ^{242}Pu.

AVAILABILITY OF ^{241}Am AND ^{243}Am FROM POWER REACTORS

For almost 10 years now, numerous writers$^{1,21-29}$ have emphasized that large quantities of ^{241}Am and ^{243}Am are being and will continue to be produced in power reactors throughout the world The exact composition of the mixture of americium isotopes available from this source varies with reactor exposure, at an exposure of 20,000 MWd ton^{-1}, the mixture is essentially 50-50 ^{241}Am and ^{243}Am [21] Table 2 2 lists projections made recently by Baxter[1] of the availability of ^{241}Am and ^{243}Am from U. S commercial power reactors over the next 15 years. Of course, these estimates as well as earlier ones[21-29] depend very strongly on the assumptions made about reactor types and fuels and about the total U. S nuclear generating capacity. Since these bases, particularly the latter quantity, are subject to constant change,

Table 2 1

PRODUCTION OF AMERICIUM ISOTOPES BY IRRADIATION OF PLUTONIUM AT A FLUX OF 3 x 10^{15} neutrons cm^{2} sec^{1}

Fluence, 10^{22} neutrons cm^{2}	Days	Atoms produced per atom irradiated			
		^{242}Pu	^{241}Am	^{241m}Am	^{243}Am
0	0	1 00	0	0	0
2	77	0 566	0 547^{-7}*	0 106^{8}	0 154
4	154	0 290	0 121^{6}	0 237^{-8}	0 113
6	232	0 131	0 139^{-6}	0 274^{8}	0 646^{1}
8	309	0 542^{-1}	0 124^{6}	0 243^{-8}	0 313^{-1}
10	386	0 214^{1}	0 941^{7}	0 185^{8}	0 135^{1}
12	463	0 834^{-2}	0 644^{7}	0 127^{8}	0 549^{-2}
14	540	0 330^{-2}	0 410^{-7}	0 809^{-9}	0 219^{-2}
16	617	0 134^{2}	0 247^{-7}	0 488^{-9}	0 883^{-3}
18	694	0 572^{-3}	0 144^{-7}	0 285^{9}	0 367^{-3}
20	772	0 255^{-3}	0 821^{8}	0 162^{-9}	0 159^{-3}

* Exponents are powers of 10 by which the number is to be multiplied

Table 2 2

ESTIMATED U. S. ANNUAL PRODUCTION OF AMERICIUM FROM POWER REACTORS

	Annual availability of ^{241}Am in Am mixture, kg year^{1}		Annual availability of ^{243}Am in Am mixture, kg year^{1}		Annual availability of ^{241}Am from processing Pu stockpile, kg year^{1}	
Calendar year	Case A* (LWR†)	Case B‡ (LWR–U/Pu, FBR§)	Case A* (LWR†)	Case B‡ (LWR–U/Pu, FBR§)	Case A* (LWR†)	Case B‡ (LWR–U/Pu, FBR§)
1975	38	39	50	53	118	119
1980	122	225	167	384	823	806
1985	237	568	312	913	2560	2510
1990	377	695	462	645	6290	6210

*Case A Light water reactors fueled with slightly enriched uranium without plutonium or uranium (^{236}U) recycle Both cases assume 150 x 10^{9} electrical watts installed by 1980

†LWR = Light water reactors

‡Case B Light water reactors with 50% ^{236}U recycle, limited plutonium recycle, and maximum FBR additions beginning in 1980 PWR–U/Pu and FBR

§FBR = Fast breeder reactor includes liquid metal cooled fast breeder reactors projections such as those shown in Table 2 2 should be regarded only as indicative of the amounts of ^{241}Am and ^{243}Am which may be available from power reactors Hennelly[27] estimates that nuclide availability, including that of ^{241}Am and ^{243}Am, from chemical processing in the 1970s of fuels irradiated in power reactors outside the United States will be at least 50% of the U S supply in the same time period

Some suggested methods of using the ^{241}Am–^{243}Am mixture available from power-reactor fuels are discussed under the subheading "Applications of ^{243}Am " Because of the lack of any profit incentive, however, none of the actual or announced industrial fuel reprocessors in the United States has opted for recovery of americium isotopes (About 1 kg of ^{241}Am and ^{243}Am was recovered during reprocessing of Shippingport blanket fuel under ERDA aegis at the Hanford plant [30]) Certainly of interest and potentially of great significance in this latter connection is the research program[31] recently under way at several ERDA laboratories to determine if practicable ways can be found for removing all long-lived actinides from high-level Purex-process liquid waste to facilitate its subsequent treatment and storage [32] Eventual success in this venture might provide the impetus for routine recovery in the United States of the ^{241}Am and ^{243}Am in power-reactor fuel

The high-level waste resulting from the reprocessing of 40 metric tons of irradiated (20.000 MWd metric ton ^{1}) UO_2 in the West German WFK (Wiederaufarbeitungsanlage Karlsruhe) facility will contain an estimated[33] 2 kg of ^{241}Am and 0 6 kg of ^{243}Am per year As part of their "Project Actinides," German scientists are devising and testing chemical flow sheets (compare Chap 5) for recovery of the americium isotopes and subsequent irradiation to ^{252}Cf

APPLICATION OF ^{241}Am

Uses Based on Characteristic Radiations

Because of its essentially monoenergetic alpha (5 44 and 5 49 MeV) and gamma (59 6 keV) radiations, ^{241}Am is particularly suited for use as an X-ray excitation source and in a multitude of industrial and scientific gauging, thickness, density, and radiographic measurements Indeed, Seaborg[34] states that the list of applications of ^{241}Am may well be the longest of any actinide isotope Crandall[35] points out that in terms of cost, convenience, spectral purity, and lifetime, ^{241}Am is superior to all competing radioisotopes as a low-energy gamma source

Neutron sources of various sizes which use ^{241}Am to furnish alpha particles for the reaction $^{9}Be(\alpha,n)^{12}C$ find extensive use in many fields, including petroleum well logging In 1970 Baybarz[36] stated that most of the ^{241}Am recovered worldwide was used in the manufacture of neutron sources, preparation of such sources is still (1976) the major outlet for both U S and foreign-produced ^{241}Am

Table 2 3 lists specific uses of ^{241}Am in various fields and industries along with the particular radiation type and property on which they are based This compilation,

Table 2.3

CATALOG OF USES FOR ^{241}Am

Radiation		Application		
Type	Property	Field/industry	Specific use	Refs.
Gamma	Transmission	Medicine	1 Determine mineral content of bone	46-61
			2 Determine lipid content of soft tissue	62
			3 Evaluate regional pulmonary ventilation	63
			4. Determine body composition	64,65
		Industrial gauging	1. Determine thickness of plate glass	66
			2 Determine thickness of metals	67-69
			3 Determine thickness of Al materials	70
			4. Determine wire thickness	71
		Soil science	1. Measure soil moisture and density	72-79
		Hydrology	1 Radiation logging of groundwater	80
			2. Sediment concentration gauge	81
		Mineralogy	1. Determine ore concentration	82
		Miscellaneous	1. Maintain helicopter flight formation	83
			2. Dynamics of Freon fire extinguishers	84
Gamma	Backscatter*	Meteorology	1 Determine atmospheric density	85-86
		Coal	1. Determine ash content of coal	87-91
		Concrete	1. Determine cement in concrete	92
		Mineralogy	1 Mineral mining machine	93
			2. Measure iron content of ores	94
Gamma	X-ray excitation source	Mineralogy	1. On-stream analyses of minerals and slurries	95-98
			2. Analysis of ores	99-102

Table 2.3 (Continued)

Radiation		Application		
Type	Property	Field/industry	Specific use	Refs
		Analytical chemistry	1 Equipment for production of X rays	103-109
			2 Assay high purity gold	110
		Medicine	1 Thyroid diagnosis	111
		Gauging	1 Tile wear measurements	112
			2 Measure thickness of metal coatings on steel	113-117
			3 Determine paper weight density	118
Gamma	Absorption radiography	Medicine	1 Determine surface-to-volume ratio of bone	119
		Metallurgy	1 Radiography of thin sheets of Al and Mg	120
		Aerospace	1 Nondestructive testing of steel tubing	121
		Miscellaneous	1 Development of radiographic camera	122
Gamma	Gamma source	Radiation detectors	1 Calibration of detectors	123-125
			2 Preparation of low-level gamma sources	126-129
		Medicine	1 Intracranial pressure sensor	130
Alpha	Ionization	Gas density	1 Ionization gauge for gas densities	131-134
			2 Determine planetary atmospheric density	135
		Gas chromatography	1 Ionization detector	136
		Building	1 Air conditioning	137
			2 Lightning rods	138-144
			3 Smoke-density detector	145-147
		Watchmaking	1 Preparation of luminous paints	148
		Alpha detectors	1 Calibration of alpha spectrometer	149-151
		Gauging	1 Determine uniformity of thin films	152-155

(Table continues on next page.)

Table 2.3 (Continued)

Radiation		Application		
Type	**Property**	**Field/industry**	**Specific use**	**Refs.**
		Miscellaneous	1. Measure relative humidity of air	156
			2. Spinning disk aerosol generator	157
			3. Source preparation	158-164
Alpha	Neutron source	Petroleum	1. Well logging	165-168
		Soil science	1. Determine soil density and moisture content	169-173
		Moisture meter	1. Moisture content of coke	174,175
			2. Moisture content of concrete	176
		Activation analysis	1. Determine carbon in fly ash	177
			2. Determine protein in grain	178
			3. Determine fluorine in ores	179
			4. Determine silicon in cast iron	180
			5. Determine phosphorus in bone	181
		Neutron counter	1. Thermal neutron counter	182
		Neutron-source preparation	1. Preparation of (α,n) and (γ,n) sources	183-188
			2 Preparation of a ^{241}Am-Be–^{242}Cm source	189

*Backscatter methods depend on Compton scattering of gamma rays to return degraded source gamma rays to a detector near the source

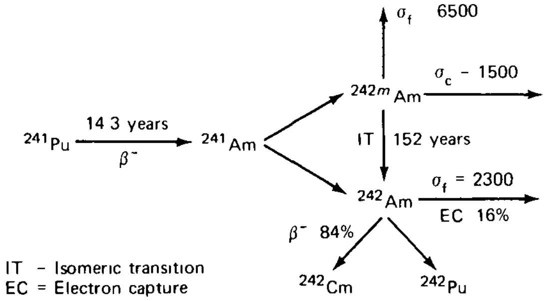
although not necessarily complete, includes examples of all the principal areas where ^{241}Am has found some actual or suggested use Applications of ^{241}Am (and, in some cases, also of ^{243}Am) have been discussed previously by Baxter,[1] Crandall,[35] Baybarz,[36] Rohrmann,[37] Seaborg,[13,34] Fowler,[38] Eichholz,[39] Muller,[40] Keller,[41] Ranschoff,[42] Strain and Leddicotte,[43] West,[44] and most recently by LeVert and Helminski.[45] The review paper by LeVert and Helminski is particularly exhaustive and provides detailed information on many of the applications mentioned in Table 2.3. In addition to those cited in Table 2.3, references to the preparation of ^{241}Am–Be neutron sources are given in Chap. 4, Sec. 4.2.2.

Use in Production of ^{242}Cm

The use of ^{241}Am as a target in nuclear reactors for the production of ^{242}Cm is potentially a very important application Alpha decay of ^{242}Cm produces ^{238}Pu, a radionuclide much in demand as an isotopic power source in space and medical applications The ^{238}Pu produced by the decay of ^{242}Cm contains minimal amounts (<0 02 ppm)[190] of the undesirable ^{236}Pu contaminant, compared to the 10 ppm or so in the ^{238}Pu produced by ^{237}Np irradiation in a light-water-reactor spectrum,[191] this is a distinct advantage for ^{238}Pu to be used in cardiac pacemakers [192]

Because of its high power output (120 W g^{-1}) and minor shielding requirements, ^{242}Cm has been projected for use in the preparation of heat sources A 900-W SNAP-11 generator fueled with 7 5 g of ^{242}Cm (as Cm_2O_3) was fabricated at ORNL,[193] whereas European[194] workers manufactured a thermoelectric battery containing 400 mg of ^{242}Cm The potential application of ^{242}Cm as an isotopic power source is limited, as Baybarz notes,[36] by its relatively short half-life (163 days), in most heat-source applications, the main criterion is that the generator supply a relatively uniform heat output for an extended period of time

The thermal-neutron-capture sequence involved in producing ^{242}Cm from pure ^{241}Am is



(2 3)

Hennelly[27] notes that ^{242}Cm product is lost by ^{242m}Am formation, by ^{242}Am fission, which is a function of neutron flux, by electron capture of ^{242}Am to form ^{242}Pu, and by ^{242}Cm alpha decay giving an optimum yield of about 0 65 g of ^{242}Cm per gram of ^{241}Am burned

APPLICATION OF ^{243}Am

Its longer half-life and lower specific activity compared to those of ^{241}Am make ^{243}Am particularly useful in determining or redetermining basic aqueous and solid state chemistry of americium, its use in such studies is steadily increasing By far, however, the most important application of ^{243}Am is its use as a target material for the production of ^{244}Cm and, when mixed with ^{244}Cm, as a target material for the manufacture of ^{252}Cf and other transuranium elements in high neutron-flux reactors

The neutron-capture sequence involved in the production of ^{244}Cm and ^{252}Cf is shown in Fig. 2.4.

Mixed ^{244}Cm–^{243}Am oxide for use in fabricating targets for irradiation in the HFIR at Oak Ridge is currently prepared by calcining cation-exchange resin containing sorbed ^{244}Cm and ^{243}Am.[195] Techniques for preparing target ^{244}Cm–^{243}Am oxide microspheres by solgel methods have also been described.[196,197] Target assemblies containing ^{243}Am and ^{244}Cm are prepared for irradiation in high-flux high-power density cores at Savannah River by uniformly mixing americium–curium oxide material with aluminum powder and pressing the material into compacts,[14] several of these compacts are canned together to form 6-in.-long slugs.

Curium-244, which has an 18-year half-life, has been proposed as an alternative to ^{238}Pu for use in isotopic power sources. Curium-244 has the advantage of a higher thermal power than ^{238}Pu but suffers from having a higher radiation level of neutrons produced by spontaneous fission. The latter failing prevents its use for biomedical purposes. Baybarz[36] mentions that, whereas ^{238}Pu heat sources are mainly limited to the thermoelectric mode of generating electric power, the thermionic mode may be envisioned for ^{244}Cm heat sources.

Americium separated from power-reactor fuel contains, as discussed previously, a mixture of ^{241}Am and ^{243}Am in varying ratios. Table 2.4, from Baxter,[1] lists the production of high-mass nuclides obtained by irradiating power-reactor americium (50-50 mixture of ^{241}Am and ^{243}Am) at a flux of 1.75 x 10^{14} neutrons cm^{-2} sec^{-1}.

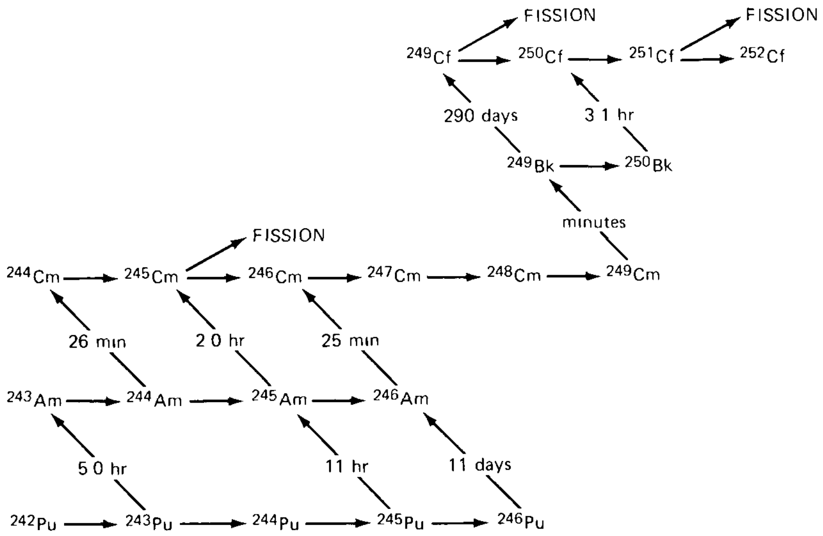


Fig. 2.4 Nuclear reactions for the production of ^{252}Cf. [From R. D. Baybarz, Recovery and Applications of the Transuranium Elements ^{237}Np, ^{238}Pu, ^{241}Am, ^{242}Cm, ^{244}Cm, and ^{252}Cf, *Atomic Energy Review*, 8: 327 (1970).]

Table 2.4

PRODUCTION OF HIGH-MASS NUCLIDES* BY IRRADIATION OF POWER-REACTOR AMERICIUM AT A FLUX OF 1.75×10^{14} neutrons cm^{-2} sec^{-1}

Fluence, 10^{22} neutrons cm^{-2}	Days	Atoms produced per single "average atom" of ^{241}Am and ^{243}Am irradiated							
		^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu	^{241}Am	^{242m}Am	^{243}Am
0							1.000		1.000
0.2	132	0.841^{-1}†	0.182^{-1}	0.278^{-2}	0.643^{-3}	0.702^{-1}	0.356	0.685^{-2}	0.833
0.4	265	0.150	0.540^{-1}	0.132^{-1}	0.437^{-2}	0.906^{-1}	0.124	0.245^{-2}	0.687
0.6	397	0.152	0.693^{-1}	0.246^{-1}	0.939^{-2}	0.960^{-1}	0.426^{-1}	0.849^{-3}	0.561
0.8	529	0.122	0.640^{-1}	0.307^{-1}	0.127^{-1}	0.978^{-1}	0.147^{-1}	0.293^{-3}	0.457
1.0	661	0.870^{-1}	0.497^{-1}	0.309^{-1}	0.137^{-1}	0.989^{-1}	0.514^{-2}	0.102^{-3}	0.371
1.2	794	0.575^{-1}	0.348^{-1}	0.272^{-1}	0.129^{-1}	0.993^{-1}	0.190^{-2}	0.377^{-4}	0.301
1.4	926	0.362^{-1}	0.228^{-1}	0.224^{-1}	0.112^{-1}	0.985^{-1}	0.784^{-3}	0.154^{-4}	0.244
1.6	1058	0.221^{-1}	0.143^{-1}	0.181^{-1}	0.940^{-2}	0.965^{-1}	0.385^{-3}	0.741^{-5}	0.199
1.8	1190	0.132^{-1}	0.872^{-2}	0.148^{-1}	0.781^{-2}	0.935^{-1}	0.229^{-3}	0.435^{-5}	0.162
2.0	1323	0.771^{-2}	0.519^{-2}	0.125^{-1}	0.663^{-2}	0.897^{-1}	0.161^{-3}	0.300^{-5}	0.132

Fluence, 10^{22} neutrons cm^{-2}	Days	Atoms produced per single "average atom" of ^{241}Am and ^{243}Am irradiated						
		^{242}Cm	^{243}Cm	^{244}Cm	^{245}Cm	^{246}Cm	^{247}Cm	^{248}Cm
0								
0.2	132	0.304	0.349^{-2}	0.189	0.175^{-2}	0.488^{-3}	0.196^{-5}	0.598^{-7}
0.4	265	0.277	0.509^{-2}	0.341	0.305^{-2}	0.188^{-2}	0.149^{-4}	0.984^{-6}
0.6	397	0.191	0.433^{-2}	0.459	0.399^{-2}	0.388^{-2}	0.440^{-4}	0.455^{-5}
0.8	529	0.119	0.300^{-2}	0.549	0.468^{-2}	0.631^{-2}	0.902^{-4}	0.129^{-4}
1.0	661	0.701^{-1}	0.189^{-2}	0.616	0.518^{-2}	0.905^{-2}	0.152^{-3}	0.279^{-4}
1.2	794	0.403^{-1}	0.112^{-2}	0.664	0.554^{-2}	0.120^{-1}	0.228^{-3}	0.515^{-4}
1.4	926	0.229^{-1}	0.651^{-3}	0.696	0.578^{-2}	0.151^{-1}	0.316^{-3}	0.849^{-4}
1.6	1058	0.129^{-1}	0.371^{-3}	0.716	0.594^{-2}	0.182^{-1}	0.412^{-3}	0.129^{-3}
1.8	1190	0.729^{-2}	0.210^{-3}	0.727	0.602^{-2}	0.214^{-1}	0.514^{-3}	0.185^{-3}
2.0	1323	0.409^{-2}	0.119^{-3}	0.730	0.605^{-2}	0.246^{-1}	0.621^{-3}	0.253^{-3}

*From Ref. 3.

†Exponents are powers of 10 by which the number is to be multiplied.

One method of using power-reactor ^{241}Am–^{243}Am mixtures is to preburn them in a thermal reactor to burn up ^{241}Am, preferentially to ^{242}Cm which would decay to ^{238}Pu[198] After the ^{243}Am-rich target mixture is chemically separated, it could be recycled to a resonance reactor for the production of ^{252}Cf An alternative, according to Christman and Cornman,[190] is to irradiate the target mixture in the resonance reactor to accelerate the production of ^{252}Cf from ^{243}Am and, at the same time, to produce ^{238}Pu from ^{241}Am Figure 2 5 shows the production yields for ^{252}Cf and ^{238}Pu which might be realized for this latter alternative with the target management schedules that are necessary because the ^{242}Cm alpha activity limits and/or delays chemical separation and target-fabrication operations

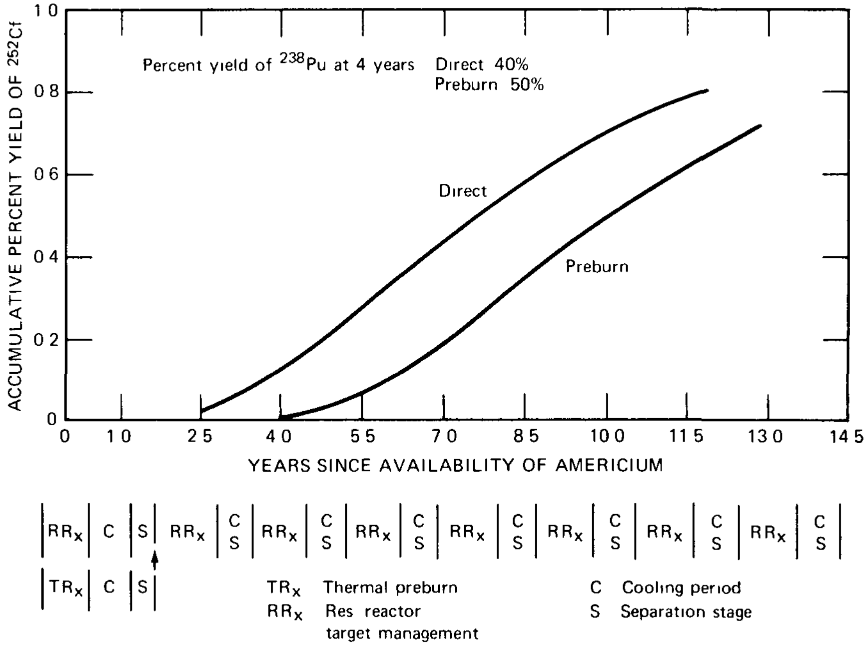


Fig. 2 5 Yields of ^{252}Cf and ^{238}Pu from americium [From R P. Christman and W. R. Cornman, Utilization of Power Reactor Americium for ^{252}Cf Production, *Transactions of the American Nuclear Society*, 12 54 (1969).]

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3 CHEMISTRY IN AQUEOUS SOLUTION

OXIDATION STATES

Americium in aqueous solutions is well known to exist in the III, IV, V, and VI oxidation states The hydrated ions $Am^{3+} \cdot aq$, $AmO_2^+ \cdot aq$, and $AmO_2^{2+} \cdot aq$ occur in the absence of complexing agents Russian workers[1a] have recently announced evidence for the production of Am(VII) by oxidation of Am(VI) in cooled, strong alkali solutions Methods of producing the individual americium ions are summarized in Table 3 1 Some additional comments on production and stabilization of the various americium oxidation states in aqueous solution follow Recent polarographic evidence for the proposed production of Am(II) in aqueous solution is also reviewed Reference is made to the electrode-potential diagrams shown on pages 55 to 58

Am(II)

Americium is the heavy homolog of europium which has a readily attained divalent state in aqueous solution Much effort has gone into attempts to establish the existence of Am^{2+} in aqueous solutions and to prepare compounds containing divalent americium The latter goal was realized in 1973, as detailed in Chap 4, by the preparation of $AmCl_2$, $AmBr_2$, and AmI_2 Leary and Mullins[1b] also have obtained evidence for the existence of divalent americium in molten salt–molten plutonium systems However, reduction conditions[2] used successfully to prepare Eu^{2+} and Sm^{2+}

Table 3.1

AMERICIUM IONS IN AQUEOUS SOLUTION

Oxidation state	Ionic form	Color in dilute $HClO_4$	Methods of preparation
III	$Am^{3+} \cdot aq$	Pink red*	1 Am(O) + HCl 2 AmO_2 + HCl (heated) 3 Am(>III) + NH_2OH, I , SO_2, etc 4 Autoreduction of Am(>III)
IV		†	1 Dissolve $Am(OH)_4$ in 13*M* NH_4F 2 Electrolytic oxidation of Am^{3+} in 10–15*M* H_3PO_4 3 $Am(OH)_4$ + alkali fluoride + $K_4P_2O_7$
V	$AmO_2^+ \cdot aq$	Yellow	1 Oxidation of Am^{3+} in 0 03*M* $KHCO_3$ solution with O_3, $S_2O_8^{2}$ or ClO 2 Dissolve Li_3AmO_4 in dilute $HClO_4$ 3 Electrolytic oxidation of Am^{3+} in 2*M* $LiIO_3$ –0 7*M* HIO_3 solution
VI	$AmO_2^{2+} \cdot aq$	Yellow brown‡	1 Oxidation of Am^{3+} in dilute acid media with $S_2O_8^{2}$ and Ag(II) 2 Electrolytic oxidation of Am^{3+} in 6*M* $HClO_4$ or in 2*M* H_3PO_4 3 Dissolve Li_6AmO_6 in dilute $HClO_4$
VII		§	1 Oxidation of AmO_2^{2+} in 3*M*–5*M* NaOH at 0–7°C with O_3 or O ion radical

*Yellow in concentrated $HClO_4$

†Pink-red Am^{4+} stable only in concentrated fluoride and phosphate solutions

‡Light brown in dilute HNO_3, green in fluoride solutions, dark brown in H_2SO_4 solutions, red in carbonate solutions

§Green-colored Am(VII) known only in alkaline solutions

will not reduce $Am^{3+} \cdot aq$ to $Am^{2+} \cdot aq$ Also, recently Jove and Pages[3] failed in attempts to reduce Am^{3+} in liquid ammonia either by electrolysis or with electrons furnished by dissolution of sodium metal

Results of several polarographic experiments with tracer concentrations of americium have been interpreted on the basis of the formation of divalent americium

Thus Myasoedov and Myuzikas[4 5] observed two waves in polarographic reduction of trivalent americium in 0 1*M* solutions of $[(C_2H_5)_4N]ClO_4$ in acetonitrile These scientists account for the two waves, the second of which is twice as high as the first, by the successive reductions $Am^{3+} + e \rightarrow Am^{2+}$ and $Am^{2+} + 2e \rightarrow Am/Hg$ David [6a] also observed two waves in the radiopolarograms of Am(III) in perchlorate medium at pH 1 to 6 which he postulated to correspond to the reductions $Am^{2+} \rightarrow Am(0)$ and $Am^{3+} \rightarrow Am(0)$

Nugent[6b] disagrees with David's interpretation of his polarographic results and states that the amalgamation of $Am^{3+} \cdot aq$ proceeds directly to Am/Hg In support of this reaction mechanism, Nugent cites a linear relation developed among standard potentials, first half-wave amalgamation potentials, and the atomic radii of the crystalline actinide metals According to Nugent, $Am^{2+} \cdot aq$ is so unstable, even at tracer concentrations, as to be essentially nonexistent

Am(III)

The stability of the higher oxidation states of the transuranium elements typically decreases with increasing atomic number In agreement with this, the trivalent state of americium is its most stable oxidation state and is the state resulting when americium metal dissolves in acids Keller[6c] notes that, even though americium is the homolog of europium, the characteristics of Am^{3+} (radius = 0 99 Å) are more like those of Nd^{3+} (radius = 0 995 Å) than those of Eu^{3+} The paramagnetic susceptibility[7a] of $Am^{3+} \cdot aq$ is 700×10^{-6} cm^3 mol^{-1} In aqueous solution, Am(III) ion is precipitated by hydroxide, fluoride, phosphate, and oxalate ions, properties of the resulting compounds are discussed in Chap 4

Friedman and Bell[7b] have recently discussed techniques for preparing $POCl_3-ZrCl_4$ solutions containing Am^{3+} and efforts to make these solutions show laser activity Friedman and Bell ascribed failure of these efforts to the short lifetime for the excited state of Am^{3+}

Hydrolysis of the Am^{3+} ion was studied by several investigators Desire, Hussonnois, and Guillaumont[8] and Desire[9a] determined the distribution of americium between aqueous $HClO_4-LiClO_4$ solutions and a benzene solution of thenoyltrifluoroacetone From their measurements, they calculate for the reaction

$$M^{3+} \cdot aq + H_2O \rightarrow MOH^{2+} \cdot aq + H^+ \qquad (3\ 1)$$

$K_1 = [MOH^{2+}][H^+]/[M^{3+}] = 1\ 2 \times 10^{-6}$ at $\mu = 0\ 1M$ and $23 \pm 1°C$

Hydrolysis of the Am^{3+} ion can also be represented by the reaction

$$M^{3+} \cdot aq + OH^- \rightarrow MOH^{2+} \cdot aq \qquad (3\ 2)$$

for which $K_2 = [MOH^{2+}]/[M^{3+}][OH^-] = [MOH^{2+}][H^+]/[M^{3+}]K_W$, where $K_W = [H^+][OH^-]$ Marin and Kikindai[10] report $K_2 = 2 \pm 0\ 2 \times 10^{11}$ at $\mu = 0\ 005M$ and

15 ± 1°C from electrophoresis measurements, whereas, from electromigration studies in NH_4ClO_4 media, Shalinets and Stepanov[11] report $K_2 = 5 \times 10^{10}$ at $\mu = 0.005M$ and 25°C.

Korotkin[12,13] states that, contrary to the simple representations shown in Eqs. 3.1 and 3.2, hydrolysis of Am^{3+} is a complicated process that commences at pHs as low as 0.5 to 1.0 and whose mechanism is determined by the nature of other cations (e.g., Li^+, Na^+, and H^+) in solution. Korotkin's conclusion is based on his extensive studies[12–13b] of the hydrolysis of $10^{-10}M$ to $10^{-6}M$ americium in $HClO_4$–$LiClO_4$, HNO_3–$LiClO_4$, HNO_3–$LiNO_3$, HNO_3–KNO_3, HNO_3–$NaNO_3$, and pure HNO_3 solutions over the pH range 1 to 11. Using paper chromatographic methods, supplemented by ion-exchange and electromigration procedures, Korotkin states that, in $HClO_4$–$LiClO_4$ ($\mu = 0.1M$) media, hydrolysis of $\leqslant 10M^{-6}$ americium proceeds according to the mechanism

$$\underset{\text{I(pH 1)}}{Am^{3+}} \rightarrow \underset{\text{II(pH 6)}}{Am(OH)^{2+}} \rightarrow \underset{\text{III}}{Am(OH)_2^+} \rightarrow \underset{\text{IV(pH > 8.5)}}{Am(OH)_3 \text{ or } [Am(OH)_2]_x^{x+}}$$

In HNO_3–$LiClO_4$ and in HNO_3–$LiNO_3$ ($\mu = 0.1M$ to $1M$) solutions, hydrolysis proceeds through the forms

$$\underset{\text{I}}{Am(NO_3)^{2+}} \rightarrow \underset{\text{II(pH 6)}}{[Am(NO_3)(OH)]^+} \rightarrow \underset{\text{III}}{[Am(OH)_2NO_3]}$$

$$\rightarrow \underset{\text{IV(pH > 8.5)}}{[Am(OH)_2]_2^{2+}} \rightarrow \underset{\text{V}}{Am(OH)_3 \text{ or } [Am(OH)_2]_x^{x+}}$$

In $0.1M$ solutions of KNO_3 and $NaNO_3$, the hydrolysis sequence, according to Korotkin, is

$$\underset{\text{I}}{Am(NO_3)^{2+}} \rightarrow \underset{\text{II}}{[Am(OH)(NO_3)]^+} \rightarrow \underset{\text{III}}{[Am(OH)(NO_3)]_2^{2+}} \rightarrow \underset{\text{IV}}{[Am(OH)(NO_3)]_2(OH)^+}$$

$$\rightarrow \underset{\text{V}}{[Am(OH)_2]_2^{2+}} \rightarrow \underset{\text{VI}}{[Am(OH)_2]_x^{x+}} \rightarrow \text{negatively charged colloids}$$

Hydrolysis of $\leqslant 10^{-6}M$ americium in pure HNO_3 is similar to that in $NaNO_3$ and KNO_3 solutions, according to Korotkin.

Korotkin[13c] recently has extended his investigations to paper chromatographic sorption of $10^{-4}M$ americium from pH 1 to 9 $HClO_4$ solutions. He concludes that at such conditions the hydrolysis mechanism may be represented by the following scheme

$$Am^{3+} \rightarrow Am(OH)^{2+} \rightarrow [Am(OH)](OH)^{+} \rightarrow Am[Am(OH)_2]^{4+} \rightarrow Am[Am(OH)_2]_n^{(3+n)^+}$$

I II III IV V

It is necessary to point out that independent experiments by other scientists to confirm or refute Korotkin's speculations about the various hydrolytic species of americium either have not yet been done or have not yet been published

Am(IV)

Because of the high value (+2.4 V) of the standard potential of the Am(IV)–Am(III) couple, tetravalent americium is unstable in most mineral acid solutions with respect to disproportionation to Am(III) and Am(V) However, stable aqueous solutions of tetravalent americium in which disproportionation does not occur even at 90°C can be prepared[14, 15] by dissolution of $Am(OH)_4$ in concentrated solutions of NH_4F, KF, RbF, and CsF The solubility of Am(IV) in 13*M* NH_4F at 25°C is 0 02*M*. This rose-colored solution probably contains the ions AmF_5^- and/or AmF_6^{2-}. Ozone oxidizes Am(IV) in 13*M* NH_4F to Am(VI), whereas iodide reduces it to Am(III). Slow reduction of Am(IV) to Am(III) occurs because of alpha radiation.

Stable solutions of tetravalent Am(IV) can also be prepared by anodic oxidation (at a platinum electrode) of Am^{3+} in H_3PO_4 solution This method of stabilizing Am(IV) was first discovered by Yanir, Givon, and Marcus.[16,17] Subsequent publications by Myasoedov and coworkers[18a, 18b] have recently confirmed and extended this preparation technique. One of their papers[18a] also presents details of the construction and operation of a suitable electrolysis cell The Russian workers report[18a] that pure Am(IV) is obtained in 10*M* to 15*M* H_3PO_4 Kinetic data for the oxidation of Am(III) in 12*M* H_3PO_4 (Fig. 3.1) show that complete oxidation to Am(IV) requires about an hour under the conditions used by Myasoedov et al

In their most recent paper, Myasoedov et al.[18b] discuss the influence of temperature and the concentrations of H_3PO_4 and americium on the completeness of electrochemical oxidation of Am(III) in 3*M* to 15*M* H_3PO_4 and the stability of the resulting Am(IV). In 3*M* to 8*M* H_3PO_4, Am(IV) disproportionates according to the scheme 3Am(IV) → 2Am(III) + Am(VI), whereas at H_3PO_4 concentrations above 10*M*, Am(IV) reduces to Am(III). The apparent rate constant for Am(IV) disproportionation increases with decreasing H_3PO_4 concentration, whereas that for reduction of Am(IV) to Am(III) increases with temperature and with decreasing americium and H_3PO_4 concentration (15*M* to 10*M*) The activation energy for the reduction of Am(IV) to Am(III) in 12*M* H_3PO_4 is 15.6 ± 1.1 kcal mol^{-1} according to results obtained by Myasoedov et al [18a]

Myasoedov, Lebedev, and Milyukova[18c] also report that Am(III) in H_3PO_4 solutions is rapidly oxidized by Ag(II) oxide and a mixture of Ag_3PO_4 and $(NH_4)_2S_2O_8$ Pure Am(IV) is obtained in 9*M* to 12*M* H_3PO_4. In 3*M* to 6*M* H_3PO_4, depending on the oxidation time, pure Am(VI) or a mixture of Am(IV) and Am(VI) are obtained

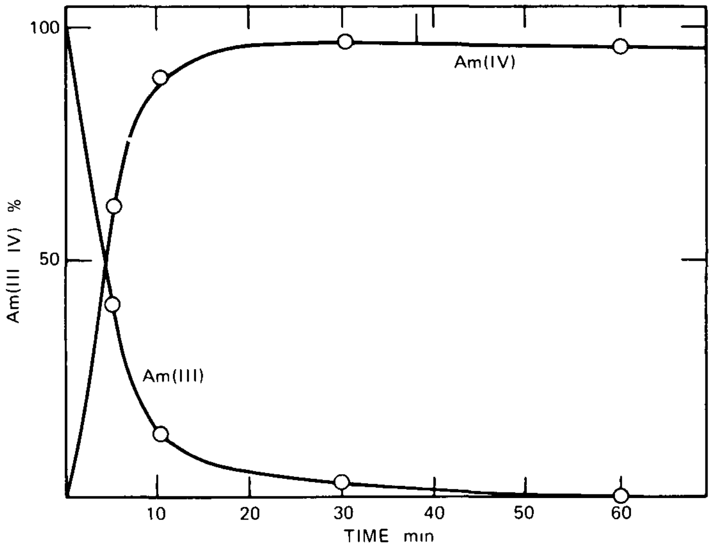


Fig. 3.1 Electrolytic oxidation of Am(III) in 12*M* H_3PO_4 [From B F Myasoedov, V M Mikhailov, I A Lebedev, O E Koiro, and V Ya Frenkel, Preparation and Stability of Am(IV) and Am(V) in Phosphoric Acid Solutions, *Radiochemical and Radioanalytical Letters* **14** 17 (1973)]

A third way of stabilizing Am(IV) in aqueous solution consists of diluting a concentrated alkali fluoride solution in which $Am(OH)_4$ has been dissolved with concentrated $K_4P_2O_7$ solution Yanir, Givon, and Marcus[17] used this approach to prepare a 0 3*M* acid solution containing Am(IV) and about 2*M* $K_4P_2O_7$ and 3*M* NH_4F Americium(IV) in this solution was very stable, being reduced only 5% in 7 hr Direct dissolution of $Am(OH)_4$ in acidified pyrophosphate solutions yielded mixtures of Am(IV) and Am(VI) with $Na_4P_2O_7$ and Am(IV) and Am(V) in $K_4P_2O_7$ solutions

Am(V)

Oxidation of Am(III) yields Am(VI) in acid solution but both Am(V) and Am(VI) in alkaline solution This behavior is in accord with that expected from electrode potentials (see pages 55 to 58) Solutions of Am(V) are conventionally prepared by controlled oxidation of Am(III) in alkali carbonate media with ozone,[19-24] peroxydisulfate,[19 23 24] or hypochlorite ion [19 23 25 26] Various solid carbonates containing the AmO_2^+ ion (see pages 139 to 141) precipitate from the resulting solutions Dilute acid solutions of AmO_2^+ containing several percent Am^{3+} can be prepared by dissolution of these solid carbonates

Americium(V) solutions free of Am(III) can be prepared by intermediate preparation of Am(VI) in 2*M* Na_2CO_3 solution [27] After 5% O_3 is bubbled through the solution for 1 hr at room temperature to oxidize Am(III) to Am(VI),

$NaAmO_2CO_3$ is precipitated by heating the solution for 30 to 60 min at 90°C. Solutions obtained by dissolution of the resulting $NaAmO_2CO_3$ contain only AmO_2^+.

Hara[28] prepared perchlorate, sulfate, and acetate solutions containing AmO_2^+ free of Am^{3+} by first extracting AmO_2^+ from $1M$ acetate buffer ($pH > 3$) solutions of Am(III) and Am(V) into $0.1M$ thenoyltrifluoroacetone in isobutanol. When the organic phase containing Am(V) was shaken with an aqueous phase having a proper pH value and composition, Am(V) was selectively stripped into the aqueous phase.

Newer methods for obtaining the AmO_2^+ ion in aqueous solution include dissolution of solid Li_3AmO_4 in dilute $HClO_4$ and electrolytic oxidation[17] of Am(III) in $2M$ $LiIO_3$–$0.7M$ HIO_3 (pH 1.47) solution. Solid Li_3AmO_4 can be prepared by the solid-state reaction:[29]

$$3Li_2O + 2AmO_2 + \tfrac{1}{2}O_2 \xrightarrow{8\text{ hr, }600^\circ C} 2Li_3AmO_4 \qquad (3.3)$$

Am(VI)

Hexavalent americium can be prepared by oxidation of lower oxidation states in either acid or alkaline solutions. In dilute, nonreducing acid solutions, powerful chemical oxidants such as $S_2O_8^{2-}$ and Ag(II) oxidize both Am(III) and Am(V) to Am(VI).[27,30a] Peroxydisulfate, however, will not oxidize Am(III) to Am(VI) completely at acidities above about $0.5M$. In $HClO_4$ solution, Ce(IV) oxidizes Am(V) to Am(VI) (Ref. 23) but only partly oxidizes Am(III) to Am(VI). Similarly ozone readily oxidizes Am(V) to Am(VI) in heated HNO_3 or $HClO_4$ solution[2] but will not oxidize macroconcentrations of Am(III) to Am(VI) in acid media even when heated.[30b]

Electrolytic oxidation of Am(III) either in $2M$ H_3PO_4 or in $6M$ $HClO_4$ produces the AmO_2^{2+} ion.[18,27] Keller[6c] also states that dissolution of Li_6AmO_6 either in water or in dilute $HClO_4$ yields a solution containing AmO_2^{2+}. Li_6AmO_6 can be made by the solid-state reaction at 360°C of Li_2O with AmO_2 in the mol ratio of 3.5 : 1 (Ref. 29).

Ozone or peroxydisulfate oxidation of either Am(III) or Am(V) in aqueous Na_2CO_3 or $NaHCO_3$ solution yields an intense red-brown colored solution thought to contain a carbonate complex of Am(VI).[22,27] This same complex is also obtained by dissolution of solid sodium americyl acetate in Na_2CO_3 or $NaHCO_3$ solutions. [Nugent,[31] in a recent review article, speculates that an Am(VII)–carbonate complex may actually be present in such solutions and suggests that the presence of such a species would be consistent with several experimental observations.] Americium(VI) in $0.1M$ to $0.5M$ $NaHCO_3$ solution is stable at 90°C to reduction by H_2O, Cl^-, and Br^- but is readily reduced by I^-, N_2H_4, H_2O_2, NO_2^-, and NH_2OH. Reduction by water occurs at 90°C in $2M$ Na_2CO_3.

Ozone oxidation of Am(III) in $2M$ Na_2CO_3 yields AmO_2^{2+} only if the temperature is maintained at ~25°C or below; at 90°C oxidation does not proceed past Am(V). Surprisingly, Am(VI) is *not* produced by O_3 oxidation of either $Am(OH)_3$ or $KAmO_2CO_3$ in $0.03M$ to $0.1M$ $KHCO_3$ solution.[22] Similarly $K_2S_2O_8$ will *not* oxidize either $Am(OH)_3$ or $NaAmO_2CO_3$ in $0.1M$ $NaHCO_3$ to Am(VI), although such oxidation is accomplished readily with $Na_2S_2O_8$. This chemistry is explained on the basis of the lower solubility of $KAmO_2CO_3$ compared to that of $NaAmO_2CO_3$.

Alkali hydroxide solutions of Am(VI) are yellow colored[22,32-34] and, according to Cohen,[33] may be easily prepared by ozone oxidation of a slurry of $Am(OH)_3$ in all the alkali hydroxides from lithium to cesium. An alternative procedure consists of oxidizing Am(III) in dilute $NaHCO_3$ solution to Am(VI) with ozone, acidifying with dilute HNO_3, and finally, adding the desired alkali hydroxide to neutralize the HNO_3 and produce an alkaline solution. Alkali hydroxide solutions of Am(VI) are not stable, and a light-tan solid precipitates a few hours after preparation. This solid is soluble in dilute mineral acids to yield a solution containing AmO_2^+ ions.

Solid Na_4XeO_6 is reported[34] to oxidize Am(III) in 12*M* to 15*M* CsF media, either with or without added HF, to Am(V) and/or Am(VI). The exact oxidation state—(V) or (VI)—of americium in the oxidized solution has not been determined.

Am(VII)

In preliminary communication, Zaitseva[35] indicated that a dark-violet solution containing Am(VII) could be obtained both by disproportionation of Am(VI) in 3*M* NaOH and by the action of strong oxidizing agents on an alkaline solution containing Am(V). Subsequent work[36] showed that the claim for Am(VII) was erroneous—the dark-violet color was due to a contamination by Fe(VI). Incidentally, attempts[37] to prepare a solid compound containing Am(VII) by careful oxidation of Li_2O–AmO_2 mixtures at 300 to 400°C in a stream of oxygen proved unsuccessful. Nugent's speculations about the existence of an Am(VII)–carbonate complex were mentioned earlier.

Krot et al.[1a] stated that aqueous solutions containing Am(VII) can be prepared by oxidation at 0 to 7°C of Am(VI) in alkaline solutions with either O^- ion radicals or ozone. Thus passage of air containing 20 to 50 mg liter^{-1} O_3 for 30 to 60 min through a light-yellow 3*M* to 4*M* NaOH solution containing 0.001*M* to 0.002*M* Am(VI) at 0 to 7°C yields a green-colored solution containing at least some Am(VII). A similar green-colored solution results on irradiation (^{60}Co) at 0°C of a 3*M* NaOH solution containing 0.001*M* to 0.002*M* Am(VI) and previously saturated with N_2O. (The N_2O functions to transform hydrated electrons produced by radiolysis to O^- ion radicals by the reaction $N_2O + e^-_{aq} = N_2 + O^-$; $S_2O_8^{2-}$ may be substituted for N_2O for the same purpose.) With either oxidant the absorbance of the green-colored solution at 370 to 450 nm is about twice that of the original Am(VI) solution and slowly decreases with time. Stability of the Am(VII) species, according to Krot et al., is greater in 5*M* NaOH than in 3*M* NaOH.

To confirm the presence of Am(VII) in the oxidized solutions, the Russian scientists made spectrophotometric studies in 1*M* to 2*M* NaOH solutions of the reactions Pu(VI) + Am(VII) = Pu(VII) + Am(VI) and 2Np(VI) + Am(VII) = 2Np(VII) + Am(V). Appearance of the characteristic spectrum of pure Pu(VII) under conditions where Am(VII) is the only oxidant provides strong evidence that the green-colored solutions prepared as described above do indeed contain some Am(VII).

Further studies of the preparation and properties of Am(VII) in aqueous solution can surely be anticipated.

THERMODYNAMIC VALUES

The heats of solution of americium metal in aqueous HCl solutions at 298.15 ± 0.05°K were redetermined in 1972 by Fuger, Spirlet, and Muller[38] using specially purified and characterized metal. Earlier (1951) measurements were made by Lohr and Cunningham[39] and Westrum and Eyring.[40] From their results, Fuger, Spirlet, and Muller[38] calculate the standard enthalpy of formation of $Am^{3+} \cdot aq$ at 298°K to be −147.4 ± 0.3 kcal mol^{-1}. This value, which is about 10% less negative than that previously accepted,[39,40] confirms the preliminary data of Morss[42] and is in line with arguments advanced by Ryan[43] and by Nugent, Burnett, and Morss.[44]

Fuger and Oetting[44b] have very recently carefully examined existing knowledge of the entropies of actinide ions. These authors have also critically evaluated available existing enthalpy and electromotive-force data and checked them for consistency with entropy data. Thermodynamic values for americium ions calculated by Fuger and Oetting are listed in Table 3.2 and are the most reliable data extant. Some earlier thermodynamic quantities for americium ions were calculated by Fuger, Spirlet, and Muller,[11] by Eyring, Lohr, and Cunningham,[45] by Gunn and Cunningham,[46] and by Hinchey and Cobble.[47]

Table 3.2

THERMODYNAMIC QUANTITIES FOR AMERICIUM IONS

				Hydration enthalpy and entropy*	
Ion	$-\Delta H^\circ f$ (298°K),† kcal mol^{-1}	$\Delta G^\circ f$ (298°K),† kcal mol^{-1}	$-S^\circ$ (298°K),† cal mol^{-1} °K^{-1}	$-\Delta H_h$, kcal mol^{-1}	$-S_h$, cal mol^{-1} °K^{-1}
$Am^{3+} \cdot aq$	147.4 ± 0.3	143.2 + 0.9	48 + 3	832	91.8
$Am^{4+} \cdot aq$	103.4 + 2.6	89.2 ± 2.4	97 + 5	1635	128
$AmO_2^+ \cdot aq$	192.4 ± 1.1	177.7 + 1.3	3 + 2		
$AmO_2^{2+} \cdot aq$	155.8 ± 0.5	141.0 + 0.8	19 + 2		

*Calculated values from Ref. 47b.
†Values from Ref. 44b.

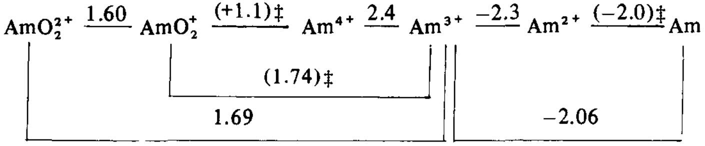
ELECTRODE POTENTIALS

Table 3.3 lists electrode potentials (1969 International Union of Pure and Applied Chemistry sign convention) for americium in various aqueous media. The potential diagram for americium in 1*M* $HClO_4$ reflects newly estimated values for the (III)–(0),

Table 3.3

ELECTRODE POTENTIALS OF AMERICIUM*†

I. 1*M* $HClO_4$



$$AmO_2^{2+} \xrightarrow{1.60} AmO_2^{+} \xrightarrow{(+1.1)\ddagger} Am^{4+} \xrightarrow{2.4} Am^{3+} \xrightarrow{-2.3} Am^{2+} \xrightarrow{(-2.0)\ddagger} Am$$

II. 1*M* OH^-

$$AmO_2(OH)_2 \xrightarrow{1.1} AmO_2OH \xrightarrow{(0.7)\ddagger} Am(OH)_4 \xrightarrow{0.5} Am(OH)_3 \xrightarrow{-2.68} Am$$

III. Phosphoric acid

$$Am(IV) \xrightarrow[10.0M \text{ to } 14.5M\ H_3PO_4]{1.75 \text{ to } 1.78} Am(III)$$

$$Am(VI) \xrightarrow[0.54M\ H_3PO_4]{1.43} Am(V)$$

$$Am(VI) \xrightarrow[4.34M\ H_3PO_4]{1.32} Am(V)$$

*In volts.

†1969 International Union of Pure and Applied Chemistry sign convention.

‡Values are determined by difference.

(III)–(II), and (IV)–(III) couples and differs slightly from those previously published.[6c,48,49] Reference is made to Nugent's recent paper[31] on the chemical oxidation states of lanthanides and actinides.

Potentials in 1*M* $HClO_4$

The potential, 1.60 ± 0.01 V, of the Am(VI)–Am(V) couple in 1*M* $HClO_4$ has been directly measured.[50] Potentials of all the other couples are calculated values.

Using their recently carefully determined value of -147.4 ± 0.3 kcal mol^{-1} for the heat of formation of $Am^{3+} \cdot aq$, Fuger, Spirlet, and Müller[38] estimate the potential of the Am(III)–Am(0) couple in 1*M* $HClO_4$ to be -2.06 ± 0.01 V. Earlier,[39,46] the potential of the (III)–(0) couple was estimated at -2.36 ± 0.04 V.

Nugent et al.[51a,51b] estimate, from various theoretical considerations, that the best value for the Am(III)–Am(II) couple is −2.3 V. They note that this calculated value is in agreement with chemical evidence which indicates that the americium potential should be appreciably greater than the corresponding californium potential of −1.6 V. The standard potential of the Am(III)–Am(II) couple has previously been listed at $\leqslant -1.5$ V (Refs. 3, 6c, 48, 52, 53).

The standard potential of the Am(IV)–Am(III) couple in 1*M* $HClO_4$ was originally estimated[46] as 2 44 V and was later revised by Cunningham[54] to 2 8 V Nugent et al ,[55] using a variety of new calculational procedures, estimate that the standard potential of the (IV)–(III) couple lies in the range 2 0 to 2 5 V From their direct measurements of a value of 1 78 V for the (IV)–(III) couple in 10*M* H_3PO_4, Stokely and Baybarz[55] calculate a value of 2 34 V for the couple in 1*M* $HClO_4$ An average value of 2 4 V is shown in Table 3 3 for the (IV)–(III) couple

Gunn,[56] from measurements of the heat of reduction of Am(VI) to Am(III) by the Fe^{2+} ion, estimated the potential of the Am(VI)–Am(III) couple at 1 70 V A value of 1 67 V for this couple was estimated by Nigon[57] on the basis of a study of the oxidation of Am(III) to Am(VI) by the Ce(IV) ion An earlier[27] estimate of 1 8 V for the (IV)–(III) couple was in error due to a misinterpretation of the effect of acidity on the oxidation of Am(III) to Am(VI) by the $S_2O_8^{2-}$ ion In passing it should be noted that the currently accepted potentials of both the (VI)–(III) and (VI)–(V) couples are based on results of measurements made 20 years ago when americium chemistry was in its infancy Repetition of these measurements with long-lived ^{243}Am would be helpful

Potentials shown in Table 3 3 for the Am(II)–Am(0), Am(V)–Am(III), and Am(V)–Am(IV) couples are calculated from those listed for the other couples The new values assigned to the (III)–(0) and (III)–(II) couples lead to a value of –1 9 V for the (II)–(0) couple, which is substantially changed from the potential of <–2 7 V customarily shown[6c,48] Nugent[6b] assigns a value of –2 0 V to the (II)–(0) couple As a reflection of the change in the (IV)–(III) potential from 2 44 to 2 4 V, the potential of the (VI)–(V) couple is calculated to be 1 1 V, only slightly more positive than the value of 1 04 V previously calculated[6c,48] for this potential

Potentials in 1*M* OH$^-$

Standard potentials of americium in 1*M* OH$^-$ solution (Table 3 3) were originally calculated in 1952 by Latimer[58a] from estimates of the solubility products of $Am(OH)_3$ and $Am(OH)_4$ Subsequently, Penneman, Coleman, and Keenan[32] suggested that the standard potential of the $Am(OH)_3$–$Am(OH)_4$ couple should be revised from +0 4 V to at least –0 5 V From recent studies of the reaction of Am(VI) with Np(VI) in 0 01*M* to 12*M* NaOH and with Pu(VI) in 3*M* to 14*M* NaOH Nikolaevskii, Shilov, and Krot[58b] estimate that the potential of the Am(VI)–Am(V) couple in 1*M* NaOH is ~0 65 V rather than the 1 1 V estimated by Latimer [58a] Peretrukhin, Nikolaevskii, and Shilov[58c] have investigated the polarographic behavior of Am(V) and Am(VI) in 1*M* to 10*M* NaOH From their data these authors give the following potential scheme

$$\begin{tikzcd}[column sep=large] \begin{matrix}1M\ \text{NaOH}\\ \\ 10M\ \text{NaOH}\end{matrix} & \text{Am(VI)} \arrow[r, dash, "0\ 68", "0\ 63"'] & \text{Am(V)} \arrow[r, dash, "0\ 25 < E_0 < 0\ 50", "0\ 17 < E_0 < 0\ 50"'] & \text{Am(IV)} \arrow[r, dash, "E_0 < 0\ 25", "E_0 < 0\ 18"'] & \text{Am(III)} \end{tikzcd}$$

Further revision of Latimer's calculated potentials for americium in alkaline solutions is in order, particularly so since there is evidence[59] that the solubility product of $Am(OH)_3$ is of the order of 3×10^{-18} rather than $2\ 7 \times 10^{-20}$ as estimated by Latimer [58a]

Potentials in H_3PO_4

The formal potentials of the Am(IV)–Am(III) and Am(VI)–Am(V) couples in H_3PO_4 solutions which are listed in Table 3 3 were determined by direct potentiometry [55,60]

AUTOREDUCTION EFFECTS

Species (e g , H_2O_2 and $HO_2^\bullet$ radicals) produced by alpha radiolysis of water reduce the higher oxidation states of americium in aqueous solution eventually to stable Am(III) Because of its lower specific activity, the rate of autoreduction of ^{243}Am(>III) is much less than that of ^{241}Am(>III) Autoreduction of Am(VI) has been studied in $HClO_4$ (Refs 46, 61-64), H_2SO_4 (Refs 62-64), and HNO_3 (Ref 62) solutions while autoreduction of Am(V) has been followed in $HClO_4$ (Refs 46, 61, 63, 64), HNO_3 (Ref 62), and HCl (Ref 65) media Zaitsev et al [62] postulate the following reactions to account for the observed kinetics of autoreduction of AmO_2^{2+} and AmO_2^+ ions in the aqueous, air saturated solutions

$$H_2O \rightarrow H + \dot{O}H \qquad (3\ 4)$$

$$H + O_2 \rightarrow HO_2^\bullet \qquad (3\ 5)$$

$$\dot{O}H + \dot{O}H \rightarrow H_2O_2 \qquad (3\ 6)$$

$$AmO_2^{2+} + HO_2^\bullet \rightarrow AmO_2^+ + O_2 + H^+ \qquad (3\ 7)$$

$$AmO_2^{2+} + H_2O_2 \rightarrow AmO_2^+ + HO_2^\bullet + H^+ \qquad (3\ 8)$$

$$AmO_2^+ + 2HO_2^\bullet + 2H^+ \rightarrow Am^{3+} + 2O_2 + 2H_2O \qquad (3\ 9)$$

$$AmO_2^+ + \dot{O}H \rightarrow AmO_2^{2+} + OH \qquad (3\ 10)$$

This reaction scheme assumes that H_2O_2 is consumed only in reducing Am(VI), whereas Am(V) is reduced only by $HO_2^\bullet$ radicals Americium(V) may be oxidized to Am(VI) by $\dot{O}H$ radicals, and this reaction competes with that of hydrogen formation

All investigators concur that autoreduction of Am(VI) is kinetically zero order with respect to the AmO_2^{2+} ion and first order with respect to total americium concentration, i e ,

$$-\frac{d[\mathrm{Am(VI)}]}{dt} = \frac{d[\mathrm{Am(V)}]}{dt} = k_1\,[\mathrm{Am}_{\mathrm{total}}] \qquad (3.11)$$

In both $HClO_4$ and H_2SO_4 media, the rate constant k_1 falls off with increasing acid concentration (Table 3.4). Indeed, Zaitsev and coworkers[62] did not observe any reduction of $^{241}AmO_2^{2+}$ in 12*M* $HClO_4$ over a period of 300 hr! This result is explained by Zaitsev et al. on the basis that in concentrated $HClO_4$ the predominant alpha radiolytic species are Cl_2 and ClO_2 which do not reduce Am(VI) or Am(V).

Table 3.4

RATE CONSTANTS FOR AUTOREDUCTION OF ^{241}Am(VI) AND ^{241}Am(V)

$HClO_4$				H_2SO_4			HNO_3*		HCl†	
M	k_1,‡ hr^{-1}	k_2,§ hr^{-1}	Ref.	*M*	k_1, hr^{-1}	Ref.	*M*	k_1, hr^{-1}	*M*	k_2, hr^{-1}
0.2	0.040	0.020	46	0.1	0.040	62	0.5	0.069	0.5	0.0074
0.2	0.040		62	0.1	0.029	63	3.0	0.086		
0.2	0.030	0.012	63	0.5	0.025	63	6.0	0.087		
0.5	0.054		61	1.0	0.0286	62	9.0	0.103		
1.0	0.0475	0.023	61	2.0	0.0251	62	14.3	0.058		
2.0	0.032		62	2.0	0.0242	65				
4.0	0.032		62	3.0	0.017	63				
9.0	0.028		62	4.0	0.0236	64				
9.0	0.01		63	4.5	0.013	63				
12.0	0.0		62	6.0	0.018	62				
				6.5	0.012	63				
				9.0	0.012	63				
				10.0	0.022	62				

*All from Ref. 62.
†Ref. 65.
‡For Am(VI) → Am(V), see Eq. 3.11.
§For Am(V) → Am(III), see Eq. 3.14.

Zaitsev et al. also state that the falloff in k_1 with increasing H_2SO_4 concentration may be accounted for by the occurrence of the reactions

$$\dot{O}H + HSO_4^- \rightarrow OH^- + HSO_4^{\bullet} \qquad (3.12)$$

and/or

$$\dot{O}H + H_2SO_4 \rightarrow H_2O + HSO_4^{\bullet} \qquad (3.13)$$

which compete with Eq. 3.6 and thereby lower the yield of H_2O_2.

The autoreduction rate of Am(VI) in HNO_3 solutions is a factor of 1 5 to 2 higher than the maximum rate in $HClO_4$ and H_2SO_4 solutions Also, in contrast to the behavior noted in $HClO_4$ and H_2SO_4 media, the reduction rate appears to increase with increasing HNO_3 concentration, at least up to 9*M* HNO_3 According to Zaitsev the increased rate of reduction of Am(VI) in HNO_3 solutions is caused by radiolytically generated NO_2 ions that very effectively reduce Am(VI)

As regards autoreduction of Am(V) to Am(III), most investigators have stated that rate of this reaction, like that of the analogous Am(VI)–Am(V) transition, depends only on total americium concentration and is independent of Am(V) concentration, i e ,

$$-\frac{d[\mathrm{Am(V)}]}{dt} = \frac{d[\mathrm{Am(III)}]}{dt} = k_2\,[\mathrm{Am_{total}}] \tag{3 14}$$

(Values of k_2 determined in several solutions are listed in Table 3 4) Zaitsev et al[62,66] disagree and state that, at least under some conditions, the rate of autoreduction of Am(V) to Am(III) does depend on the concentration of Am(V) In any event, autoreduction of $^{241}AmO_2^+$ proceeds more slowly in 0 5*M* HCl than in 0 2*M* $HClO_4$, presumably because of preferential reaction of the primary radiolysis products with chloride species rather than with AmO_2^+ ions Slow autoreduction of AmO_2^+ in HNO_3 solutions has also been reported,[62] the maximum reduction rate of AmO_2^+ is ~1% per hour in 0 5*M* HNO_3 and 0 8% per hour in 3 0*M* HNO_3

The rate of autoreduction of ^{243}Am(VI) in 2 18*M* $HClO_4$ solution at 75 7°C is about six times what it is at room temperature[67] In 4*M* $HClO_4$–2*M* $NaClO_4$ solution, ^{241}Am(VI) autoreduces about four times faster at 75°C than at 25°C (Ref 62)

In 13*M* NH_4F, ^{241}Am(IV) autoreduces at a rate of about 4% per hour,[15] whereas, in 3*M* fluoride solution, the autoreduction rate is about 10% per hour[17] Self-reduction of Am(IV) to Am(III) in phosphoric acid solution follows first-order reaction kinetics[18] with a rate constant that is dependent on the concentrations of americium and H_3PO_4 (Fig 3 2) In 12*M* H_3PO_4 solution containing initially 0 008*M* Am(IV) (85% ^{243}Am), 27 hr are required for self reduction of half the americium

DISPROPORTIONATION

Am(IV)

In aqueous solution, Am(IV) is stable only in concentrated H_3PO_4, $K_4P_2O_7$, and fluoride (NH_4F, KF, etc) solutions (see pages 51 and 52) In other media, Am(IV) disproportionates to Am(III) and Am(V) in accordance with the large positive potential of the Am(IV)–Am(III) couple (see Table 3 3)

In HNO_3 and $HClO_4$ solutions, Am(IV) rapidly disproportionates according to the reaction[32]

$$2\mathrm{Am(IV)} \rightarrow \mathrm{Am(III)} + \mathrm{Am(V)} \tag{3 15}$$

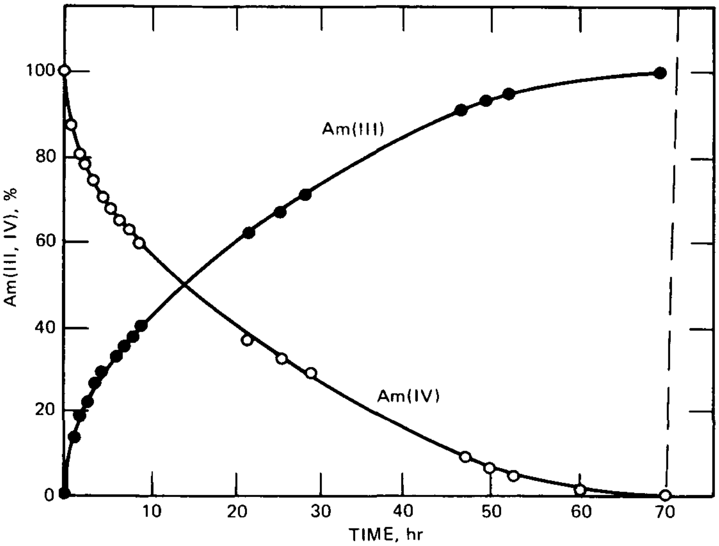


Fig. 3.2 Kinetics of the self-reduction of Am(IV) in 12*M* H_3PO_4. [From B. F. Myasoedov, V. M. Mikhailov, I. A. Lebedev, O. E. Koiro, and V. Ya. Frenkel, Preparation and Stability of Am(IV) and Am(V) in Phosphoric Acid Solutions, *Radiochemical and Radioanalytical Letters*, **14**: 17 (1973).]

Assuming a reaction second order in Am(IV), Penneman, Coleman, and Keenan[32] estimated k_1 in the equation

$$-d[\mathrm{Am(IV)}]/dt = k_1 [\mathrm{Am(IV)}]^2 \qquad (3.16)$$

to be >3.7 × 10^{-4} liter $mol^{-1} hr^{-1}$ in 0.05*M* HNO_3 at 0°C.

Conversely, dissolution of $Am(OH)_4$ in 0.05*M* to 2*M* H_2SO_4 solutions at either 0 or 25°C or of AmO_2 in 1*M* H_2SO_4 yields solutions[32,68] containing Am^{3+} and AmO_2^{2+}. These results are explained on the basis of the following mechanism:

Stage 1, simple disproportionation:

$$2\mathrm{Am(IV)} \rightarrow \mathrm{Am(III)} + \mathrm{Am(V)} \qquad (3.17)$$

Stage 2, redox reaction:

$$\mathrm{Am}^{4+} + \mathrm{AmO_2^+} \rightarrow \mathrm{AmO_2^{2+}} + \mathrm{Am}^{3+} \qquad (3.18)$$

In support of this postulated mechanism, the proportion of AmO_2^{2+} increases with increasing SO_4^{2-} and HSO_4^- concentrations at constant H^+ concentration. This means that SO_4^{2-} (or HSO_4^-) catalyzes the redox reaction since this step is not observed in HNO_3 or $HClO_4$ media.

Significantly, the average oxidation number of americium remains IV when $Am(OH)_4$ is dissolved in either $HClO_4$, HNO_3, or H_2SO_4 media[32] This result is somewhat surprising since Zaitsev et al[68] claim that the reduction of Am^{4+} by water is of increasing importance when AmO_2 is dissolved in >1*M* H_2SO_4, e g, 27% reduction in 2*M* H_2SO_4 and 64% in 6*M* H_2SO_4

Am(V)

Early studies of the disproportionation of Am(V) in $HClO_4$ (Refs 46, 63, 69, 72), H_2SO_4 (Ref 70a), HNO_3 (Ref 70a), and HCl (Ref 65) solutions were all made with ^{241}Am Results of these studies were greatly obscured by effects produced by alpha decay of the ^{241}Am isotope which, in most cases, led to autoreduction of Am(VI) to Am(V) at a rate which was approximately equal to that of the disproportionation This complicating effect resulted, as Coleman[67] has pointed out, in general disagreement regarding both the stoichiometry and kinetics of the disproportionation reaction Thus Stephanou, Asprey and Penneman[69] and, later, Hall and Markin[63] concluded that the reaction 2Am(V) → Am(VI) + Am(IV) is followed by immediate reduction of Am(IV) by water, so that the apparent reaction is 2Am(V) → Am(VI) + Am(III) Conversely, Gunn and Cunningham[46] suggested that the stoichiometry is 3Am(V) → 2Am(VI) + Am(III), during which the average oxidation number of the americium is conserved Zaitsev et al[70a] supported this latter contention

The most recent and definitive study of the kinetics of the disproportionation of Am(V) has been made by Coleman[67] using the isotope ^{243}Am to eliminate radiolytic complications Coleman investigated disproportionation of Am(V) in 3*M* to 8*M* $HClO_4$ at 25°C, in 1*M* to 2*M* $HClO_4$ at 75 7°C, and in about 2*M* HCl, H_2SO_4, and HNO_3 solutions at 75 7°C His data for disproportionation in 6*M* $HClO_4$ at 25°C are shown in Fig 3 3

In confirmation of the earlier claims of Gunn and Cunningham[46] and of Zaitsev et al,[70a] Coleman[67] finds that the stoichiometry of the disproportionation reaction in all media but HCl corresponds to

$$3Am(V) \rightarrow 2Am(VI) + Am(III) \qquad (3\ 19)$$

In HCl no Am(VI) is detected, since Am(VI) is rapidly reduced by Cl in acid media

According to Coleman,[67] the net disproportionation reaction is

$$3AmO_2^+ + 4H^+ \rightarrow 2AmO_2^{2+} + Am^{3+} + 2H_2O \qquad (3\ 20)$$

At 75 7°C in $LiClO_4$–0 97 to 1 90*M* $HClO_4$ ($\mu = 2\ 0M$) solutions, the second order rate constant depends on $[H^+]^{2\ 5}$ Coleman[67] and Newton[70b] note that this dependence suggests that two activated complexes are involved, one formed from two AmO_2^+ and two H^+ and the other from two AmO_2^+ and three H^+ Assuming, as Coleman did, these activated complexes are involved in parallel rate-determining steps, the rate law is given by

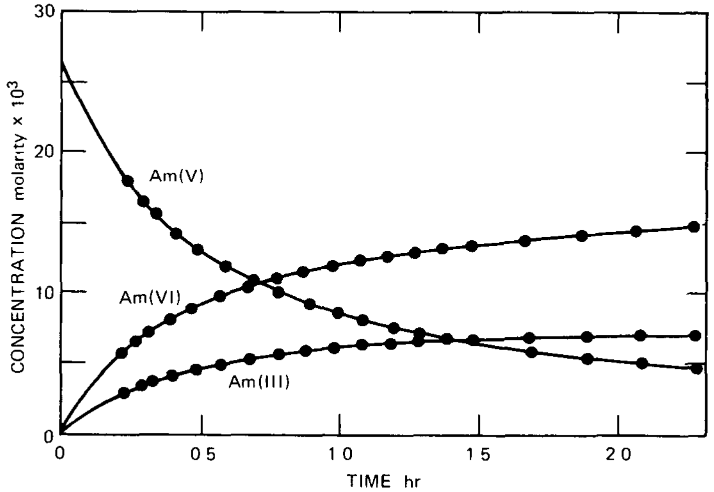


Fig. 3.3 Disproportionation of Am(V) in 6*M* $HClO_4$ at 25°C [From J S Coleman, The Kinetics of the Disproportionation of Americium(V) *Inorganic Chemistry* 2 53 (1963)]

$$\frac{d[Am(V)]}{dt} = k_2\,[AmO_2^+]^2\,[H^+]^2 + k_3\,[AmO_2^+]^2\,[H^+]^3 \tag{3 21}$$

with $k_2 = (6\ 94 \pm 1\ 01) \times 10^{-4} M^{-3}\ sec^{-1}$ and $k_3 = (4\ 63 \pm 0\ 71) \times 10^{-4} M^{-1}\ sec^{-1}$

Newton[70b] states, however "Despite the fact that the rate law above is very satisfactory, an ambiguity in interpretation remains If the same two activated complexes are formed consecutively, rather than in parallel steps, the rate law is

$$\frac{-d[Am(V)]}{dt} = [AmO_2^+]\left(\frac{1}{k_2'\,[H^+]^2} + \frac{1}{k_3'\,[H^+]^3}\right)^{-1}$$

This equation fits the experimental results just as well as the previous one Values for k_2' and k_3' are $(2\ 57 \pm 0\ 36) \times 10^{-3} M^{-4}\ sec^{-1}$ and $(2\ 06 \pm 0\ 33) \times 10^{-3} M^{-4}\ sec^{-1}$, respectively These values reproduce the data with a root mean square deviation of 3 2% and a maximum deviation of 6 6% In order to distinguish between the two rate laws, measurements would have to be extended at least down to 0 7*M* $HClO_4$ where the two calculated values for the apparent second-order rate constants would differ by 10% "

Using, in part, temperature-dependence data obtained by Coleman, Newton estimated thermodynamic quantities of activation for the disproportionation of Am(V) Results of his calculations are given in Table 3 4a

Coleman also notes that at 75 7°C the disproportionation rates in 2*M* HNO_3, HCl, and H_2SO_4 are, respectively, 4 0, 4 6, and 24 times as great as that in 2*M* $HClO_4$,

Table 3.4a

NET ACTIVATION PROCESSES AND THERMODYNAMIC QUANTITIES FOR THE DISPROPORTIONATION OF Am(V)[a]

Net activation process	ΔG^*, kcal mol^{-1}	ΔH^*, kcal mol^{-1}	ΔS^*, cal mol^{-1} deg^{-1}
$2AmO_2^+ + 2H^+ \rightleftharpoons [*]^{4+}$	26.17	15.4 ± 0.3	31 ± 1
$2AmO_2^+ + 3H^+ \rightleftharpoons [*]^{5+}$	26.81	9.4 ± 0.5	−50 ± 1.2

[a] Adapted from T. W. Newton, The Kinetics of the Oxidation–Reduction Reactions of Uranium, Neptunium, Plutonium, and Americium in Aqueous Solutions, USAEC Report TID-26506, 1974.

whereas at ~25°C the reaction rate increased 450 times in going from 3*M* to 8*M* $HClO_4$.

Coleman also observed the reaction

$$Am^{3+} + 2AmO_2^{2+} + 2H_2O \rightarrow 3AmO_2^+ + 4H^+ \qquad (3.22)$$

the reverse of the disproportionation reaction, on addition of Am(III)–Am(VI) mixtures to $Al(ClO_4)_3$ buffer at pH 4 and on neutralization of Am(III)–Am(VI) mixtures with $NaHCO_3$. Studies of the kinetics of Eq. 3.22 have not been made.

KINETICS OF OXIDATION–REDUCTION REACTIONS

A long-neglected area of americium chemistry has been the determination of the rate laws and mechanism of the various oxidation–reduction reactions of americium ions in aqueous solution. Several recent papers by Japanese and Russian workers suggest, however, that this situation may be changing. The following paragraphs summarize data for the few reactions that have been studied in detail and supplement information presented in earlier review papers by Hindman,[71] by Newton and Baker,[72] and by Gourisse.[73] An important up-to-date reference is the ERDA Critical Review by Newton.[70b]

Peroxydisulfate Oxidation of Am(III) in Acid Media

Japanese workers[74-76] have studied kinetics of oxidation of Am(III) to Am(VI) by $S_2O_8^{2-}$ ion, in both the presence and absence of Ag^+ ion, in 0.06*M* to 0.4*M* HNO_3 solutions at 40 to 70°C. Kinetics of this reaction, in the absence of Ag^+ ion, in 0.09*M* to 0.6*M* HNO_3 at 45.6 to 69.0°C have also been investigated by Russian scientists.[77] The general pattern of the oxidation reaction (Fig. 3.4) involves (1) an induction

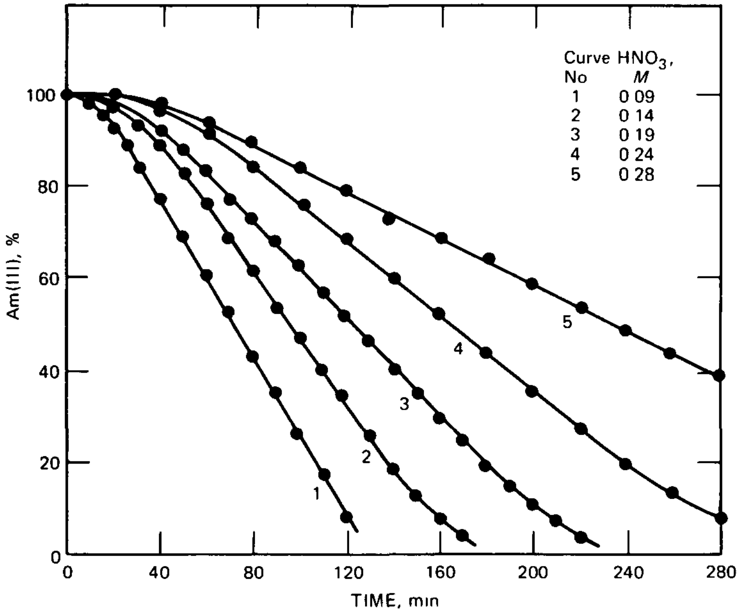


Fig. 3.4 Kinetics of oxidation of Am(III) by peroxydisulfate (50.6°C, $[S_2O_8^{2-}]_0 = 0.40M$). [From V. A. Ermakov, A. G. Rykov, G. A. Timofeev, and G. N. Yakovlev, Investigation of the Kinetics and Redox Reactions of the Actinide Elements. XX. Kinetics and Mechanisms of the Interaction of Americium(III) and (V) with Peroxydisulfate Ions in Nitric Acid Solution, *Radiokhimiya*, 13: 826 (1971) through *Soviet Radiochemistry (English Translation)*, 13: 851 (1971).]

period; (2) a linear region of constant rate; and (3) a region of gradually decreasing rate, particularly at higher HNO_3 concentrations. Reaction rates are dependent on temperature and on the concentrations of HNO_3, $S_2O_8^{2-}$, and, when present, Ag^+. Newton[70b] states that the stoichiometry of the oxidation reaction is

$$\tfrac{3}{2}S_2O_8^{2-} + Am^{3+} + 2H_2O \rightarrow 3SO_4^{2-} + AmO_2^+ + 4H^+ \qquad (3.23)$$

Both the Japanese and Russian workers concur that the oxidizing agent is not the $S_2O_8^{2-}$ ion itself but secondary products (e.g., SO_4^-, OH, and $HS_2O_8^-$) resulting from its thermal decomposition.

Using micromolar concentrations of ^{241}Am(III), Ohyoshi, Jyo, and Shinohara[76] found the oxidation reaction to be first order with respect to both Am^{3+} and $S_2O_8^{2-}$ concentrations and to follow the rate expression

$$\frac{-d[Am(III)]}{dt} = K_h(k_1 + k_2[Ag^+])[S_2O_8^{2-}][Am(III)] \cdot 1/[H^+] \qquad (3.23a)$$

where K_h is the dissociation constant of $H_2S_2O_8^-$ and k_1 and k_2 refer to the silver ion uncatalyzed and catalyzed paths, respectively (Some values for k_1 and k_2 are listed in Table 3.5.) The energies of activation are 33.3 kcal mol^{-1} for k_1 and 17.4 kcal mol^{-1} for k_2. This activation energy for k_1 was recalculated by Newton[70b] from k vs T data in the original Japanese paper. Newton notes that the value of 28.6 kcal mol^{-1} reported by Ohyoshi, Jyo, and Shinohara[76] for the k_1 path is clearly in error.

Table 3.5

RATE CONSTANTS FOR PEROXYDISULFATE OXIDATION OF Am(III)

{$[\text{Am(III)}]_0$‡ = $4.0 \times 10^{-6}M$; $[NH_4S_2O_8]_0$† = $2.0 \times 10^{-2}M$; $[HNO_3]_0$† = $6.0 \times 10^{-2}M$; $\mu = 0.50M$}

Temp., °C	k_2,‡ M^{-2} min^{-1}	k_1,§ M^{-1} min^{-1}
40	162	0.013
50	420	0.093
60	915	0.36
70	1820	1.45

†Subscript zero means initial concentration.
‡Silver-catalyzed path. Eq. 3.23.
§Uncatalyzed path. Eq. 3.23.

Conversely, Ermakov et al.,[77] on the basis of studies with millimolar amounts of ^{243}Am(III), claim that the rate of oxidation of Am(III) (in the absence of Ag^+) in the linear portion of the kinetic curves does not depend on the Am(III) concentration and is given by

$$\frac{-d[\text{Am(III)}]}{dt} = (a - b[H^+])\,[S_2O_8^{2-}]\,[\text{Am(III)}]^0$$
$$= \frac{2}{3}\left(k_1 - \frac{k_4[H^+]}{1+x}\right)[S_2O_8^{2-}]_0 = k_{III} \qquad (3.24)$$

At 50.6°C, $a = 4.9 \times 10^{-5}$ min^{-1} and $b = 0.9 \times 10^{-4} M^{-1}$ min^{-1}. In Eq. 3.24, $[S_2O_8^{2-}]_0$ is the initial concentration of the peroxydisulfate ion, $x = k_5/k_6[H_2O]$, and k_1, k_4–k_6 are rate constants for the following reactions:

$$S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^{\dot{-}} \qquad (3.25)$$

$$S_2O_8^{2-} + H^+ \xrightarrow{k_4} HSO_4^- + SO_4^{\dot{-}} \qquad (3.26)$$

$$SO_4^{\dot{-}} \xrightarrow{k_5} SO_3 + O \qquad (3.27)$$

$$SO_4^{\dot{-}} + H_2O \xrightarrow{k_6} H_2O_2 + SO_3 \qquad (3.28)$$

Peroxydisulfate Oxidation of Am(V) in HNO_3

Ermakov et al.[77] have also investigated the kinetics of the oxidation of Am(V) by $S_2O_8^{2-}$ ion in 0.09 to 0.6*M* HNO_3 media at 45.6 to 60°C. According to Newton,[70b] the stoichiometry of this reaction is

$$\tfrac{1}{2}S_2O_8^{2-} + AmO_2^{+} \rightarrow SO_4^{2-} + AmO_2^{2+} \qquad (3.29)$$

Ermakov and his coworkers account for their results on the basis of the rate law

$$\begin{aligned} \frac{-d[Am(V)]}{dt} &= (a' - b'[H^+])\,[S_2O_8^{2-}]\,[Am(V)]^0 \\ &= 2\left(k_1 \quad \frac{k_4[H^+]}{1+x}\right)[S_2O_8^{2}]_0 = k_V \end{aligned} \qquad (3.30)$$

where x, k_1, k_4, and $[S_2O_8^{2-}]_0$ are defined as for Eq. 3.24. At 50.6°C $a' = 1.5 \times 10^{-5}$ min^{-1} and $b' = 2.7 \times 10^{-4} M^{-1}$ min^{-1}.

From Eqs. 3.24 and 3.30, it follows that the ratio k_V/k_{III} should equal 3 for similar conditions of acidity and temperature. This has been confirmed by Ermakov et al.[77]

Peroxydisulfate Oxidation of Am(III) in K_2CO_3 Media

Just as in acid media, the rate of oxidation of Am(III) by peroxydisulfate in K_2CO_3 solutions is determined by the rate of thermal decomposition of the $S_2O_8^{2-}$ ion. In contrast to behavior in acid media, however, peroxydisulfate oxidation of Am(III) in carbonate solutions proceeds through the intermediate formation of Am(V). These conclusions were established by Ermakov et al.[78] who studied oxidation of 0.001*M* to 0.003*M* Am(III) in 1.3*M* to 2.46*M* K_2CO_3 solutions by 0.025*M* to 0.1*M* $S_2O_8^{2-}$ at temperatures in the range 58 to 83°C. Under such conditions the rate of oxidation of Am(III) to Am(V) is independent of the total Am and K_2CO_3 concentrations and equals the rate of decomposition of $S_2O_8^{2-}$ ions. The rate of oxidation of Am(V) to Am(VI) is directly proportional to both the total americium concentration and the $S_2O_8^{2-}$ concentration and is inversely proportional to the K_2CO_3 concentration.

The effective activation energy of $S_2O_8^{2-}$ oxidation of Am(III) to Am(V) in K_2CO_3 solutions is about 33.9 kcal mol^{-1} which is close to the activation energy (33.5 kcal mol^{-1}) of the thermal decomposition of $S_2O_8^{2-}$ ions according to the reaction $S_2O_8^{2-} \rightarrow 2SO_4^{\bullet -}$.

Reduction of Am(VI) in Acid Peroxydisulfate Solutions

In high acid ($\geqslant 1M$ HNO_3) solutions at 50 to 70°C, thermal decomposition products of the $S_2O_8^{2-}$ ion reduce Am(VI) to Am(V). For this reduction, Rykov et al.[79a] propose the rate law

$$\frac{-d[\mathrm{Am(VI)}]}{dt} = k_{VI}[S_2O_8^{2-}]_0 = 2\left(\frac{k_4[H^+]}{1+x} - k_1\right) \qquad (3.31)$$

where $[S_2O_8^{2-}]_0$ is the initial concentration of the peroxydisulfate ion, $x = k_5/k_6[H_2O]$ and k_1, k_4, k_5, and k_6 are the rate constants for Eqs. 3.25, 3.26, 3.27, and 3.28, respectively.

The results of Rykov et al.[79a] thus indicate that the mechanism of reduction of Am(VI) in the presence of $S_2O_8^{2-}$ ions is identical with that proposed (see page 67) for oxidation of Am(V). The direction of the process—oxidation of Am(V) or reduction of Am(VI)—is determined by the ratio of the contributions of the primary processes of thermal decomposition of $S_2O_8^{2-}$ ions. At low acidities where Eq. 3.25 predominates, oxidation of Am(V) predominates. At high acidities, where the catalytic pathway of decomposition (Eq. 3.26) dominates, Am(VI) is reduced. The hydrogen-ion concentrations where the reaction paths change are temperature dependent.

Reduction of Am(VI) by Hydrogen Peroxide

Using ^{243}Am in $LiClO_4$–$HClO_4$ media, Woods, Cain, and Sullivan[79b] studied kinetics of the reaction

$$2AmO_2^{2+} + H_2O_2 \rightarrow 2AmO_2^+ + 2H^+ + O_2 \qquad (3.32)$$

These workers report that the empirical form of the rate law for Eq. 3.32 at 25°C and $\mu = 1.00M$ is

$$\frac{-d[AmO_2^{2+}]}{dt} = k[AmO_2^{2+}][H_2O_2][H^+]^{-0.12} \qquad (3.33)$$

Over the range of hydrogen-ion concentrations from $0.98M$ to $0.1M$, $\log k = 4.952 \pm 0.007 - 0.12 \pm 0.01 \log [H^+]$.

Reduction of Am(VI) by Other Reductants*

Shilov, Nikolaevskii, and Krot[79c] have reported results of qualitative spectrophotometric studies of the reaction of $2 \times 10^{-4}M$ to $10^{-3}M$ ^{241}Am(VI) in dilute HNO_3 solutions with various reducing agents. According to their data (Table 3.5a),

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*Woods and Sullivan [*Inorganic Chemistry,* **13**: 2774 (1974)] studied the reaction between AmO_2^{2+} and NpO_2^+ in $1M$ (H,Li)ClO_4. The rate law is:

$$\frac{-d[\mathrm{Am(VI)}]}{dt} = k[\mathrm{Am(VI)}][\mathrm{Np(V)}]$$

At 25°C, k is $(2.45 \pm 0.4) \times 10^4$ M^{-1} sec^{-1}; for this reaction, $\Delta H^* = 6.66 \pm 0.08$ kcal mol^{-1} and $\Delta S^* = -16.2 \pm 0.3$ cal mol^{-1} deg^{-1}.

Table 3.5a

REDUCTION OF Am(VI) BY SEVERAL REDUCING AGENTS*

$\{[\mathrm{Am(VI)}]_0 = 2 \times 10^{-4}–10^{-3}; 25°\mathrm{C}\}$

Reductant				Final solution	
Reagent	Concentration, *M*	Medium	Reaction rate	Am(V), %	Am(III), %
Oxalic acid	0.022	0.5*M* HNO_3	Very fast	56	44
	0.15	0.5*M* HNO_3	Very fast	57	43
	0.15	pH = 6.0	Very fast	57	43
Tartaric acid	0.0025	0.5*M* HNO_3	$t_{1/2}$ = 3 min	64	36
	0.0025	pH = 4.0	$t_{1/2}$ = 10 sec	63	37
Citric acid	0.0025	0.5*M* HNO_3	$t_{1/2}$ = 1 min	76	24
HCl	0.09	0.5*M* HNO_3	$t_{1/2}$ = 18 min	100	0
HCOOH	0.0025	pH = 4.0	$t_{1/2}$ = 10 min	100	0
HCHO	0.0024	0.1*M* HNO_3	$t_{1/2}$ = 2 min	100	0
Li_2SO_3	0.01	0.1*M* HNO_3	Very fast	100	0
NH_2OH	0.0025	0.1*M* HNO_3	Very fast	100	0
H_2O_2	0.0025	0.1*M* HNO_3	Very fast	100	0
N_2H_4	0.0025	0.1*M* HNO_3	Very fast	100	0

*From V. P. Shilov, V. B. Nikolaevskii, and N. N. Krot, Some Characteristics of the Reaction of Americium(VI) with Reducing Agents in Aqueous Solutions, *Radiokhimiya,* **15**: 871 (1973) through *Soviet Radiochemistry (English Translation),* **15**: 881 (1973).

oxalic acid and other organic compounds commonly regarded as complexing agents reduce Am(VI) rapidly to approximately equal mixtures of Am(III) and Am(V), whereas other reagents (H_2O_2, etc.) reduce Am(VI) initially only to Am(V). Mechanisms and rate laws involved in reduction of Am(VI) and Am(V) by H_2O_2 are discussed on pages 68 and 69–70, respectively. Detailed studies of the kinetics of reduction of Am(VI) by other reducing agents listed in Table 3.5a have not been reported.

Reduction of Am(V) by Hydrogen Peroxide

From their studies of the reduction of AmO_2^+ to Am^{3+} by H_2O_2 in 0.1*M* $HClO_4$, Zaitsev et al.[80] deduced the rate law

$$\frac{-d[\mathrm{AmO_2^+}]}{dt} = k[\mathrm{AmO_2^+}][\mathrm{H_2O_2}] \qquad (3.34)$$

where k = 14.8 ± 1.5, 21.6 ± 2.2, and 30.3 ± 3.0 liters mol^{-1} hr^{-1} at 25, 30, and 35°C, respectively. The activation energy for the reduction reaction is thus 13.2 kcal mol^{-1}.

The only other reported studies of the Am(III)–Am(V)–H_2O_2–$HClO_4$ system have been made by Damien and Pages.[81,82a] They report that the rate at which

AmO_2^+ is reduced is inversely proportional to the $HClO_4$ concentration and also is strongly dependent on the initial $[Am^{3+}]_0/[AmO_2^+]_0$ and $[H_2O_2]_0/[AmO_2^+]_0$ concentration ratios. In 0.2*M* $HClO_4$ at 26°C, the rate data could be described satisfactorily by the relation[81]

$$\frac{-d[AmO_2^+]}{dt} = \frac{k[AmO_2^+]_0[H_2O_2]_0}{1 + k'[Am^{3+}]_0/[AmO_2^+]_0} \qquad (3.35)$$

where $k = 3.3$ liters mol^{-1} hr^{-1} and $k' = 0.13$ $(liter\ mol^{-1}\ hr^{-1})^2$. Damien and Pages[82a] suggested that a more general rate law for this system is

$$\frac{-d[AmO_2^+]}{dt} = k[AmO_2^+] + k'[AmO_2^+]^2 \qquad (3.36)$$

where k' and k are a function, respectively, of acidity and H_2O_2 concentration. Damien and Pages did not attempt to determine these constants.

Reduction of Am(V) by Np(IV) in $HClO_4$ Media

Blokhin, Ermakov, and Rykov[82c] used a spectrophotometric procedure to study the kinetics of the Np(IV)–Am(V) reaction in 0.23*M* to 1.97*M* $HClO_4$ at temperatures in the range 35.0 to 54.6°C. Depending on the initial concentrations of Np(IV) and Am(V), the reaction products are either Np(V) and Am(III) or Np(VI) and Am(III). The reaction rate falls rapidly with increasing acidity. Under the assumption of constant Am(IV) concentration, the kinetic data follow the rate law

$$\frac{d[Am^{3+}]}{dt} = k_1'[Np^{4+}][AmO_2^+] + k_2'[NpO_2^+][AmO_2^+] \qquad (3.37)$$

where k_1' and k_2' are, respectively, rate constants for Eqs. 3.38 and 3.39.

$$Np^{4+} + AmO_2^+ \xrightarrow{k_1'} NpO_2^+ + Am^{4+} \qquad (3.38)$$

$$NpO_2^+ + AmO_2^+ \xrightarrow{k_4'} NpO_2^{2+} + Am^{4+} \qquad (3.39)$$

Values of k_1' and k_2' are given in Ref. 82c. The authors of this reference also calculate the following standard thermodynamic activation parameters for Eq. 3.37: $\Delta H^* = 30 \pm 1$ kcal mol^{-1}, $\Delta G^* = 20.7 \pm 1.0$ kcal mol^{-1}, and $\Delta S^* = 31 \pm 3$ cal mol^{-1} deg^{-1}.

Reduction of Am(V) by Np(V) in $HClO_4$ Media

Rykov, Timofeev, and Chistyakov[82d] have determined spectrophotometrically the rate of the reaction

$$2NpO_2^+ + AmO_2^+ + 4H^+ \rightarrow 2NpO_2^{2+} + Am^{3+} + 2H_2O \qquad (3.40)$$

Kinetic data were collected in perchlorate media ($\mu = 2\ 0M$) at temperatures in the range 24 7 to 44 1°C According to these workers, reduction of Am(V) by Np(V) is an irreversible second-order reaction with a rate law given by

$$\frac{-d[AmO_2^+]}{dt} = -\frac{1}{2}\frac{d[NpO_2^+]}{dt} = k[NpO_2^+][AmO_2^+] \qquad (3\ 41)$$

The rate of the reduction of Am(V) by Np(V) increases with acidity, at 24 7°C and $[H^+] = 0\ 53M$, $k = 0\ 71$ mol^{-1} min^{-1} whereas at 29 8°C and $[H^+] = 1\ 89M$, $k' = 6\ 10$ mol^{-1} min^{-1} Standard thermodynamic activation parameters calculated by Rykov, Timofeev, and Chistyakov[82d] for Eq 3 40 are $\Delta H^* = 15\ 2$ kcal mol^{-1}, $\Delta G^* = 20\ 0$ kcal mol^{-1}, and $\Delta S^* = -16$ cal mol^{-1} deg^{-1}

Reduction of Am(V) by Np(V) in Na_2CO_3 Media

Kinetics of the reduction of Am(V) by Np(V) in Na_2CO_3 solutions have been investigated spectrophotometrically by Chistyakov, Ermakov, and Rykov[82e] The stoichiometry of the reduction reaction corresponds to the equation

$$4H^+ + AmO_2^+ + 2NpO_2^+ \rightarrow Am^{3+} + 2NpO_2^{2+} + 2H_2O \qquad (3\ 42)$$

Kinetics of this reaction were studied at 50 5 to 69 7°C in 0 45M to 1 71M Na_2CO_3 solution containing 0 0013M Np(V) and 0 000655M ^{243}Am Under these conditions, kinetics of the Am(V)–Np(V) reaction in Na_2CO_3 media follow the same rate law (Eq 3 41) as that followed in $HClO_4$ media In 1 71M Na_2CO_3 at 64°C, the rate constant, k , is 150 ± 15 The effective activation energy of Eq 3 42 is independent of Na_2CO_3 concentration and is 14 5 ± 1 0 kcal mol^{-1}

Reduction of Am(V) by U(IV) in $HClO_4$ Media

At 11 2 to 36 0°C in 0 51M to 2 50M $HClO_4$, the reaction between Am(V) and U(IV) proceeds according to the reaction

$$AmO_2^+ + U^{4+} \rightarrow Am^{3+} + UO_2^{2+} \qquad (3\ 43)$$

Spectrophotometric measurements of Blokhin, Ermakov, and Rykov[82f] show that the rate law for this reduction reaction is given by

$$\frac{d[Am^{3+}]}{dt} = k[AmO_2^{2+}][U^{4+}] \qquad (3\ 44)$$

In 2 0M $HClO_4$ at 19 5°C, $k = 725 \pm 30$ Standard thermodynamic activation parameters for Eq 3 43 are $\Delta H^* = 18 \pm 1$ kcal mol^{-1}, $\Delta G^* = 15\ 2 \pm 0\ 2$ kcal mol^{-1}, and $\Delta S^* = 9 \pm 3$ cal mol^{-1} deg^{-1}

Self-Reduction of Am(VI) and Am(V) in Acid Peroxydisulfate Solution

Self-reduction of Am(VI) and Am(V) in various acid solutions is discussed on pages xxx to xxx. Ermakov et al.[83] have now studied self-reduction of Am(VI) and Am(V) at 18°C in $0.1M$ to $0.2M$ HNO_3 solutions containing $0.10M$ to $0.41M$ $(NH_4)_2S_2O_8$. Alpha radiation doses ranged from 0.95×10^{21} to 9.64×10^{21} eV liter^{-1} min^{-1}. Under such conditions the rate of reduction of Am(VI) is independent of its concentration but is a function of dose rate and the concentration of $S_2O_8^{2-}$ ions. No Am(III) is observed until all the Am(VI) is reduced to Am(V). In the presence of $S_2O_8^{2-}$ ions, radiolytic reduction of Am(V) proceeds more slowly than that of Am(VI).

SOLUTION ABSORPTION SPECTRA

Am(III)

A representative list of the various solutions in which the absorption spectra of the Am^{3+} ion have been measured is compiled in Table 3.6. Table 3.7 lists molar absorptivities at maximum absorption wavelengths for Am(III) in various media. These data as well as similar results presented later for Am(IV), (V), and (VI) should be used with some caution, taking into account that the accuracy of the resolution of the narrower absorption peaks may depend on the resolving power of the instrument with

Table 3.6

ABSORPTION SPECTRUM OF AM(III)

Media	References	Typical spectrum
$0.2M$–$10.4M$ HNO_3	26, 64, 84	Fig. 3.5a
$0.2M$–$10M$ HCl	64, 65, 85	Fig. 3.5b
$0.2M$–$10.0M$ H_2SO_4	64, 86	
$0.1M$–$0.5M$ $HClO_4$, $DClO_4$	2, 27, 48, 64, 65, 87–91	Fig. 3.5c
$4M$–$13.7M$ LiCl	92	
$11.4M$ LiBr	84	Fig. 3.6a
$6.0M$ K_2CO_3	84	Fig. 3.6a
40 wt % K_2CO_3	26	
$7.37M$ MgI_2	84	
$10M$ H_3PO_4	18	Fig. 3.6b
Saturated KF	93	Fig. 3.7a
Ethanolic HCl	88, 94, 95	Fig. 3.7b
Fused $LiNO_3$–KNO_3	96	Fig. 3.7c

Table 3.7

PROMINENT ABSORPTION BANDS OF AMERICIUM(III) IN VARIOUS SOLUTIONS

Absorption maximum, nm	Molar absorptivity, liters mol^{-1} cm^{-1}	Media	Ref.
1302	0 2	0 5*M* $DClO_4$	89
1050	7 7	0 5*M* $DClO_4$	89
874	1 1	0 5*M* $DClO_4$	89
818	44 0	40 wt % K_2CO_3	26
815	61 9	10*M* H_2SO_4	64
813	66 3	0 5*M* $DClO_4$	89
811	64 4	0 1*M* $HClO_4$	64
811	43 0	10*M* HNO_3	64
811	41 0	1*M* HNO_3	26
510	105 0	$LiNO_3$–KNO_3 eutectic	96
508	270 0	40 wt % K_2CO_3	26
505 5	260 0	11 44*M* LiBr	84
505	70 0	13 7*M* LiCl	92
505	168 0	10*M* HNO_3	64
503	378 0	0 1*M* $HClO_4$	64
503	379 0	12*M* H_3PO_4	18
501 2	170 0	Saturated KF	93
377	18 6	0 1*M* $HClO_4$	64
360	15 5	0 1*M* $HClO_4$	88
335	12 9	0 1*M* $HClO_4$	88
235	2790 0	13 7*M* LiCl	92

which they were measured. In perchlorate media, major peaks in the absorption spectrum of Am^{3+} occur at 503 and 811 nm. Shifts in the position of these peaks and/or changes in molar absorptivity which occur in other media are evidence for formation of various americium complexes.

Theoretical calculations of the electronic energy bands in the Am^{3+} ion have been performed by several investigators[91,97-100] Such calculations revealed[97,98] an unexpected $^7F_0 \leftrightarrow {}^5D_1$ transition at about 17,500 cm^{-1} which had not been observed previously Subsequently a weak band near the calculated energy level was observed in a concentrated americium solution.[100] The observed intensity of this band is consistent with a weak electric dipole mechanism.[99] The theoretical calculations also predict transitions between the ground $^7F_0$ state and even J-levels to be more intense than those to excited odd J-levels[91,98] The observed spectrum of Am^{3+} in $LiNO_3$–KNO_3 eutectic is in good agreement with the latter prediction

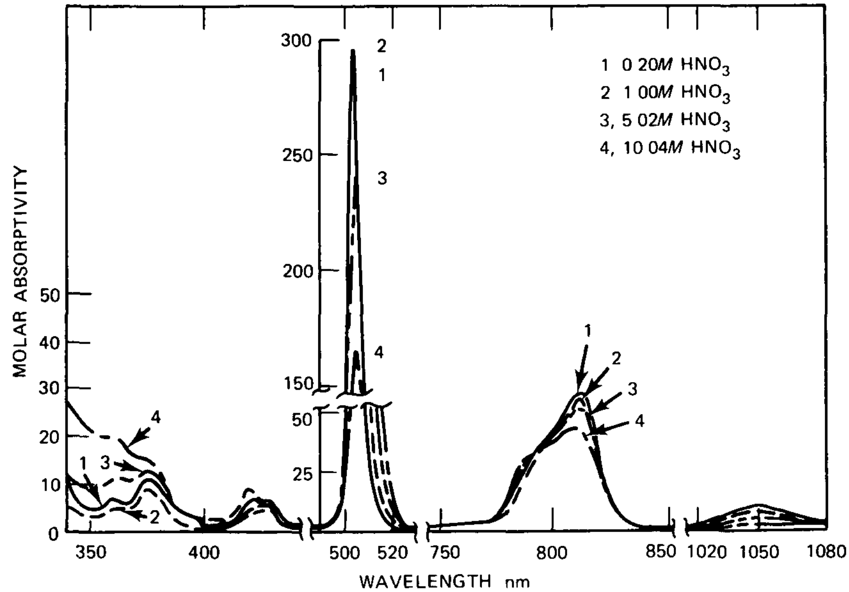

Fig. 3.5a Absorption spectrum of Am(III) in HNO_3. (From G. N. Yakovlev and V N. Kosyakov, Spectrophotometric Studies of the Behavior of Americium Ions in Solution, in *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955,* Vol. 7, p. 363, United Nations, New York, 1956)

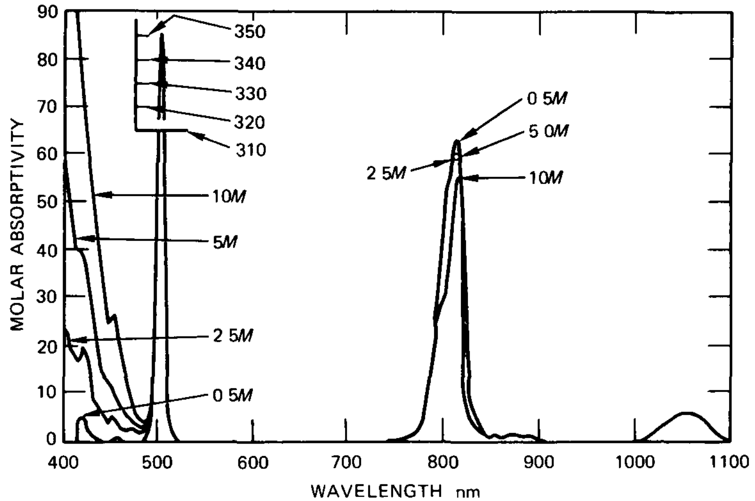

Fig. 3.5b Absorption spectrum of Am(III) in HCl [From G R Hall and P D Herniman, The Separation and Purification of Americium-241 and the Absorption Spectra of Trivalent and Quinquevalent Americium Solutions, *Journal of the Chemical Society (London),* p 2214 (1954)]

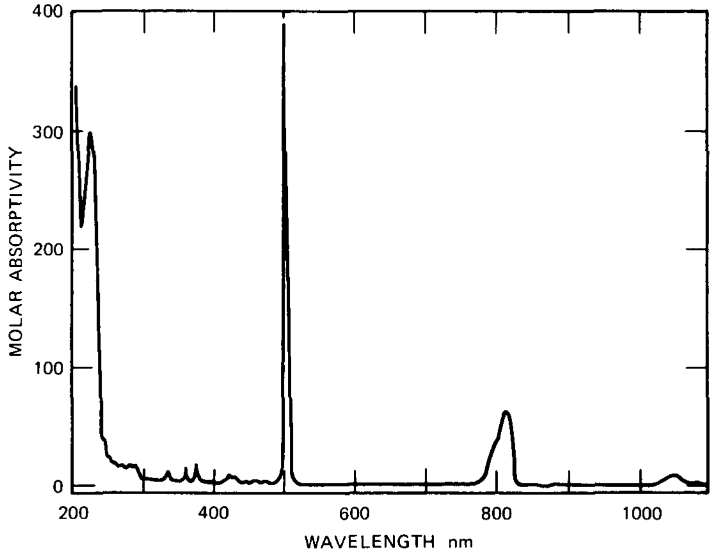

Fig. 3.5c Absorption spectrum of Am(III) in diluted $HClO_4$. [From T H Keenan, Americium and Curium, *Journal of Chemical Education*, 36: 27 (1959).]

Am(IV)

The solution spectrum[14 15] of Am(IV) has been measured in 10*M* to 12*M* NH_4F (Refs. 14, 15) (Fig 3.8a) and in 12*M* KF (Ref. 101) (Fig 3 8b), in the two solutions, resemblance of the spectrum in band energy and intensity (Table 3 8) is evident The spectrum in 13*M* NH_4F and 12*M* KF also resembles very closely that of solid AmF_4 (see pages 145 and 146).

Varga et al[101] have recently published an account of the first attempts at interpretation of the absorption spectrum of Am^{4+} in aqueous 12*M* KF and solid AmF_4, including term assignments Agreement between experimental and calculated levels was generally excellent Correspondence between the calculated results obtained for Am^{4+} in KF and AmF_4 was very close. Identical interpretations for the low energy levels were obtained, but some differences were found among the higher energy terms

Am(V)

The solution spectrum of Am(V) has been determined in 0.1*M* H_2SO_4 (Ref 26) (Fig 3 9a), 0 5*M* to 5 0*M* HCl (Ref 65) (Fig 3.9b) and in dilute $HClO_4$ (Refs. 27, 48, 88) (Fig. 3 9c) Molar absorptivities at maximum absorption peaks are listed in Table 3 8.

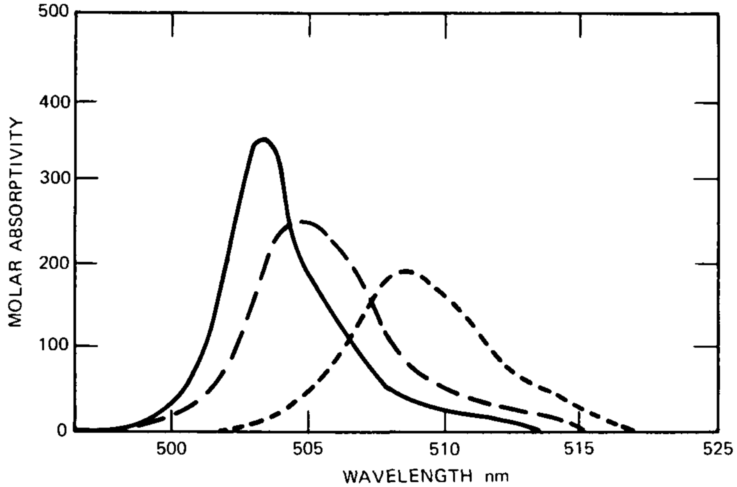

Fig. 3.6a The 503-nm band in the Am(III) spectrum ——, 1M $HClO_4$, - - -, 11.4M LiBr, – –, 6.0M K_2CO_3 solutions [From M. Shiloh, M. Givon, and Y. Marcus, A Spectrophotometric Study of Trivalent Actinide Complexes in Solutions III Americium with Bromide, Iodide, Nitrate, and Carbonate Ligands, *Journal of Inorganic and Nuclear Chemistry*, **31**: 1807 (1969).]

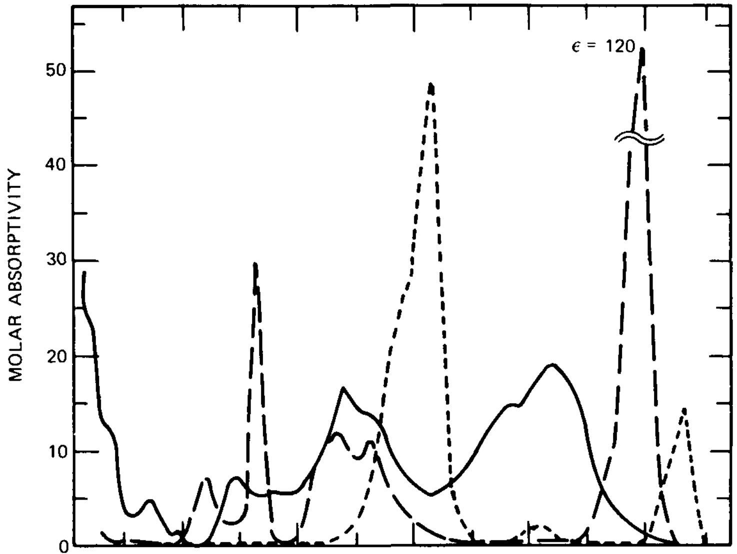

Fig. 3.6b Absorption spectrum of Am(III) in 10M H_3PO_4, - - -, Am(IV) in 10M H_3PO_4, ——, and Am(VI) in 5M H_2PO_4, – – – [From E. Yanir and M. Givon, Higher Oxidation States of Americium in Phosphate Solutions, *Inorganic and Nuclear Chemistry Letters*, Supplement to *Journal of Inorganic and Nuclear Chemistry*, **5**: 369 (1969).]

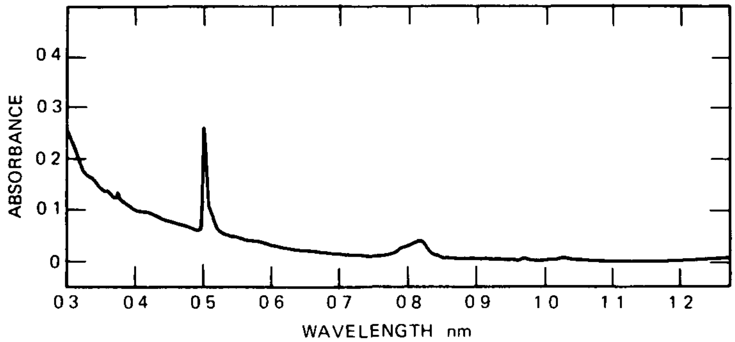

Fig. 3.7a Absorption spectrum of Am(III) in saturated KF solution. (From C. E Thalmayer and D. Cohen, Actinide Chemistry in Saturated Potassium Fluoride Solution, in *Lanthanide/Actinide Chemistry*, R. F. Gould (Ed.), Advances in Chemistry Series, p 256, 1971)

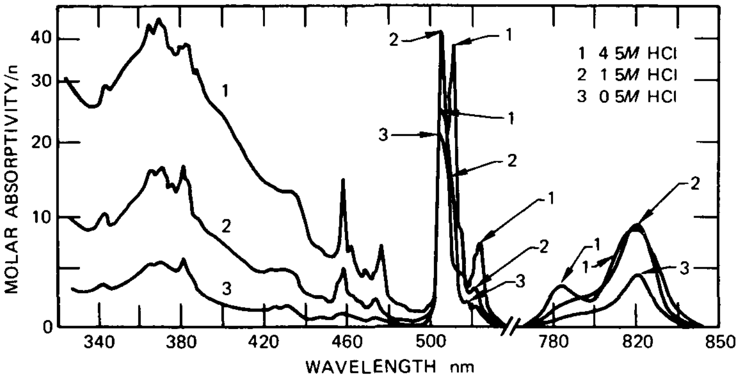

Fig. 3.7b Absorption spectrum of Am(III) in ethanolic HCl (for curves 1, 2, and 3 n = 1, 10/3, and 10, respectively). [From Yu. A. Barbanel, A. G. Gorskii, and V. P. Kotlin, Absorption Spectra of Am(III) in Standard Solutions of HCl, *Radiokhimiya*, **13**: 305 (1971) through *Soviet Radiochemistry (English Translation)*, **13**: 314 (1971).]

To interpret the spectra of the $5f^4$ AmO_2^+ ion, Varga et al[103] made ab initio relativistic calculations of various spectroscopic parameters. These calculated parameters were used to initiate least-squares fits to 15 electronic energy levels of aqueous AmO_2^+ in 1*M* $DClO_4$–D_2O. Correlation with 35 lower levels of the f^4 intermediate spin–orbit coupling diagram allowed term assignments to be made to the experimental aquo-ion levels.

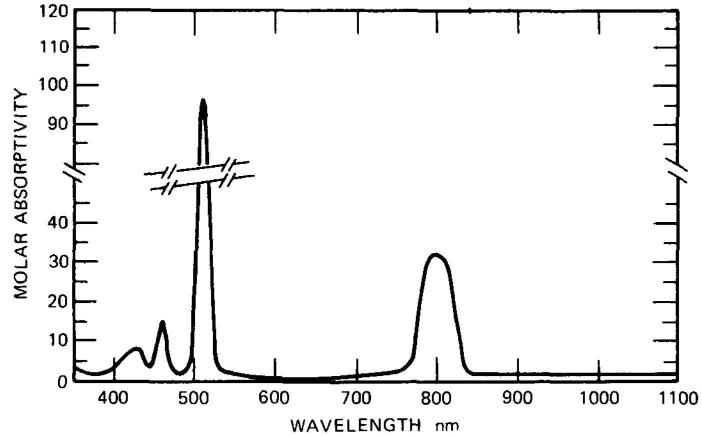

Fig. 3.7c Absorption spectrum of Am(III) $LiNO_3$–KNO_3 eutectic at 170°C. (From D. M. Gruen, S. Fried, P. Graf, and R. L. McBeth, The Chemistry of Fused Salts, in *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958,* Vol. 28, p. 112, United Nations, Geneva, 1958.)

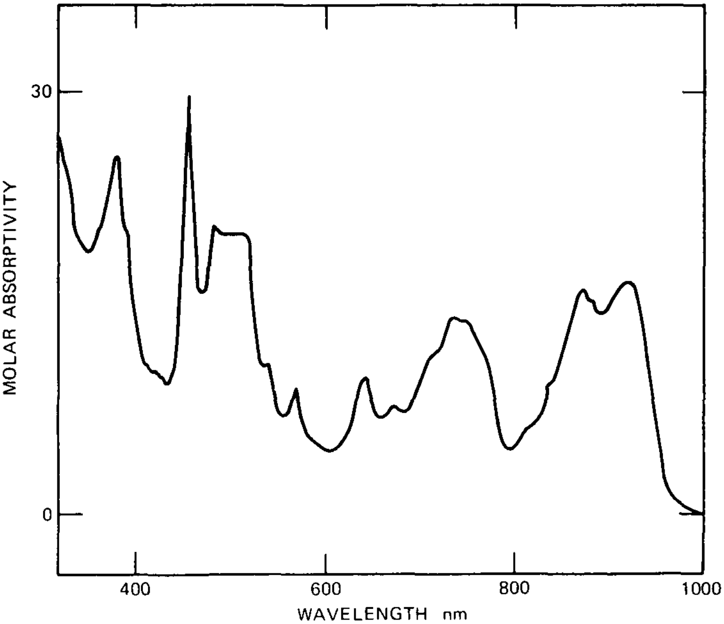

Fig. 3.8a Absorption spectrum of Am(IV) in 13*M* NH_4F [From L. B. Asprey and R. A. Penneman, Preparation and Properties of Aqueous Tetravalent Americium, *Inorganic Chemistry,* **1**: 134 (1962).]

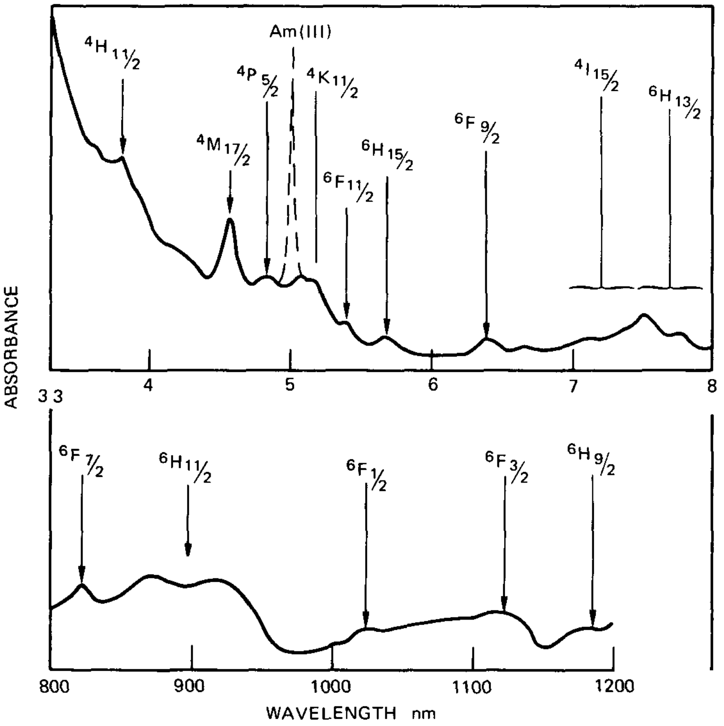

Fig. 3.8b Absorption spectrum of Am^{4+} in 12*M* KF, room temperature, 1-cm cells The observed peak at 500 nm for Am(III) indicates incomplete oxidation of the sample. [From L. P. Varga, R. D. Baybarz, M. J. Reisfeld, and L. B. Asprey, Electronic Spectra of the 5f^5 and 5f^9 Actinides Am^{4+}, Pa^{3+}, Bk^{2+}, Cf^{3+}, and Es^{4+} *Journal of Inorganic and Nuclear Chemistry* 35. 2775 (1973)]

Am(VI)

Table 3 9 lists various aqueous media in which the spectrum of Am(VI) has been measured Molar absorptivity values are shown in Table 3 8 The spectrum of Am(VI) in acid media is not strongly affected by changes in ionic environment Only small shifts in band energies and/or intensities occur in different acids or at different acidities[18 63 104] The spectrum of Am(VI) in carbonate solutions (Fig 3 12a), in 1*M* CsOH (Fig 3 12b), and in acid solutions differs markedly

Varga, Reisfeld, and Asprey[106] calculated the spectrum of the AmO$_2^{2+}$ ion from the f^3 intermediate spin–orbit coupling diagrams Except for the lower energy levels, agreement between calculated and observed (in 0 1*M* HClO$_4$) spectra was poor, however The electron delocalization associated with the covalent character of the Am–O bond is believed[103] responsible for the deviation between calculated and observed spectroscopic parameters

Table 3.8

PROMINENT ABSORPTION BANDS OF AMERICIUM(IV) (V), (VI), AND (VII) IONS IN VARIOUS SOLUTIONS

Ion	Absorption maximum, nm	Molar absorptivity, liters mol ^{1} cm ^{1}	Media	Ref.
Am(IV)*	920	26 0	12M H_3PO_4	18a
	742	18 0	12M H_3PO_4	18a
	456	30 0	13M NH_4F	15
Am(V)	900	6 0	0 1M $HClO_4$	64
	720	66 0	0 1M H_2SO_4	26
	715	59 0	0 1M $HClO_4$	88
	646	9 5	0 1M $HClO_4$	88
	515	48 0	0 1M H_2SO_4	26
	514	44 4	0 5M HCl	65
	514	35 7	5M HCl	65
	513	45 0	0 1M $HClO_4$	88
	415	12 0	0 1M $HClO_4$	88
Am(VI)	996	194 0	12M H_3PO_4	18a
	996	120 0	5M H_3PO_4	17
	995	86 4	2M $HClO_4$	102
	757	10 4	0 1M $HClO_4$	88
	713	11 4	0 1M $HClO_4$	88
	663	30 5	0 1M $HClO_4$	88
	619	12 6	0 1M $HClO_4$	88
	548	12 8	0 1M $HClO_4$	88
	400	500 0	3 5M NaOH	1a
Am(VII)	740	330 0	3 5M NaOH	1a
	400	1600 0	3 5M NaOH	1a

*Molar absorptivities of Am(IV) in 12M H_3PO_4 at 333, 357, 384, 416, and 454 nm are, respectively, 1363 ± 19, 1029 ± 11, 701 ± 10, 365 ± 12, and 138 ± 9 [18b]

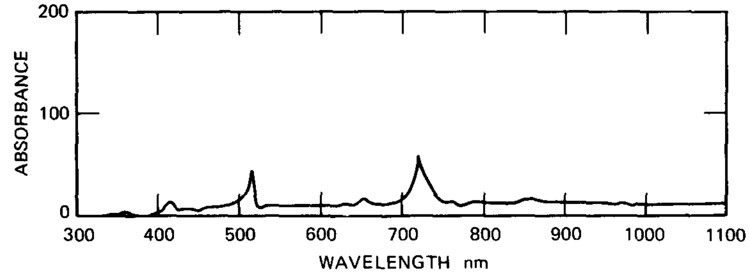

Fig. 3.9a Absorption spectrum of Am(V) in 0 1M H_2SO_4 [From L B Werner and I Perlman, The Pentavalent State of Americium, *Journal of the American Chemical Society*, 73: 495 (1951)]

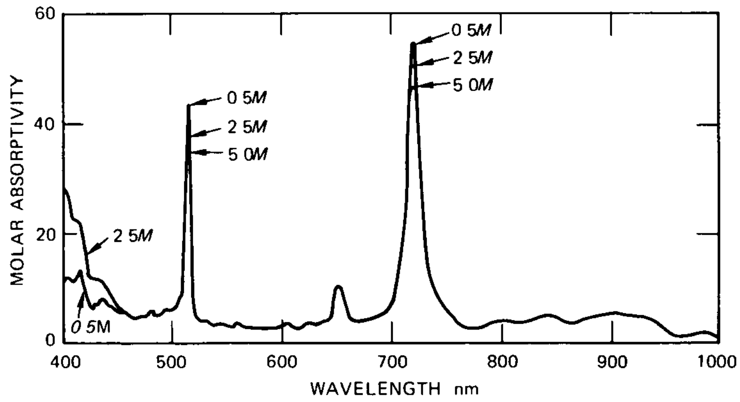

Fig. 3.9b Absorption spectrum of Am(V) in HCl [From G R Hall and P D Herniman, The Separation and Purification of Americium-241 and the Absorption Spectra of Tervalent and Quinquevalent Americium Solutions, *Journal of the Chemical Society (London)*, p 2214 (1954)]

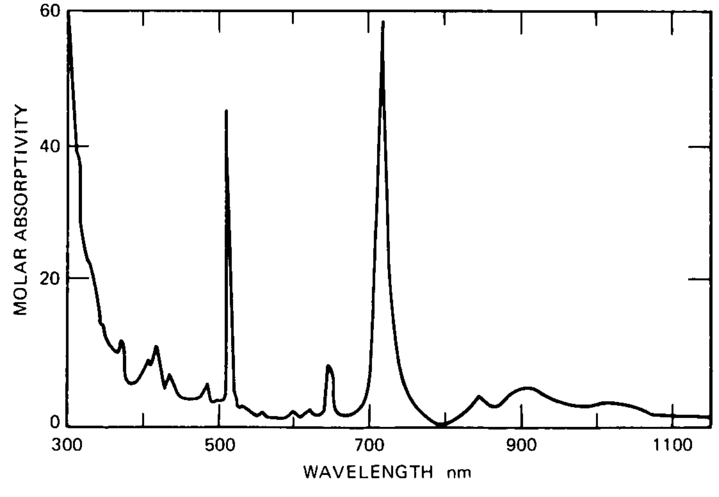

Fig. 3.9c Absorption spectrum of Am(V) in 1M $HClO_4$ (From R A Penneman and L B Asprey, A Review of Americium and Curium Chemistry, in *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy Geneva, 1955*, Vol 7, p 355, United Nations, New York, 1956)

Bell^{107} has compared band positions of the transuranium actinyl spectra including those of AmO_2^+ and AmO_2^{2+} with the spacings between positions of the UO_2^{2+} bonds 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, and the transuranium actinyl ions are represented with the uranyl core and a

Table 3.9

SOLUTION ABSORPTION SPECTRUM OF Am(VI)

Media	References	Typical spectrum
0 2*M*–14 3*M* HNO_3	30, 104	Fig 3 10a
0 1*M*–6 0*M* H_2SO_4	63	Fig 3 10b
0 1*M*–2 0*M* $HClO_4$	27, 48, 64, 88	Fig 3 11a
5 0*M*–12 0*M* H_3PO_4	17, 18a	Fig 3 6b
1*M* HF	105	
0 1*M* $Na_4P_2O_7$	22	Fig 3 11b
0 1*M* Na_2CO_3	22	Fig 3 12a
1 0*M* CsOH	33	Fig 3 12b

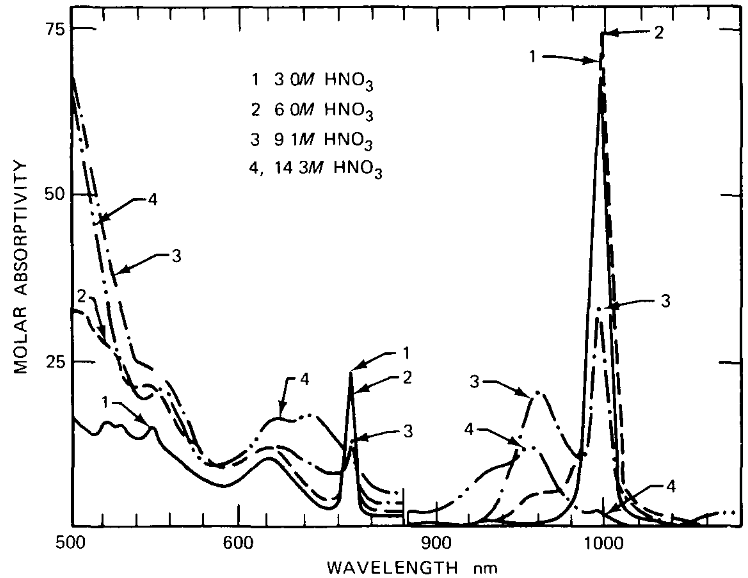

Fig. 3.10a Absorption spectrum of Am(VI) in HNO_3 (From G N Yakovlev and V N Kosyakov, An Investigation of the Chemistry of Americium, in *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955,* Vol 28, p 373, United Nations, Geneva, 1956)

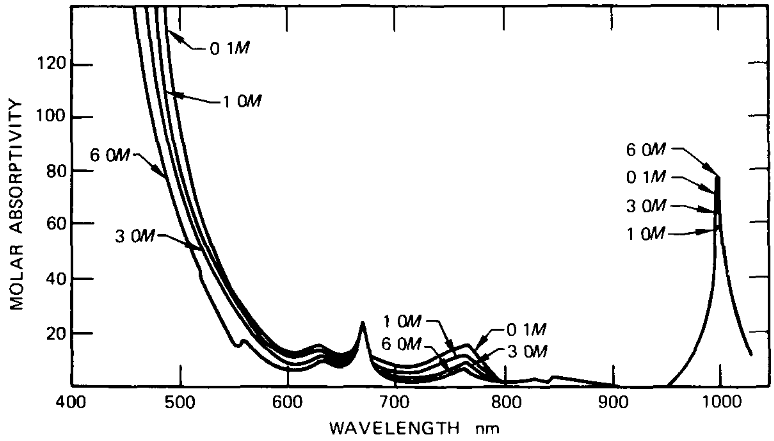

Fig. 3.10b Absorption spectrum of Am(VI) in H_2SO_4 [From G R Hall and T L Markin, The Self-Reduction of Americium(V) and (VI) and the Disproportionation of Americium(V) in Aqueous Solutions, *Journal of Inorganic and Nuclear Chemistry*, 4: 296 (1957)]

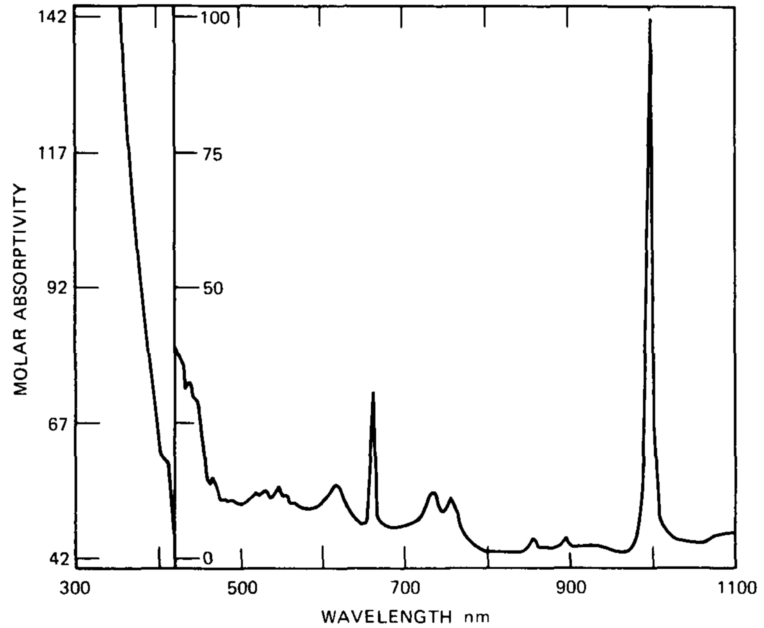

Fig. 3.11a Absorption spectrum of Am(VI) in 1M $HClO_4$ (From R A Penneman and L B Asprey, A Review of Americium and Curium Chemistry, in *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955,* Vol 7, p 355, United Nations, New York, 1956)

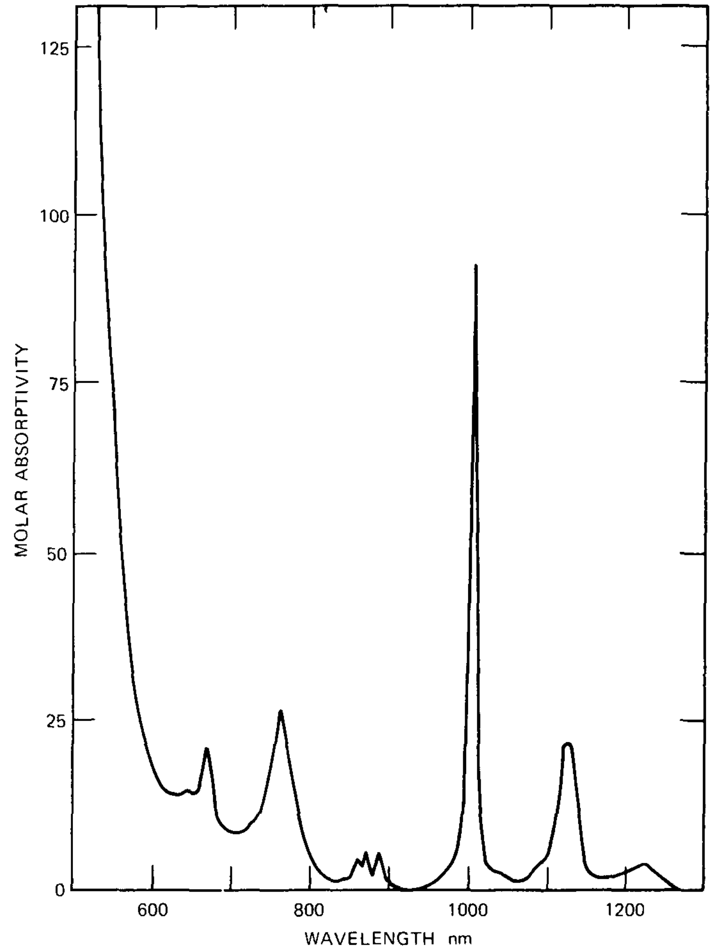

Fig. 3.11b Absorption spectrum of Am(VI) in 1*M* $Na_4P_2O_7$ [From J S Coleman, T K Keenan, L H Jones, W T Carnall, and R A Penneman, Preparation and Properties of Americium(VI) in Aqueous Carbonate Solutions, *Inorganic Chemistry* 1· 58 (1963)]

progressive increase of electrons in the first two orbitals lying above the bonding orbitals

Am(VII)

Green-colored solutions believed to contain some Am(VII) are prepared (see pages 54 and 55) by oxidation of Am(VI) in 3*M* to 5*M* NaOH at 0 to 7°C with either O_3 or the O ion radical The absorption spectra of Am(VI) and Am(VII) in 3 5*M* NaOH as measured by Krot et al [1] are shown in Fig 3 12c

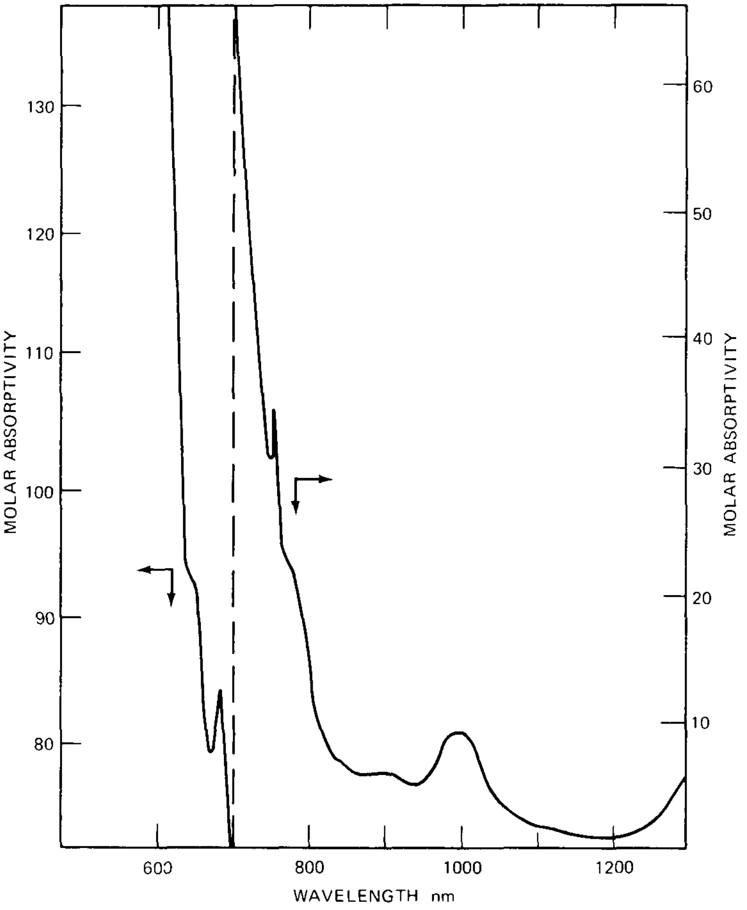

Fig. 3.12a Absorption spectrum of Am(VI) in 0 1M Na_2CO_3 [From J S Coleman, T K Keenan, L H Jones, W T Carnall, and R A Penneman, Preparation and Properties of Americium(VI) in Aqueous Carbonate Solutions, *Inorganic Chemistry*, 1: 58 (1963)]

COMPLEXES OF AMERICIUM IONS

Tabulated Formation Constants

Formation constants and pertinent experimental conditions under which they were determined are collected in Tables 3 10 and 3 11 for complexes of Am^{3+} with inorganic and organic ligands, respectively (A few complexes for which formation constants have not yet been measured are also cited) This listing is believed complete

(Text continues on page 99)

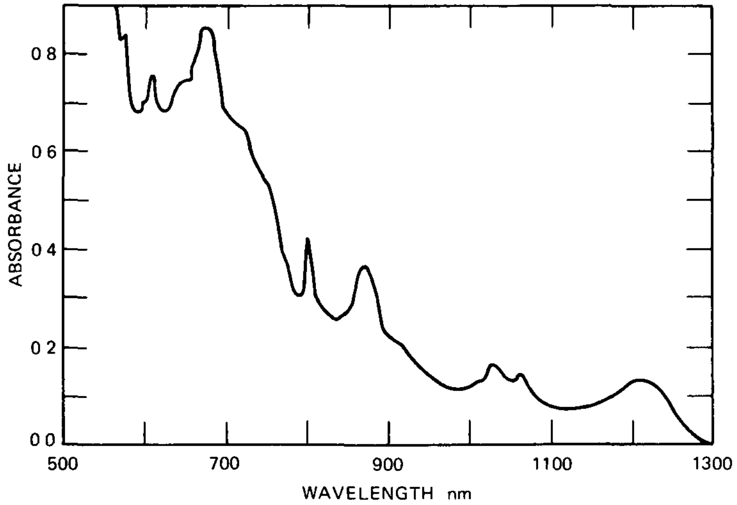

Fig. 3.12b Absorption spectrum of Am(VI) in 1*M* CsOH [From D Cohen, Americium(VI) in Basic Solution, *Inorganic and Nuclear Chemistry Letters* Supplement to *Journal of Inorganic and Nuclear Chemistry*, 8: 533 (1972)]

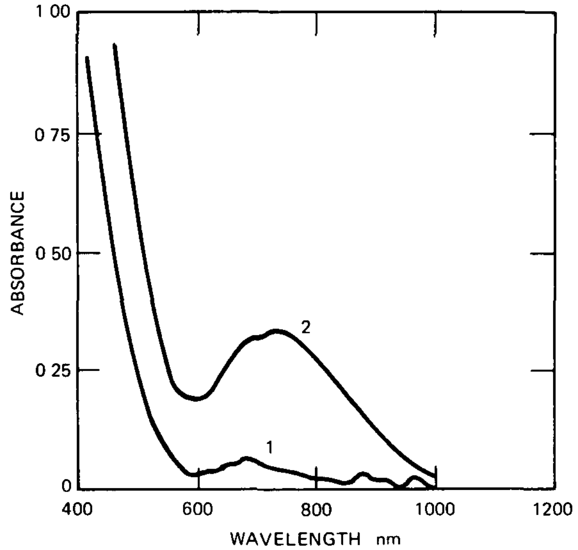

Fig. 3.12c Absorption spectra of Am(VI) and Am(VII) in 3 5*M* NaOH 1, 0 0194*M* Am(VI), 2, 0 0194*M* Am–50% Am(VII) and 50% Am(VI) [From N N Krot, V P Shilov, V B Nikolaevskii, A K Nikaev, A D Gel'man, and V I Spitsyn, Preparation of Americium in Heptavalent State, *Doklady Akademii Nauk SSSR (U S S R)*, 217: 589 (1974) through USAEC Report ORNL-tr-2828, Oak Ridge National Laboratory, 1974]

Table 3.10

COMPLEXES OF AMERICIUM WITH INORGANIC LIGANDS

Ref.	Method	Temp., °C	Ionic strength (μ), M	Medium	Log of formation constants β_1	β_2	Other
	Bromide (Br), Refs 84, 108						
84	Spec	25		8 74–11 4M LiBr	–3 3 + 0 1 ($AmBr^{2+}$)		
	Carbonate (CO_3), Refs 64, 84						
84	Soly	25		0 1–0 6M K_2CO_3			$[Am(OH)(CO_3)_3]^4$
	Chloride (Cl^-), Refs 92, 95, 108-119						
92	Spec	25(?)		13 7M LiCl	–2 21 ± 0 08 ($AmCl^{2+}$)	4 70 ± 0 08 ($AmCl_2^+$)	
109	SX	30 ± 0 1	1 0	$LiClO_4$–LiCl	–0 25 + 0 015		
				$HClO_4$–HCl	0 14 + 0 024	–0 53 ± 0 044	
				$NaClO_4$ NaCl	0 027 ± 0 01	–0 55 + 0 13	
				NH_4ClO_4–NH_4Cl	0 117 ± 0 017	0 033 ± 0 020	
110	IX	26 ± 1	1 0	$HClO_4$–HCl	–0 057 ± 0 098	–0 82	
				$NaClO_4$–NaCl, pH 3 0	0 15 ± 0 03		
111	SX	22 + 1	1 0	$HClO_4$–HCl	–0 046 ± 0 010		
112, 113	SX	25	4 0	4M $NaClO_4$	–0 15 ± 0 07	–0 69 ± 0 10	
114	IX		0 5	0 5M $HClO_4$	–0 24		
115	Relax				0 03	1 0	
116	IX	20	4.0	$HClO_4$–HCl	–0 16 ± 0 02	–0 75 ± 0 14	
118	Spec	25(?)		*			K_6† 150 ± 20
				‡			K_6‡ 60 ± 20
	Fluoride (F), Refs 120a, 120b						
120a	SX	25	0 5	$NaClO_4$–NaF	3 39 ± 0 01 (AmF^{2+})	6 11 ± 0 03 (AmF_2^+)	β_3 = 9 0 (AmF_3)
120b	SX	25	1 0	$NaClO_4$	2 49 ± 0 02		
	Hydroxide (OH^-), Refs 9a-11						
11	EM	25	0 005	$HClO_4$–NH_4ClO_4	10 7 ± 0 1 ($AmOH^{2+}$)	20 9§ [$Am(OH)_2^+$]	

(Table continues on next page)

Table 3.10 (Continued)

Ref.	Method	Temp., °C	Ionic strength (μ), M	Medium	Log of formation constants		
					β_1	β_2	Other
10	PEP	15 ± 1	0 005	HCl–KCl	11 32 ± 0 02		
9	SX	23 ± 1	0 1	$HClO_4$–$LiClO_4$	8 3		
	Nitrate (NO_3), Refs 84, 109-111, 121-126						
84	Spec	25		8 0*M* $LiNO_3$	1 3 ± 0 1 ($AmNO_3^{2+}$)		
122	IX	20–25	1 0	1 0*M* NH_4ClO_4, pH 1 5	0 60		
123	SX	25 ± 0 02	1 0	$HClO_4$–HNO_3	0 25 ± 0 02		
109	SX	30 ± 0 1	1 0	NH_4ClO_4–HNO_3	0 23	0 13 [$Am(NO_3)_2^+$]	
110	IX	26 ± 1		$NaClO_4$–$NaNO_3$, pH 3 0	0 20 ± 0 03		
				$HClO_4$ HNO_3, pH 1 0	0 15 ± 0 03	−0 40	
111	SX	22 ± 1	1 0	$HClO_4$–HNO_3	0 25 ± 0 07		
121	SX	20 ± 1	8 0	8 0*M* $HClO_4$	−0 33	−0 77	β_3 = −1 4 [$Am(NO_3)_3$]
124	SX		1 0	1 0*M* $NaClO_4$, pH 3 0	−0 26		
126	SX	25	2 01	NH_4NO_3–HNO_3	0 20 ± 0 03		
	Perchlorate (ClO_4), Ref 127						
127	SX	25	2 0	HBF_4–$HClO_4$	−0 07 ± 0 03 ($AmClO_4^{2+}$)		
	Phosphate (H_2PO_4), Refs 128, 129						
128	IX	20 ± 1	1 0	1 0*M* NH_4Cl	1 48 [$Am(H_2PO_4)^{2+}$]	2 10 ($Am(H_2PO_4)_2^+$)	β_3 = 2 85 [$Am(H_2PO_4)_3$] β_4 = 3 4 [$Am(H_2PO_4)_4$]
129	IX	25 + 0 1	0 2	0 2*M* NH_4ClO_4		1 69 + 0 78	
	Sulfate (SO_4^{2-}), Refs 110, 112, 122, 124, 130-135						
110	IX	26 ± 1	1 1 3	$NaClO_4$, pH 3 0	1 49 ($AmSO_4^+$)	2 47 [$Am(SO_4)_2$]	
124	SX		1–1 3	$NaClO_4$, pH 3 0	1 47	2 59	
122	IX	20–25	0 75	0 75*M* $NaClO_4$, pH 3 5	1 78		
130	IX		1 5	1 5*M* NH_4ClO_4, pH 3 5	1 76	2 11	
112, 131	SX	25	1 0	1 0*M* $NaClO_4$	1 57 ± 0 09	2 66 + 0 08	
132	SX	25 ± 0 1	2 0	2 0*M* $NaClO_4$	1 43 ± 0 06	1 83 ±0 12	

133	IX	27	1 0	$HClO_4$–H_2SO_4	1 22 ± 0 01		β' = 0 54 ± 0 03 [$Am(HSO_4)_2^+$]
				$NaClO_4$–Na_2SO_4, pH 3 0	1 48 ± 0 01	2 35 ± 0 01	
134	SX	24–25	0 5	0 5*M* $NaClO_4$	1 85 ± 0 01	2 79 ± 0 01	
	IX	25	0 5	0 5*M* $NaClO_4$	1 86 ± 0 01	2 73 ± 0 01	
	Thiocyanate (SCN^-), Refs 109, 112, 126, 136-141a, 141b						
109	SX	30 ± 0 1	1 0	$LiClO_4$ + LiSCN	0 06 ± 0 04 ($AmSCN^{2+}$)	0 24 ± 0 03 [$Am(SCN)_2^+$]	
				$NaClO_4$–NaSCN	0 17 ± 0 05	0 51 ± 0 03	
				NH_4ClO_4–NH_4SCN	0 12 ± 0 06	0 56 ± 0 02	
112, 136	SX	25	5 0	5 0*M* $NaClO_4$	0 85 ± 0 05		β_3 = 0 55 ± 0 15 [$Am(SCN)_3$] β_4 = 0 0 + 0 15 [$Am(SCN)_4^-$]
126	SX	25	2 0	NH_4NO_3–NH_4SCN	0 55 ± 0 15	0 74 + 0 03	β_3 = 0 87 ± 0 03
137	IX		0 5	0 5*M* NH_4ClO_4	0 66 + 0 03 (μ=0)		
			5 0	5 0*M* NH_4ClO_4	0 24		β_3 = –0 04
138	IX	25	1 0	$NaClO_4$–NaSCN	0 50 ± 0 01	0 84 ± 0 07	
139	SX		5 0	5 0*M* $NaClO_4$	0 60 ± 0 06		
140	SX	25 + 0 1	1 0	$NaClO_4$ + NaSCN, pH 2 0	0 36 ± 0 03	–0 01 ± 0 20	β_3 = 0 22 ± 0 26
141a	Spec	22 ± 1	1 0	1 0*M* $NaClO_4$	0 76 ± 0 03	0 83 ± 0 07	
141b	SX	25	5 0	$NaClO_4$ + NaSCN	0 59 ± 0 05		
	Trimetaphosphate ($P_3O_9^{3-}$), Ref 142						
142	IX	25 + 0 1	0 2	NH_4ClO_4, pH 2 4	2 48 ± 0 04 (AmP_3O_9)		β_1' = 2 21 + 0 21 ($AmHP_3O_9^+$)

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*85 vol % succinonitrile–15 vol % acetonitrile

†Equilibrium constant for reaction $AmCl_5^{2}$ + Cl → $AmCl_6^{3}$

‡Propylene carbonate

§Estimated value

TABLE 3.11

COMPLEXES OF AMERICIUM WITH ORGANIC LIGANDS

Ref.	Method	Temp., °C	Ionic strength (μ), M	Medium	Log of formation constants		
					β_1	β_2	Other
	Acetic acid (HAc), Refs 28, 143-147						
143	IX	20	0 5	9 0M HAc	2 28 ($AmAc^{2+}$)	3 84 ($AmAc_2^+$	β_3 = 4 78 ($AmAc_3$) β_4 = 5 7 ($AmAc_4$) β_5 - 6 66 ($AmAc_5^{2}$) β_6 = 7 62 ($AmAc_6^{3}$)
144	Pot T	20	1 0	1 0M NH_4ClO_4	1 81	3 20	β_3 = 4 57, β_4 = 5 7 β_5 = 6 73, β_6 - 7 73
145	SX	25 + 0 1	2 0	2 0M NH_4ClO_4	1 95 + 0 11		
146	IX	20	0 5	0 5M $NaClO_4$	1 99 + 0 01	3 27 + 0 07	β_3 = 3 9
147	IX	25(?)	0 2	?	2 15	3 83	
		25(?)	0 5	?	2 30	3 81	
		25(?)	1 0	?	2 08	3 62	
28	SX	~25		0 1 1 0M Ac	1 40 (AmO_2Ac)	2 51 (AmO_2Ac_2)	
	α Alanine (ALAN), Ref 148						
148	SX	25	2 0	2 0M $NaClO_4$	0 79 ($AmALAN^{2+}$)		
	Anthranil *N N*-diacetic acid (H_3ADA), Refs 149, 150						
149 150	IX	25	0 1	0 1M NH_4ClO_4	8 92 (AmADA)	14 5 ($Am(ADA)^{3}$)	
	Arsenazo III (AZ), Refs 151a, 151b						
151a	Spec			HAc, HNO_3	AmAz	$AmAZ_2$	$AmAZ_3$
151b	Spec			pH 3 6	AmO_2AZ		
	N Benzoylphenylhydroxylamine (NBPHA), Ref 152						
152	SX						β = ? $[Am(NBPHA)_3]$
	Benzoyltrifluoroacetone (HBTA), Ref 153						
153	SX	25	0 1	NH_4ClO_4			β_3 - 14 84 $[Am(BTA)_3]$
	Citric acid (H_3Cit), Refs 154-160						
154, 155	Spec	25	1 0	1 0M $NaClO_4$	6 96 (AmCit)	10 3 $[Am(Cit)_2^{3}]$	β_1 = 4 53 ($AmHCit^+$) β(?) - 5 61 ($AmCitOH^-$)

155	IX	25	0 1	0 1*M* $NaClO_4$	9 16 + 0 03		β'_1 − 7 00
			0 5	0 5*M* $NaClO_4$	8 73 ± 0 066		β'_1 = 6 29
			1 0	1 0*M* $NaClO_4$	6 72 + 0 05		β'_1 = 4 24
156	IX	25	0 1	0 1*M* NaH_2Cit	6 74	11 55	β'_1 = 5 31 β'_2 = 8 23 [$Am(HCit)_2$]
157	IX			1 0*M* NH_4Cl	7 11	14 0	β''_3 = 8 29 [$Am(H_2Cit)_3$]
158	PEP			0 04*M*		9 66	
	Decanohydroxamic acid (HDHA), Ref 161						
161	SX	20	0 1	0 1*M* $NaClO_4$			β(?) = [$Am(DHA)_3 \cdot 2H_2(DHA)_2$]
	1,2 Diaminocyclohexanetetraacetic acid (H_4DCTA), Refs 162 165						
162	EM	20 ± 0 5	0 1	KCl + HCl	18 34 (AmDCTA)		β'_1 = 2 87 (AmHDCTA)
163	IX	25 ± 1	0 1	0 1*M* NH_4ClO_4	18 79		
164	IX	80		0 001*M* H_4DCTA +0 02*M* ammonium α hydroxyisobutyrate	18 79§		
165	SX	20	0 1	0 1*M* NH_4Cl	18 21		
	1,2 Diaminopropanetetraacetic acid (H_4DTPrA), Ref 155						
155	IX	25	0 1	0 1M $NaClO_4$	17 69 (AmDTPrA)		β'_1 = 9 79 (AmHDTPrA)
	Dibutyl-(PP')-ethane-(1,2)-diphosphonic acid (H_2B_2EDP), Ref 166						
166	SX	25	1 0	1 0*M* $NaClO_4$			β'_1 = 14 52 ($Am(HB_2EDP)_3$)
	5,7-Dichloro 8-Hydroxyquinoline (HDCO), Refs 167, 168						
167	SX	25 ± 0 5	0 1	0 1*M* $(NH_4,H)ClO_4$			β_3 = 21 93 ($Am(DCO)_3$)
	Diethylenetriaminepentaacetic acid (H_5DTPA), Refs 150, 169 178						
150	IX	25	0 1	0 1*M* NH_4ClO_4	23 07 ($AmDTPA^{2}$)		β'_1 = 14 06 (AmHDTPA)
169	IX	25	0 1	0 1*M* NH_4ClO_4	22 92		
170	EM	25 + 0 2	0 1	0 1*M* KNO_3	22 74		β'_1 = 14 3
171	SX		0 1		23 2		
172	Spec	25	0 1		23 2		
173	Spec	25	0 1	0 1*M* NH_4ClO_4	24 03		
174	Spec	20 ± 0 1	0 5	$HClO_4$, HNO_3	22 09		
175	IX	25	0 1	0 1*M* NH_4ClO_4	23 32		
176	IX	25	1 0	1 0*M* NH_4ClO_4	21 3		β'_1 = 15 46
	Diethylphosphinylproprionic acid (HDEPP), Ref 179						
179	IX	25	0 5	NH_4ClO_4 $HClO_4$	1 76 ($AmDEPP^{2+}$)	3 16 [$Am(DEPP)_2^+$]	

(Table continues on next page)

Table 3.11 (Continued)

Ref.	Method	Temp., °C	Ionic strength (μ), M	Medium	Log of formation constants		
					β_1	β_2	Other
	Diglycolic acid (H_2DGA), Ref 180						
180	Spec	25.2	0.1	0.1M NH_4ClO_4	6.47 ($AmDGA^+$)	10.96 [$Am(DGA)_2$]	β_3 = 13.83 [$Am(DGA)_3^3$]
	Dioctyl-(PP')-ethane-(1,2)-diphosphonic acid (H_2O_2EDP), Ref 166						
166	SX	25	1.0	1.0M $NaClO_4$			β_1' = 19.53 [$Am(HO_2EDP)_3$]
	Diphosphine dioxides,* Ref 181						
181	SX	25	2.0	2.0M $NaNO_3$	1.43 [$Am(NO_3)_3$ · (1,1-DiPO)] 6.56 [$Am(NO_3)_3$ · 2(1,4-DiPO)] 5.92 [$Am(NO_3)_3$ · 2(1,5-DiPO)]		
	Ethylenediamine-*bis*-isopropylphosphonic acid (H_4EDIP), Ref 182						
182	EM	25	0.1	0.1M KNO_3	18.00 (AmEDIP)		β_1' = 6.26 (AmH_3EDIP^{2+}) β_1'' = 8.94 (AmH_2EDIP^+) β_1''' = 13.95 (AmHEDIP)
	Ethylenediamine-*bis*-methylphosphonic acid (H_4EDMP), Refs 183, 184						
183	EM	25	0.1	0.1M KNO_3	16.57 (AmEDMP)		β_1' = 6.15 (AmH_3EDMP^{2+}) β_1'' = 7.90 (AmH_2EDMP^+) β_1''' = 12.23 (AmHEDMP)
184	IX	25	0.5	0.5M NH_4ClO_4			β_1' = 6.12 (AmH_2EDMP^+)
	Ethylenediaminetetraacetic acid (H_4EDTA), Refs 155, 160, 165, 173, 185–190						
155	IX	25	0.1	0.1M $NaClO_4$	18.15 (AmEDTA)		
			0.5	0.5M $NaClO_4$	16.36		β_1' = 9.68 (AmHEDTA)
			1.0	1.0M $NaClO_4$	15.72		
155	Spec	25 + 0.2	1.0	$NaClO_4$, $HClO_4$	15.33	22.10 [$Am(EDTA)_2^5$]	β_1' = 8.94 (AmHEDTA)
165	SX	20	0.1	0.1M NH_4Cl	16.91 ± 0.04		
173	Spec	25	0.1	0.1M NH_4ClO_4	18.06		
185	IX	25 + 0.02	0.1	0.1M NH_4ClO_4	18.16 ± 0.10		
186	IX		1.0	1.0M NH_4ClO_4	18.03 ± 0.13		β_1' = 10.29 (AmHEDTA)
187	EM	25 ± 0.5	0.1	HCl + KCl	17.0		β_1' = 9.21 (AmHEDTA)
188	IX	80	0.1	0.001M H_4EDTA +0.2M α-hydroxyisobutyrate	17.14		

190	EM	25 ± 0 1	0 1	0 1*M* KNO$_3$	17 00 ±0 09		β'_1 = 9 21 (AmHEDTA) β = 19 98 (AmOHEDTA^{2})
	Ethylenediaminetetramethylphosphonic acid (H$_8$EDTMP), Ref 191						
191	EM	25 + 0 1	0 1	0 1*M* KNO$_3$	22 47 + 0 08 (AmEDTMP^{5})		β'_1 = 4 8 + 0 6 (AmH$_5$EDTMP) β''_1 = 7 33 + 0 09 (AmH$_4$EDTMP) β'''_1 = 11 17 ± 0 07 (AmH$_3$EDTMP) β''''_1 = 14 90 ± 0 06 (AmH$_2$EDTMP) β'''''_1 = 18 45 + 0 08 (AmHEDTMP)
	Ethylenediaminetetrapropionic acid (H$_4$EDTP), Ref 155						
155	Spec	25 + 0 2	1 0	NaClO$_4$, HClO$_4$	18 84 ± 0 02 (AmEDTP)		β_1 = 12 31 (AmHEDTP)
	Ethyleneglycol *bis* 2 aminoethyltetraacetic acid (H$_4$EGTA), Ref 150						
150	IX	25	0 1	0 1*M* NH$_4$ClO$_4$	18 22 (AmEGTA)		
	Glycine (HGLYCN), Ref 192						
192	SX	25	2 0	2 0*M* NaClO$_4$	0 69 ± 0 02 (AmGLYCN^{2+})		
	Glycolic acid (HGLYC), Refs 146 155, 193						
146	IX	20	0 5	0 5*M* NaClO$_4$	2 82 (AmGLYC^{2+})	4 85 [Am(GLYC)$_2^+$]	β_3 = 6 30 [Am(GLYC)$_3$]
193	SX	25	2 0	2 0*M* NaClO$_4$	2 59		
155	Spec	25 + 0 2	1 0	NaClO$_4$, HClO$_4$	2 44 + 0 02	4 29 ± 0 2	β_3 = 5 20
155	IX	25	0 5	0 5*M* NaClO$_4$	2 57 + 0 02	4 01 + 0 1	
	Hydrazine-*N N*-diacetic acid (H$_2$HyDA), Ref 155						
155	IX	25	0 1	0 1*M* NaClO$_4$	10 74 (AmHyDA$^+$)	20 20 [Am(HyDA)$_2$]	
	Hydrazineiminodiacetic acid (H$_2$HyIDA), Ref 194						
194	EM	25	0 1	0 1*M* KNO$_3$	10 98 (AmHyIDA$^+$)	19 97 [Am(HyIDA)$_2$]	β'_1 = 4 13 (AmHHyIDA^{2+})
	2-hydroxycyclohexylethylenediaminetriacetic acid (H$_3$HCEDTA), Ref 155						
155	IX	25	0 1	0 1*M* NaClO$_4$	16 09 (AmHCEDTA)		β_1 = 7 44 (AmHHCEDTA$^+$)
	N'(2 hydroxyethyl)ethylene-*N,N,N'*–triacetic acid (H$_3$NHEDTA), Refs 150, 155 173, 195, 196a						
150, 195	IX	25	0 1	HClO$_4$, NH$_4$ClO$_4$	15 72 (AmNHEDTA)	22 47 [Am(NHEDTA)$_2^3$]	
156	Spec	25 ± 0 2	1 0	HClO$_4$, NH$_4$ClO$_4$	14 84	22 18	
173	Spec	25	0 1	0 1*M* NH$_4$ClO$_4$	16 18		
196a	IX	22	0 15	HCl, KCl	15 34		
	Hydroxyethylidenediphosphonic acid (HEDPA), Ref 196b						
196b	SX	25	0 1	HNO$_3$–NaNO$_3$			β_3 = ? [Am(H$_3$EDPA)$_3^3$)]

(Table continues on next page)

Table 3.11 (Continued)

Ref.	Method	Temp., °C	Ionic strength (μ), M	Medium	Log of formation constants β_1	β_2	Other
	N'(2-hydroxyethyl)iminodiacetic acid (H_2NHIDA), Refs 149, 150, 173, 197, 198						
149, 150	IX	25	0.1	0.1M NH_4ClO_4	9.14 ($AmNHIDA^+$)	17.04 [$Am(NHIDA)_2$]	
173	Spec	25	0.1	0.1M NH_4ClO_4	9.80	17.01	
197	SX		0.1		9.3 ± 0.1		
198	EM	25	0.1	0.1M KNO_3	9.3 + 0.13	16.5 + 0.2	
	α Hydroxyisobutyric acid (HIBA), Refs 155, 199-201						
155	Spec	25 + 0.2	1.0	$HClO_4$, $NaClO_4$	2.68 ($AmIBA^{2+}$)	4.38 [$Am(IBA)_2^+$]	
155	IX	25 + 0.2	0.5	0.5M NH_4ClO_4	2.88 ± 0.01	4.03 ± 0.02	
199	IX		0.5	NH_4ClO_4 + NH_4IBA	2.38	4.67	β_3 - 5.12 [$Am(IBA)_3$]
200	IX				2.72	4.69	β_3 = 5.64
201	SX		0.5				β_3 = 6.1
	bis Hydroxymethylphosphinic acid (HMPA), Ref 202						
202	IX	25	0.2		1.76 + 0.06 ($AmMPA^{2+}$)	2.48 ±0.02 [$Am(MPA)_2^+$]	
	Hydroxymethylphosphonic acid (HMP'A), Ref 202						
203	IX	25	0.2	0.2M NH_4ClO_4	1.55 ($AmMP'A^{2+}$)	3.18 [$Am(MP'A)_2^+$]	
	o Hydroxyphenyliminodiacetic acid (H_2HPIDA), Ref 204						
204	SX	25 ± 0.1	0.1	0.1M NH_4ClO_4	6.80 [$Am(HPIDA)^{2+}$]	11.9 [$Am(HPIDA_2^+$]	
	2 Hydroxypropane-1-3-diaminetetraacetic acid (H_4PDTA), Ref 173						
173	Spec	25	0.1	0.1M NH_4ClO_4	AmPDTA		Am_2PDTA^{2+}
	8 Hydroxyquinoline (HOX), Refs 152, 167, 168						
152	SX						$Am(OX)_3$
167	SX	25 + 0.5	0.1	0.1M $(NH_4,H)ClO_4$			$Am(OH)(OX)_2$
	8 Hydroxyquinoline-5-sulfonic acid (H_2OXSA) Ref 205						
205	IX	25 + 0.2	0.1	0.1M NH_4ClO_4	8.64 + 0.09 ($AmOXSA^+$)		
	Iminodiacetic acid (H_2IDA), Refs 150, 155, 173, 180, 206						
150	IX	25	0.1	0.1M NH_4ClO_4	7.37 ($AmIDA^+$)	12.39 ($Am(IDA)_2$)	
155	Spec	25 ± 0.2	1.0	$HClO_4$, $NaClO_4$	6.14		
173	Spec	25	0.1	0.1M NH_4ClO_4	6.94		β_1 - 3.34 [$Am(IDA)_5^7$]
206	Spec	25		0.005M H_2IDA			$Am(IDA)_3^3$

	7-Iodo-8 hydroxyquinoline 5-sulfonic acid (H_2IOXSA), Ref 205						
205	IX	25 + 0 2	0 1	0 1M NH_4ClO_4	6 92 ($AmIOXSA^+$)		
	β Isopropyltropolone (HIPT), Ref 153						
153	SX	25	0 1	NH_4ClO_4			β_3 = 21 37 [Am(IPT)$_3$]
	Lactic acid (HLACT), Refs 148, 207-208						
148	SX	25	2 0	2 0M NH_4ClO_4	2 52 ($AmLACT^{2+}$)	4 77 [$Am(LACT)_2^+$]	β_3 = 5 98 [Am(LACT)$_3$]
207	IX		0 5	0 5M NH_4ClO_4	2 77	4 64	
208a	SX	20	0 5	0 5$M$$NH_4ClO_4$			β_3 = 5 71 ± 0 03
208a	IX	20	0 5	0 5M NH_4ClO_4			β_3 = 5 73
208b	PEP	10	1 5	KCl + HLACT	2 57	4 21	
	N Methyliminodiacetic acid (H_2MIDA), Ref 150						
150	IX	25	0 1	0 1M NH_4ClO_4	7 01 ($AmMIDA^+$)	12 51 [Am(MIDA)$_2$]	
	6 Methyl-2-picoline acid (HMAPS), Ref 205						
205	IX	25 ± 0 2	0 1	0 1M NH_4ClO_4	4 26 ($AmMAPS^{2+}$)		
	6-Methyl 2-picolyliminodiacetic acid (H_2MPIDA), Ref 150						
150	IX	25	0 1	0 1M NH_4ClO_4	8 38 ($AmMPIDA^+$)		
	Methylolethylphosphoric acid (HMEPA), Ref 203						
203	IX	25	0 2	0 2M NH_4ClO_4	1 79 ± 0 12 ($AmMEPA^{2+}$)		
	(Methylphenylphosphinyl)-methylphenylphosphinic acid (HMPPA), Ref 209						
209	SX	25	0 2	0 2M NH_4ClO_4	3 35 ($AmMPPA^{2+}$)		
	Methylphosphinic acid (HMPA), Ref 210						
210	IX	25 + 0 2	0 5	NH_4ClO_4	2 79† ($AmMPA^{2+}$)		
	Napthoyltrifluoroacetone (HNTA), Ref 153						
153	SX	25	0 1	NH_4ClO_4			β_3 = 18 31 (Am(NTA)$_3$)
	Nitrilodiaceticmonobutyric acid (H_3NDMBA), Refs 211, 212						
211, 212	IX	25	0 1	NH_4ClO_4			β'_1 = 3 53 (AmHNDMBA)
	Nitrilodiaceticmonoproprionic acid (H_3NDAPA), Refs 211, 212						
211, 212	IX	25	0 1	NH_4ClO_4	10 54 (AmNDAPA)	17 83 [$Am(NDAPA)_2^{3-}$]	β'_1 = 4 02 (AmHNDAPA)
	Nitrilodiaceticmonovaleric acid (H_3NDAVA), Refs 211, 212						
211, 212	IX	25	0 1	NH_4ClO_4			β'_1 = 3 47 (AmHNDAVA)

(Table continues on next page)

Table 3.11 (Continued)

Ref.	Method	Temp., °C	Ionic strength (μ), M	Medium	Log of formation constants		
					β_1	β_2	Other
	Nitrilotriacetic acid (H_3NTA), Refs 155, 165, 176, 180, 211-215b						
155	IX	25 + 0 2	0 1	0 1M $NaClO_4$	11 72 + 0 02 (AmNTA)		
			0 5	0 5M $NaClO_4$	10 84 + 0 06		
165	SX	20	0 1	0 1M NH_4ClO_4	10 70	19 71 [$Am(NTA)_2^3$]	
176	IX	20	1 0	1 0M NH_4ClO_4	10 87		
180	IX	25 6	0 1	0 1M NH_4ClO_4	11 91	20 18	
211	IX	25	0 1	NH_4ClO_4 $HClO_4$	11 52	20 24	
212	IX	25	0 1	0 1M (NH_4,$HClO_4$)	11 68	20 47	
214	Spec	24 6	0 1	0 1M NH_4ClO_4	11 99	21 1	
215b		20	0 1		11 65	19 52	β_3 = 13 56 [$AmNTA(HNTA)^2$]
	Nitrosophenylhydroxylamine (cupferron), Ref 152						
152	SX					$Am(Cupf)_2$	
	Oxalic acid (H_2Ox), Refs 160, 165, 170, 186 189, 215-217b						
165	SX	20	0 1	0 1M NH_4Cl		8 3 [$Am(Ox)_2$]	β_3 = 11 8 [$Am(Ox)_3^3$]
186	IX		1 0	1 0M NH_4Cl		9 95	β_4 = 11 0 [$Am(HOx)_4$]
215a	Soly	25	0 0	$HClO_4$–H_2Ox	7 10 ($AmOx^+$)	11 2	β_3 = 12 3
160	IX	20 25	0 2	0 2M NH_4ClO_4	5 99	10 1	
216	EM	25	0 1	NH_4Cl–HCl	6 45	10 5	
217	SX	25	1 0	1 0M $NaClO_4$	4 63	8 35	β_3 = 11 2
170	IX	25	0 5	0 5M $NaClO_4$	3 8 + 0 02	8 61 ± 0 01	
217b	Spec	25 + 0 1	0 25	Oxalate, pH 1–5	3 27 (AmO_2Ox)	2 09 [$AmO_2(Ox)_2^3$]	
	1 Phenyl-3-methyl-4-acetyl pyrazolone-5 (HPMAP), Ref 218						
218	SX	25	0 1	0 1M NH_4ClO_4			β_3 = 12 23 [$Am(PMAP)_3$]
	1 Phenyl-3 methyl-4-benzoyl pyrazolone-5 (HPMBP), Ref 218						
218	SX	25	0 1	0 1M NH_4ClO_4			β_3 = 16 49 [$Am(PMBP)_3$]
	1-Phenyl 3-methyl-4-trichloroacetyl-pyrazolone-5 (HPMTCP), Ref 218						
218	SX	25	0 1	0 1M NH_4ClO_4			β_3 = 7 47 [$Am(PMTCP)_3$]
	1 Phenyl-3-methyl-4 trifluoroacetyl-pyrazolone-5 (HPMTFP), Ref 218						
218	SX	25	0 1	0 1M NH_4ClO_4			β_3 = 9 70 [$Am(PMTFP)_3$]

	Phosphonoacetic acid (H_3PAA), Ref 219						
219	IX	25	0 2	NH_4ClO_4			$\beta_1'' = 2\ 75\ [Am(H_2PAA)^{2+}]$ $\beta_1''' = 5\ 15\ (AmHPAA^+)$ $\beta_2''' = 8\ 5\ [Am(HPAA)_2^-)]$
	Pyridine-2-carbonic acid (HAPS) Ref 205						
205	IX	25 + 0 2	0 1	0 1*M* NH_4ClO_4	4 28 + 0 05 ($AmAPS^{2+}$)	7 99 ± 0 03 [$Am(APS)_2^+$]	$\beta_3 = 10\ 51 + 0\ 05\ [Am(APS)_3]$
	α-Picolinic acid-*N* oxide (HAPSNO), Ret 205						
205	IX	25 + 0 2	0 1	0 1*M* NH_4ClO_4	3 09 + 0 07 ($AmAPSNO^{2+}$)	5 49 + 0 07 [$Am(APSNO)_2^+$]	
	2-Picolyliminodiacetic acid (H_2PIDA) Refs 149 150						
149, 150	IX	25	0 1	0 1*M* NH_4ClO_4	8 96 ($Am(PIDA^+)$)	17 71 ($Am(PIDA)$)	
	Propanetricarboxylic acid (H_3PTA), Ret 154, 155						
154, 155	Spec	25	1 0	1 0*M* $NaClO_4$	5 61 ± 0 07 (AmPTA)		$\beta_1' = 4\ 96 + 0\ 02\ (AmHPTA^+)$
	α-Pyridylacetic acid (HAPAA) Ret 205						
205	IX	25 ± 0 2	0 1	0 1*M* NH_4ClO_4	3 63 + 0 07 ($AmAPPA^{2+}$)		
	Pyridine 3-carboxylic acid [Nicotinic acid] (HNIC), Ref 205						
205	IX	25 ± 0 2	0 1	0 1*M* NH_4ClO_4	3 18 + 0 07 ($AmNIC^{2+}$)		
	Pyridine 2 6-dicarboxylic acid (H_2PDA), Ref 205						
205	IX	25 + 0 2	0 1	0 1*M* NH_4ClO_4	9 33 ± 0 09 ($AmPDA^+$)	16 51 ± 0 09 [$Am(PDA)$]	
	Pyruvic acid (HPRUV), Ret 148						
148	SX	25	2 0	2 0*M* $NaClO_4$	2 03 ($AmPRUV^{2+}$)	3 34 [$Am(PRUV)_2^+$]	$\beta_3 = 3\ 87\ (Am(PRUV)_3)$
	bis 3-Methoxy-salicylidenealdehydeethylenediimine (B-3 MoxSEDI), Ref 220						
220	SX	25(?)	0 3	0 3*M* KNO_3			$\beta = 6\ 59\ [AmH(B\ 3MoxSEDI)\ ]$
	bis-Salicylidenealdehydeethylenediimine (BSEDI), Ref 220						
220	SX	25(?)	0 3	0 3*M* KNO_3			$\beta_2' - 4\ 94\ [AmH(BSEDI)_2]$
	Squaric acid (H_2Sq), ‡Ref 221						
221	IX	25	1 0	$HClO_4-NH_4ClO_4$	2 17 ($AmSq^+$)	3 10 ($Am(Sq)_2$)	
	Tartaric acid (H_2TART), Refs 157, 165, 222						
157	IX			1 0*M* NH_4Cl		10 7 [$Am(TART)_2$]	
165	SX	20	0 1	0 1*M* NH_4Cl	3 9 ($AmTART^+$)	6 8	
222	PLP	(?)	(?)	(?)		7 88	

(Table continues on next page)

Table 3.11 (Continued)

Ref.	Method	Temp., °C	Ionic strength (μ), M	Medium	Log of formation constants β_1	β_2	Other
	Taurine-*N*,*N*-diacetic acid (H_3TDA), Ref 150						
150	IX	25	0 1	0 1M NH_4ClO_4	8 08 (AmTDA)		β'_1 = 2 29 ($AmHTDA^+$)
	Tetraethylenepentaammeheptaacetic acid (H_7TPHA), *Ref* 173						
173	Spec	20 + 0 1	0 1	0 1M NH_4ClO_4	(?)($AmTPHA^{4}$)	(?)[$Am(TPHA)_2^{11}$]	
	Thenoyltrifluoroacetone (HTTA); Refs 153, 223						
153	SX	25	0 1	NH_4ClO_4	3 4($AmTTA^{2+}$)	8 5 [$Am(TTA)_2^+$]	β_3 = 13 3 [$Am(TTA)_3$]
	Thiodiglycolic acid (H_2TDGA), Ref 180						
180	Spec	25 6	0 1	0 1M NH_4ClO_4	3 52 + 0 08 ($AmTDGA^+$)	5 66 ± 0 07 ($Am(TDGA)_2$)	β'_1 = 2 06 + 0 08 ($AmHTDGA^{2+}$)
	Thioglycolic acid (HTGLYC), Ref. 146						
146	IX	20	0 5	0 5M NH_4ClO_4	1 55($AmGLYC^{2+}$)	2 60 [$Am(TGLYC)_2^+$]	(?) [$Am(TGLYC)_3$]
	p-Toluenesulfonic acid(pTSAH), Ref 127						
127	SX	25	2 0	$HClO_4$–pTSAH	–0 028 ± 0 028 ($AmpTSA^{2+}$)		
127	SX	25	2 0	HBI_4–pTSAH	0 075 ± 0 018		
	Triethylenetetraaminehexaacetic acid (H_6TTHA); Refs 150, 173						
150	IX	25	0 1	0 1M NH_4ClO_4			β'_1 = 18 13 ($AmHTTHA^{2}$) β''_1 = 11 85 (AmH_2TTHA)
173	Spec	25	0 1	0 1M NH_4ClO_4	27 61 ($AmTTHA^{3}$)		β = 30 97 (Am_2TTHA) β = 9 15 [$Am_2H_2(TTHA)_3^{10}$]

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*1,1–DiPO = $(C_6H_{13})_2P(O)CH_2(O)P(C_6H_{13})_2$, 1,4 DiPO = $(C_6H_{11})_2P(O)(CH_2)_4(O)P(C_6H_{11})_2$; 1,5 DiPO = $(C_6H_{11})_2P(O)(CH_2)$ $(O)P(C_6H_{11})_2$

†At μ = 0

‡Diketocyclobutenediol

§Calculated value at 25°C and μ = 0 1M

for all data reported prior to 1974 * Earlier compilations of formation constants of americium complexes are those of Jones and Choppin,[47b] Martell and Sillen,[224] Marcus, Givon, and Shiloh,[225a] Keller,[6c] and Gel'man et al [225b]

The following abbreviations are used in Tables 3 10 and 3 11 Spec, spectrophotometry, Soly, solubility, SX, solvent extraction, IX, ion exchange, Relax, relaxation, EM, electromigration, Pot T, potentiometric titration, and PEP, paper electrophoresis

The constants k_1 and β_1 shown in Tables 3 10 and 3 11 are defined for the reaction of a cation M with a ligand L as follows

$$k_1 = \beta_1 = \frac{[ML]}{[M][L]},\ k_2 = \frac{[ML_2]}{[ML][L]},\ k_3 = \frac{[ML_3]}{[ML_2][L]},\ \text{etc}$$

$$\beta_2 = \frac{[ML_2]}{[M][L]^2},\ \beta_3 = \frac{[ML_3]}{[M][L]^3},\ \text{etc}$$

and

$$\beta_2 = k_1 k_2,\ \beta_3 = k_1 k_2 k_3,\ \text{etc}$$

Complexes with Inorganic Ligands

All the formation constants listed in Table 3 10 are for complexes formed by Am(III) Keller[6c] observes that the complex formation of trivalent americium is probably better known than that of any other trivalent actinide element but that very little work has been done on complexes of Am(>III) Color changes (Table 3 1) indicate existence of Am(VI) nitrate, sulfate, and fluoride complexes There is also spectrophotometric evidence[226] for the existence in 1*M* NaOH solution of a peroxide complex of Am(V) Quantitative data are lacking for the identity of these latter complexes and their formation constants

Attempts to seek correlations within the data on formation constants of actinide complexes are largely frustrated, as pointed out by Jones and Choppin,[47b] by the wide range of ionic strengths and supporting electrolytes used However, at an ionic strength of 1 0*M* to 2 0*M*, the stability sequence for complexes of Am(III) with monovalent inorganic ligands appears to be

$$F > H_2PO_4^- > SCN^- > NO_3 \geqslant Cl > ClO_4^-$$

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*A recent paper by E M Rogozina, L F Konkina, and D K Popov published in *Radiokhimiya* **16** 383 (1974) [*Soviet Radiochemistry (English Translation)* **16**. 382 (1974)] lists formation constants for complexes formed by Am(III) with various amino acids

(The formation constant for $AmSCN^{2+}$ recently determined by Chianizia, et al[126] is notably out of line with values measured by other investigators) Americium(*III*) forms relatively strong complexes with SO_4^{2-} and $P_3O_9^{3-}$ ions

The complexing behavior of $Am^{3+} \cdot aq$ indicates it, like other actinide and lanthanide ions, is a Chatt–Ahrland[227] type "A" or Pearson[228a] "hard" cation with a characteristic coordination number[118] of 8 or 9 in aqueous solution Association of Am^{3+} with inorganic ligands proceeds initially through electrostatic interactions to form outer-sphere complexes In some cases (e g , F , SO_4^{2}), however, there is thermodynamic evidence (see pages 75 and 77) that the ligand displaces the water of hydration, at least to some extent, to form inner-sphere complexes Spectrophotometric results of Marcus and Shiloh[92 108] also provide evidence for inner-sphere complexation of chloride and nitrate to Am^{3+} in concentrated LiCl and $LiNO_3$ solutions, respectively Preparation of the solid compound $[(C_6H_5)_3PH]_3$ and $AmCl_6$, containing the octahedral hexahalide complex $AmCl_6^{3-}$, has been described by Ryan[119] Spectra of solutions of $[(C_6H_5)_3PH]_3$ $AmCl_6$ in propylene carbonate and in 15 vol % acetonitrile–85% vol % succinonitrile were measured by Marcus and Bomse[118]

The stability of Am^{3+} complexes in many cases is similar to that of complexes of lanthanides of equal ionic radius In some cases, however, where bonding presumably involves f electrons, the stability of the Am^{3+} complex is slightly greater than that of the corresponding lanthanide complex[228b] Advantage can be taken of this difference in stability to effect a separation of Am^{3+} from lanthanide elements The properties of Am^{3+}–chloride and thiocyanato complexes are particularly useful (Chap 5) for this latter purpose. Ion-exchange studies[225,229–232] with both anion resins and long-chain amine hydrohalides show that Am^{3+} in concentrated LiCl and HCl solutions is complexed with the probable formation of the species $AmCl_4$ and LiA_2AmCl_6 in the organic resin and amine phases, respectively (In the LiA_2AmCl_6 species, A^+ is the result of the dissociation of one chloride ion from an amine hydrochloride aggregate[233]) The predominant aqueous-phase species in the concentrated LiCl and HCl solutions is $AmCl_2^+$

Complexes with Organic Ligands

Other than those for acetate, diethylenetriaminepentaacetic acid (DTPA), ethylenediaminetetraacetic acid (EDTA), and oxalate complexes of Am(V), all the data in Table 3 11 are for complexes of Am(III). The higher oxidation states of americium are relatively strong oxidizing agents and are not stable in the presence of most organic complexants

For three-quarters of the approximately 80 different organic ligands listed in Table 3.11, formation constants of complexes with Am(III) have been measured only once by a single group of investigators. The accuracy of these formation constants cannot be fully determined in the absence of comparative data. In contrast, formation constants for complexes of Am(III) with hydroxycarboxylic (e. g., citric, glycolic, lactic, and tartaric) and aminopolycarboxylic (H_5DTPA, H_4EDTA, H_3NTA, etc) acids so useful in separative work have been determined by many investigators using a variety of experimental conditions and techniques. For these latter complexants, with some obvious exceptions (e.g., data for citric and tartaric acids), formation constants determined by the several investigators for a particular complex at a given ionic strength are in fairly good agreement

Examination of the results in Table 3.11 reveals that aminopolycarboxylic acids complex Am(III) more strongly than do either hydroxycarboxylic or aminoalkylpolyphosphoric acids (e. g., ethylenediamine-bis-methylenephosphonic acid) Keller[6c] observes that in the series of α-hydroxycarboxylic acids (e g., glycolic and lactic) the stability of the americium complex decreases with increasing number of carbon atoms The stability of the complexes of Am^{3+} with aminopolycarboxylic acids increases linearly (Fig 3 13) with the number of bound donor atoms of the ligand Reference has already been made to the changes in the absorption spectrum of Am^{3+} as the result

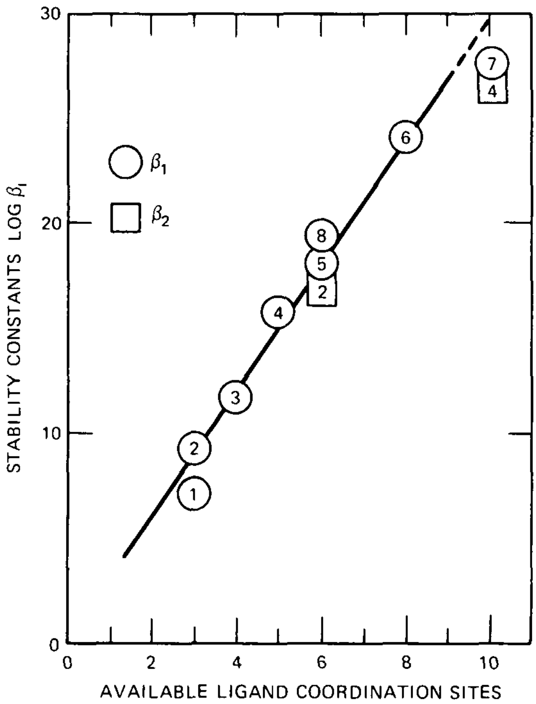
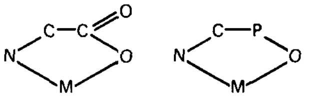


Fig. 3.13 Correlation of stability constants with number of available coordination sites 1, iminodiacetic acid, 2, N-hydroxyethyliminodiacetic acid, 3, nitrilotriacetic acid, 4, N-hydroxyethylethylenediaminetriacetic acid, 5, ethylenediaminetetraacetic acid, 6, diethylenetriaminepentaacetic acid, 7, triethylenetetraaminehexaacetic acid, 8, diaminocyclohexanetetraacetic acid [From C Keller, *The Chemistry of the Transuranium Elements*, Verlag Chemie GmbH, Weinheim, 1971]

of complex formation; illustrative of such changes is the spectrum of Am^{3+} in 0.1*M* $NaClO_4$–0.005*M* H_3NTA solutions at different pHs (Fig. 3.14).

Various Russian scientists[234–238] are currently seeking ways to estimate and correlate the strengths of complexes of Am^{3+} and other trivalent actinides and lanthanides with various organic ligands. Shalinets,[235] in particular, suggests a "rule of additivity of the strength of rings" according to which, under similar steric conditions, the logarithm of the thermodynamic formation constant of the complex is proportional to the sum of the strengths of the individual rings

e.g.,



, etc.

contained in it; i.e.,

$$\log \beta_0^0 = \sum_i N_i \epsilon_i \qquad (3.45)$$

where N_i and ϵ_i are, respectively, the number and strength of the rings in the complex and β_0^0 is the thermodynamic formation constant calculated by means of the Davies equation from the formation constant determined at a particular ionic strength. Shalinets[235] has estimated ϵ values for various rings as well as discussed the influence of various factors such as the basicity of the donor atoms, the presence of substituents in the ring, and the number and size of the rings. The general utility and validity of Shalinet's approach has not been completely established, but, in a few test cases at least, formation constants of americium chelates calculated by Eq. 3.45 are in good agreement with experimental data.

Americium(III) also forms many neutral organic-phase soluble salts and chelate adducts [e.g., $Am(NO_3)_3 \cdot 3(RO)_3PO$] with various organophosphorus compounds and also with thenoyltrifluoroacetone. Formulas and formation constants for some of these entities are listed in Chap. 5; more complete listings are given in Refs. 6c, 147, and 201.

Thermodynamics and Kinetics

Thermodynamic functions have been determined for only a few complexes of Am^{3+}. These data, which are collected in Table 3.12, provide evidence for the structures of these complexes in aqueous solution. The thermodynamic changes on complexation of Am^{3+} are the result of two contributions: exothermic enthalpy and negative entropy due to the association of the cation with the ligand and endothermic enthalpy and positive entropy due to the dehydration of the cation and anion. A high positive net change of the entropy indicates inner-sphere complexing. Thus, from the magnitude of the ΔH and ΔS terms for $AmSO_4^+$, Carvalho and Choppin[243] conclude that the degree of inner-sphere complexation present is at least comparable to, and

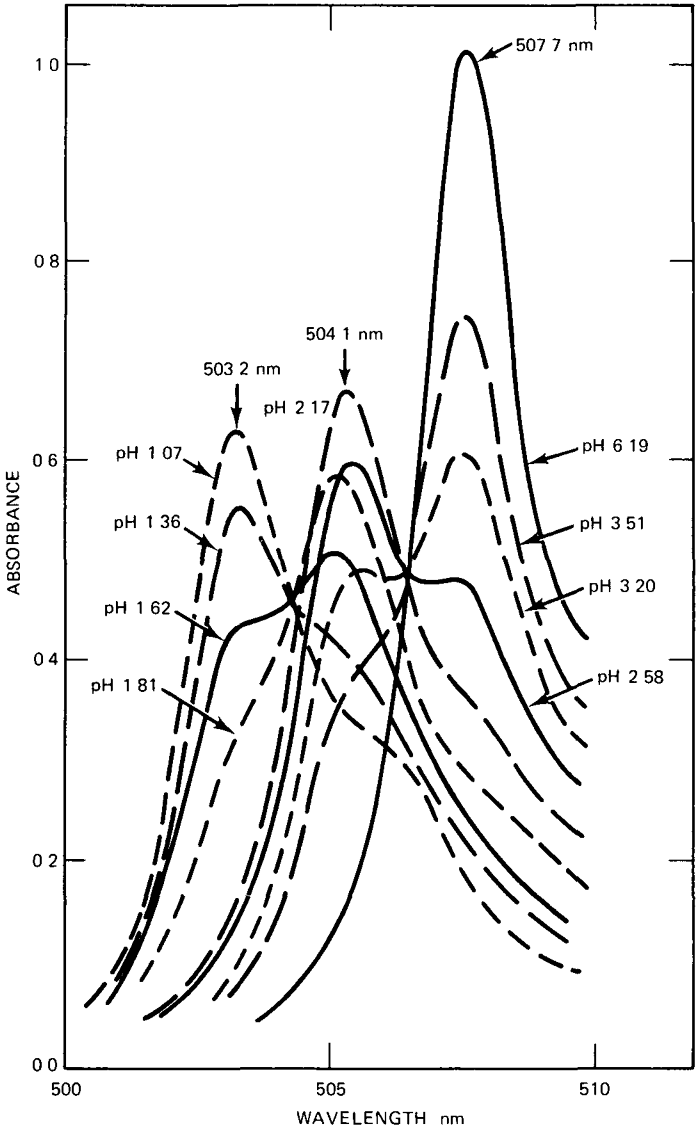


Fig. 3.14 Absorption spectrum of Am(III) in 0 1*M* NaClO$_4$ –0 005*M* H$_3$NTA solution at different pHs [From S H Eberle and C S Sabau, The Thermodynamics of Am(III)–Nitrilotriacetic Acid Complexes, *Radiochemical and Radioanalytical Letters,* 11: 77 (1972)]

Table 3.12

THERMODYNAMIC FUNCTIONS FOR COMPLEXES OF Am(III)

Method*	Conditions	Reaction	ΔG, kcal mol ^{1}	ΔH, kcal mol ^{1}	ΔS, cal mol ^{1} deg ^{1}	Ref.
Acetic acid (HAc)						
Tdm(SX)	2 0*M* NH_4ClO_4	$Am^{3+} + Ac \rightarrow AmAc^{2+}$	−2 68 ± 0 03	4 3 ± 0 3	23 4 ± 1	239
Diglycolic acid (H_2DGA)						
Tdm(Spec)	0 1*M* NH_4ClO_4	$Am^{3+} + DGA^{2} \rightarrow AmDGA^{+}$	−8 75 + 0 03	0 6 ± 0 71	31 ± 2	180
		$AmDGA^{+} + DGA^{2} \rightarrow Am(DGA)_2$	−6 20 ± 0 07	1 6 + 0 8	26 ± 3	180
		$Am(DGA)_2 + DGA^{2} \rightarrow Am(DGA)_3^{3}$	−3 93 ± 0 08	0 8 ± 0 2	16 ± 1	180
Ethylenediaminetetraacetic acid (H_4EDTA)						
Cal	0 1*M* KCl, 25°C	$Am^{3+} + EDTA^{4} \rightarrow AmEDTA$	24 78	−4 67 ± 0 25	67 5 ±2	240
Fluoride (F)						
Tdm(SX)	1 0*M* $NaClO_4$	$Am^{3+} + F \rightarrow AmF^{2+}$	4 10 ± 0 80	7 64	39 3	241
Tdm(Sol)	0 1*M* $HClO_4$	$Am^{3+} + F \rightarrow AmF^{2+}$	−5 58	5 23	31 8	242
Glycine (HGLYCN)						
Tdm(SX)	2 0*M* $NaClO_4$	$Am^{3+} + GLYCN \rightarrow AmGLYCN^{2+}$	−0 93 ± 0 02	2 9 ± 0 4	13 ± 2	192
Iminodiacetic acid (H_2IDA)						
Tdm(Spec)	0 1*M* NH_4ClO_4	$Am^{3+} + HIDA \rightarrow AmHIDA^{2+}$	−1 79 ±0 15	−14 99 ± 1 52	−44 3 ± 5 7	180
		$Am^{3+} + IDA^{2} \rightarrow AmIDA^{+}$	−9 64 ± 0 01	−1 19 ± 0 32	28 4 ± 1 1	180
		$AmIDA^{+} + IDA^{2} \rightarrow Am(IDA)_2$	7 59 ± 0 04	−3 14 ± 1 68	14 9 ± 5 6	180
		$Am(IDA)_2 \cdot aq \rightarrow Am(IDA)_2(OH)^{2}$	10 70 ± 0 09	10 8 ± 1 2		180
Tdm(Spec)	0 005*M* H_2IDA, 15–90°C	$Am + IDA^{2} \rightarrow AmIDA^{+}$	−3 to −2	6 9 ± 1 2	13 1 ± 3 7	206
Nitrilotriacetic acid (H_3NTA)						
Tdm(Spec)	0 1*M* NH_4ClO_4	$Am^{3+} + NTA^{3-} \rightarrow AmNTA$	16 31 ± 0 04	0 67 ± 0 46	56 1 ± 0 46	180, 214
		$AmNTA + NTA^{3} \rightarrow Am(NTA)_2^{3-}$	12 32 ± 0 09	−5 7 ± 0 8	22 3 ± 2 8	180, 214

Sulfate (SO_4^{2})						
Tdm(SX)	2 0*M* $NaClO_4$	$Am^{3+} + SO_4^{2} \rightarrow AmSO_4^{+}$	−2 0	4 4	21	243
Thiocyanate (SCN^-)						
Tdm(SX)	1 0*M* $NaClO_4$	$Am^{3+} + SCN \rightarrow AmSCN^{2+}$	−0 69 ± 0 02	−4 36 ± 0 30	−12 3 ± 1 0	138
		$Am^{3+} + SCN^- \rightarrow AmSCN^{2+}$	−0 81 + 0 07	2 53 ± 0 29	11 2	139
Tdm(SX)	1 0*M* $NaClO_4$	$Am^{3+} + SCN \rightarrow AmSCN^{2+}$	−0 47 ± 0 02	1 6 ± 0 7	7 ± 2	140
		$Am^{3+} + 3SCN^- \rightarrow Am(SCN)_3$	−0 19 ± 0 15	−6 4	20 ± 15	140
		$AmSCN^{2+} + 2SCN \rightarrow Am(SCN)_3$	0 28 ± 0 16	−8 5	−27 + 16	140
Tdm(SX)	5 0*M* (ClO_4 + SCN)10–55°C	$Am^{3+} + 3SCN^- \rightarrow Am(SCN)^{2+}$	−0 813 + 0 074	2 81 ± 0 49	12 0 + 1 6	141b
Thiodiglycolic acid (H_2TDGA)						
Tdm(Spec)	0 1*M* NH_4ClO_4	$Am^{3+} + HTDGA \rightarrow AmHTDGA^{2+}$	−2 75 + 0 19	−7 08 ± 0 98	−14 5 ± 3 9	180
		$Am^{3+} + TDGA^{2} \rightarrow AmTDGA^{+}$	−4 88 ± 0 09	6 76 ± 1 12	39 1 ± 4 2	180
		$AmTDGA^{+} + TDGA^{2} \rightarrow Am(TDGA)_2^{-}$	−2 85 + 0 12	8 88 ± 0 66	39 4 ± 2 4	180

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*Tdm, temperature dependence measurements, Spec, spectrophotometry, cal, calorimetry, SX, solvent extraction, Sol, solubility probably exceeds, that of the outer-sphere complexation By the same criteria, monodentate complexes of Am^{3+} with fluoride, glycine, and ethylenediaminetetracetic, nitrilotriacetic and diglycolic acids are all also inner sphere complexes Jones and Choppin[47b] emphasize the importance of the disruption of the hydration sphere of Am^{3+} and other actinide ions in complexing thermodynamics Their estimates of the entropy and enthalpy of hydration of Am^{3+} and Am^{4+} are listed in Table 3 2

On the basis of the limited data available, Moskvin[244] has presented some generalizations of the thermodynamics of the formation of actinide ions in aqueous solutions His analysis includes discussion of the heat capacities of triply charged actinide ions and the changes in their heat capacities on hydration and when transferred from a crystal lattice to solution Moskvin concludes that further accumulation of thermochemical data for actinide ions, including those of americium, is one of the most urgent contemporary problems in actinide chemistry

Kinetics of the exchange reaction

$$\mathrm{EuEDTA} + \mathrm{Am}^{3+} \rightarrow \mathrm{Eu}^{3+} + \mathrm{AmEDTA} \qquad (3\ 46)$$

were studied in an aqueous acetate buffer solution of $\mu = 0\ 1M$ [245-247] In the pH range 5 5 to 6 5, Choppin and Williams[245] find that the exchange obeys the overall rate law

$$\mathrm{Rate} = \left\{\frac{k_A^1\ [\mathrm{EuEDTA}\ ]\,[\mathrm{Am}^{3+}]}{[\mathrm{Eu}^{3+}]} - k_C\ [\mathrm{AmEDTA}\ ]\right\}\ [\mathrm{H}^+]$$

$$+ \left\{k_B^1\ [\mathrm{EuEDTA}^-]\ [\mathrm{Am}^{3+}] - k_D^1\ [\mathrm{Eu}^{3+}]\,[\mathrm{AmEDTA}\ ]\right\} \qquad (3\ 47)$$

Equation 3 47 correlates with a reaction that proceeds via two pathways, the first set of braces can be associated with an acid-catalyzed mechanism, and the second set represents an acid independent reaction path The two paths have approximately equal probability at pH 6 4 Activation parameters[247] for the exchange reaction are $\Delta H^* = 10\ 7$ kcal mol^{-1} and $\Delta S^* = -12\ 2$ cal mol^{-1} deg^{-1}

El-Rawi,[248] in a recently published thesis, reported results of studies of the kinetics of complexing of americium by the aminopolycarboxylic acids, H_5DTPA, H_4EDTA, *N*-hydroxyethylethylenediaminetriacetic acid ($H_3NHEDTA$), and diaminocyclohexanetetraacetic acid (H_4DCTA) Rates of ligand exchange between Am^{3+} and LaX were studied According to El Rawi,[248] ligand exchange proceeds as a first-order reaction in the presence of excess LaX Respective rate constants for the ligand exchange increase in the order $H_3NHEDTA > H_4EDTA > H_5DTPA > H_4DCTA$, H_4DCTA reacts especially slowly, probably because of steric hindrance to chelate formation Two different reaction mechanisms appear operative in this system (1) direct reaction of Am(III) and LaX and (2) a hydrogen ion catalyzed dissociative reaction $LaX\text{-}(H^+) \rightarrow HX\,(Am) \rightarrow AmX$

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4 METAL, ALLOYS, AND COMPOUNDS

METAL

Preparation

Americium metal is usually prepared by one of the following four methods:

1. Vapor phase reduction of AmF_3 with barium (or lithium) metal

$$2AmF_3 + 3Ba \xrightarrow[\text{vacuum}]{1100-1250^\circ C} 2Am + 3BaF_2 \tag{4.1}$$

2. Reduction of AmO_2 with lanthanum metal

$$AmO_2 + \tfrac{4}{3}La \xrightarrow[\text{vacuum}]{1500-1600^\circ C} Am + \tfrac{2}{3}La_2O_3 \tag{4.2}$$

3. Bomb reduction of AmF_4 with calcium metal

$$AmF_4 + I_2 + 3Ca \rightarrow Am + 2CaF_2 + CaI_2 \tag{4.3}$$

4. Thermal decomposition of Pt_5Am

$$Pt_5Am \xrightarrow[10^{-5}\text{ torr}]{1550^\circ C} Am + 5Pt \tag{4.4}$$

Westrum and Eyring[1] and later Graf et al.[2] made use of Eq. 4.1 to prepare the first microgram amounts of americium metal. Subsequently McWhan et al.[3] and McWhan, Cunningham, and Wallmann[4] prepared milligrams of americium metal by reduction of AmF_3 with barium. These workers stress that the AmF_3 be completely dehydrated, if it is not, the resulting metal will be contaminated with AmO. Also, according to McWhan, Cunningham, and Wallmann,[4] well-agglomerated metal is obtained only when Eq. 4.1 is performed at temperatures above 1200°C.

Lanthanum reduction of AmO_2 (Eq. 4.2) and subsequent distillation of the americium metal from tantalum equipment yield americium of very high (99.9+%) purity. This scheme has been used by various workers[3,6] to prepare milligram to gram quantities of americium metal. Equipment used by Wade and Wolf[5] to produce 200 g of metal is shown in Fig. 4.1. Successful production of americium by Eq. 4.2 is enhanced by the 10^4-fold difference in americium–lanthanum volatilities.

The bomb method (Eq. 4.3) was applied by Conner[7] to prepare americium metal on a gram scale, AmF_4 for use in Eq. 4.3 was prepared by fluorination of AmO_2 with

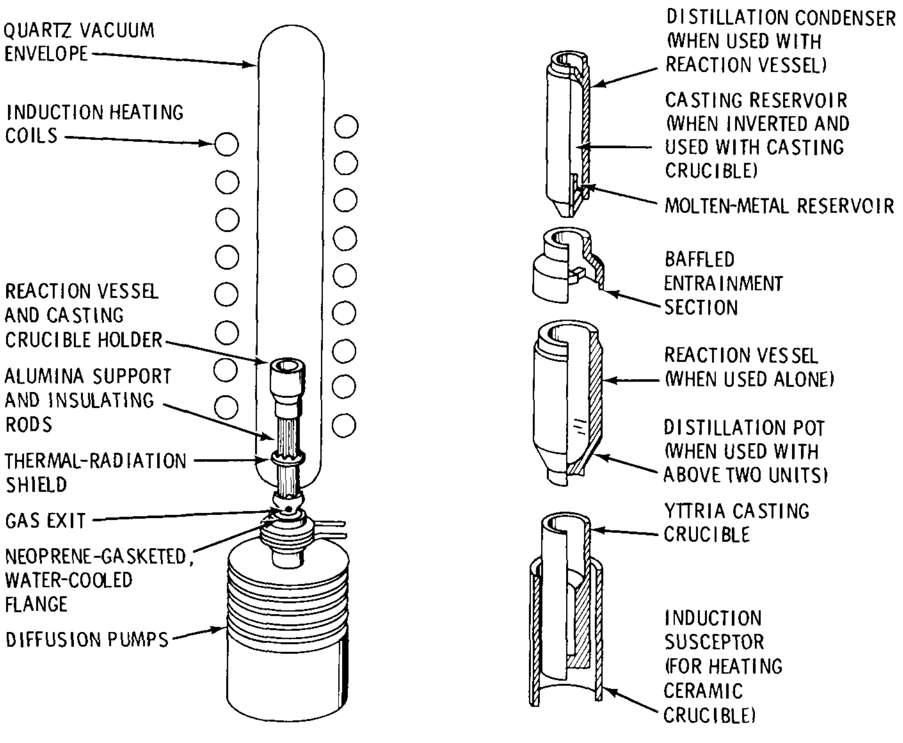

Fig. 4.1 Apparatus for preparation of americium metal by Eq. 4.2. [From W. Z. Wade and T. Wolf, Preparation and Some Properties of Americium Metal, *Journal of Inorganic and Nuclear Chemistry*, **29**: 2577 (1967).]

F_2. Reductions were performed in either tantalum or MgO crucibles in steel pressure vessels. Reduction yields of 34 to 64% of impure americium metal were obtained. (The exothermic reaction between calcium and I_2 was used to supply the heat required for good metal coalescence.) Conner believes that with further development the thermite bomb method will offer an inexpensive means for producing americium metal in good yield and of high purity.

Preparation of americium metal by thermal decomposition of the intermetallic compound Pt_5Am (see page 129) is a very recent development.[8,10] In the tests of Muller, Reul, and Spirlet,[8] 4 g of Pt_5Am were decomposed at 1550°C and 10^{-6} torr; the resulting americium metal, after further distillation in tantalum equipment, was as pure as that obtained by Eq. 4.2.

Properties

Americium metal is silvery, ductile, nonmagnetic, and very malleable. Selected physical properties are listed in Table 4.1. Of the two definitely established crystalline forms of americium metal, the double hexagonal close-packed (dhcp) phase is the stable one at room temperature and is generally the one obtained by reduction of AmF_3 or by thermal dissociation of Pt_5Am. The reaction between AmO_2 and lanthanum (Eq. 4.2) has been reported variously to yield pure dhcp phase,[11a] pure face-centered cubic (fcc) phase,[4] and a mixture of dhcp and fcc phases.[3,6] Workers at the European Institute for Transuranium Elements[16f] recently prepared the fcc form by condensation of americium vapor on thin tungsten wires spot-welded behind a 1-mm slit in a tantalum disk. The americium metal condensed on the tantalum disk showed the dhcp structure. After storage at liquid-nitrogen temperatures for 3 weeks, the fcc phase started to transform into the dhcp modification. McWhan et al.[3] also observed the fcc phase to transform to the dhcp on cooling the metal at dry-ice temperature.

McWhan, Cunningham, and Wallmann[4] originally reported that the melting point of americium metal is 994 ± 7°C and that the dhcp → fcc phase transition occurs between 600 and 700°C. Later work demonstrates that the melting point is about 1170°C and that there is a solid–solid transition at about 1070°C. Sari, Muller, and Benedict,[16a] in recent metallographic and differential thermal-analysis studies with high-purity americium metal, conclude that there is no phase transition between 600 and 700°C. Stephens, Stromberg, and Lilley[12] suggest that americium metal may undergo a dhcp → fcc phase transformation at 600 to 700°C and an fcc → bcc (body-centered cubic) transformation at 994 to 1070°C. Confirmatory evidence for this hypothesis is lacking.

In addition to the properties listed in Table 4.1, Stephens, Stromberg, and Lilley[12] have determined the phase diagram, compressibility, and electrical resistance of americium at room temperature over the range 35 to 120 kbars. Hall et al.[16e] used an adiabatic technique to measure the specific heat, C_p, of vapor-deposited ^{241}Am metal from 15 to 300°K. According to Hall et al.,[16e] the temperature dependence of the

Table 4.1

SELECTED PROPERTIES OF AMERICIUM METAL

Property	Value(s)*	Refs.
Crystallographic data		
Symmetry	(<~1070°C) dhcp	2 4
	($\overline{>}$~1070°C) fcc	3 4
Space group	$P6_3/mmc$	2–4
Lattice parameters	dhcp a = 3 4681 Å, c = 11 241 Å	3, 4
	fcc a = 4 894 Å	3, 4
Density	13 671 g cm ^{3} (calculated)	4
	13 671 g cm ^{3} (observed)†	5
Metallic radius (CN 12)	1 73 Å	3, 4
Melting point	1176°C, 1173°C	12
Boiling point‡	2284°K	11a
Coefficient of thermal expansion	α_a = 7 5 + 0 2 x 10^{-6}°C^{-1}	4
	α_c = 6 2 + 0 2 x 10^{-6}°C^{-1}	4
Compressibility at 1 atm	0 00277 kbar ^{1} at 23°C	12
Vapor pressure	log p (atm) = 6 578 + 0 046– (14,315 + 55)T(990 1358°K)	11b, 13, 14
Magnetic susceptibility	$\chi_{20°C}$ = (881 + 46) x 10 ^{6} cm^{3} mol ^{1}	4, 15a, 15b
Magnetic moment	1 36 Bohr magnetons	15a
Microhardness (Vickers) at 25°C	800 MN m ^{2}	16a
Electrical resistivity	68 $\mu\Omega$ cm (300°K), 71 $\mu\Omega$ cm (298°K)	16b, 16c
Crystal entropy (S^0_{298})	13 2‡, 13 06 cal mol ^{1}°K ^{1}	11b, 16d, 16e
Heat of vaporization at boiling point‡	55 021 kcal mol ^{1}	11b
Entropy of vaporization at boiling point‡	24 08 cal mol ^{1}°K ^{1}	11b
Transformation temperature	(600–700°C?), 1079°C, 1072°C, 1074 1175°C	4, 5, 12, 16a
Heat of transformation	1 40 kcal mol ^{1}	5
Heat of fusion	3 44 kcal mol ^{1}	5
Heat of solution in aqueous HCl		
1*M* HCl	147 3 kcal mol ^{1}	11a
1.5*M* HCl	147 1 kcal mol ^{1}	11a
6*M* HCl	147 7 kcal mol ^{1}	11a

*For the double hexagonal close-packed form unless otherwise indicated

†By immersion in monobromobenzene

‡Calculated value

measured specific heat with minimum self-damage does not fit a simple Debye model However, a reasonable assumption of the electronic contribution gives a strongly temperature-dependent Debye temperature Schenkel, Schmidt, and Spirlet[16c] used a potentiometric method to measure the electrical resistivity of a 1 89-μm-thick layer of americium metal between 300 and 3 6°K, up to 20°K the electrical resistivity varies with temperature as $T^{2\ 8}$ Ward, Muller, and Kramer[11b] used the heats of transition and melting measured by Stephens et al [12] to arrive at the following equation for americium liquid log p (atm) = 5 185 – 13,191/T

Self-irradiation studies of ^{241}Am metal at 4.5 and 78°K were performed by Schenkel, Schmidt, and Spirlet.[16c] From the equation $\Delta p = 17.43\ \mu\Omega\text{-cm}\ (1 - e^{\alpha t})$, the time constant, α, for the rate of self-damage was 0.0204 hr^{-1}. Hall et al.[16e] found that, for samples of ^{241}Am self-damaged below 10°K for times up to 112 hr, annealing takes place over the temperature range 50 to 250°K with three main stages clearly visible.

Hexagonal americium metal[17] shows no magnetic hyperfine coupling at temperatures as low as 1.7°K.

When heated, americium metal reacts with halogens, H_2, O_2, N_2, carbon, boron, antimony, etc., and with $HgBr_2$ and HgI_2. These reactions are considered on pages 131 to 171. Americium also forms alloys with a number of metals (e.g., beryllium and platinum). These are discussed on pages 127 and 129. Americium dissolves[1,11a] readily in aqueous HCl but is insoluble[18,19] in liquid NH_3.

From considerations of its atomic radius, Zachariasen[20,21a,21b] assigns a valency of four to americium metal—the so-called "thoride" hypothesis. Hill,[22a,22b] Jullien, Galleani D'Agliano, and Coqblin,[22c] and others, however, believe there is abundant evidence to adopt the viewpoint that americium metal is trivalent with an f^6 electronic configuration and is the first rare-earth-like metal in the transactinium series.

ALLOYS AND INTERMETALLIC COMPOUNDS

Preparation and properties of alloys and intermetallic compounds formed by americium with the metals Al, Be, Bi, Hg, Ir, La, Np, Ni, Os, Pd, Pt, Pu, Rh, and Th are reviewed here.* (For convenience, binary compounds of americium with the elements Sb, As, Se, and Te are discussed on pages 131 and 132 and 164 to 166.) A complete phase diagram is known only for the plutonium–americium system.

Aluminum–Americium System

Runnals[23] patented a method for making americium–aluminum alloys in which a mixture of aluminum metal and an americium halide is heated in a vacuum of 10^{-3} torr at 700 to 1200°C until the americium is reduced and alloyed.

Homogeneous americium–aluminum alloys containing 2 to 53 wt.% americium can be prepared by reaction of aluminum, AmO_2, and Na_3AlF_6 (cryolite) at 1100 to 1200°C (Refs. 24a and 24b). This technique is being used by German scientists at

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*Preparation of the binary compounds Al_2Am, Fe_2Am, Co_2Am, and Ru_2Am has now been reported.[205] The first three of these compounds have the cubic Cu_2Mg type of structure, whereas Ru_2Am is isostructural with Os_2Am, which has the $MgZn_2$ type of structure. All these compounds, except Fe_2Am, exhibit almost temperature independent paramagnetism; Fe_2Am is ferromagnetic with an estimated curie temperature of ~400°K.

Karlsruhe, as part of their Actinide Project, to prepare gram quantities of aluminum–5 to 10 wt % americium alloys for irradiation in various European reactors.[25,26] Equipment used for preparation of such aluminum–americium alloys is described in Refs. 25 and 26.

Beryllium–Americium System

Runnals and coworkers[23,27,28] used Eq. 4.5 to prepare milligram amounts of ^{241}Am–beryllium alloys for use as neutron sources

$$2AmF_3 + xBe \xrightarrow[10^{\ 3}\ \text{torr}]{700-1200°C} 2Am \cdot (x-3)Be + 3BeF_2 \qquad (4.5)$$

The BeF_2 readily distills leaving a fluoride-free alloy. Runnals and Boucher[28] prepared alloys with beryllium/americium atomic ratios of 263 1 and 14 1. The intermetallic compound, $AmBe_{13}$, is present in the 14 1 alloy, $AmBe_{13}$ is fcc with a = 10.283 Å.

Recently, Brachet and Vasseur[29] developed a method for making aluminum–beryllium neutron sources by reduction of AmO_2 with beryllium according to Eq 4.6

$$AmO_2 + 15Be \xrightarrow{1200-1300°C} 2BeO + AmBe_{13} \qquad (4.6)$$

Using Eq. 4.6, Brachet and Vasseur[29] obtained an alloy that emitted 3.75×10^6 neutrons g^{-1} sec^{-1} The yield of such a source was 2×10^6 neutrons sec^{-1} Ci^{-1} of emitter

Bismuth–Americium System

Reaction[30] of metallic bismuth vapor with either americium metal or americium hydride in a sealed, evacuated quartz tube for 48 hr at 975°C produces AmBi. This metallide has the NaCl structure with a = 6.338 ± 0 0012 Å, after annealing 14 days at 800°C, a = 6 335 ± 0 0019 Å.

Mercury–Americium System

Bouissières and Legoux[31a] first prepared an amalgam of americium by equilibrating a sodium citrate solution of $AmCl_3$ ($10^{-12}M$ to $10^{-6}M$ americium) for 90 min in an H_2 atmosphere with a 0 027 wt % lithium amalgam. The yield of americium amalgam decreased steadily as the pH of the initial citrate solution increased from 2 to 8, reaching zero at the latter pH. In this latter respect the mercury–americium system resembles the mercury–lanthanum system.[31b] David and Bouissieres[31c] now find that amalgamation of americium by electrolytic reduction of $10^{-6}M$ Am^{3+} in a lithium citrate solution at a mercury cathode is a first-order reaction. The time required to form the americium amalgam increases with increased lithium citrate concentration.

Reaction of Am^{3+} in 0.4*M* to 0.8*M* acetic acid with sodium amalgam results in rapid and almost complete ($\geqslant$98%) amalgamation of the americium[32]

Iridium–Americium System

Reduction of AmO_2 with highly purified H_2 in the presence of iridium metal—the so-called coupled reduction[33a-c]—yields at 1550°C the intermetallic compound Ir_2Am (Eq. 4.7)

$$2H_2 + AmO_2 + 2Ir \xrightarrow[1550^\circ C]{60\ hr} Ir_2Am + 2H_2O \tag{4.7}$$

The Ir_2Am phase has the cubic Cu_2Mg type of structure with a = 7.55 Å.

Lanthanum–Americium System

Lanthanum–americium alloys containing 0.92 to 2.37 at % americium dissolved in fcc β-lanthanum have been produced by arc-melting the constituent metals[34] The lattice parameters for these alloys deviate only slightly from the Vegard line, an indication that the effective size of americium in lanthanum is very close to that of elemental americium (1.73 Å radius) Small amounts of americium (<1.5 at %) dissolved in β-lanthanum produce an unusually weak depression of the superconducting transition temperature T_c of β-lanthanum.[35] To account for this latter observation, Hill et al[35] suggest that americium atoms in lanthanum are likely to be trivalent and to possess the f^6 electron configuration, which has no first-order magnetic moment

Neptunium–Americium System

Through alpha decay, ^{241}Am metal automatically becomes a neptunium–americium alloy. The magnetic behavior of such an alloy ($\simeq$0.5 wt.% neptunium) was studied recently by Dunlap et al.[36a] using the Mossbauer effect of the 59.6-keV X-ray in ^{237}Np. A small local moment on neptunium in americium was found

Nickel–Americium System

Lam and Mitchell[36b] prepared Ni_2Am by arc-melting the requisite amount of the pure elements in an argon–helium atmosphere for several hours at 800 to 1000°C. Cubic Ni_2Am has the Cu_2Mg type of structure (space group *Fd3m*) with a = 6.99 Å.

Osmium–Americium System

Hexagonal Os_2Am (space group Pb_3/mmc) was prepared by Lam and Mitchell[36b] by the same method used to make Ni_2Am. Lattice constants of Os_2Am are a = 5.320 Å and c = 8 849 Å

Palladium–Americium System

Coupled reduction of Am_2O_3 with palladium, according to the conditions of Eq. 4 8, yields the compound Pd_3Am, which has the ordered Cu_3Au structure

$$Am_2O_3 + 6Pd + 3H_2 \xrightarrow[40\text{–}60\ \text{hr}]{1300\ \ 1400^\circ\text{C}} 3H_2O + 2Pd_3Am \qquad (4.8)$$

The lattice constant of Pd_3Am is 4 158 Å

Platinum–Americium System

Pt_2Am. When performed at 1400°C, Eq. 4.7, with platinum substituted for iridium, yields pure Pt_2Am.[33] This alloy phase has the cubic Cu_2Mg structure with a = 7.615 Å.

Pt_5Am. Intermetallic Pt_5Am, which is obtained[33a,33b] by Eq 4.9,

$$Am_2O_3 + 10Pt + 3H_2 \xrightarrow{40\ \text{hr}-1200^\circ\text{C}} 2Pt_5Am + 3H_2O \qquad (4.9)$$

has the orthorhombic Pt_5Sm type of structure with a = 5.319 Å, b = 9 09 Å, and c = 26.42 Å Mention has already been made (see pages 122 to 124) of the preparation of americium metal by thermal decomposition of Pt_5Am in a vacuum Interestingly, for the noble metals iridium, palladium, platinum, and rhodium, the M_5Am compound is known only for platinum.

Plutonium–Americium System

The plutonium–americium phase diagram is shown in Fig. 4.2. This diagram was constructed by Ellinger, Johnson, and Struebing[37-39] from X-ray diffraction studies of plutonium–americium alloys containing 1.48 to 95 ± 1 at.% americium. The principal feature of the plutonium–americium system is the continuous series of solid solutions between δ-plutonium and β-americium which are stable at room temperature in the composition range from about 6 to 80 at.% americium. In contrast to the extensive solid solubility of americium in δ-plutonium, the solubility of americium in bcc ε-plutonium is about 8 at.% at 665 ± 15°C. The maximum solubility of plutonium in americium appears to be less than 5 at.%.

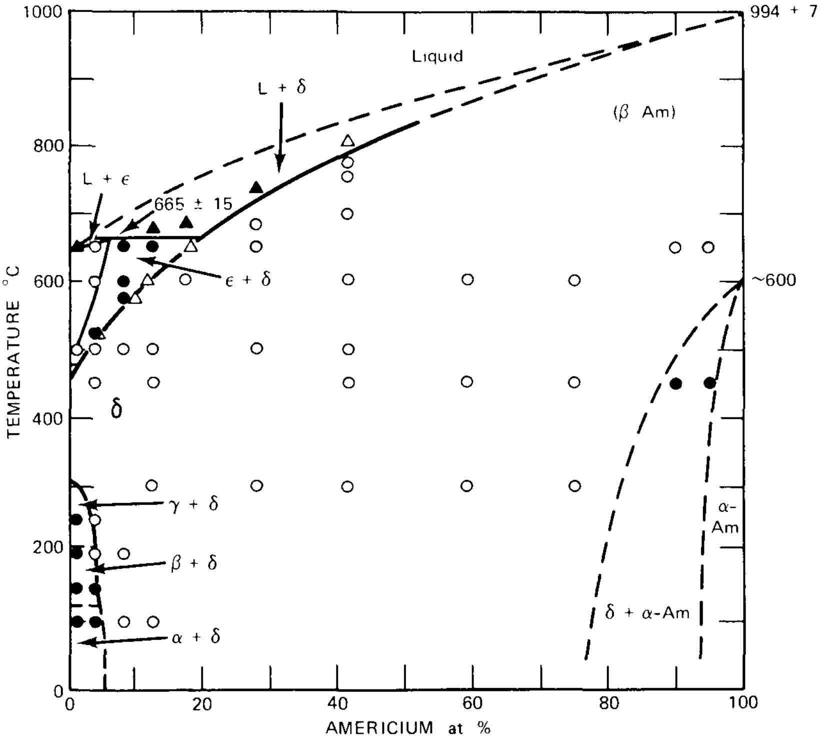

Fig. 4.2 The plutonium–americium phase diagram Unlabeled Greek letters refer to plutonium phases ○, one-phase alloy, ●, two-phase alloy, ▲, liquid present, △, X-ray parametric [From F H Ellinger, K A Johnson, and V O Struebing, The Plutonium–Americium System, *Journal of Nuclear Materials,* **20**: 83 (1966)]

Rhodium–Americium System

Rh_2Am. This intermetallic phase is prepared[33b] by the same coupled reduction technique (see Eq. 4.7) used to make Ir_2Am and Pt_2Am. Also, like Ir_2Am and Pt_2Am, the cubic Rh_2Am phase has the Cu_2Mg structure with a = 7 548 Å

Rh_3Am. This intermetallic compound has the ordered Cu_3Au type of structure with a = 4.098 Å. It is made by coupled reduction of AmO_2 with rhodium for 60 hr at 1550°C in a H_2 atmosphere.

Thorium–Americium System

For use as Mossbauer sources, Adair[40] prepared thorium–0 54 to 5.0 wt.% americium alloys by both levitation and arc melting of prepressed mixtures of americium and thorium metals. The high vapor pressure of americium metal at the melting point of thorium dictates that the levitation process be carried out in an inert atmosphere rather than in vacuum to avoid loss of americium

COMPOUNDS

Inorganic Compounds of Americium

The known (January 1976) inorganic compounds of americium, for which compositions are established, are listed in Table 4 2 along with some of their properties (Compounds of americium with organic ligands including acetate and oxalate are discussed on pages 166 to 171) Other properties and methods of preparing these compounds are discussed in the accompanying text A few additional inorganic compounds whose compositions have not been definitely established are also mentioned

Generally, the compounds listed in Table 4.2 have been arranged in alphabetical order of the inorganic ligand. Oxyhalides are included with the corresponding binary halides, as are the ternary halides Following the practice established by Keller,[41] ternary and polynary oxides of americium containing one or more of the elements Na, K, Ba, Sr, Cm, Zr, Hf, Th, Ta, Nb, and Pa are included with the binary oxides Certain other ternary oxides ($AmAsO_4$, $AmBO_3$, $AmVO_4$, etc), however, are discussed separately

Some of the compounds listed in Table 4.2 (e.g , oxides and binary halides) are well-characterized, gram amounts having been prepared by many investigators in several countries using both ^{241}Am and ^{243}Am. Conversely, only microgram or milligram quantities of many of these compounds have been synthesized and these by a single scientist using ^{241}Am. Verification of the procedures used to prepare these latter compounds and their properties should be provided by programs currently under way both abroad and in U. S. Energy Research and Development Administration laboratories.

Aluminate. *$AmAlO_3$* Hexagonal $AmAlO_3$ crystals[41,42] are produced when coprecipitated $Am(OH)_3$ and $Al(OH)_3$ (1 1) are heated in H_2 for 2 to 8 hr at 1250°C. The crystals have the distorted perovskite structure of $LaAlO_3$

Antimonide. *AmSb.* Mitchell and Lam[43] prepared AmSb by heating equimolar amounts of ^{241}Am metal and high-purity antimony under vacuum for 1 hr at 630°C The temperature was gradually raised to 850°C, and the AmSb was held at this temperature for 7 hr before cooling to room temperature Subsequently the AmSb was heat-treated at 100°C for 24 hr, furnace cooled, and then heated at 400°C for 10 days Roddy[30] also prepared AmSb by reacting ^{243}Am metal with antimony metal for 24 hr at 775 to 900°C in an evacuated quartz bulb. The lattice parameter measured by

Roddy ($a = 6.240$ Å) was in excellent agreement with that ($a = 6.238$ Å) reported by Mitchell and Lam.[43]

Magnetic susceptibility measurements[44] on AmSb give a temperature-independent value of $(1250 \pm 100) \times 10^{-6}$ emu mol^{-1} for the range $4.2°K < T < 320°K$.

Am_4Sb_3. Charvillat et al.[44b] prepared Am_4Sb_3 by heating $^{241}AmH_3$ in a Pyrex tube at 550°C with a quantity of elemental antimony corresponding to the stoichiometry 4 : 3. The resulting product contained two phases, AmSb and a second phase with the bcc structure of anti-Th_3P_4 type. The lattice parameter of Am_4Sb_3 is $a = 9.2392 \pm 0.0005$ Å.

Arsenate. *$AmAsO_4$*. Light-pink $AmAsO_4$ is produced by heating at 1000°C the residue obtained from evaporation[41,45] of a 1 : 1 solution of $Am(NO_3)_3$ and $(NH_4)_2HAsO_4$.

Arsenide. *AmAs*. Vapor-phase reaction of excess metallic arsenic with $^{241}AmH_3$ for a week at 330°C yields AmAs.[46] The resulting product contains two phases—metallic arsenic and a cubic NaCl-type phase that Charvillat and Damien[46] label AmAs by analogy with the corresponding plutonium and neptunium monoarsenides. A single AmAs phase is obtained by heating the mixture AmAs + arsenic at 330°C in a high vacuum.

The lattice parameter ($a = 5.880 \pm 0.0012$ Å) of AmAs prepared by Roddy[30] by heating ^{243}Am metal and arsenic metal for 24 hr at 675°C and then 7 days at 400°C was somewhat larger than the value of 5.8753 Å measured by Charvillat and Damien. Roddy found that heating samples of AmAs for 10 hr at 1000°C produced a slight decrease in the lattice parameters. Weak lines corresponding to AmO were observed in the X-ray pattern of the resulting material. According to Roddy, the reduction in size of the unit cell suggests the possibility of the existence of solid solution between AmAs and AmO; this phenomenon may have occurred in the preparation of Charvillat and Damien, or the slight difference in lattice parameters may be the result of isotope effects.

Kenellakopulos et al.[15a] measured the magnetic susceptibility of AmAs between liquid helium and room temperature. The effective magnetic moment of AmAs is 1.14 Bohr magnetons; AmAs exhibits an antiferromagnetic transition at 13°K.

Borate. *$AmBO_3$*. Orthorhombic $AmBO_3$ results from the solid-state reaction[41,42] of stoichiometric amounts of AmO_2 and B_2O_3 or H_3BO_3 for 12 hr in air at 900°C. The light-pink borate is soluble in concentrated mineral acids. It has the aragonite structure of the low-temperature modification of $LaBO_3$ and $NdBO_3$.

Borides. *AmB_4*. Tetragonal AmB_4 forms when a mixture of americium metal and boron in the atomic ratio 33 : 67 is heated in a vacuum at 800 to 2100°C in a ZrB_2 crucible.[47] Uranium, neptunium, and plutonium all form diborides, but americium does not. Eick and Mulford[47] attribute this to the large metallic radius of americium.

(Text continues on page 138.)

Table 4.2 INORGANIC COMPOUNDS OF AMERICIUM

				Crystal structure					
					Space group or structure type	Lattice constants			
Type	**Formula**	**Color**	**Density, g cm^{-3}**	**Symmetry**		**a, Å**	**b, Å**	**c, Å**	**α(β), deg**
Aluminate	$AmAlO_3$	Pink	9.40	Hexagonal	$R\bar{3}m$	5.336		12.91	
Antimonide	AmSb			fcc	$Fm3m$	6.239			
Arsenate	$AmAsO_4$	Pink	8.13	Monoclinic	$P2_1/n$	6.89	7.06	6.62	105.5
Arsenide	AmAs			fcc	$Fm3m$	5.880			
Beryllide	$AmBe_{13}$		4.38	fcc	$Fm3c$	10.283			
Bismuthide	AmBi			fcc	$Fm3c$	6.338			
Borate	$AmBO_3$	Pink	8.48	Orthorhombic	$Pnam$	5.053	8.092	5.738	
Borides	AmB_4			Tetragonal	$P4/mbm$	7.105		4.006	
	AmB_6			Simple cubic	$Pm3m$	4.115			
Bromides	$AmBr_2$	Black		Tetragonal	$P4/n$	11.59		7.121	
	$AmBr_3$	White	6.79	Orthorhombic	$Ccmm$	12.66	4.064	9.144	
	$AmBr_3 \cdot 6H_2O$	Light brown	3.51	Monoclinic	$P2/n$	9.955	6.783	8.166	92.75
	$[(C_6H_5)_3PH]_3AmBr_6$								
Carbide	Am_2C_3	Black		bcc	$I\bar{4}3d$	8.276			
Carbonates	$Am_2(CO_3)_3 \cdot 2H_2O$	Pink							
	$Am_2(CO_3)_3 \cdot 4H_2O$	Pink							
	$NH_4AmO_2CO_3$			Hexagonal	$C6/mmc$				
	$CsAmO_2CO_3$	Tan		Hexagonal	$C6/mmc$	5.123		11.538	
	$KAmO_2CO_3$	Light (?)		Hexagonal	$C6/mmc$	5.112		9.740	
	$K_3AmO_2(CO_3)_2$	Tan							
	$K_5AmO_2(CO_3)_3$			Orthorhombic					
	$RbAmO_2CO_3$		6.06	Hexagonal	$C6/mmc$	5.12		10.46	
Chlorides	$AmCl_2$	Black		Orthorhombic	$Pbnm$	8.963	7.573	4.532	
	$AmCl_3$	Pink	5.78	Hexagonal	$P6_3/m$	7.382		4.214	
	$AmCl_3 \cdot 6H_2O$	Yellow rose		Monoclinic	$P2/n$	9.702	6.567	8.009	93.62
	AmOCl	Pink	8.95	Tetragonal	$P4/nmm$	4.00		6.78	

(Table continues on next page)

Table 4.2 (Continued)

				Crystal structure					
					Space group or structure type	Lattice constants			
Type	Formula	Color	Density, g/cm³	Symmetry		a, Å	b, Å	c, Å	α(β), deg
Chloride complexes	$CsAmCl_4$	Yellow							
	$CsAmCl_4 \cdot 4H_2O$	Yellow							
	Cs_3AmCl_6	Yellow							
	$Cs_2NaAmCl_6$	Yellow		fcc	$Fm3m$	10 86			
	$AmCl_3-2(C_2H_5)_4NCl$								
	$[(C_6H_5)_3PH]_3AmCl_6$								
	$Cs_3AmO_2Cl_4$	Green							
	$Cs_2AmO_2Cl_4$	Dark red		Cubic*		15 1			
Fluorides	AmF_3	Pink	9 56	Hexagonal	$P\bar{3}c1$	7 004		7 225	
	AmF_4	Rose tan	7 34	Monoclinic	$C2/c$	12 56	10 58	8 25	125 9
	AmO_2F_2	Brown	6 50	Hexagonal†	$R\bar{3}m$	4 136		15 85	
Fluoride complexes	$NaAmF_4$	Pink	7 02	Hexagonal	$P6$	6 109		3 731	
	$KAmF_4$								
	KAm_2F_7	Pink		Cubic		5 857			
	$(NH_4)_4AmF_8$	Red							
	$LiAmF_5$	Pink	6 19	Tetragonal	$I4_1/a$	14 63		6 449	
	$K_7Am_6F_{31}$		6 09	Hexagonal†	$R\bar{3}$	14 938		10 293	
	$Na_7Am_6F_{31}$		6 23	Hexagonal†	$R\bar{3}$	14 48		9 665	
	Rb_2AmF_6	Pink	5 52	Orthorhombic	$Cmcm$	6 962	12 001	7 579	
	$KAmO_2F_2$	Tan	5 97	Rhombohedral	$R\bar{3}m$	6 78			36 25
	$RbAmO_2F_2$	Yellow	6 90	Rhombohedral	$R\bar{3}m$	6 789			36 25
Germanate	$AmGeO_4$	Dark brown	8 95	Tetragonal	$I4_1/a$	5 04		11 03	
Hydrides	AmH_2	Black	10 55	fcc	$Fm3m$	5 348			
	AmH_3		9 32	Hexagonal	$P\bar{3}c1$	6 68		6 75	
Hydroxide	$Am(OH)_3$	Pink	7 24	Hexagonal	Pb_3/m	6 426		3 745	
Iodides	AmI_2	Black		Monoclinic		7 677	8 311	7 925	98 46
	$\alpha\ AmI_3$			Orthorhombic	$Ccmm$	4 31	14 03	9 92	

	β AmI_3	Yellow	6 04	Hexagonal	$R3$	7 42		20 55	
	$AmOI$			Tetragonal		4 011		9 204	
Iridium	Ir_2Am			Cubic	$Fd3m$	7 55			
Molybdates	α $Am_2(MoO_4)_3$			Tetragonal	$I4_1/a$	5 24		11 52	
	β $Am_2(MoO_4)_3$			Orthorhombic		9 095	10 527	10 820	
	$LiAm(MoO_4)_2$			Tetragonal	$I4_1/a$	5 20		11 39	
	$NaAm(MoO_4)_2$			Tetragonal	$I4_1/a$	5 25		11 55	
	$Na_5Am(MoO_4)_4$					11 515		11 429	
	$K_2Am_2(MoO_4)_4$								
	$K_{10}Am_2(MoO_4)_8$								
Nickel	Ni_2Am			Cubic	$Fd3m$	6 99			
Nitride	AmN	Black	13 53	fcc	$Fm3m$	5 000			
Osmium	Os_2Am			Hexagonal	$P6_3/mmc$	5 320		8 849	
Oxides, binary	AmO	Black	13 6	fcc	$Fm3m$	5 045			
	$A\text{-}Am_2O_3$	Tan	11 68	Hexagonal	$P\bar{3}m1$	3 817		5 971	
	$B\text{-}Am_2O_3$		11 89	Monoclinic	$C2/m$	14 38	3 52	8 92	100 4
	$C\text{-}Am_2O_3$	Red brown	10 49	Cubic	$Ia3$	11 03			
	AmO_2	Dark brown	11 66	fcc	$Fm3m$	5 377			
Oxides, ternary									
Lithium and sodium	$LiAmO_2$								
	Li_2AmO_3								
	Li_8AmO_6			Hexagonal	Li_8PbO_6	5 62		15 96	
	Li_3AmO_4	Brown	6 52	Tetragonal	$LiUO_4$	4 459		8 355	
	Li_7AmO_6	Brown	4 62	Hexagonal	$R\bar{3}$	5 54		15 65	
	Li_4AmO_5	Black brown	5 91	Tetragonal	$I4/m$	6 666		4 415	
	Li_6AmO_6			Hexagonal	Li_6ReO_6	5 174		14 59	
	Na_2AmO_3	Black brown	6 63	Monoclinic	$C2/c$	5 92	10 26	11 23	100 12
	Na_3AmO_4			fcc	$Fm3m$	4 757			
	Na_4AmO_5		5 27	fcc	$Fm3m$	4 70			
	Na_6AmO_6			Hexagonal	Li_6ReO_6	4 76		16 10	
Barium and strontium	$BaAm_2O_4$								
	$BaAmO_3$	Black brown	8 51	Cubic	Perovskite	4 356			
	Ba_3AmO_6	Dark brown	7 28	Cubic	$F\bar{4}3m$	8 81			

(Table continues on next page)

Table 4.2 (Continued)

Type	Formula	Color	Density, g/cm³	Crystal structure					
				Symmetry	Space group or structure type	Lattice constants			
						a, Å	b, Å	c, Å	α(β), deg
	$SrAm_2O_4$								
	$SrAmO_3$			Cubic	Perovskite	4 23			
	Sr_3AmO_6			Cubic	Ba_3WO_6				
Curium		See Table 4 3							
Zirconium, hafnium, and thorium		See Figs 4 10 and 4 11							
Niobium, tantalum, and protactinium	α $AmNbO_4$	Light brown	8 43	Monoclinic	$I2$	5 444	11 25	5 141	94 95
	β $AmNbO_4$ (660°C)	Light brown	8 30	Tetragonal	$I4_1/a$	5 30		11 34	
	$Am_{0\ 33}NbO_3$	Yellow brown	6 19	Pseudo tetragonal	$P4/mmm$	3 819		7 835	
	Ba_2AmNbO_6	Brown	7 57	Cubic	$F\bar{4}3m$	8 520			
	$AmNbTiO_6$	Yellow brown	7 18	Orthorhombic	$Pnam$	5 34	11 00	7 53	
	$AmTaO_4$		10 3	Monoclinic	$I2$	5 489	11 21	5 115	95 37
	$Am_{0\ 33}TaO_3$		8 69	Tetragonal	$I4_1/a$	3 889		7 820	
	Ba_2AmTaO_6		8 54	Cubic	$F\bar{4}3m$	8 518			
	$AmTaTiO_6$		8 54	Orthorhombic	$Pnam$	5 33	10 95	7 49	
	$AmPaO_4$	Pink	10 95	fcc	$Fm3m$	5 458			
	Ba_2AmPaO_6		8 23	Cubic	$F\bar{4}3m$	8 793			
Palladium	Pd_3Am	Metallic		Simple cubic	$Pm3m$	4 158			
Phosphates	$AmPO_4$	Pink	7 91	Monoclinic	$P2_1/n$	6 73	6 93	6 41	103 5
	$AmPO_4 \cdot 0\ 5H_2O$	Pink	6 70	Hexagonal	$C6_22$	6 99		6 39	
Platinum	Pt_2Am	Metallic		Cubic	$Fd3m$	7 66			
	Pt_5Am	Metallic			Pt_5Sm	5 319	9 090	26 42	
Rhodium	Rh_2Am	Metallic		Cubic	$Fd3m$	7 548			
	Rh_3Am	Metallic		Simple cubic	$Pm3m$	4 098			
Scandate	$AmScO_3$	Pink		Orthorhombic	$P6nm$	5 540	5 785	8 005	

Selenides	$AmSe_{1.8}$	Black		Tetragonal		4 096		8.347	
	Am_3Se_4			bcc	$I\bar{4}3d$	8 728			
Silicate	$AmSiO_4$	Dark brown	7 56	Tetragonal	$I4_1/amd$	6 87		6 20	
Sulfates	$Am_2(SO_4)_3 \cdot 8H_2O$	Yellow pink		Monoclinic	$C2/c$	13 619	6 837	18 405	102 7
	$Am_2(SO_4)_3$	White							
	$KAm(SO_4)_2$								
	$NaAm(SO_4)_2 \cdot 2H_2O$								
	$KAm(SO_4)_2 \cdot H_2O$								
	$RbAm(SO_4)_2 \cdot 3H_2O$								
	$CsAm(SO_4)_2 \cdot 4H_2O$								
	$TlAm(SO_4)_2 \cdot 4H_2O$								
	$K_3Am(SO_4)_3 \cdot H_2O$								
	$K_8Am_2(SO_4)_7$								
	$Cs_8Am_2(SO_4)_7$								
	$Tl_8Am_2(SO_4)_7$								
	$\{[Co(NH_3)_6]HSO_4\}_2 \cdot \{AmO_2(SO_4)_3\} \cdot nH_2O$	Orange		Cubic					
Sulfides	AmS			fcc	$Fm3m$	5 592			
	$AmS_{1.9}$	Black		Tetragonal		3 938		7 981	
	α-Am_2S_3	Black		Orthorhombic	$Pnma$	3 98	7 39	15 36	
	γ-Am_2S_3		8 50	bcc	$I\bar{4}3d$	8 434			
	$Am_{10}S_{14}O_3$‡			Tetragonal	$I4_1/acd$	14 87		19 73	
Tellurides	$AmTe_2$			Tetragonal		4 366		8 969	
	$AmTe_3$			Orthorhombic	$Bmmb$	4 399	4 339	25.57	
	Am_2Te_3			Orthorhombic	$Pbnm$	11 93	12 12	4.33	
	Am_3Te_4			bcc	$I\bar{4}3d$	9 394			
Tungstate	$Am_2(WO_4)_3$			Tetragonal	$I4_1/a$				
Vanadates	$AmVO_3$	Ochre	9 57	Orthorhombic	$Pbnm$	5 45	5 58	7 76	
	$AmVO_4$	Red brown	6 89	Tetragonal	$I4/amd$	7 31		6 42	
Xenates	$Am_4(XeO_6)_3 \cdot 40H_2O$	Orange							

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*Monoclinic form also known

†Hexagonal–rhombohedral

‡Also referred to as β-Am_2S_3

Eick and Mulford[47] point out that the AmB_4 phase exhibits a wide range of stoichiometry.

When heated, AmB_4 decomposes according to the reaction

$$3AmB_4(s) \rightarrow 2AmB_6(s) + 2Am(g) \qquad (4.10)$$

AmB_6. Arc-melting a mixture of the elements in the americium/boron atomic ratio 10:90 in an argon atmosphere produces simple cubic AmB_6 (Ref. 47). This compound evaporates congruently.

Bromides. The only reported solid compounds of americium with bromine are $AmBr_2$, $AmBr_3$, $AmBr_3 \cdot 6H_2O$, and $[(C_6H_5)_3PH]_3AmBr_6$.

$AmBr_2$. Synthesis of $AmBr_2$ can be accomplished[48,49] on a multimilligram scale by oxidation of americium metal with $HgBr_2$ in accordance with Eq. 4.11.

$$Am + HgBr_2 \xrightarrow[\text{vacuum}]{300^\circ C} AmBr_2 + Hg \qquad (4.11)$$

Stoichiometric amounts of americium metal and $HgBr_2$ are placed in a quartz tube, sealed in vacuum, and heated at 300°C for 4 days. Subsequently the mercury is distilled to the opposite end of the tube and sealed off. The $AmBr_2$ is then annealed 10 days at 400°C. Black $AmBr_2$ is isostructural with $EuBr_2$ and, at room temperature, is stable in an argon atmosphere for at least 4 weeks.

$AmBr_3$. Americium(III) bromide is a high-melting solid that can be purified by vacuum sublimation at temperatures above 850°C. It can be prepared

1. By reaction[50,51] of AmO_2 with $AlBr_3$ at 500°C according to Eq. 4.12.

$$3AmO_2 + 4AlBr_3 \rightarrow 3AmBr_3 + 2Al_2O_3 + \tfrac{3}{2}Br_2 \qquad (4.12)$$

2. By the metathetical reaction[52]

$$AmCl_3 + 3NH_4Br \xrightarrow[\text{H}_2\text{ atmos}]{400-500^\circ C} AmBr_3 + 3NH_4Cl \qquad (4.13)$$

3. By controlled vacuum thermal decomposition[53] of $AmBr_3 \cdot 6H_2O$

$$AmBr_3 \cdot 6H_2O \xrightarrow[10^{-4}-10^{-3}\text{ torr}]{60-170^\circ C} AmBr_3 + 6H_2O \qquad (4.14)$$

Zachariasen[54] and Asprey, Keenan, and Kruse[52] have determined that orthorhombic $AmBr_3$ has the $PuBr_3$ type of structure. Visible and near infrared spectra[51] have been recorded for solid $AmBr_3$. Liquid bromine does not oxidize $AmBr_3$ in nonaqueous solvents.[55]

$AmBr_3 \cdot 6H_2O$. Anhydrous $AmBr_3$ is hygroscopic and, when exposed to oxygen-free water vapor, takes up water corresponding to the formation of

$AmBr_3 \cdot 6H_2O$ (Ref 53) Vacuum evaporation of aqueous HBr solutions containing trivalent americium yields a product of composition close to $AmBr_3 \cdot H_2O$

$[(C_6H_5)_3PH]_3AmBr_6$ The triphenylphosphonium salt of the $AmBr_6^3$ ion was prepared on a microscale by precipitation from a nearly anhydrous ethanol solution of $AmBr_3$ and $(C_6H_5)_3PH$ which was almost saturated with HBr (Ref 56) Properties of the precipitated salt have not been determined

Carbide. *Am_2C_3* Americium sesquicarbide forms when americium metal is arc melted with high-purity graphite in an argon–helium atmosphere[57] The bcc crystal contains eight molecules per unit cell and is isostructural with Pu_2C_3

Nuclear gamma resonance spectra obtained using a source of Am_2C_3 show a pure quadrapole spectrum down to 1 8°K No magnetic ordering is seen[44]

Carbonates. *$Am_2(CO_3)_3 \cdot xH_2O$* Weigel and ter Meer[58] report that hydrolysis of an aqueous solution of Am(III) trichloroacetate yields $Am_2(CO_3)_3 \cdot 2H_2O$ (Eq 4.15)

$$2Am(CCl_3 \cdot COO)_3 + 5H_2O \rightarrow Am_2(CO_3)_3 \cdot 2H_2O + 3CO_2 + 6CHCl_3 \qquad (4\ 15)$$

Conversely, Fang[59] finds that addition of a CO_2-saturated solution of $NaHCO_3$ to a solution of $AmCl_3$ and washing the filtered precipitate with a CO_2-saturated aqueous solution produce $Am_2(CO_3)_3 \cdot 4H_2O$

According to Weigel and ter Meer,[60] thermal decomposition of $Am_2(CO_3)_3 \cdot 2H_2O$ in a vacuum proceeds as follows

$$Am_2(CO_3)_3 \cdot 2H_2O \xrightarrow{-2H_2O} Am_2(CO_3)_3 \xrightarrow{-2CO_2} Am_2O_2CO_3 \xrightarrow{-CO_2} Am_2O_3$$

Keller and Fang[61] observed the following sequence for thermal decomposition of $Am_2(CO_3)_3 \cdot 4H_2O$ in air

$$Am_2(CO_3)_3 \cdot 4H_2O \xrightarrow{-4H_2O} Am_2(CO_3)_3 \xrightarrow{-CO_2} Am_2O(CO_3)_2$$

$$\xrightarrow{+\frac{1}{2}O_2} Am_2O(CO_3)_2 \xrightarrow{-2CO_2} 2AmO_2$$

$NH_4AmO_2CO_3$ Crystals of $NH_4AmO_2CO_3$ precipitate when a dilute solution of Am(III) in 1*M* $(NH_4)_2CO_3$ is oxidized to Am(V) with ozone or peroxydisulfate[62]

$CsAmO_2CO_3$ Keenan[63] reports that $CsAmO_2CO_3$ precipitates when a slurry of pink $Am(OH)_3$ in 0 5*M* $CsHCO_3$ is treated with 5% O_3 in O_2 for 1 hr at 92°C

$K_{2x+1}AmO_2(CO_3)_{1+x}$ Several different potassium Am(V) double carbonates can apparently be prepared depending on precipitation conditions of pH and K_2CO_3 concentration Thus $KAmO_2CO_3$ is precipitated[64,65] from 0 03*M* to 0 1*M* $KHCO_3$ at pH 7 This compound[65] can be prepared most easily by O_3 oxidation of $Am(OH)_3$ in

0.03*M* $KHCO_3$. In an alternative synthesis, an Am(V) solution is first prepared by addition of a stoichiometric amount of KI to an $AmO_2(NO_3)_2$ solution After benzene extraction of the liberated I_2, $KHCO_3$ is added to neutralize acid and to make the final solution 0.1*M* $KHCO_3$ The light-colored precipitate that forms is digested 3 to 4 hr at 90°C and is then washed with 0.1*M* $KHCO_3$, absolute ethyl alcohol, and acetone.

Tan, finely divided $K_3AmO_2(CO_3)_2$ precipitates[66] when a solution of Am(III) in 3 5*M* K_2CO_3 is oxidized with O_3, $K_2S_2O_8$, or $KClO_2$. The solubility of $K_3AmO_2(CO_3)_2$ in 3.5*M* K_2CO_3 at 23°C corresponds to 10 to 40 mg Am liter [1]

According to Yakovlev and Gorbenko-Germanov,[67] the compound $K_5AmO_2(CO_3)_3$ precipitates when Am(III) in concentrated (>5*M*) K_2CO_3 is oxidized with ozone, $K_2S_2O_8$, or HClO.

Nigon et al.[62] also obtained a potassium Am(V) double carbonate by heating a K_2CO_3 solution containing Am(III) and KOCl to 80°C. Neither the K_2CO_3 concentration nor the composition of the resulting orthorhombic bisphenoids was stated.

$RbAmO_2CO_3$ Crystals of $RbAmO_2CO_3$ precipitate when a dilute solution of Am(III) in 10*M* Rb_2CO_3 is oxidized to Am(V) with ozone or peroxydisulfate [62,68]

$Na_{2x+1}AmO_2(CO_3)_{1+x}$. Werner and Perlman[69] obtained a sodium Am(V) double carbonate of unknown composition by oxidizing Am(III) in K_2CO_3 solution with NaClO. Later, in a slightly modified procedure, Nigon et al [62] also prepared a sodium Am(V) double carbonate of unknown composition by adding NaClO to a solution of Am(III) in Na_2CO_3 and digesting the resulting solution at 80°C. The refractive index of the resulting crystals (probably belonging to the monoclinic system) was between 1.58 and 1.60. More recently, Coleman et al.[65] state that, when Am(VI) in 2*M* Na_2CO_3 (previously prepared at a lower temperature) is heated to 90°C even with O_3 present, it is largely reduced to Am(V) within 1 hr, and sodium Am(V) carbonate precipitates. These workers did not establish the composition of the double carbonate but noted that it is readily oxidized to Am(VI) by O_3 at room temperature or by 0.001*M* $Na_2S_2O_8$ at 90°C in $NaHCO_3$ solutions $\leq 1M$.

Barium Am(VI) Carbonate. Addition of $Ba(NO_3)_2$ to Am(VI) carbonate solution precipitates a red-brown barium americium carbonate of undetermined composition.[65]

Calcium Am(VI) Carbonate. This salt precipitates when $Ca(NO_3)_2$ is added to Am(VI) carbonate solution,[65] its composition has not been determined

Sodium Am(VI) Carbonate. A crystalline Am(VI) carbonate forms when 1 ml of saturated $Na_2CO_3 \cdot NaHCO_3$ solution is added to 0.2 mmol of solid sodium Am(VI) acetate.[65] The same compound can be prepared by adding methanol to a solution of Am(VI) in 0.1*M* $NaHCO_3$. Other syntheses of sodium Am(VI) carbonates were performed by O_3 oxidation of $Am(OH)_3$ slurries in the presence of about 1 to 8 mols of $NaHCO_3$ per mol of Am(III). Solid sodium Am(VI) carbonates were obtained[65] by evaporation of the resulting solutions in a stream of O_3 The infrared spectra of solid sodium Am(VI) carbonate establishes the presence of the oxygen–americium–oxygen group in the carbonate complex

Chlorides. *$AmCl_2$* Oxidation of americium metal with $HgCl_2$ in a vacuum at 300°C produces $AmCl_2$ (Eq 4 16) [48,49]

$$\mathrm{Am + HgCl_2 \xrightarrow[\text{vacuum}]{300^{\circ}C} AmCl_2 + Hg} \qquad (4\ 16)$$

$AmCl_3$ Four methods of preparing anhydrous $AmCl_3$ are known

1 Reaction of AmO_2 with CCl_4 at 800 to 900°C (Refs 50, 51, and 70),

$$\mathrm{AmO_2 + 2CCl_4 \xrightarrow{800\ 900^{\circ}C} AmCl_3 + 2COCl_2 + \tfrac{1}{2}Cl_2} \qquad (4\ 17)$$

2 Reaction of AmO_2 with HCl (Refs 71 and 72),

$$\mathrm{AmO_2 + 4HCl \xrightarrow{500\ 600^{\circ}C} AmCl_3 + \tfrac{1}{2}Cl_2 + 2H_2O} \qquad (4\ 18)$$

3 Evaporation to dryness of an HCl solution of Am^{3+} containing NH_4Cl and subliming NH_4Cl from the residue [52]

4 Dehydration[73] of $AmCl_3 \cdot 6H_2O$ by heating in a stream of HCl followed by vacuum sublimation of $AmCl_3$

The enthalpy of formation[73,74] of $AmCl_3$ at 209°C was originally reported at −249 ± 3 kcal mol^{-1} A more accurate value[11] for the enthalpy of formation is −233 7 ± 0 4 kcal mol [1] The anhydrous trichloride sublimes at about 800°C

Zachariasen[54] and subsequently Asprey, Keenan, and Kruse[52] and Fuger[75] determined the lattice constants and crystal symmetry of $AmCl_3$ using powder methods A refined crystal structure for $AmCl_3$ has recently been worked out by Burns and Peterson[72] using single-crystal data Their lattice constants are listed in Table 4 2 Burns and Peterson[72] calculate from their data the ionic radius of Am^{3+} to be 0 984 ± 0 003 Å

The coefficients of the thermal expansion of the lattice constants[75] of $AmCl_3$ between 20°C and 608°C are $\alpha_a = (2\ 40 \pm 0\ 1) \times 10^{5}\ {}^{\circ}C^{1}$ and $\alpha_c = (1\ 38 \pm 0\ 1) \times 10^{5}\ {}^{\circ}C^{1}$

Gruber and Conway[76] have measured the absorption spectrum and Zeeman effect of Am^{3+} in $LaCl_3$ The absorption spectrum of $AmCl_3$ at liquid N_2 temperatures has been determined by Pappalardo, Carnall, and Fields [51]

The solubility[77] of $AmCl_3$, at either 25 or 40°C, decreases from about 0 11*M* in 9*M* LiCl to about 0 04*M* in 13*M* LiCl

$AmCl_3 \cdot 6H_2O$ For use in single-crystal X ray diffraction studies, Burns and Peterson[78] prepared $AmCl_3 \cdot 6H_2O$ crystals by dissolving about 100 mg of AmO_2 in excess 6*M* HCl and allowing the solution to evaporate Stover and Conway[79]

published part of the absorption spectrum of $AmCl_3 \cdot 6H_2O$ at room temperature and at liquid N_2 temperature.

AmOCl. Templeton and Dauben[80] state that americium oxychloride was first prepared by L. B. Asprey by accidental contamination in an experiment designed to yield Am_2O_3 by H_2 reduction of AmO_2. Normally AmOCl is prepared by vapor-phase hydrolysis[81a] of $AmCl_3$ according to Eq. 4.19

$$AmCl_3(s) + H_2O(g) \rightarrow AmOCl(s) + 2HCl(g) \qquad (4.19)$$

Koch is also reported[81a] to have prepared AmOCl by heating Am_2O_3 at 500°C in a mixture of HCl and H_2O vapors.

Equilibrium constants for Eq. 4.19 at various temperatures between 682 and 800°K were initially measured in 1953 by Koch and Cunningham.[81a] From their results, Koch and Cunningham derived the expression $\Delta G^\circ \text{ (kcal)} = 22.38 + 6.4 \times 10^{-3} T \log T + 1.8 \times 10^{-7} T^2 - 22/T - 52.31 \times 10^{-3} T$ for the free-energy function of Eq. 4.19. Weigel, Wishnevsky, and Hauske[81b] (in 1975) redetermined equilibrium constants for Eq. 4.19 using both ^{241}Am and ^{243}Am. Weigel and coworkers report the heat of formation of AmOCl at 298°K is 225.7 kcal mol^{-1}. This value is in excellent agreement with the value 226.0 ± 0.2 kcal mol^{-1} calculated by Fuger, Spirlet, and Muller[11a] from the earlier data of B. B. Cunningham, A. Broido, and C. W. Koch.

Chloride Complexes. Solid chloride complexes of Am(III), (V), and (VI) were synthesized by Bagnall, Laidler, and Stewart,[82,83a] by Ryan,[56] and by Marcus and Shiloh.[84]

$CsAmCl_4 \cdot 4H_2O$. Hydrated cesium tetrachloroamericate(III) precipitates from concentrated solutions of Am(III) in HCl saturated with gaseous HCl on addition of CsCl.[83a] The americium–chlorine stretching frequencies occur at 235 and 197 cm^{-1}. X-ray powder results for $CsAmCl_4 \cdot 4H_2O$ are listed in Ref. 83a but have not been interpreted.

$CsAmCl_4$. Bagnall, Laidler, and Stewart[83a] prepared $CsAmCl_4$ by heating $CsAmCl_4 \cdot 4H_2O$ in a stream of HCl at approximately 320°C for 1 hr. The americium–chlorine stretching frequency of the anhydrous compound occurs at 218 cm^{-1}. Marcus and Shiloh[84] also prepared $CsAmCl_4$ by evaporating together aqueous 3*M* HCl solutions of CsCl and $AmCl_3$ at a 1:1 mol ratio.

Cs_3AmCl_6. A compound of this composition was obtained by evaporating aqueous 3*M* HCl solutions of CsCl and $AmCl_3$ at a 3:1 mol ratio.[84] Conversely, Bagnall, Laidler, and Stewart[83a] also prepared Cs_3AmCl_6 by adding the stoichiometric amount of CsCl in 6*M* HCl to an ethanolic solution of hydrated $AmCl_3$ saturated with gaseous HCl. The americium–chlorine stretching frequency of Cs_3AmCl_6 occurs at 214 cm^{-1}. X-ray powder results for Cs_3AmCl_6 have not been interpreted.

$Cs_2NaAmCl_6$. Face-centered cubic $Cs_2NaAmCl_6$ is obtained[83a] when an HCl solution of Am(III) and a 2:1 mol mixture of CsCl and NaCl is evaporated to dryness

According to Bagnall, Laidler, and Stewart,[83a] this mixed cation complex is unique in that no other combinations of alkali metal cations yield analogous products From 15 to 70°K, $Cs_2NaAmCl_6$ has temperature-independent paramagnetism with $\chi_m = 5400 \times 10^{-6}$ emu mol^{-1}. Below 15°K the susceptibility increases slightly, presumably due to the presence of some additional paramagnetic impurity [83b]

$AmCl_3 \cdot 3CsCl \cdot yLiCl$ ($y \simeq 20$) Marcus and Shiloh[84] prepared this solid by evaporating aqueous 3*M* HCl solutions of $AmCl_3$ and CsCl (mol ratio = 3 1) containing excess LiCl.

$AmCl_3 \cdot x(C_4H_9)_4NCl \cdot yLiCl$ ($x \simeq 17$, $y \simeq 260$) Marcus and Shiloh[84] find that two liquid phases are produced from ethanol solutions of hydrated $AmCl_3$ and $(C_4H_9)_4NCl$ which contain a large excess of LiCl A yellow solid of the above-mentioned composition is formed from the upper liquid phase upon evaporation of the ethanol

$AmCl_3 \cdot 2(C_2H_5)_4NCl \cdot yLiCl$ ($y \simeq 0$, 1, and y) Yellow solids precipitate[84] when acetone is added to ethanol solutions of hydrated $AmCl_3$ and $(C_2H_5)_4NCl$ In the absence of LiCl, $AmCl_3 \cdot 2(C_2H_5)_4NCl$ precipitates, whereas $AmCl_3 \cdot 2(C_2H_5)NCl \cdot LiCl$ precipitates in the presence of stoichiometrically equal amounts of LiCl When excess LiCl is present, the yellow precipitate is $AmCl_3 \cdot 2(C_2H_5)_4NCl \cdot yLiCl$

$AmCl_3 \cdot x(C_{12}H_{25})_3NHCl$ ($x \simeq 25$) From a saturated solution of hydrated $AmCl_3$ in trilaurylammonium hydrochloride in toluene, Marcus and Shiloh[84] obtained $AmCl_3 \cdot x(C_{12}H_{25})_3NHCl$ as a yellow waxlike solid upon evaporation of the toluene This material can be recovered unchanged after dissolution in benzene.

$[(C_6H_5)_3PH]_3AmCl_6$ Analogous to the corresponding bromide compound (see page 139), the triphenyl phosphonium salt of $AmCl_6^{3-}$ can be prepared[56,85] by precipitation from nearly anhydrous ethanol solutions of $AmCl_3$ and $(C_6H_5)_3PH$ which are almost saturated with HCl Quantities of $[(C_6H_5)_3PH]_3AmCl_6$ that contain 3 to 4 mg of americium are stable to radiation damage for about 2 days and then turn dark yellow and char [85]

$Cs_3AmO_2Cl_4$ * Green cesium dioxotetrachloroamericate(V), isostructural with $Cs_3NpO_2Cl_4$, is precipitated by ethanol from a solution of Am(V) hydroxide and CsCl in 6*M* HCl and also by treating $CsAmO_2CO_3$ with concentrated HCl saturated with CsCl.[83a] Previously, $Cs_3AmO_2Cl_4$ was erroneously formulated as the trimeric cluster $Cs_8(AmO_2)_3Cl_{11}$ (Ref 82) The americium–chlorine stretching frequency for $Cs_3AmO_2Cl_4$ occurs at 290 cm^{-1}

$Cs_2AmO_2Cl_4$. A dark-red solid, $Cs_2AmO_2Cl_4$, is obtained when $Cs_3AmO_2Cl_4$ is treated with concentrated HCl [82] Brown[86] states that this unusual oxidation is

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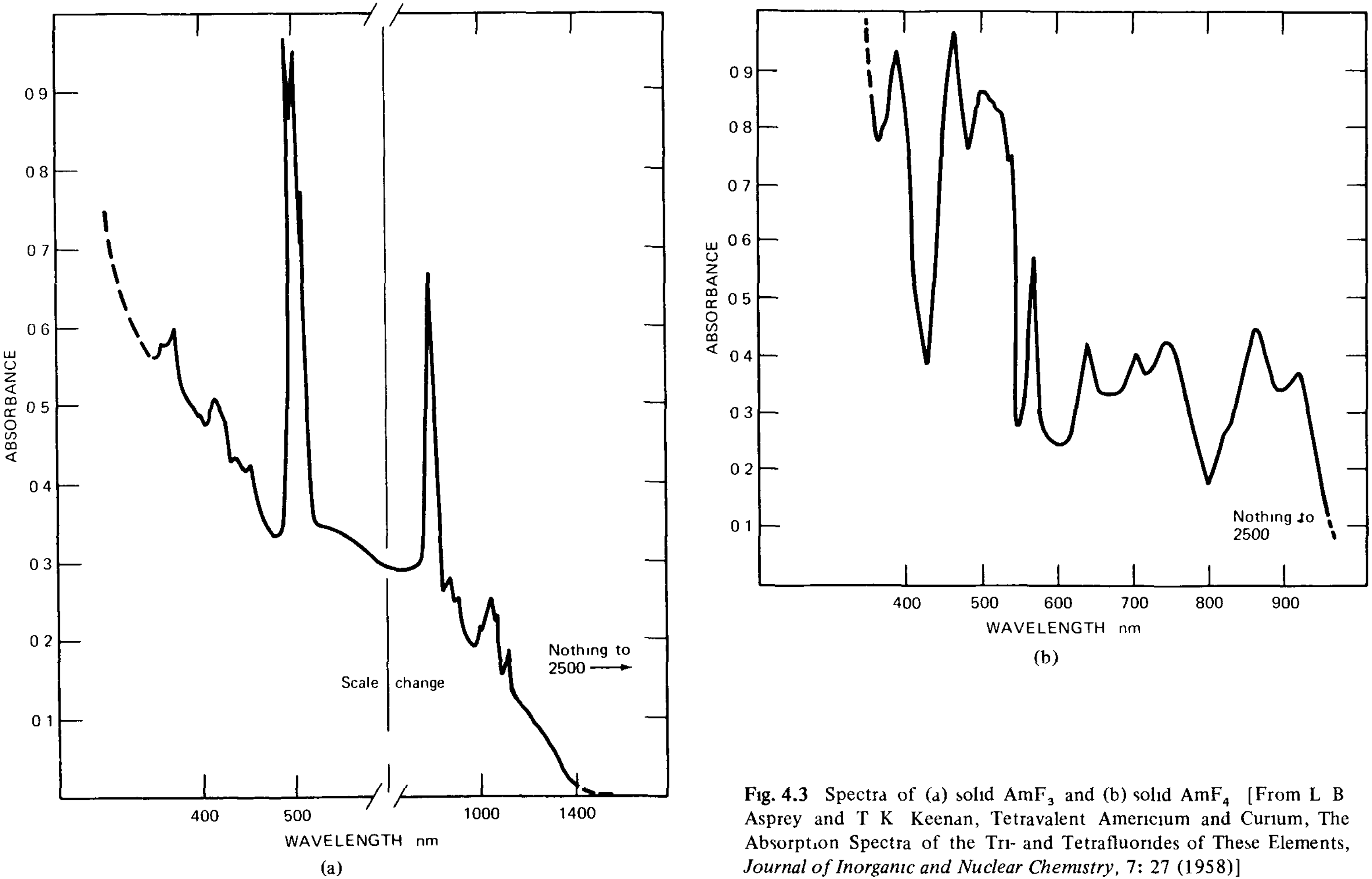
*Additional studies of the preparation and properties of $Cs_3AmO_2Cl_4$ have been reported recently by Vodovatov and his Russian colleagues.[206]



(a)

(b)

Fig. 4.3 Spectra of (a) solid AmF_3 and (b) solid AmF_4 [From L B Asprey and T K Keenan, Tetravalent Americium and Curium, The Absorption Spectra of the Tri- and Tetrafluorides of These Elements, *Journal of Inorganic and Nuclear Chemistry*, 7: 27 (1958)] probably due to the high-lattice-energy stabilization of $Cs_2AmO_2Cl_4$. The cubic form of $Cs_2AmO_2Cl_4$, when washed repeatedly with small volumes of concentrated HCl, is reported[83a] to transform to a monoclinic form.

Fluorides. *AmF_2.* Stable AmF_2 is unknown. Formation of divalent americium in single crystals of CaF_2 has been reported, however.[87-89] Single crystals of CaF_2 grown with 0.1 to 0.2 wt % Am are initially light pink, but they darken to a brown color on standing. Visible and electron paramagnetic resonance spectroscopic examination of the resulting crystals indicates the presence of Am^{2+} in an f^7 configuration. Americium(III) incorporated in the CaF_2 lattice may also be reduced with calcium metal or electrolytically.

AmF_3. The anhydrous trifluoride can be prepared by:

1. Hydrofluorination at 600 to 700°C for 1 hr of either $Am(OH)_3$ or AmO_2 (Refs. 1, 50, and 86).
2. Drying of hydrated AmF_3 precipitated from aqueous solution (Refs. 4, 52, and 90).
3. Heating hydrated AmF_3 precipitated from aqueous solution[91] with an excess of $NH_4F \cdot HF$ at 700°C.
4. Metathesis of $AmCl_3$ with NH_4F according to Eq. 4.20.

$$AmCl_3 + 3NH_4F \xrightarrow[H_2]{400\text{–}450^\circ C} AmF_3 + 3NH_4Cl \qquad (4.20)$$

Hydrated AmF_3 can be satisfactorily dried and dehydrated by washing with ethanol or ether and heating in air at 85°C under an infrared lamp.[90] Alternatively, dehydration can also be effected successfully by flowing HF or a mixture of H_2 and HF at 400 to 500°C over the hydrated fluoride.[52]

The melting point[91] of AmF_3 is 1393 ± 20°C. Americium(III) fluoride has the LaF_3 structure; its crystal structure has been determined by Templeton and Dauben[80] and most recently by Asprey, Keenan, and Kruse.[52] Magnetic susceptibilities for AmF_3 at 295, 199, and 77°K are[92] 1040×10^{-6}, 1290×10^{-6}, and 1740×10^{-6} cm^3 mol^{-1}, respectively. The solid state spectrum of AmF_3, as determined by Asprey and Keenan,[93] is given in Fig. 4.3(a). The Mossbauer spectrum for AmF_3 has also been reported.[94,95]

Vapor-pressure data for AmF_3[96-98] are represented reliably[97] by the equation

$$\log P_{torr} = -(34628/T) + 34.007 - 7.048 \log T \; (1126\text{–}1469^\circ K)$$

The free energy of sublimation (kcal mol^{-1}) is given by $\Delta G = 112.65 + 32.34T \log T - 155.5T$. Ryan[99] estimates the heat of formation of solid AmF_3 as −380 kcal mol^{-1}.

Reduction of AmF_3 to americium metal is discussed on page 122. Americium(III) trifluoride[52] is stable in H_2 at 500°C.

AmF_4 Reaction of either AmF_3 or AmO_2 with F_2 at 400 to 500°C yields AmF_4 (Refs 90, 93, and 100) Conner[101] recently used this approach to prepare multigram quantities of AmF_4 Fried[50] showed that AmF_4 cannot be prepared by heating AmF_3 in O_2–HF mixtures

Lattice constants of AmF_4 have been measured by Asprey,[90] by Keenan and Asprey,[102a] and most recently by Asprey and Haire,[102b] AmF_4 is isomorphous with UF_4, NpF_4, and PuF_4 Gas evolves when water is added to AmF_4, and the tetrafluoride is converted into birefringent aggregates that give the characteristic spectrum of Am(III) The solid state spectrum[93] of AmF_4 is shown in Fig 4 3(b)

The vapor pressure of AmF_4 in the range 729 to 900°C can be represented[100,103] by the equation $\log P_{torr} = -(11911\ 5/T) + 9\ 337$ AmF_4 is thermodynamically unstable above 635°C The estimated[99] heat of formation of AmF_4 is –399 kcal mol^{1}

AmF_6 All attempts[104,105] to prepare AmF_6 have been unsuccessful

AmO_2F_2 Keenan[106] prepared americyl fluoride by the reaction (at –196°C) of solid sodium americyl acetate with anhydrous HF containing a small amount of F_2 The hexagonal AmO_2F_2 is isostructural with other actinyl(VI) difluorides

Fluoride Complexes Various fluoride complexes of Am(III) ($NaAmF_4$, $KAmF_4$, and K_2AmF_7) and Am(IV)[$(NH_4)_4AmF_8$, $K_7Am_6F_{31}$, and $Na_7Am_6F_{31}$] are known Two complexes of Am(V) ($KAmO_2F_2$ and $RbAmO_2F_2$) are also known

$NaAmF_4$ Keller and Schmutz report[107,108] that $NaAmF_4$ can be synthesized by heating AmO_2 with either NaF or Na_2CO_3 in an HF–H_2 mixture at 450 to 650°C (According to these workers, $NaAmF_4$ is the first fluoride complex of americium to be prepared by a high-temperature solid state reaction) Keenan[109] showed later that exposure of $Na_7Am_6F_{31}$ to H_2 for 16 hr at 300°C converts it to $NaAmF_4$ Lattice constants of hexagonal $NaAmF_4$ have been measured,[108] but other details of the chemistry of this compound are lacking

$KAmF_4$ Solid-state reaction of equimolar amounts of KF and AmF_3 at 350 to 650°C in an HF–H_2 atmosphere produces[108] $KAmF_4$ X-ray diffraction and other properties of this compound have not been reported

KAm_2F_7 Pink, cubic KAm_2F_7 is reported to result from reaction of 2 mols of KF with 1 mol of AmF_3 at 350 to 650°C in an HF–H_2 atmosphere [108]

$(NH_4)_4AmF_8$ Freshly prepared $Am(OH)_4$ dissolves in 13*M* NH_4F solution up to an Am(IV) concentration of 5 g liter^{1} When this solubility is exceeded at room temperature, red crystals precipitate [110] These crystals, by analogy with the isostructural tetravalent uranium compound, are formulated as $(NH_4)_4AmF_8$ The solubility of $(NH_4)_4AmF_8$ in 13*M* NH_4F is about 0 02*M* No further studies of this compound have been made

$LiAmF_5$ This compound results[111] when the residue from evaporation of an HCl solution containing stoichiometric (1 1) amounts of lithium and americium is treated with F_2 at 350°C for ≃16 hr Lattice constants of tetragonal $LiAmF_5$ have been measured by Keenan,[111] $LiXF_5$-type compounds are known for X = Th, Pu, U, Np, Pu, and Cm also [112]

$K_7Am_6F_{31}$ Preparation of $K_7Am_6F_{31}$ is by evaporation of a 7 1 mixture of potassium/americium from HF solution, subsequently the dried residue is treated[113] with F_2 for 16 hr at 350°C. (At the time of its original preparation,[90] $K_7Am_6F_{31}$ was formulated as "$KAmF_5$ ") Trends in the 7 6 potassium/actinide(IV) series for actinides from thorium to curium inclusive are discussed by Keenan.[113]

$Na_7Am_6F_{31}$ This compound is completely analogous to the $K_7Am_6F_{31}$ described above and is prepared in a similar manner.[109] A 7 6 sodium/actinide(IV) series analogous to the 7 6 potassium/actinide(IV) series is also known [109,113] Reduction of $Na_7Am_6F_{31}$ with H_2, as noted earlier, produces $NaAmF_4$.

Rb_2AmF_6 The procedure recommended by Keenan[114] for preparation of Rb_2AmF_6 involves equilibration of freshly prepared $Am(OH)_4$ with aqueous RbF and HF at 0°C. The precipitate so formed is heated for about 70 hr at 150°C in F_2. Synthesis of Rb_2AmF_6 from $RbAmO_2CO_3$ has also been accomplished [115] Optical properties and the solid absorption spectrum of Rb_2AmF_6 were determined by Kruse and Asprey [115] The lattice parameters of orthorhombic Rb_2AmF_6 have been measured by Keenan [114]

Keenan points out that, although $Rb_7Am_6F_{31}$ is not known, the 7 6 rubidium compounds are known from thorium to plutonium. Conversely, the 2 1 Rb_2MF_6 series includes americium and curium but not Th(IV) and Pu(IV).

$KAmO_2F_2$ Addition of a saturated solution[116] of KF to an acid solution of AmO_2^+ (prepared by dissolution of $KAmO_2CO_3$ in dilute HNO_3) precipitates tan $KAmO_2F_2$ The rhombohedral crystal ($CaUO_4$ type) contains AmO_2^+ ions and is built up of layers containing $AmO_2F_2^-$ ions held together by potassium ions

$RbAmO_2F_2$ Keenan[117] made $RbAmO_2F_2$ by addition of saturated RbF solution to AmO_2^+ in 0 01*M* HCl. On standing overnight in contact with an acidic RbF solution, $RbAmO_2F_2$ is reduced to Rb_2AmF_6 (Ref. 115).

Germanate. *$AmGeO_4$* Both thermal and hydrothermal methods[41,118] can be used to prepare $AmGeO_4$ Pure, dark-brown $AmGeO_4$ is produced when $Am(OH)_4$ and excess GeO_2 in a 1*M* $NaHCO_3$ solution are heated 7 days at 230°C. Bright-brown $AmGeO_4$, contaminated with AmO_2 and Am_2O_3, results when AmO_2 and GeO_2 are heated 8 hr in O_2 at 1000°C.

The thermal decomposition of $AmGeO_4$ starts at about 1050°C. Keller[118] suggests formation and decomposition of $AmGeO_4$ can be represented by the reaction sequence

$$AmO_2 + GeO_2 \xrightarrow[T_1\ \ T_2(H_2O)]{} \alpha\text{-}AmGeO_4 \xrightarrow[T_3]{} \beta\ AmGeO_4 \xrightarrow[T_4]{} AmO_2 + GeO_2$$

where $T_2 \ll T_1 < T_3 > T_4 \gg T_2$. Alpha $AmGeO_4$ has the scheelite structure, and β $AmGeO_4$ has the zircon structure.

Hydrides. That americium metal reacts with H_2 to form hydrides has been known almost since the discovery of americium.[1,119] Only recently, however, has a detailed study[120,121] of the americium–hydrogen system shown the existence of two hydride phases: fcc AmH_{2+x} $(0 \leqslant x \leqslant 0.7)$ and hexagonal AmH_3. Pressure isotherms for the composition AmH_2 to AmH_3 are shown in Fig. 4.4. Conversion of $AmH_{2.7}$ to AmH_3 is sluggish. At hydrogen to americium <2, a two-phase region consisting of AmH_2 and americium metal exists.

According to Olson and Mulford,[120] the partial pressure of H_2 above AmH_2 between 773 and 1073°K follows the relation log p (atm) = 7.190 − 8812/T. For the reaction

$$Am(s) + H_2(g) \rightarrow AmH_2(s) \tag{4.21}$$

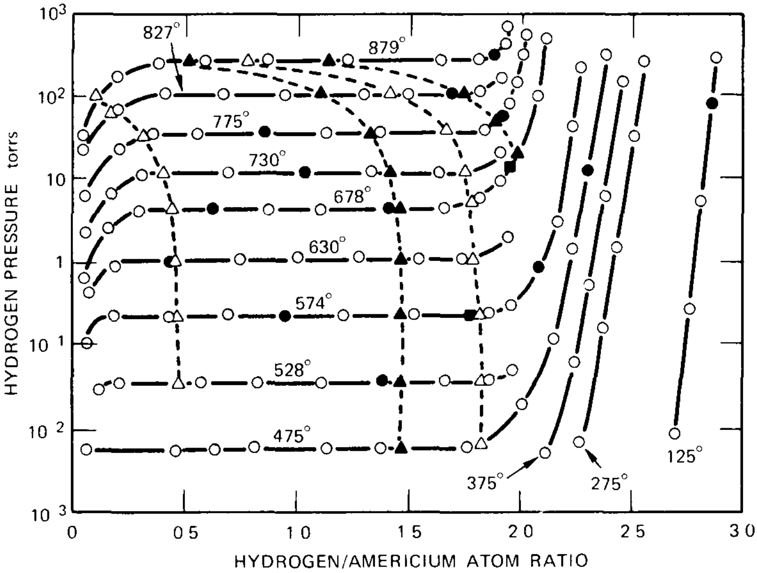


Fig. 4.4 Family of isotherms in the solid solution–dihydride–trihydride region of the americium–hydrogen system. Solid lines, varying hydrogen at constant temperature (○, hydrogen added, ●, hydrogen removed). Dashed lines, varying temperature with prehydrided samples (△, increasing temperature series, ▲, decreasing temperature series). [From J. W. Roddy, The Actinide Hydrides. The Americium–Hydrogen System, *Journal of Inorganic and Nuclear Chemistry*, 35: 4141 (1973).]

Olson and Mulford[120] reported $\Delta H = -40.3$ kcal mol^{-1} and $\Delta S = -30.0$ cal mol^{-1} deg^{-1}. Recent work[121] at Oak Ridge National Laboratory puts these values at $\Delta H = -45.5$ kcal mol^{-1} and $\Delta S = 37.3$ cal mol^{-1} deg^{-1}.

Utilizing the Solution Theory, Messer and Park[122] have calculated the excess heat and entropies of mixing in the americium–hydrogen system.

Hydroperoxide. Slow neutralization with NH_4OH of a 0.1*N* acid solution of Am(III), which is also 0.2*N* H_2O_2, leads to a yellow-brown color at a pH of about 5. Further addition of NH_4OH yields a yellow-brown precipitate, which, according to Buijs and Louwrier,[123] is quite distinct from $Am(OH)_3$ and is probably a hydroperoxide of Am(III). The hydroperoxide is insoluble in saturated NH_4F but converts to $Am(OH)_4$ when treated at 90°C with 10*N* KOH for 1 day.

Hydroxides. *$Am(OH)_3$.* An amorphous hydrous gel precipitates when ammonia or alkali is added to a solution of an Am(III) salt.[124-126] This precipitate consists of particles about 15 to 20 Å in diameter.[125] Aging of this gel in water for 1 hr at 80°C yields rod-like or scroll-like particles of crystalline $Am(OH)_3$ which are isostructural with hexagonal $Nd(OH)_3$ (Refs. 124, 126). After several months of aging in water, the $Am(OH)_3$ structures disintegrate to give small amorphous particles. In the solid state, $Am(OH)_3$ converts to crystalline AmO_2. The rate of conversion to the dioxide is dependent on storage conditions.

Weaver and Shoun[127] find that Am^{3+} can be completely precipitated from chloride or nitrate media at an NaOH/americium ratio of 2.4. For this stoichiometry, they calculate, at NaOH/americium ratios of 1.0 to 1.5, that K_{SP} is $[Am^{3+}][OH^-]^{2.4} = (3.4 \pm 0.3) \times 10^{-18}$ and that the solubility in water is $(K_{SP}/2.4^{2.4})^{1/3.4} = 3.9 \times 10^{-6}M$.

Figure 4.5 is a thermogram of a sample of $Am(OH)_3$ heated in oxygen; the $Am(OH)_3$ contained small amounts of nitrate and carbonate.[124] Although the DTA (differential thermal analysis) peaks and TGA (thermogravimetric analysis) changes are only tentatively assigned, the change at 1000°C is believed to be due to the decomposition of carbonate, whereas the change at about 300°C is thought to result from a loss of nitrate. Changes below 300°C are assigned to loss of water. The final product obtained after cooling to room temperature was confirmed by X-ray analysis to be AmO_2.

$Am(OH)_4$. A brown-black precipitate forms when a slurry of $Am(OH)_3$ is oxidized either with hypochlorite in weak base or with peroxydisulfate in strong (7*M*) base.[128,129] This precipitate is referred to as $Am(OH)_4$ by Penneman, Coleman, and Keenan[129] but is perhaps better termed hydrous AmO_2. Treatment[125] of americium "hydroperoxide" (this page) with strong KOH also yields $Am(OH)_4$. The estimated solubility[129] product (K_{SP}) of $Am(OH)_4$ is about 10^{-56}.

When tetravalent americium is precipitated with hydroxide, the resulting crystalline material gives electron diffraction patterns identical[125] to those obtained for AmO_2. When a mixture of Am(III) and (IV) hydroxides is precipitated, the crystalline

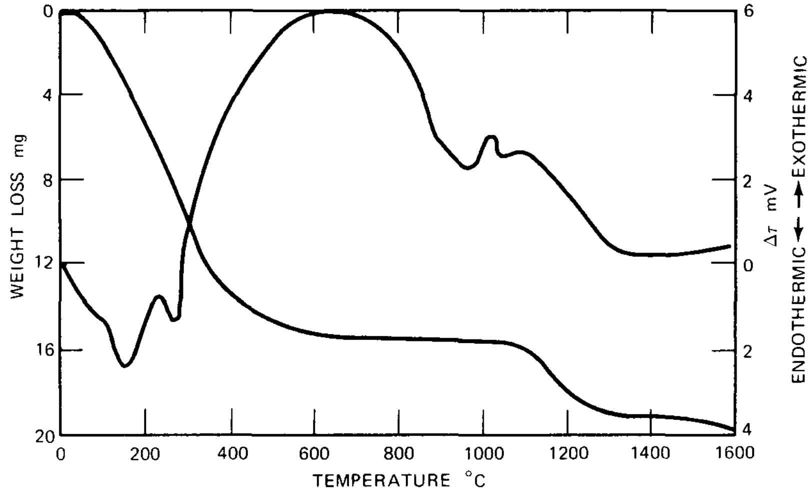


Fig. 4.5 Thermogram of $Am(OH)_3$.

products consist of mixtures of rod-like $Am(OH)_3$ particles and symmetrical particles of hydrous dioxide

Iodides. *AmI_2.* Combining americium metal with HgI_2 according to Eq. 4.22 (Refs. 48 and 130) gives AmI_2

$$Am + HgI_2 \xrightarrow[\text{vacuum}]{300°C} AmI_2 + Hg \qquad (4.22)$$

Reaction conditions are identical to those used to prepare $AmBr_2$ (see page 138) except that the black granular AmI_2 is annealed 3 days at 550°C rather than for 10 days at 400°C. The americium–iodine distance in AmI_2 is in the range 3 28 to 3 40 Å. The only notable feature of the absorption spectrum of AmI_2 is a weak, very broad band peaking at 837 nm. Americium(II) iodide melts with decomposition at about 700°C. Its effective magnetic moment is $\mu_{eff} = 6.7 \pm 0.7$ Bohr magnetons.[121]

AmI_3. What is termed α-AmI_3 is prepared[51] by heating AmO_2 at 500°C with either AlI_3 or a mixture[50] of aluminum metal and I_2 and separating the reaction products by fractional sublimation Zachariasen[54] found the resulting AmI_3 to have an orthorhombic structure

Americium(III) triiodide can also be made by Eq. 4.23 (Refs. 52 and 131)

$$AmCl_3 + 3NH_4I \xrightarrow[400\text{–}900°C]{\Delta} AmI_3 + 3NH_4Cl \qquad (4.23)$$

where a flow system is used to sweep volatile NH_4Cl from the reaction zone. The triiodide (β-AmI_3) made by Eq. 4 23 has a hexagonal structure and cannot be converted to an orthorhombic form even on annealing at various temperatures.[131] Treatment of β-AmI_3 with H_2 at 900°Cdoes not yield AmI_2

Pappalardo, Carnall, and Fields[51] have measured the visible and near infrared spectra of AmI_3 at low temperatures. Maslov and Maslov[132] estimate that the heat of formation for AmI_3 from americium and I_2 is -146 ± 5 to 10 kcal mol^{-1}. (From recent thermochemical data, Ryan[99] calculates a value of -139 ± 3 to 5 kcal mol^{-1})

AmOI Pure AmOI can be obtained by heating AmI_2 in moist air at 400°C (Ref. 130). Its properties have not yet been determined.

Molybdates. *$Am_2(MoO_4)_3$*. Solid-state reaction[133,134] between MoO_3 and AmO_2 at 700 to 900°C yields a ternary oxide of the empirical composition $Am_2Mo_3O_{12}$. X-ray diffraction data show that the low-temperature (⩽850°C) α-form of this compound has the vacancy scheelite structure whereas the stable high-temperature β-form has an orthorhombic form.

$LiAm(MoO_4)_2$ The compound $LiAm(MoO_4)_2$ results when an equimolar mixture of Li_2MoO_4 and $Am_2(MoO_4)_3$ is heated[134] at 550°C This compound has the scheelite structure and is isostructural with $LiGd(MoO_4)_2$.

$NaAm(MoO_4)_2$ Two phases result from solid-state reaction[134] of Na_2MoO_4 and $Am_2(MoO_4)_3$ at 550°C. One of these is $NaAm(MoO_4)_2$ which, like $LiAm(MoO_4)_2$, has the scheelite structure.

$Na_5Am(MoO_4)_4$ This compound,[134] which also forms when Na_2MoO_4 and $Am_2(MoO_4)_3$ are heated 24 hr at 550°C, melts congruently at 654°C The crystal structure of $Na_5Am(MoO_4)$ is the same as that of $Na_5La(WO_4)_4$.

$K_2Am_2(MoO_4)_4$ and $K_{10}Am_2(MoO_4)_8$. Two homogeneous phases of the empirical composition $K_2Am_2(MoO_4)_3$ and $K_{10}Am_2(MoO_4)_8$ apparently form when K_2MoO_4 and $Am_2(MoO_4)_3$ are heated[134] at 600°C. X-ray diffraction data indicate that these compounds are not isostructural with those of sodium and lithium.

Nitrate. *$Am(NO_3)_3 \cdot xH_2O$* Several reports, e.g., Ref 70, cite use of solid $Am(NO_3)_3 \cdot xH_2O$ [made by thermal evaporation of a purified $Am(NO_3)_3$–HNO_3 solution] as an intermediate in preparation of other americium compounds But, surprisingly, the chemical and physical properties of solid $Am(NO_3)_3 \cdot xH_2O$, including its crystal structure, have apparently not been determined.

Nitride. *AmN* Akimoto[135-137a] prepared micrograms of AmN by reacting AmH_3 for 30 min at 800°C and also by direct reaction of americium metal and N_2 at 750°C. Potter and Tennery[137b] disclosed a cyclic process for the preparation of finely divided AmN which involves incrementally dehydriding AmH_3 and nitriding the metal.

Milligram amounts of AmN have been recently synthesized by Charvillat et al.[137c] by heating AmH_3 under a high-purity N_2 atmosphere in a sealed tube. The AmN thus produced has the cubic NaCl structure. Its effective magnetic moment is 136 Bohr magnetons.[15]

Tagawa[138] has recently reviewed the phase behavior and crystal structure of the actinide nitrides.

Binary Oxides. *AmO.* Zachariasen[139] in a 1949 article reported the lattice constant of impure cubic AmO but did not give any details of how the compound is made. Akimoto[135-137a] claims to have prepared microgram amounts of AmO by reacting metallic americium at 850°C with the stoichiometric amount of oxygen gas generated by thermal decomposition of Ag_2O. He reports AmO is a brittle material with a grayish metallic luster. Attempts to prepare milligram to gram amounts of AmO have apparently not been made.

In connection with studies of the vaporization behavior of substoichiometric PuO_2, Ackermann, Faircloth, and Rand[140] found the vapor pressure of AmO between 1600 and 2200°K to obey the relation

$$\log p\,(\text{atm}) = (8.19 \pm 0.41) - (25{,}650 \pm 760)/T$$

Am_2O_3. Americium sesquioxide is obtained by reduction of AmO_2 with H_2 at 600 to 1000°C. The crystal structure of the resulting Am_2O_3 depends on the reduction temperature. Cubic (Mn_2O_3-type structure), red-brown C-type Am_2O_3 is produced at 600°C (Refs. 80 and 141), and hexagonal (La_2O_3-type structure), tan A-type Am_2O_3 is obtained[80] at 800°C. The melting point of hexagonal Am_2O_3 is 2205 ± 15°C (Ref. 142); the cubic-to-hexagonal transition occurs at about 800°C (Ref. 143). Chikalla and Eyring[144] state that cubic Am_2O_3 is capable of dissolving excess oxygen and exists, at room temperature, over a wide range of stoichiometry. The upper boundary is at about $AmO_{1.67}$.

It is not yet clear whether or not monoclinic sesquioxide (B-type Am_2O_3) can be prepared. Chikalla and Eyring[144] interpreted some of their X-ray data to indicate that B-type Am_2O_3 forms when oxide samples with oxygen/americium ratios between 1.51 and 1.54 are quenched from 800°C or above. In subsequent work, Berndt et al.[145a] and Maier[145b] were unable to confirm the earlier observations of Chikalla and Eyring.[144] Their results show that only A-type Am_2O_3 exists in the range 900 to 1500°C. Berndt et al. note, however, that in the americium–samarium–oxygen system, pure B-type Am_2O_3–Sm_2O_3 exists at 1250 to 1550°C at 8 to 10 mol % Sm_2O_3. They suggest, therefore, that the diffraction lines observed by Chikalla and Eyring[144] might have originated from a small amount of samarium impurity in their americium oxide sample.

On the basis of their recent studies with carefully purified ^{241}Am, Keller and Berndt[146a] state that B-type monoclinic sesquioxide with the exact stoichiometry Am_2O_3 does not exist. These workers report that hexagonal Am_2O_3 is the only stable modification for $<700°C \leq T \leq 1550°C$. Keller and Berndt,[146a] in agreement with the observations of Maier et al., note that a monoclinic form of Am_2O_3 can be stabilized by incorporation of small amounts of lanthanum oxides.

Chikalla et al.[142] have drawn up a stability diagram for actinide sesquioxides (Fig. 4.6). Their diagram includes transformation temperature data obtained by Foex and Traverse[146b] and Warshaw and Roy[146c] for lanthanides Baybarz[146d] has also given a stability diagram for several of the actinide sesquioxides including Am_2O_3. Chikalla and Turcotte[146e] note that the resin-bead technique used by Baybarz to obtain data for berkelium and californium can result in large amounts of residual impurities and, for that reason, question the validity of Baybarz's diagram.

AmO_2. Thermal decomposition in air or oxygen at 700 to 900°C of such americium compounds as $Am(NO_3)_3$ (Refs. 70 and 147), $Am(OH)_3$ (Ref. 123), $Am_2(CO_3)_3 \cdot 4H_2O$ (Ref 61), or $Am_2(C_2O_4)_3$ (Ref 141) produces dark-brown AmO_2. Cubic AmO_2 crystallizes with a fluorite structure. The lattice constant of $^{241}AmO_2$ has been determined by Zachariasen et al.,[139,148a] Dauben and Templeton,[80] and most recently by Keller [41] Keller and also Chikalla and Eyring[144] note that, because of the high alpha activity of ^{241}Am, a continuous destruction of the lattice of $^{241}AmO_2$ takes place with the formation of Frenkel defects According to Keller,[41] the lowest value of the lattice constant of $^{241}AmO_2$, obtained immediately after preparation, is a = 5 377 Å. After 3 months' storage, the lattice constant is 5.395 Å. The lattice constant of $^{243}AmO_2$ at 25°C is 5.3743 Å (Ref. 148a). [Thermal expansion of AmO_2 can be calculated from the expression $a_t = 5\ 3733 + 4\ 34 \times 10^{-5}\ t + 14.3 \times 10^{-9}\ t^2$, where a_t is the lattice constant (Å) at any temperature t (°C) [148b]]

McHenry[149] observed that the melting point of a composition near AmO_2, when heated in helium, increased with increasing rate of heating Melting points of 1750 and 2120°C, respectively, were noted at heating rates of 0.3 and 1.50°C min^{-1}. According to Chikalla and Turcotte,[146e] McHenry's results must certainly refer to a grossly substoichiometric oxide since the oxygen dissociation pressure over $AmO_{2.00}$ is 1 atm at about 1000°C (Ref 150). However, on the basis of an extrapolation of other actinide dioxide data, Chikalla and Turcotte[146e] state that the expected melting point of AmO_2 is 2175°C

The vapor pressure of AmO_2 between 1600 and 2200°K is given by the relation[140]

$$\log p\ (\text{atm}) = (7\ 28 \pm 0.19) - (28260 \pm 360)/T$$

The dioxide dissolves readily in aqueous HCl solutions with evolution of chlorine and in aqueous HNO_3 and H_2SO_4 solutions with evolution of oxygen, particularly when heated Using data obtained originally by Eyring, Lohr, and Cunningham[141] for the heat of solution of AmO_2 in 6 02*M* HNO_3–0.1*M* HBF_4, Fuger, Spirlet, and Muller[11a] calculate the enthalpy of formation of AmO_2 at 298°K as $\Delta H_f^\circ = -224\ 3 \pm 0.6$ kcal mol^{-1}

Chikalla and Eyring[150] used a thermogravimetric isopiestic technique to measure the oxygen dissociation pressures over stoichiometric americium dioxide Their results (Fig 4.7) show that the partial pressure of oxygen above AmO_{2-x} increases sharply

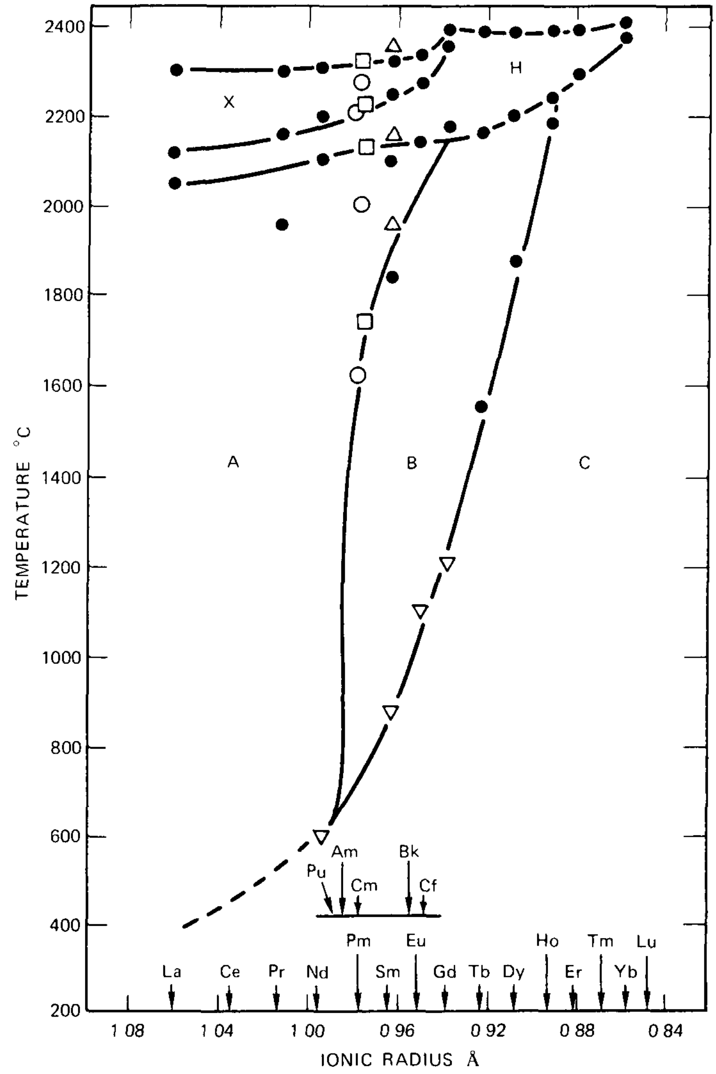


Fig. 4.6 Stability diagram of polymorphic forms of lanthanide and actinide sesquioxides ● and ▽ are results of Foex and Traverse[146b] and Warshaw and Roy,[146c] respectively ○, □, and △ are transformation temperatures in Cm_2O_3, Pm_2O_3, and Sm_2O_3 found by Chikalla et al [142] (from T D Chikalla, C E McNeilly, J L Bates, and J J Rasmussen, High Temperature Phase Transformations in Some Lanthanide and Actinide Oxides, in *Proceedings of the International Colliquium on High Temperature Phase Transformation,* Centre National de la Recherche Scientifique, Publication No 205, 1973)

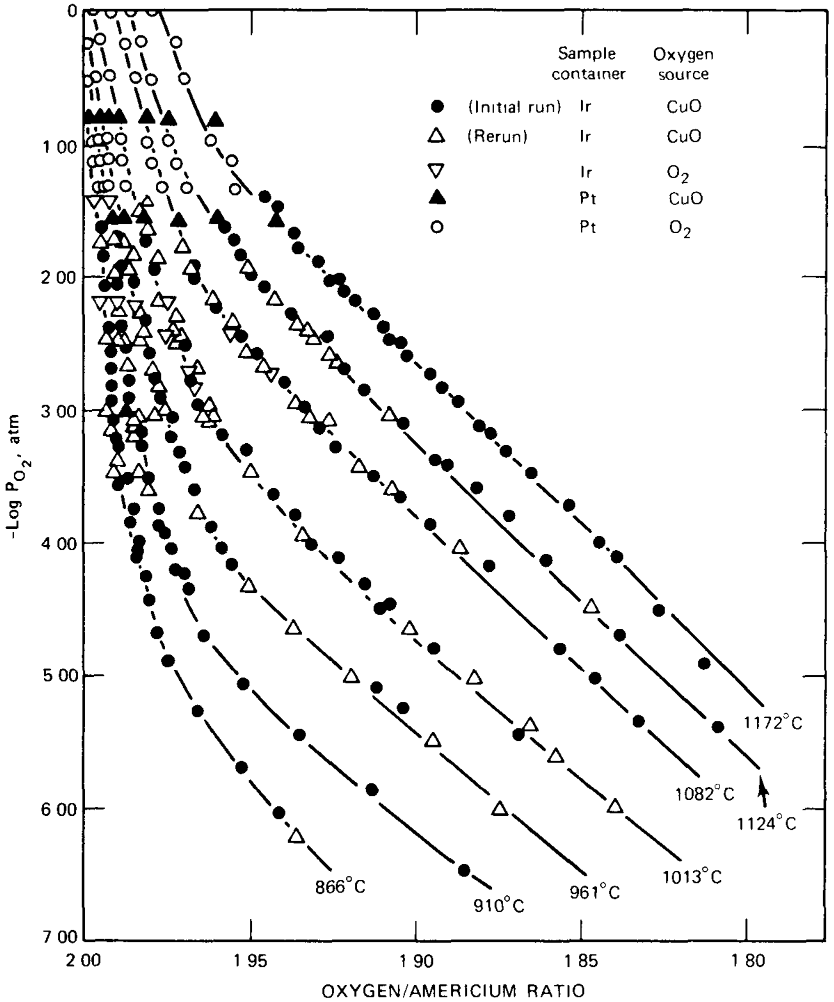


Fig. 4.7 Dissociation-pressure isotherms for AmO_x [From T D Chikalla and L Eyring Dissociation Pressures and Partial Thermodynamic Quantities for Americium Oxides, *Journal of Inorganic and Nuclear Chemistry,* 29: 2281 (1967)]

both with the temperature and with the oxygen/americium ratio. Asprey and Cunningham[151] also studied the thermal decomposition of AmO_2 The relative partial molar enthalpy and entropy of solution of O_2 in AmO_{2-x} calculated from the results of both sets of investigators are in reasonable agreement.

Figure 4.8 is the phase diagram for the americium–oxygen system derived by Sari and Zamorani[152a] and Sari, Tebaldi, and Pietra[152b] using DTA and ceramographic procedures. According to this diagram an oxygen-deficient fcc single-phase AmO_{2-x}

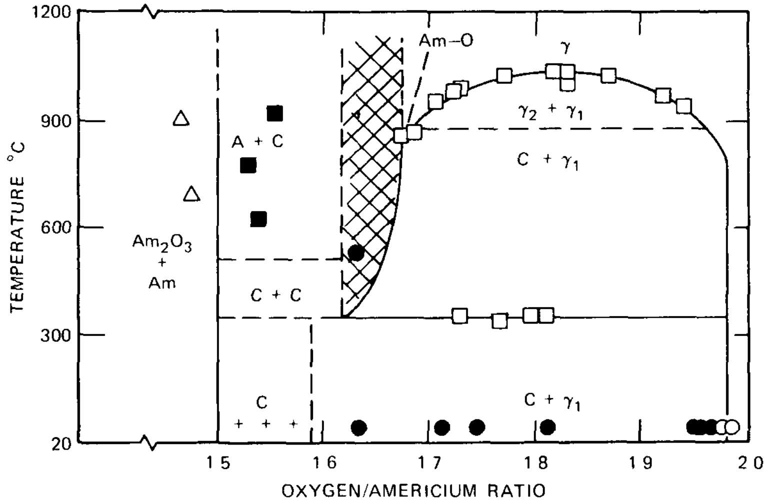


Fig. 4.8 Low-temperature americium–oxygen phase diagram. A = hexagonal Am_2O_3, C = low-temperature bcc Am_2O_3, C′ = high-temperature bcc Am_2O_3, γ, γ_1, γ_2, = fcc AmO_{2-x}. □ = results of DTA measurements. All other points represent results of micrographic analysis. [From C. Sari and E. Zamorani, An Investigation in the Americium Oxide System, *Journal of Nuclear Materials*, 37: 324 (1970).]

exists at temperatures above 1020°C and for $1.7 \leqslant$ oxygen/americium $\leqslant 2.0$. At room temperature the compound $AmO_{1.98}$ is in equilibrium with a bcc phase of the approximate composition $AmO_{1.59}$. The low-temperature bcc phase takes up additional oxygen at temperatures higher than 350°C and extends into a region of composition $1.63 \leqslant$ oxygen/americium $\leqslant 1.68$. For higher oxygen/americium ratios, this phase is in equilibrium with AmO_{2-x} up to 1020°C, whereas, for lower oxygen/americium ratios, it is in equilibrium with a hexagonal Am_2O_3.

Chikalla and Eyring[144] analyzed (X-ray diffraction) quenched samples taken across the entire compositional width $1.50 <$ oxygen/americium < 2.00; their results show the formation of bcc phase (α) in the range $1.50 <$ oxygen/americium < 1.67. Samples annealed in the higher oxygen/americium region could not be quenched but always gave a two-phase mixture of $AmO_{2.00}$ and a phase of estimated composition $AmO_{1.8}$. By implication it is suggested that another diphasic region must exist in the interval $1.67 <$ oxygen/americium < 1.8.

Chikalla and Turcotte[153a] have suggested that there is a greater complexity in the 1.67 to 1.80 region of the americium–oxygen system than indicated in Fig. 4.8. More recently, on further consideration of the Sari–Zamorani phase diagram for AmO_2, Chikalla and Turcotte[146e] state, "The partial pressure data in Fig. 4.7 and the phase diagram suggested by Sari and Zamorani are in direct conflict. The thermodynamic data suggest that the region $AmO_{1.95}$–$AmO_{1.85}$ is single-phased to temperatures below 900°C, whereas the diphasic dome reported by Sari and Zamorani extends to well above 1000°C. In the other fluorite-related systems examined in this region, including plutonium, berkelium (Turcotte, unpublished), cerium, and praseodymium, there is indeed evidence of a diphasic region but only at temperatures near or below 600°C.

"With the exception of the diphasic dome at high temperatures, which is a dome that we believe is disproved by the equilibrium thermodynamic studies, there are no real data presented which justify construction of any detailed phase diagram. That given by Sari and Zamorani relies entirely on the hope that AmO_x is much like PuO_x."

Karraker[153b] studied the magnetic properties of AmO_2, over the temperature ranges 15 to 50°K and 50 to 100°K, $\mu_{eff} = 1.3$ and 1.53 Bohr magnetons, respectively. Karraker also notes that AmO_2 is antiferromagnetic at temperatures below about 8.5 ± 0.5°K.

Ternary Oxides with Lithium and Sodium. *Lithium.* Solid-state reaction of Li_2O and AmO_2 in various proportions at temperatures in the range 350 to 1000°C leads to a variety of brown-colored ternary oxides.[41,154,155] The following compounds are known

Am(VI)	Li_6AmO_6 and Li_4AmO_5
Am(V)	Li_7AmO_6 and Li_3AmO_4
Am(IV)	Li_8AmO_6 and Li_2AmO_3
Am(III)	$LiAmO_2$

Figure 4.9, due to Keller,[41] summarizes the thermal stability of these compounds and the conditions for their preparation.

Sodium. The following listed ternary oxides of americium with sodium can be prepared by solid-state reaction of Na_2O or Na_2O_2 with AmO_2.[41,154,155]

Am(VI)	Na_6AmO_6 and Na_4AmO_5
Am(V)	Na_3AmO_4
Am(IV)	Na_2AmO_3

Conditions for preparation of these compounds and their thermal stability were reported by Keller[41] and are shown in Fig. 4.10.

Ternary Oxides with Barium and Strontium. *Barium.* The following ternary oxides are known in the barium–americium–oxygen system.[41,156]

Am(VI)	Ba_3AmO_6
Am(IV)	$BaAmO_3$
Am(III)	$BaAm_2O_4$ ($BaO \cdot Am_2O_3$)

Medium-brown Ba_3AmO_6 is obtained by heating a finely pulverized mixture of BaO and AmO_2 (3.05:1) in O_2 for 8 hr at 800 to 1000°C (Refs. 41, 156). This compound dissolves in dilute acids.

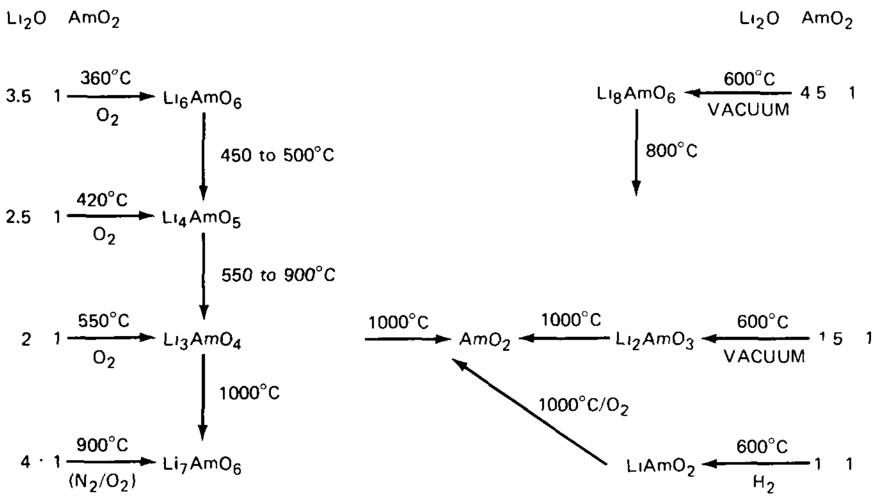


Fig. 4.9 Preparation conditions and thermal stability of compounds in the system lithium–americium–oxygen. [From C. Keller, The Solid State Chemistry of Americium Oxides, in *Lanthanide/Actinide Chemistry*, R. F. Gould (Ed.), Advances in Chemistry Series, American Chemical Society, Washington, 1967.]

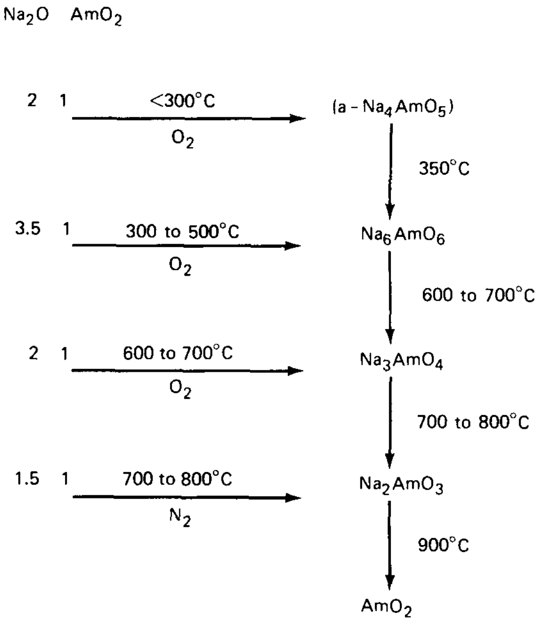


Fig. 4.10 Preparative conditions and thermal stability of compounds in the system sodium–americium–oxygen. [From C. Keller, The Solid State Chemistry of Americium Oxides, in *Lanthanide/Actinide Chemistry*. R. F. Gould (Ed.), Advances in Chemistry Series, American Chemical Society, Washington, 1967.]

Dark brown $BaAmO_3$ forms when a mixture[41] of BaO (or $BaCO_3$) and AmO_2 (1.09:1) is heated in air at 1250°C for 30 hr. Synthesis of $BaAmO_3$ can also be effected by thermal decomposition of Ba_3AmO_6 at temperatures above 1100°C. $BaAmO_3$ dissolves in dilute acids with disproportionation of Am(IV).

Reduction[41] of $BaAmO_3$ with H_2 at 1250°C produces $BaAm_2O_4$ ($BaO \cdot Am_2O_3$), which has the structure of $CaFe_2O_4$.

Strontium. In the strontium–americium–oxygen system, the following compounds exist:[41,156]

Am(VI)	Sr_3AmO_6
Am(IV)	$SrAmO_3$
Am(III)	$SrAm_2O_4$ ($SrO \cdot Am_2O_3$)

These compounds are completely analogous to those in the barium–americium–oxygen system and are prepared by similar solid-state reactions.

Ternary Oxides with Curium. Curium(IV) is stabilized[157] by formation of solid solutions of CmO_x in AmO_2. Table 4.3 lists the phases known in the americium–curium–oxygen system for oxygen/americium + curium > 1.5.

Ternary Oxides with Zirconium, Hafnium, and Thorium. *Zirconium.* A one-phase solid solution with the fluorite structure exists above 18 mol % AmO_2 in the AmO_2–ZrO_2 system at 1200 to 1400°C (Fig. 4.11).

Figure 4.12 shows the phases present in the $AmO_{1.5}$–ZrO_2 system at 1200°C (Refs. 41, 158). Besides the pure starting components, two one-phase regions exist: a tetragonal solid solution of 0 to 6 mol % $AmO_{1.5}$ and a cubic solid solution of about 32 to 55 mol % $AmO_{1.5}$. According to Keller,[41] "In the cubic solid solution, in whose region exists $Am_2Zr_2O_7$ with the pyrochlore-type structure, a continuous transition from the fluorite phase to the pyrochlore phase can be observed."

Hafnium. The americium–hafnium–oxygen system has not been studied as intensively as the corresponding americium–zirconium–oxygen system. Qualitatively,[41,158] a one phase solid solution with the fluorite structure exists in the AmO_2–HfO_2 system, but the extent of the solid-solution region is unknown. Keller[41] reports that the $AmO_{1.5}$–HfO_2 system is considerably more simple than the $AmO_{1.5}$–ZrO_2 system. According to Keller, a 1:1 compound $Am_2Hf_2O_7$ with the pyrochlore structure exists in the $AmO_{1.5}$–HfO_2 system.

Thorium. Thoria and AmO_2 form a complete series of solid solutions.[41,158] Keller[41] states, "The solubility of $AmO_{1.5}$ in ThO_2 at 1300°C is about 50 mol %. In this case the pure fluorite structure remains, the lack of oxygen is balanced by the formation of statistically distributed oxygen holes. An exact determination of the solubility of $AmO_{1.5}$ in ThO_2 is possible in practice only by quoting a large margin of error because the lattice constants of ThO_2 ($a = 5.599$ Å) and those of the cubic $AmO_{1.5}$ ($a/2 = 5.515$ Å) are relatively close to each other, and, moreover, the quality

Table 4.3

PHASES IN THE SYSTEM AMERICIUM–CURIUM–OXYGEN

		Phase						
				Lattice constants, Å				
Composition*	**Cations present**	**Formula**	**Symmetry**	a	b	c	β	**Conditions**
$2.00 \leqslant O/M \leqslant 1.98$	Am^{4+}, Cm^{4+}	$(Am_{0.30}, Cm_{0.70})O_{2.00}$	fcc	5.368				350°C in O_2
$1.93 \leqslant O/M \leqslant 1.80$	Am^{4+}, Cm^{4+}, Cm^{3+}	$(Am_{0.30}, Cm_{0.70})O_{1.83}$	fcc	5.433				550°C in O_2
$1.80 \leqslant O/M \leqslant 1.68$	Am^{4+}, Cm^{4+}, Cm^{3+}	$(Am_{0.30}, Cm_{0.70})O_{1.085}$	Rhombohedral	6.687			99.47°	760°C in He
$1.72 \leqslant O/M \leqslant 1.52$	Am^{4+}, Am^{3+} Cm^{4+}, Cm^{3+}	$(Am_{0.30}, Cm_{0.70})O_X$	bcc	10.935 11.004				990°C in He 915°C in 4% H_2/He
$O/M = 1.50$	Am^{3+}, Cm^{3+}	$(Am_{0.64}, Cm_{0.36})O_{1.5}$	Monoclinic	14.321	3.665	8.926	100.17°	1100°C in 4% H_2/He
$O/M = 1.50$	Am^{3+}, Cm^{3+}	$(Am_{0.64}, Cm_{0.36})O_{1.5}$	Hexagonal	3.980		5.980		1500°C in 4% H_2/He

*M = americium + curium

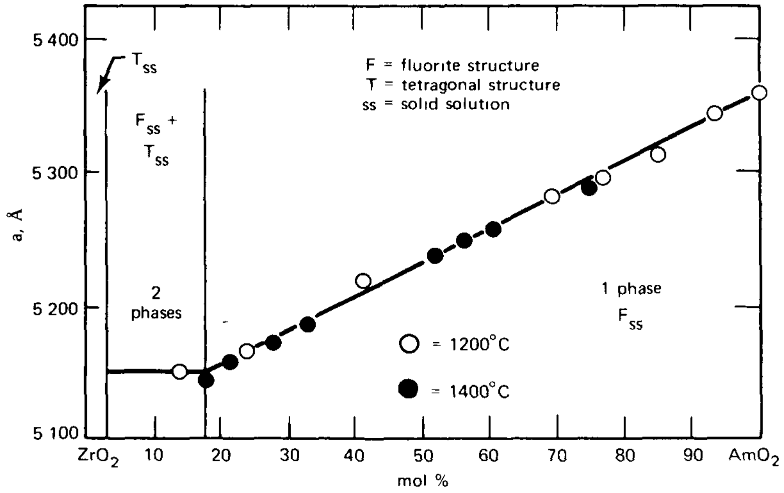


Fig. 4.11 The AmO_2-ZrO_2 system. [From C. Keller, The Solid State Chemistry of Americium Oxides, in *Lanthanide/Actinide Chemistry*, R. F. Gould (Ed.), Advances in Chemistry Series, American Chemical Society, Washington, 1967.]

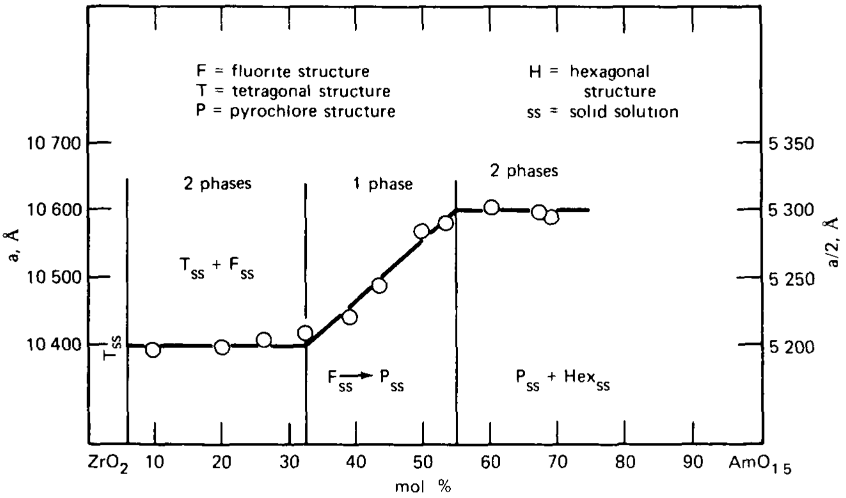


Fig. 4.12 The $AmO_{1.5}-ZrO_2$ system—lattice constants and solid solutions at 1200°C [From C. Keller, The Solid State Chemistry of Americium Oxides, in *Lanthanide/Actinide Chemistry*, R. F. Gould (Ed.), Advances in Chemistry Series, American Chemical Society, Washington, 1967.]

of X-ray powder patterns of samples above 50 mol % $AmO_{1\ 5}$ leaves much to be desired "

Oxides with Niobium, Tantalum, and Protactinium *Niobium* $AmNbO_4$ Monoclinic α $AmNbO_4$ is produced by the solid-state reaction of AmO_2 and Nb_2O_5 ($2AmO_2\ \ Nb_2O_5$) for 24 hr at 1200°C (Refs 41, 45) When heated, α $AmNbO_4$ transforms to β $AmNbO_4$ at 600 ± 20°C (Ref 45), β $AmNbO_4$, which has the tetragonal scheelite structure, is unstable below 660°C and cannot be stabilized even by fast quenching

$Am_{0\ 33}NbO_3$ When mixed in the proportions $2AmO_2\ \ 3Nb_2O_5$, AmO_2 and Nb_2O_5 react at 1200°C in H_2, air, or a vacuum to produce pale-rose $Am_{0\ 33}NbO_3$ (Refs 41 and 42) This compound is isostructural with tetragonal $La_{0\ 33}TaO_3$

Ba_2AmNbO_6 At 1300°C, α-$AmNbO_4$ reacts with BaO to form Ba_2AmNbO_6 (Refs 41 and 45) This latter compound has the "ordered" perovskite structure This compound can also be synthesized by direct solid-state reaction of AmO_2, Nb_2O_5, and BaO (Ref 45)

$AmNbTiO_6$ Yellow-brown orthorhombic $AmNbTiO_6$ is easily prepared by reaction of α-$AmNbO_4$ with TiO_2 at 1150°C for 24 hr in air [41,45]

Tantalum Solid-state reactions between Ta_2O_5 and AmO_2 yield α-$AmTaO_4$, β-$AmTaO_4$, and $Am_{0\ 33}TaO_3$ (Refs 41, 42, and 45), these compounds and the conditions for their preparation are completely analogous to those already described for the americium–niobium–oxygen system The compounds Ba_2AmTaO_6 and $AmTaTiO_6$ are also known[41,45] and are prepared like the corresponding niobium compounds

Protactinium $AmPaO_4$ The solid-state reaction[45] between AmO_2 and Pa_2O_5 ($2AmO_2\ \ PaO_3$) for 8 hr at 1100°C results in a double oxide $[Am_{0\ 5}(III),Pa_{0\ 5}(V)]O_2$ (= $AmPaO_4$) that, according to Keller,[41] has a fluorite-type structure with a statistical distribution of metal ions The double oxide[45] is insoluble in acids but can be solubilized by fusion with $K_2S_2O_7$

Ba_2AmPaO_6 At 1350 to 1400°C $(Am_{0\ 5},Pa_{0\ 5})O_2$ reacts with BaO or $BaCO_3$ to form Ba_2AmPaO_6 (Refs 41, 45, 159) The latter compound has an ordered perovskite type of structure [41]

Phosphate $AmPO_4 \cdot xH_2O$ Light pink Am(III) phosphate precipitates when a dilute solution of either H_3PO_4, Na_2HPO_4, or $(NH_4)_2HPO_4$ is added to a weakly acidic ($[H^+] < 0\ 1M$)Am^{3+} solution [45] Hexagonal $AmPO_4 \cdot 0\ 5H_2O$ is obtained when the precipitate is dried at 200°C or lower temperature Anhydrous $AmPO_4$ is obtained at higher drying temperatures The anhydrous compound[45] is stable up to 1000°C and can also be obtained by direct reaction of stoichiometric amounts of AmO_2 and $(NH_4)_2HPO_4$ at 600 to 1000°C Dilute acid solutions readily dissolve $AmPO_4 \cdot 0\ 5H_2O$, but monoclinic $AmPO_4$ dissolves only in boiling acid solution

Phosphide AmP Charvillat et al [44b,137c] synthesized AmP by reaction at 580°C of red phosphorus on AmH_3 in a sealed quartz tube The monophosphide has the cubic NaCl structure with a = 5 7114 ± 0 0003 Å

Scandate $AmScO_3$ Pink $AmScO_3$ forms when stoichiometric proportions of AmO_2 and Sc_2O_3 are heated in highly purified H_2 at 1100 to 1700°C (Ref 160) A convenient starting material for the solid state reaction is obtained by coprecipitation of the hydroxides of americium and scandium

According to Keller and Berndt[146] oxidation of $AmScO_3$ or the solid-state reaction of AmO_2–Sc_2O_3 mixtures results in the formation of a fluorite phase Keller and Berndt also find that AmO_2 takes up small amounts of Sc_2O_3 into solid solution, 0 5 mol % at 1100°C to 4 7 mol % at 1550°C But even in this system there is some loss of oxygen of AmO_2 at high temperatures leading to an increased solubility of Sc_2O_3 in $AmO_{2\ x}$

Selenides $AmSe$ Charvillat et al [137c] prepared AmSe by reacting AmH_3 with a stoichiometric amount of selenium at 800°C in a vacuum The resulting product after pelletizing and further heating at 1100 to 1200°C contained two phases—Am_3Se_4 (Th_3Pu_4 structures) and a second phase (NaCl structure) that Charvillat et al identified as cubic AmSe

$AmSe_{2\ x}$ Nonstoichiometric black $AmSe_{2\ x}$ is prepared by heating an excess of selenium metal with AmH_3 for 1 week at 400°C under high vacuum[161] X ray diffraction analyses indicate the resulting product is a nonstoichiometric compound with a composition near $AmSe_{1\ 8}$ Roddy[30] has also prepared what appears to be tetragonal $AmSe_2$ by heating ^{243}Am metal or hydride with selenium metal for 24 hr at 950°C His results also suggest that a range of homogeneity may exist in the americium–selenium system

Am_3Se_4 Body-centered cubic Am_3Se_4 results when a mixture of 50 wt % americium metal and 50 wt % selenium metal is heated for 1 hr at 217°C and then 7 hr at 850°C before furnace cooling to room temperature[43] Roddy[30] also prepared Am_3Se_4 by heating ^{243}Am metal with metallic selenium 24 hr at 950°C X-ray diffraction measurements show that the products of such preparations contain at least two phases that persist even after heat-treating for 10 to 14 days at 750 to 800°C The major phase[44] in the final product is Am_3Se_4, which is isostructural with Th_3P_4 and is without magnetic ordering down to 4 2°K

Silicate $AmSiO_4$ Hydrothermal reaction of $Am(OH)_4$ with excess SiO_2 in 1*M* $NaHCO_3$ solution for 1 week at 230°C yields brown $AmSiO_4$ that has the zircon structure[119] On heating, $AmSiO_4$ decomposes to AmO_2 and SiO_2 without forming intermediate silicates A process for manufacturing alpha sources has been patented[162] which consists of fixing onto a metallic or ceramic support a layer of an enamel containing $^{241}AmSiO_4$ This layer is obtained by melting an enamel powder containing ^{241}Am on the surface of the support

Sulfates. *$Am_2(SO_4)_3 \cdot xH_2O$.* Evaporation of a neutral solution of Am(III) sulfate yields thick, tabular, pale yellow-pink crystals of $Am_2(SO_4)_3 \cdot 8H_2O$ of lengths up to 0.5 mm.[163] Crystals of the octahydrate, after being dried in air, are stable for several days.

On the basis of analyses for americium, sulfate, and water, Yakovlev et al [164] assign the formula $Am_2(SO_4)_3 \cdot 5H_2O$ to the precipitate obtained by adding ethanol to a solution of Am(III) in 0.5*M* H_2SO_4

Hall and Markin[70] prepared white anhydrous $Am_2(SO_4)_3$ by heating hydrated americium sulfate to a temperature of 550 to 650°C in air Thermogravimetric data obtained by these workers are shown in Fig 4.13. Anhydrous $Am_3(SO_4)_3$ does not take up water when cooled to room temperature in air

Am(III) Double Sulfates The following double sulfates[100,164,165] can be prepared by addition of an alkali metal sulfate solution to a solution of Am(III) in 0.5*M* H_2SO_4

$KAm(SO_4)_2$
$NaAm(SO_4)_2 \cdot H_2O$
$KAm(SO_4)_2 \cdot 2H_2O$
$RbAm(SO_4)_2 \cdot 4H_2O$
$CsAm(SO_4)_2 \cdot 4H_2O$
$TlAm(SO_4)_2 \cdot 4H_2O$
$K_3Am(SO_4)_3 \cdot H_2O$
$K_8Am_2(SO_4)_7$
$Cs_8Am_2(SO_4)_7$
$Tl_8Am_2(SO_4)_7$

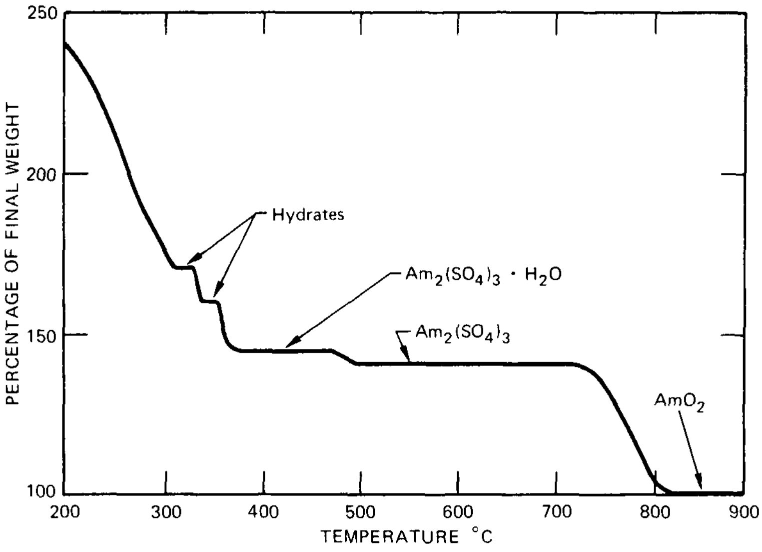


Fig. 4.13 Thermogravimetric analysis of $Am_2(SO_4)_3 \cdot xH_2O$ [From G R Hall and T. L Markin, The Alpha Half-Life of Americium-241, *Journal of Inorganic and Nuclear Chemistry*, **4**: 137 (1975)]

Ratios of $[M^+]/[Am^{3+}]$ (M = Na, K, Rb, Cs, or Tl) at which the various double sulfates precipitate are given in Ref 164 The absorption spectra of certain of the crystalline double salts between 400 and 800 nm at 80, 200, and 300°K have also been reported,[164] but, apparently, X ray diffraction data for the double sulfates have not been obtained Coprecipitation of trace amounts of Am^{3+} with K_2SO_4 and $La_2(SO_4)_3$ has also been studied [166 168]

$\{[Co(NH_3)_6]HSO_4\}_2\{AmO_2(SO_4)_3\} \cdot nH_2O$ Hexammine cobalt(III) americyl(VI)–sulfate is prepared by addition of hexammine cobalt(III) ions to an aqueous sulfate solution containing AmO_2^{2+} (Ref 169) The orange cubic crystals (diamond type structure) are isostructural with the corresponding UO_2^{2+} and NpO_2^{2+} compounds No precipitate forms, however, in an ammonium sulfate solution containing Am(III) and hexammine cobalt(III) ions [170]

Sulfides Am_2S_3 The alpha form of americium sesquisulfide is obtained[171] by vapor phase reaction for 4 days of a stoichiometric amount of sulfur with AmH_3 in a quartz and Pyrex tube sealed under high vacuum The quartz end of the tube is kept at 500°C, and the Pyrex part is maintained at 300°C to prevent sulfur from condensing

When heated in a vacuum[171] at 1300°C, α Am_2S_3 changes to pure γ-Am_2S_3 Pure γ-Am_2S_3 can also be prepared[50] by passing a mixture of H_2S and CS_2 gases over heated (1400 to 1500°C) AmO_2 for 5 min The crystal structure of γ Am_2S_3 has been determined by Zachariasen [172]

AmS Thermal decomposition[171] of α-Am_2S_3 in vacuum at 650°C yields AmS as well as γ-Am_2S_3 The americium–sulfur distance in cubic AmS is 2 796 Å

$AmS_{2\ x}$ Americium disulfide[161] is prepared by the same procedure used to make $AmSe_{2\ x}$—namely, by heating under vacuum an excess of sulfur with AmH_3 for 1 week at 400°C Analogous to $AmSe_{2\ x}$, the coarse black disulfide is a nonstoichiometric compound with a composition near $AmS_{1\ 9}$ The americium–sulfur distance is 2 93 Å in good agreement with an ionic binding between Am^{3+} and S^2

$Am_{10}S_{14}O(\beta\ Am_2S_3)$ When heated[173] at 1100°C in a high vacuum, α-Am_2S_3 transforms into β Am_2S_3 The formula of the β-Am_2S_3, according to Damien, Marcon, and Jove,[173] is more properly written $Am_{10}S_{14}O$ The tetragonal oxysulfide is isostructural with the rare earth and plutonium β sesquisulfides

Tellurides $AmTe$ To prepare americium monotelluride, Charvillat et al [137c] heated milligram amounts of AmH_3 with a stoichiometric quantity of elemental tellurium at 800°C in a vacuum The resulting product after pelletizing and further heating at 1100 to 1200°C contained two phases—Am_3Te_4 (Th_3Pu_4 structure) and a second phase (NaCl structure) that Charvillat et al identified as cubic AmTe

$AmTe_3$ Americium tritelluride[174] is prepared by vapor-phase reaction (120 hr at 350°C in a sealed tube) of excess tellurium (americium/tellurium = 3 5) on AmH_3 Orthorhombic $AmTe_3$ is isostructural with the corresponding rare-earth tritellurides

$AmTe_2$ Thermal dissociation of $AmTe_3$ at 400°C in a high vacuum ($<10^{-5}$ torr) yields tetragonal $AmTe_2$. The ditelluride is isostructural with the rare-earth ditellurides and likely has the Fe_2As type of structure. Damien[174] states that $AmTe_2$ prepared as described above is a tellurium-deficient compound, $AmTe_{2-x}$, with a rather large homogeneity range between 400 and 600°C.

Am_2Te_3 At temperatures[175] above 600°C, $AmTe_2$ dissociates into Am_2Te_3. By analogy with isostructural rare earth sesquitellurides, Damien and Charvillat[175] label Am_2Te_3 as an η form.

Am_3Te_4 The η-Am_2Te_3 phase is stable up to around 850°C, at 900°C, Am_3Te_4 is formed.[175] The latter compound was first prepared by Mitchell and Lam[43] using experimental procedures completely identical to those already described (see page 161) for preparation of Am_3Se_4. Body-centered cubic Am_3Te_4 is isostructural with Th_3P_4 and is without magnetic ordering[44] down to 4.2°K.

Oxytelluride? In the pattern of Am_3Te_4, Damien and Charvillat[175] assign four diffraction lines, which cannot be indexed in the bcc system, to an americium oxytelluride.

Tungstate Analogous to the reaction with MoO_3 (see page 151), solid-state reaction of WO_3 and AmO_2 at 700 to 900°C yields a ternary oxide of the empirical composition $Am_2W_3O_{12}$ (Ref. 133). This compound has the scheelite structure corresponding to the formula $Am_2(WO_4)_3$.

Vanadates. Red-brown $AmVO_4$ forms when AmO_2 is heated (10 hr at 600°C followed by 10 hr at 1000°C) with V_2O_5 in air.[41,42,45] $AmVO_4$ has the tetragonal zircon structure. Reduction with H_2 at 1200°C converts $AmVO_4$ to ochre-colored $AmVO_3$ with the $GdFeO_3$ structure.

Xenate. Addition of solid sodium perxenate to K_2CO_3 and Na_2CO_3 solutions of Am(III) precipitates Am(III) perxenate, $Am_4(XeO_6)_3 \cdot 40H_2O$ (Ref. 176). The color of the precipitate is orange when wet and orange tan when dried under vacuum at room temperature. The compound can be water washed without decomposition or loss by solubilization. Its solubility in distilled water at ≃23°C is $4.6 \times 10^{-5} M$. Americium perxenate dissolves in acids with evolution of gas to form Am(V) and Am(VI). Marcus and Cohen[176] report that Am(III) perxenate shows the characteristic absorption bands of Am(III) in the visible and near-infrared regions, as well as the characteristic infrared absorption at 650 to 680 cm^{-1} for the xenon–oxygen vibration in perxenate.

Compounds of Americium with Organic Ligands

Relatively few solid compounds of americium with organic ligands have yet been prepared, those known as of January 1976 are listed in Table 4.4. As revealed in the

Table 4.4

COMPOUNDS OF AMERICIUM WITH ORGANIC LIGANDS

No.	Organic reagent ligand	Compound	
		Formula	Color
1	Acetate	$NaAmO_2(OOCCH_3)_3$	Lemon yellow
2	Acetylacetone	$Am(C_5H_7O_2)_3 \cdot H_2O$	Pale rose
3	Benzoyltrifluoroacetone	$Am(C_{10}H_6F_3O_2)_3 \cdot 3H_2O$	Pale rose
4	Cyclooctatetraene	$KAm(C_8H_8)_2 \cdot 2THF^*$	Yellow
5	Cyclopentadiene	$Am(C_5H_5)_3$	Flesh
6	Dipivaloylmethane	$Am(C_{11}H_{19}O_2)_3$	
7	Formate	$Am(HCOO)_3 \cdot 0\ 2H_2O$	Pink
8	Hexafluoroacetylacetone	$CsAm(C_5HF_6O_2)_4 \cdot H_2O$	Yellow
9	8-Hydroxyquinoline	$Am(C_9H_6NO)_3$	Yellow green
10	5-chloro-8-hydroxyquinoline	$Am(C_9H_5ClNO)_3$	Dark green
11	5,7-dichloro-8-hydroxyquinoline	$Am(C_9H_4Cl_2NO)_3$	Green
12	Oxalate	$Am_2(C_2O_4)_3 \cdot 10H_2O$	Pink
13	Phthalocyanine	$Am(C_{32}H_{16}N_2)_2$	Dark violet
14	Pyridine-2-carboxylic acid	$AmO_2(C_5H_4NCOO)_2$	Red brown
15	Pyridine 2-carboxylic acid	$HAmO_2(C_5H_4NCOO)_3$	Red brown
16	Pyridine *N* oxide carboxylic acid	$AmO_2[C_5H_4N(O)COO]_2$	
17	Thenoyltrifluoroacetone	$Am(C_8H_4F_3O_2S)_3 \cdot 3H_2O$	Pale rose

*THF = tetrahydrofuran

ensuing discussion, aside from $Am_2(C_2O_4)_3$ which is well characterized, very little is known about either the preparation or properties of compounds of americium with organic ligands This situation will surely change in the future as ^{243}Am becomes more available and as interest in the bonding parameters of americium in compounds with cyclopentadiene and similar ligands continues to build

Acetate. Sodium Am(VI) acetate [$NaAmO_2(OOCCH_3)_3$] precipitates when sodium acetate is added to an acid solution of Am(VI) (Refs 177-179) The lattice constant of the lemon-yellow cubic crystals (space group = $P2_1/3$) is 10 653 ± 0 002Å, and their refractive index is 1 528 ± 0 002 (Ref 178) From infrared measurements, Jones[180] has determined the force constant of the americium–oxygen bond in $NaAmO_2(OOCCH_3)_3$ to be 6 12 megadynes $Å^{-1}$

Acetylacetone Dropwise addition of ammonia to an aqueous Am^{3+} solution containing a small excess of acetylacetone precipitates at pH 6 to 6 3 pale-rose $Am(C_5H_7O_2)_3 \cdot H_2O$ (Ref 181a) The crystalline precipitate obtained after stirring for 24 hr is recrystallized from ethanol and dried in air over silica gel or P_2O_5 It decomposes to AmO_2 when heated in air at 200 to 400°C

Benzoyltrifluoroacetone. To prepare $Am(C_{10}H_6F_3O_2)_3 \cdot 3H_2O$, an aqueous Am(III) solution adjusted to pH 4 5 is added dropwise, with warming, to slightly less than the stoichiometric amount of $NH_4C_{10}H_6F_3O_2$ (Ref 181a) The pale-rose precipitate is recrystallized from ethanol and dried in air When heated in air at 200 to 400°C, $Am(C_{10}H_6F_3O_2)_3 \cdot 3H_2O$ decomposes directly to AmO_2

Cyclooctatetraene. Karraker[181b] has recently announced preparation of potassium *bis*(cyclooctatetraenyl)Am(III) by the reaction of $K_2C_8H_8$ in tetrahydrofuran (THF) solution with $^{241}AmI_3$ Metal analysis of the solid is consistent with the formula $KAm(COT)_2 \cdot 2THF$, whereas X-ray powder-diffraction patterns show it to be isostructural with $KPu(COT)_2 \cdot 2THF$ The compound $KAm(COT)_2 \cdot 2THF$ decomposes in water and burns when exposed to air The absorption spectrum of $KAm(COT)_2 \cdot 2THF$ in THF solution shows the characteristic spectrum of Am^{3+}

Cyclopentadiene. Tri(cyclopentadienide)Am(III), $Am(C_5H_5)_3$, is prepared by reacting either $AmCl_3$ (Refs 182, 183a, and 183b) or AmF_3 (Ref 183c) with molten $Be(C_5H_5)_2$ according to Eqs 4 24 and 4 25

$$2AmCl_3 + 3Be(C_5H_5)_2 \xrightarrow{65°C} 2Am(C_5H_5)_3 + 3BeCl_2 \tag{4 24}$$

$$2AmF_3 + 3Be(C_5H_5)_2 \xrightarrow{70°C} 2Am(C_5H_5)_3 + 3BeF_2 \tag{4 25}$$

Baumgartner et al [182] state that pure $Am(C_5H_5)_3$ can be obtained by fractional sublimation at 10^{5} torr and 160 to 205°C The flesh-colored compound does not melt below 330°C when heated in argon but darkens at higher temperatures. Unlike $Pu(C_5H_5)_3$, $Am(C_5H_5)_3$ is not pyrophoric, it decomposes only slowly in air [182] In water or dilute acids, the compound decomposes, with evolution of gas and deposition of white flocks, to give a rose-colored Am(III) solution

The infrared spectrum of $Am(C_5H_5)_3$ shows characteristic absorption bands at 768/795 cm^{-1}, 841 cm^{-1}, 1007 cm^{-1}, 1448 cm^{-1}, and 3078 cm^{-1} (Ref 184) The room-temperature absorption spectrum of $Am(C_5H_5)_3$ between 4455 cm^{-1} and 40,000 cm^{-1} has been measured [185] On the basis of the published absorption spectrum, Nugent et al [186] estimate that the organometallic bonding in $Am(C_5H_5)_3$ is highly ionic with a covalency only about 2 8 ± 0 2% relative to the corresponding bands of Am^{3+}_{aq} For this reason they state that $Am(C_5H_5)_3$ should be designated as a tricyclopentadienide rather than as a tricyclopentadienyl

The magnetic moment of $Am(C_5H_5)_3$ is reported[187] to be 1 74 Bohr magnetons

Dipivaloylmethane. Danford et al [188] at Oak Ridge National Laboratory precipitate $Am(C_{11}H_{19}O_2)_3$ by adding aqueous Am(III) sulfate to a solution of dipivaloylmethane (dpm) (2,2,6,6-tetramethyl-3,5-heptanedione) and NaOH in 70% aqueous ethanol Following the precipitation step, two-thirds of the mother liquor is removed by vacuum evaporation The precipitate is extracted with ethanol, one-quarter volume of water is added to the alcohol extracts, and the ethanol is evaporated in a stream of nitrogen to reprecipitate the complex The precipitate, after drying in vacuo at room temperature, is purified by sublimation at 124 to 135°C at 10^{5} torr for 1 5 hr It melts at 215 to 218°C after softening at 205°C (Ref 183c) Monoclinic unit-cell dimensions are [183c] a = 12 2(2) Å, b = 28 3(3) Å, c = 22 4(3) Å, β = 106 4(9)°

Sakanoue and Amano[189] have recently determined the volatility of $Am(C_{11}H_{19}O_2)_3$ [$Am(dpm)_3$] and various lanthanide dipivaloylmethanato complexes at 180°C and 10^{-3} torr Their results yield the following order for the volatilities

$$\mathrm{La(dpm)_3} < \begin{matrix}\mathrm{Pr(dpm)_3} \\ \mathrm{Am(dpm)_3}\end{matrix} < \begin{matrix}\mathrm{Eu(dpm)_3} \\ \mathrm{Gd(dpm)_3}\end{matrix} < \mathrm{Sc(dpm)_3}$$

Sakanoue and Amano[189] also determined that $Am(dpm)_3$ was less volatile than $Th(dpm)_3$, $Pu(dpm)_3$, or $Cf(dpm)_3$

Formate Hydrated Am(III) formate [$Am(HCOO)_3 \cdot 0\ 2H_2O$] crystals form when $Am(OH)_3$ is dissolved in concentrated formic acid at 50°C and the excess acid is evaporated [58] The lattice constants of the hexagonal pink crystals are a = 10 55 Å and c = 4 07 Å

Weigel and ter Meer[60] report that thermal decomposition of $Am(HCOO)_3$ proceeds according to the following reaction sequence

$$\mathrm{Am(HCOO)_3} \xrightarrow{300-350^\circ C} \mathrm{AmO(HCOO)} + \mathrm{H_2} + \mathrm{CO} + \mathrm{CO_2} \qquad (4\ 26)$$

$$2\mathrm{AmO(HCOO)} \xrightarrow{400-500^\circ C} \mathrm{Am_2O_3CO_3} + \mathrm{H_2} + \mathrm{CO} \qquad (4\ 27)$$

$$\mathrm{Am_2O_2CO_3} \xrightarrow{520^\circ C} \mathrm{Am_2O_3} + \mathrm{CO_2} \qquad (4\ 28)$$

Hexafluoroacetylacetone. Yellow $CsAm(C_5HF_6O_2)_4 \cdot H_2O$ precipitates when an excess of $CsC_5HF_6O_2$ in 50 vol % ethanol is added to an $AmCl_3$ solution and the solution is evaporated to half its volume [188,190] A product melting at 189 to 191°C results when the yellow crystals are washed with water and dried in air The melting point increases to 193 to 194°C after vacuum sublimation at 130 to 140°C at 10^{6} torr (Ref 188) According to Ref 191, "It is not clear whether this increase in melting point is due to dehydration, for the pale-rose, anhydrous compound is obtained when the monohydrate is recrystallized from 1 butanol "

Hydroxyquinoline *8 Hydroxyquinoline* Keller, Eberle, and Mosdzelewski[192] report that yellow-green $Am(C_9H_6NO)_3$ precipitates when an Am(III) solution is added dropwise to a pH 5 5 to 6 5 solution of 8-hydroxyquinoline in 0 1*M* ammonium acetate At 25°C, $Am(C_9H_6NO)_3$ is soluble in ether, acetone, methanol, dioxane, and chloroform to the extent of only 2 5 × 10^{5} to 7 × 10^{5} mols liter^{-1}

5-Chloro-8-Hydroxyquinoline. Dark-green $Am(C_9H_5ClNO)_3$ precipitates on addition of an Am(III) solution to a pH 5.1 to 5.9, 30 vol.% dioxane solution of 5-chloro-8-hydroxyquinoline in 0.1*M* ammonium acetate.[192]

5,7-Dichloro-8-Hydroxyquinoline. Addition of an Am(III) solution to a 65 vol.% dioxane solution of 5,7-dichloro-8-hydroxyquinoline in 0.1*M* ammonium acetate at pH 5.7 to 6.0 precipitates green $Am(C_9H_4Cl_2NO)_3$ (Ref. 192). This compound and also $Am(C_9H_5ClNO)_3$ are about 1000-fold more soluble in ether, acetone, methanol, dioxane, and chloroform than is $Am(C_9H_6NO)_3$. The absorption spectrum of $Am(C_9H_6Cl_2NO)_3$ in $CHCl_3$ exhibits a band at 3900 Å characteristic of *tris* chelates.

Oxalate. Pink, monoclinic $Am_2(C_2O_4)_3 \cdot 10H_2O$ precipitates from a slightly acidic or neutral solution of Am^{3+} on addition of oxalic acid or suitable alkali oxalate solution (Refs. 100, 141, 150, 193, and 194). Lattice constants of the crystalline hydrate are $a = 11.19$ Å, $b = 9.63$ Å, and $c = 10.24$ Å with $\beta = 114.4°$. The space group[58] is *P*2/*b*. The solubility product[195] of Am(III) oxalate in 0.2*M* to 0.3*M* $HClO_4$ is 2.2×10^{-31}. Attempts to measure the solubility product in water were unsuccessful. The solubility of Am(III) oxalate in nitric acid–oxalic acid solutions has been measured by Burney and Porter.[196]

From their recent X-ray diffraction studies, Weigel and ter Meer[58] conclude that the value of x in $Am_2(C_2O_4)_3 \cdot xH_2O$ is 10. [Previously the number of water molecules in hydrated Am(III) oxalate was thought to vary with the conditions of precipitation and drying; values of $x = 7$ (Ref. 197), 9 (Ref. 100), and 11 (Ref. 193) were reported.] Weigel and ter Meer[58] note that Nd^{3+} and Am^{3+} have nearly the same ionic radius. Ollendorff[198] has shown that Nd(III) oxalate is $Nd_2(C_2O_4)_3 \cdot 10H_2O$. Plutonium(III) and Cm(III) are also decahydrates.[199]

Weigel and ter Meer[60] studied the thermal decomposition of $Am_2(C_2O_4) \cdot 10H_2O$ in air using mass spectrometric identification of gaseous decomposition products and X-ray identification of solid residues. Their results, listed in Table 4.5, extend and modify those reported earlier by Markin[197] for decomposition of the "heptahydrate." Radiolytic decomposition of ^{241}Am(III) oxalate to yield first anhydrous Am(III) carbonate (15 to 20 days) and then its pentahydrate (50 to 60 days) is a first-order reaction with a rate constant of 0.22 d^{-1} (Ref. 200).

Phthalocyanine. Weighable amounts of $Am(C_{32}H_{16}N_8)_2$ have been prepared by reaction of AmI_3 at 200°C with phthalodinitride in 1-chloronapthene.[201] According to Lux,[202] $Am(C_{32}H_{16}N_8)_2$ is the first Am(IV) compound with organic ligands to be prepared. Dark-violet $Am(C_{32}H_{16}N_8)_2$ sublimes without decomposition at 550°C at 10^{-5} torr and is stable in air.[202] Spectroscopic evidence also indicates[202] that americium also forms a mono(phthalocyaninato) compound which sublimes at 450 to 500°C at 10^{-5} torr.

Pyridine Carboxylates. *Pyridine-2-Carboxylates.* Addition of pyridine-2-carboxylic acid (C_6H_5NCOOH) to a solution of AmO_2^{2+} precipitates either americyl(VI)

Table 4.5

THERMAL DECOMPOSITION OF $Am_2(C_2O_4)_3 \cdot 10H_2O$

Initial phase	Temperature interval	Final phase
$Am_2(C_2O_4)_3 \cdot 10H_2O$	25 50°C	$Am_2(C_2O_4)_3 \cdot 6H_2O$
$Am_2(C_2O_4)_3 \cdot 6H_2O$	50 340°C (over 4 hydrate forms)	$Am_2(C_2O_4)_3$
$Am_2(C_2O_4)_3$	390–430°C	$Am_2(CO_3)_3$
$Am_2(CO_3)_3$	430 470°C	$Am_2O(CO_3)_2$
$Am_2O(CO_3)_2$	470–520°C	$Am_2O_2CO_3$
$Am_2O_2CO_3$	520 610°C	Am_2O_3

pyridine-2-carboxylate $[AmO_2(C_6H_5NCOO)_2]$ or a complex acid of the composition $H[AmO_2(C_6H_5NCOO)_3]$ (Refs 203, 204) The particular compound precipitated depends, as discussed in Ref 203, upon solution pH and the concentration of the pyridine carboxylic acid Both compounds are crystalline red-brown powders soluble in pyridine The $H[AmO_2(C_6H_5NCOO)_3]$ compound decomposes to AmO_2 at about 340°C

*Pyridine-*N*-Oxide-2-Carboxylate* Americyl(VI) pyridine-*N*-oxide-2-carboxylate, $AmO_2[C_6H_5N(O)COO]_2$, precipitates when pyridine-*N*-oxide-2-carboxylic acid is added to an aqueous AmO_2^{2+} solution[204] The precipitate is soluble in pyridine and dimethyl sulfoxide and, when heated, dehydrates at 100°C and decomposes at temperatures above 200°C

Thenoyltrifluoroacetone Preparation of Am(III) thenoyltrifluoroacetone $[Am(C_8H_4F_3O_2S)_3 \cdot 3H_2O]$ is accomplished in exactly the same way (see pages xxx to xxx) as the benzoyltrifluoroacetone complex[181] The pale-rose precipitate decomposes directly to AmO_2 when heated in air at 200 to 400°C

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5 RECOVERY; SEPARATION; PURIFICATION

INTRODUCTION

Present-day technology for recovery and purification of americium involves principally aqueous ion exchange and solvent extraction methods supplemented, in some cases, by precipitation processes. Using the chemistry discussed in Chaps. 3 and 4, these procedures are applied not only to recover and separate americium from a variety of aqueous feedstocks, including high-level Purex-process waste, but also to purify it from curium and lanthanides. Although methods used primarily for analytical purposes or tested only on a laboratory-scale are cited, emphasis in this review is on those aqueous procedures used either currently or previously to recover and purify gram to kilogram amounts of americium.

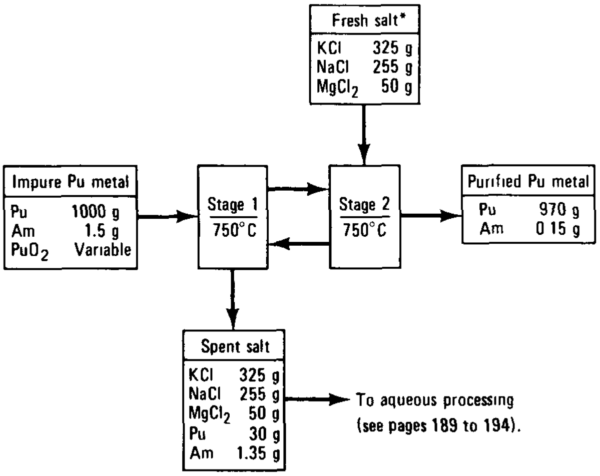
Only little use has thus far been made of nonaqueous methods for separating and purifying americium—a notable exception is the pyrochemical process used at the Energy Research and Development Administration (ERDA) Rocky Flats Plant to remove ^{241}Am from molten plutonium metal. The pyrochemical process, as well as significant features of americium chemistry in other nonaqueous processes, is described in the first part of this chapter.

PYROCHEMICAL PROCESSES

Rocky Flats Americium Extraction Processes

Currently at the ERDA Rocky Flats Plant, a countercurrent molten-salt extraction process is used to purify multikilogram amounts of plutonium metal from ^{241}Am which grows in by beta decay of ^{241}Pu (Refs. 1 to 4). This two-stage batch purification scheme, which is based partly on earlier molten salt–molten metal studies at Los Alamos Scientific Laboratory (LASL)[5] and Argonne National Laboratory (ANL),[6] removes about 90% of the americium from plutonium metal typically contaminated with 200 to 2000 ppm ^{241}Am.

The charge to the first stage of this Rocky Flats process (Fig. 5.1) consists of plutonium metal contaminated with ^{241}Am and gram quantities of PuO_2 and a salt initially composed of KCl–47.1 mol % NaCl–5.8 mol % $MgCl_2$ which has previously been contacted in Stage 2 with plutonium metal partially depleted in americium.* This charge, contained in a tantalum crucible, is heated under an argon atmosphere in a resistance furnace at 750°C; the molten phases are stirred 1 hour at 750°C with a flat-bladed tantalum stirrer and then cooled to room temperature. [A specially designed tilt-pour furnace is being tested for use in the molten-salt extraction



*Salt/metal ratio variable, depending on ^{241}Am content of Pu metal

Fig. 5.1 Rocky Flats molten-salt americium extraction process.

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*According to Knighton et al.,[382] the $MgCl_2$ content of the salt has been increased from 8 to 30 mol %, whereas the salt/metal ratio has been decreased from 0.56 to 0.056.

process.[7]] Plutonium metal resulting from Stage 1 is contacted in Stage 2 with fresh KCl–NaCl–$MgCl_2$ salt under the same conditions as in Stage 1. The particular salt/metal ratio used depends on the ^{241}Am content of the feed plutonium and is chosen to ensure removal of about 90% of the americium; a typical salt/metal ratio is[2] 0.56.* Salt from Stage 1, which has had two contacts with plutonium metal, is currently processed by aqueous methods (see pages 190 to 194) for recovery of americium and plutonium values. Originally[3,4] the process was operated in a cross-current mode with a salt composed of KCl–49.1 mol % NaCl–1.8 mol % $MgCl_2$. Countercurrent operation with a salt phase containing 5.8 mol % $MgCl_2$ reduces the amount of americium-bearing salt which must be subsequently processed.

In the Rocky Flats process, americium is oxidized by $MgCl_2$ and $PuCl_3$ by the following reactions:

$$Am^0 + \tfrac{3}{2}MgCl_2 \rightarrow AmCl_3 + \tfrac{3}{2}Mg^0 \qquad (5.1)$$

$$Am^0 + PuCl_3 \rightarrow AmCl_3 + Pu^0 \qquad (5.2)$$

Knighton[8] notes that distribution of americium between metal and salt phases correlates with the $\tfrac{3}{2}$ power of the $MgCl_2$ mole fraction. This indicates that americium in the salt phase is present in the trivalent state (Eq. 5.1) rather than as Am^{2+}, which might be expected from the work of Mullins, Beaumont, and Leary.[9a,9b] Plutonium oxide has also been shown to extract americium from plutonium metal;[9c] the side reaction between PuO_2 and americium in Stage 1 (Fig. 5.1) enhances removal of americium from the metal phase.

Current research effort by personnel at the Rocky Flats Plant on the americium extraction process is centered on reducing still further the salt/metal ratio and in developing nonaqueous methods of recovering americium and plutonium values from spent salt.* With respect to the former objective, recent tests[8] (Table 5.1) show that, at corresponding $MgCl_2$ contents, the value of the americium distribution coefficient is much higher with an NaCl–$CaCl_2$–$MgCl_2$ salt than with the NaCl–KCl–$MgCl_2$ mixture. In verification of these distribution data, countercurrent, two-stage production-scale tests with a 45 mol % NaCl–50 mol % $CaCl_2$–5 mol % $MgCl_2$ salt demonstrated satisfactory (>90%) removal of americium from plutonium metal containing about 1500 ppm ^{241}Am at a salt/metal ratio of 0.2.

A potential disadvantage of substituting $CaCl_2$ for KCl is that the aqueous methods (see pages 190 to 194 and 233 to 243) currently used to process spent extraction salt will not easily separate americium from large amounts of calcium. A pyrochemical procedure involving reduction with calcium metal appears suitable, however, for recovery of americium and plutonium values from both spent NaCl–$CaCl_2$–$MgCl_2$ and NaCl–KCl–$MgCl_2$ salts.[8] In addition to a metal button containing plutonium and americium contaminated with magnesium and calcium, the

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*See footnote on page 185.

Table 5.1

AMERICIUM PARTITION BETWEEN MOLTEN PLUTONIUM AND $NaCl-CaCl_2-KCl-MgCl_2$ SALTS

$MgCl_2$, mol %	Americium distribution coefficient (K_d)*	
	$NaCl-KCl-MgCl_2$	$NaCl-CaCl_2-MgCl_2$
5	3.1	13
10	8.7	20
15	15.9	29
20	24.5	39
30	45.0	60
40	69.2	85
50	97.0	112

*K_d = wt.% Am in salt/wt.% Am in metal.

products of the reduction reaction are a white salt (four parts) and a black salt (one part) with some metallic modular inclusions. Preliminary indications are that the white salt contains sufficiently small amounts of americium and plutonium (typically $10^{-4}-10^{-3}$ g Pu/g salt and 10^{-5} g Am/g salt) that it can be discarded without further processing or, possibly, reused. Hydroxide precipitation methods (pages 190 to 194) can be used to recover and purify americium and plutonium from acid solutions of the metal button and black salt.

Also under development for removing plutonium and americium from chloride melts is a pyrochemical process that involves scrubbing the molten salt with an Mg–90 wt.% Zn alloy. The resulting scrub alloy buttons can be satisfactorily dissolved in 4*M* HNO_3–0.2*M* HF solution to prepare feedstock for further aqueous processing.

Americium Chemistry in Other Pyrochemical Systems

Mullins and Leary[10] patented a method of separating americium from plutonium which involves bubbling a mixture of oxygen and argon gas into a molten salt containing both elements. Plutonium precipitates as PuO_2, whereas americium stays in solution.[11]

In connection with their studies of salt transport processes,[12] ANL investigators[13] determined distribution coefficients of americium and other actinides between molten $MgCl_2$ and liquid zinc–magnesium alloys at 800°C. On the basis of these and other data, pyrochemical processes for separating americium from curium have been patented.[14,15] These processes involve contacting a molten halide salt containing americium, curium, and at least 50 wt.% $MgCl_2$ with either magnesium–zinc or a magnesium–cadmium alloy; curium is taken up by the alloy, whereas americium remains in the salt phase.

Studies in support of the development of a Molten Salt Breeder Reactor (MSBR) are currently under way in the United States[16 18] One method considered for the processing of MSBR fuel involves selective reduction of protactinium and rare earths from the molten fluoride salt into liquid bismuth, followed by the preferential transfer of the rare earths into an acceptor salt, such as LiCl or LiBr Ferris and his coworkers[19 22] in their studies of this process have determined the equilibrium distribution of americium (and other transuranium elements) between liquid bismuth and molten LiCl, LiBr, and several $LiF-BeF_2-ThF_4$ solutions at temperatures in the range 600 to 750°C At each temperature the distribution coefficients (mole fraction in the bismuth phase divided by mole fraction in the salt phase) for most of the solutes obeyed the relation $D_M = (N_{Li}^n)(K_M)$, in which the superscript n is the oxidation number of solute M^{n+} in the salt phase and N_{Li} is the mole fraction of lithium in the bismuth phase For N_{Li} ranging from 10^{-5} to 0 3, the oxidation number of americium in the salt varied between 3+ and 2+, depending on temperature and salt-phase composition In molten LiCl and in 66 7 mol% LiF–33 3 mol% BeF_2 at 600°C, however, a significant fraction of the americium appears to be present in the divalent state This evidence for existence of Am^{2+} parallels the observations of Mullins, Beaumont, and Leary[9a] for the $Am-PuCl_3$ system

The distribution coefficient, D = (g Am/g metal phase) (g Am/g salt phase), of americium between molten aluminum metal and molten $AlCl_3-KCl$ is[23] 1 96 * McKenzie, Fletcher, and Bruce[24] measured the distribution of plutonium, americium, and certain fission products between neutron-irradiated aluminum–plutonium alloys and molten bismuth An equal volume of bismuth extracts 75% of the plutonium and 93% of the americium

Foos, Guillaumont, and Mesplede have measured the partition of americium at 150 to 160°C between molten $LiNO_3-KNO_3$ phases and solutions of either tri-*n*-butyl phosphate (TBP),[25-27] triphenyl phosphonate (TPPO),[25-27] tri-*n*-octylphosphine oxide (TOPO),[28] or a series of diphenyldiphosphine dioxides[28 29] $[(C_6H_5)_2PO(CH_2)_nPO(C_6H_5)_2$ = n-DPO, where n = 2, 3, 4, and 6] in a eutectic of polyphenyls (The spectrum of Am^{3+} in molten $LiNO_3-KNO_3$ is shown in Chap 3, Fig 3 7c) From logarithmic plots of distribution ratio vs organophosphorus extractant concentration, the following organic species were identified $Am(NO_3)_3 \cdot 2TBP$, $Am(NO_3)_3 \cdot 2TPPO$, $Am(NO_3)_3 \cdot TOPO$, $Am(NO_3)_3 \cdot$ 2-DPO, $Am(NO_3)_3 \cdot$ 2(3-DPO), and $Am(NO_3)_3 \cdot$ 2(4-DPO) For the diphenyldiphosphine dioxides, the following order of extractant strength was observed

$$6\ DPO \ll 4\text{-}DPO < 3\text{-}DPO < 2\text{-}DPO$$

In this system, 6 DPO does not extract americium Foos, Guillaumont, and Mesplede[25 29] note that TOPO extracts lanthanides very well from fused $LiNO_3-KNO_3$ but Am^{3+} only poorly, suggesting an effective separation scheme

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*At 275°C and an $AlCl_3$ KCl mole ratio of 1 14

Polish workers investigated the distribution at 180°C of uranium, plutonium, and americium between a KCl–CuCl eutectic melt and solutions of TBP, dibutylphosphoric acid (HDBP), and tri-*n*-octylamine in biphenyl.[30] Absorption spectra of Am(III) in molten pyridinium and some alkali metal chlorides indicate americium is present as the octahedral complex $AmCl_6^{3-}$ (compare Chap. 3, pages 99 and 100) in such systems.[31]

PRECIPITATION PROCESSES

For the first 15 years or so after its discovery, many different precipitation processes were used extensively to recover and purify microgram to gram amounts of americium. Highlights of these processes, which are now primarily only of historical interest, are presented here; amplified discussion of several early precipitation schemes is given in articles by Penneman and Keenan[32] and by Thompson et al.[33] Nowadays, of course, ion exchange and solvent extraction technology have largely supplanted precipitation processes for recovering americium. Even so, for special purposes, precipitation processes still find applications, and these are discussed on pages 190 to 194. Attention is also directed to the discussion in Chap. 4 of the properties of AmF_3, $Am_2(C_2O_4)_3$, $K_3AmO_2(CO_3)_2$, and other insoluble compounds of Am(III) and Am(V).

Precipitation Processes: Historical

Important contributions in the very early days of americium chemistry were made by Cunningham,[34] Wallman,[35] Werner,[36-38] and Thompson.[39] Cunningham isolated the first pure americium by precipitation of AmF_3 and $Am(OH)_3$, and Werner and Thompson devised various schemes for isolation of trace quantities of americium including its precipitation as an insoluble Am(V) carbonate and by carrying on $Ta_2O_5 \cdot xH_2O$ precipitated by heating a carbonate solution containing Ta(V) and Am(V).

Subsequently workers in several countries used precipitation methods to purify milligram and even gram amounts of ^{241}Am from plutonium and other contaminants. For example, Milsted, Herniman, and Hall[40-42] in England devised methods for the separation of 10 to 25 mg ^{241}Am from aged plutonium stocks; their isolation scheme included steps in which americium was concentrated and purified by precipitation of AmF_3 and $Am_2(C_2O_4)_3 \cdot 10H_2O$. Later, in 1956, Butler and Merritt[43] in Canada combined precipitation [$Am(OH)_3$ and AmF_3] and ion-exchange techniques to separate and purify 0.8 g of ^{241}Am from 2 kg of aged plutonium; as in the earlier British work, a gross separation from plutonium was first made by precipitating plutonium peroxide from acid solution. Yakovlev and Kosyakov[44] reported on the separation of a gram of ^{241}Am from plutonium and other impurities by precipitation of $K_8Am_2(SO_4)_7$ and $K_3AmO_2(CO_3)_2$. American scientists[45-47] in the 1950s also devised and tested several precipitation schemes for isolation and purification of macro amounts of americium The precipitation process developed by LASL workers to concentrate americium from impure feedstocks is shown in Fig 5 2

Also in this early period, results obtained during the development of analytical procedures for and the fundamental chemistry of americium established that micro concentrations of Am(III) coprecipitate quantitatively with LaF_3 (Refs 48 to 51), CeF_3 (Refs 32 and 51 to 53), $La_2(C_2O_4)_3$ (Refs 54 to 57), CaC_2O_4 (Ref 46), K_2SO_4 (Ref 58), $KLa(C_2O_4)_2$ (Refs 59 and 60), and $BiPO_4$ (Refs 32, 61, and 62) Yakovlev and Gorbenko-Germanov[63] also showed that Am(V) in alkaline medium is quantitatively coprecipitated with $K_4UO_2(CO_3)_3$ and $K_4PuO_2(CO_3)_3$ Hermann[56] also reported that a partial separation of americium from lanthanum could be obtained by fractional precipitation of $La_2(C_2O_4)_3$ from homogeneous solutions involving the slow hydrolysis of dimethyl oxalate to generate the precipitant, americium is enriched in the precipitate

Pressly[64] devised an interesting precipitation process for separating Am(III) from Pm(III) In this scheme Am^{3+} and Pm^{3+} are coprecipitated as fluorides, which are then dissolved in a mixture of boric and nitric acids The resulting solution is made 3*M* H_2SiF_6, on heating, H_2SiF_6 partially decomposes into volatile HF and SiF_4, whereby PmF_3 precipitates while Am^{3+} stays in solution Earlier, Werner[38] and Thompson[39] also used to advantage the soluble complex formed by Am^{3+} with fluosilicate ions to isolate micrograms of americium from rare earths

Kuznetsov and Akimova[65] found that microgram amounts of Am(III) coprecipitate with the black solids precipitated by the addition of the dyes methyl violet, crystal violet, or methylene blue to solutions containing americium and one of the compounds benzene-2 arsonic acid<1-azo-7>1,8-dihydroxynaphthalene-3,6-disulfonic acid (Arsenazo), 2-hydroxy-5-nitro-naphthalene-4-sulfonic acid-<1-azo-2>-1-hydroxynaphthalene (Eriochrome black T), or benzene-2-carboxyl-<1-azo-7>-1,8-dihydroxynaphthalene-3, 6-disulfonic acid The extent of coprecipitation of Am^{3+} varies with pH but is essentially 100% at pH's $\geqslant$6 0 Americium(III) is also carried by the precipitate formed by addition of 1,8-diaminonaphthalene chloride to a solution containing ammonium oxalate and oxalic acid [65]

Present-Day Precipitation Processes

Flow sheets currently used[66] at the Transuranium Processing Plant at Oak Ridge National Laboratory (ORNL) to purify the ^{243}Am—^{244}Cm fraction recovered from both High Flux Isotope Reactor (HFIR) and Savannah River reactor PuO_2 and/or AmO_2—CmO_2 targets include two cycles of oxalate precipitation to remove miscellaneous metallic impurities European workers[67, 68] have also used an oxalate precipitation process to purify americium and curium separated from irradiated ^{243}Am targets

A precipitation process for separating gram to kilogram amounts of curium from americium is still used occasionally [68, 69, 74] In this process (Fig 5 3), Am(III) in

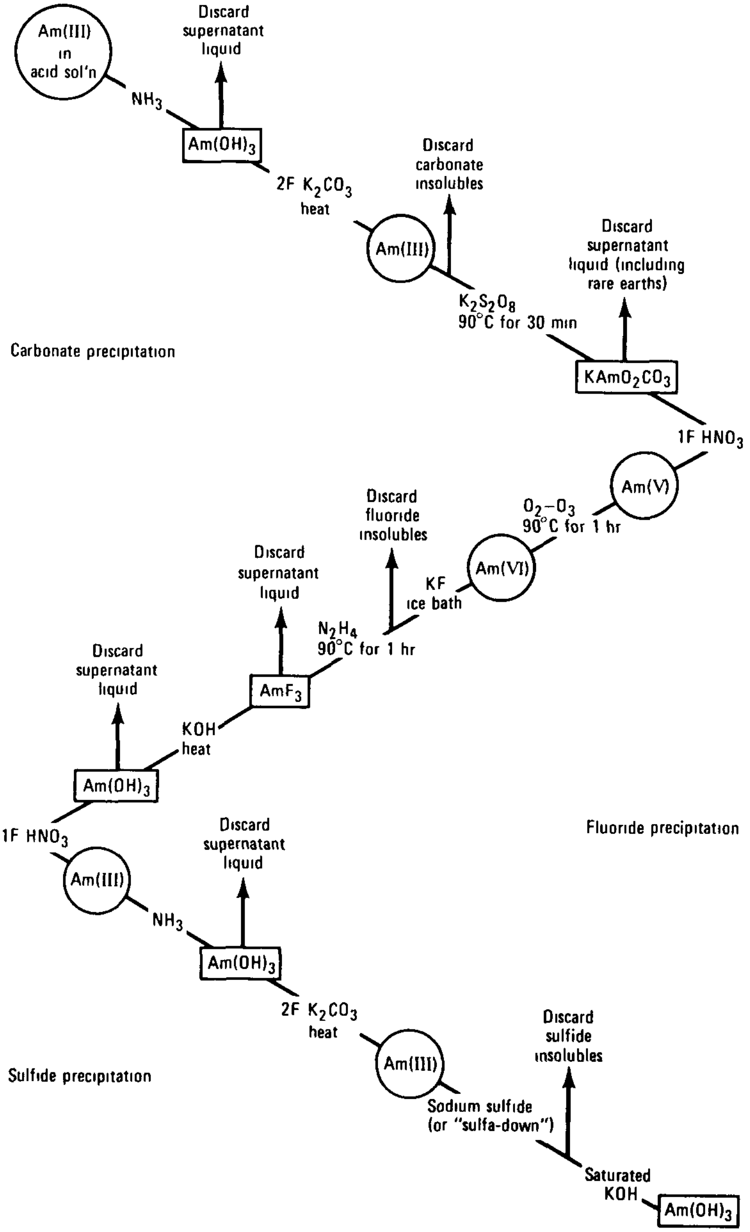


Fig. 5.2 Typical precipitation process developed for the recovery and purification of gram amounts of americium.[47]

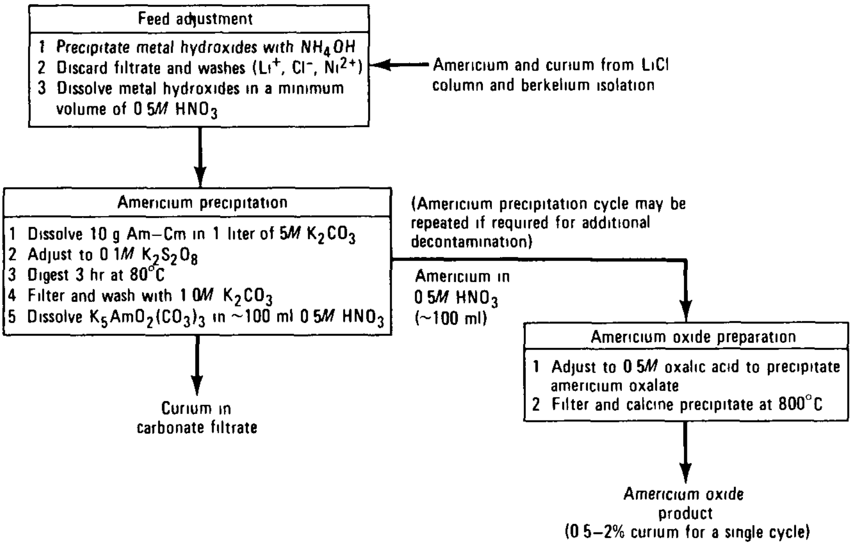


Fig. 5.3 Americium–curium separation by precipitation of $K_5AmO_2(CO_3)_3$. [From R. E. Leuze and M. H. Lloyd,[76] Processing Methods for the Recovery of Transplutonium Elements, in *Progress in Nuclear Energy, Process Chemistry*, Series III, C. E. Stevenson, E. A. Mason, and A. T. Gresky (Eds.), Vol. 4, page 549, Pergamon Press, Inc., New York, 1970.]

concentrated ($\geqslant 3M$) K_2CO_3 solution is oxidized to Am(V) at 80°C with ozone, NaOCl, or $K_2S_2O_8$ and subsequently precipitated as $K_5AmO_2(CO_3)_3$; Cm(III) is not oxidized and remains as a soluble complex in the carbonate solution. [As early as 1952, Stephanou and Penneman[49] found that Cm(III) could be separated from americium by oxidizing the latter to Am(VI) with $K_2S_2O_8$ and precipitating CmF_3.] Equipment used at the Savannah River Plant for large-scale precipitation separation of americium and curium has been described by Kishbaugh et al.[73]

A process based on precipitation of the double sulfate $Am_2(SO_4)_3 \cdot Na_2SO_4 \cdot H_2O$ (compare pages 164 and 165) with lanthanum as carrier was successfully used[75,76] at the Savannah River Plant to recover 200 g of americium and curium from the aqueous raffinate remaining after solvent extraction recovery of plutonium from highly irradiated plutonium–aluminum alloy (see Chap. 2, Fig. 2.2). Solutions of $NaHSO_4$, NaOH, and $La(NO_3)_3$ were added to the nitrate-based raffinate to adjust its composition to approximately 5.5M Na^+, 0.5M Al^{3+}, 1M SO_4^{2-}, 5M NO_3^-, 0.5 g La^{3+} liter^{-1}, <25 mg Am^{3+} liter^{-1}, and <25 mg Cm^{3+} liter^{-1} at pH 0.5. Best results for recovering americium and curium were obtained by adding $La(NO_3)_3$ carrier and then adjusting the sulfate concentration to 1.0M to 1.5M by addition of $NaHSO_4$. Subsequently the solution was adjusted to pH 0.5 to 1.0 by adding 50 wt.% NaOH and digested 6 hr at 70°C to form the double sulfates. After centrifugation, the sulfate precipitate was washed with dilute Na_2SO_4 solution and then metathesized to hydroxides by treatment with NaOH solution. The resulting hydroxides were washed and dissolved in HNO_3 to provide a concentrated americium–curium fraction for further purification at the Oak Ridge Transuranium Processing Plant.

Variables affecting carrier precipitation of americium and curium double sulfates were studied by Burney; his results, including data for solubility of carrier-free americium and curium double sulfates, have been summarized by Leuze and Lloyd.[76] On the basis of experience at the Savannah River Plant, the double sulfate precipitation process provides an adequate way of concentrating americium and purifying it from gross amounts of such impurities as iron and aluminum. Its principal disadvantage, as noted by Leuze and Lloyd[76] is that the americium–curium product is contaminated with gross amounts of lanthanum which must be removed in further purification steps.

Until very recently when it was replaced by a cation-exchange process, a hydroxide precipitation process was routinely used at the Rocky Flats Plant to recover americium and plutonium values from the spent $NaCl–KCl–MgCl_2$ mixture obtained from pyrochemical extraction of ^{241}Am from aged plutonium metal (pages 185-187).[77] The chloride salt residue was dissolved in hot 1*M* HCl, and the plutonium and americium precipitated as hydroxides with 3*M* KOH. After the precipitate was washed with 0.5*M* KOH, it was filtered and then dissolved in 3*M* HNO_3 in preparation for separating americium and plutonium by an ion-exchange process. This precipitation process had several deficiencies: (1) slow filtration because of the gelatinous nature of the precipitate, (2) carry-over of magnesium that caused inefficiency in subsequent processing, and (3) a high carry-over of chloride ion that caused equipment corrosion. To circumvent these difficulties, Miner and Hogan[78] developed a new selective, hydroxide precipitation process based on the slow decomposition of urea; the precipitate formed from the slow release of hydroxyl ions is fairly crystalline, easily filtered, and substantially free of magnesium and chloride. This latter homogeneous precipitation process has not been operated under plant-scale conditions.

Proctor et al.[79-81] at the Rocky Flats Plant use precipitation processes to purify gram quantities of production-grade AmO_2 from cerium and other rare earths. In one process, adopted from the work of Zaozerskii and Patkin,[82] an americium solution of 30 g liter^{-1} is prepared by dissolving the impure AmO_2 in 6*M* HCl. After the addition of 20 vol.% NH_4OH to adjust the solution pH to 5, Ce(IV) peroxide is precipitated by adding 2*M* H_2O_2. Subsequently $Am_2(C_2O_4)_3$, precipitated from the peroxide filtrate, is digested 16 hr at 60°C, washed, dried, and calcined to AmO_2. Two cycles of peroxide precipitation and supplemental oxalate precipitation reduce the cerium content of the AmO_2 from as much as 50,000 ppm to <500 ppm. A more general precipitation process patented by Proctor[81] for preparing high-purity AmO_2 is depicted in Fig. 5.4. This scheme makes use of the fact that Am(VI) is soluble in the hydrofluoric acid solution used to precipitate rare earths. Coupling of the fluoride precipitation step with tail-end precipitation of $Am_2(C_2O_4)_3$ to remove lead and silver impurities yields AmO_2 containing only 500 to 600 ppm total impurities. The scheme shown in Fig. 5.4 was used by Proctor[83] recently to purify 57 g of americium from 200 g of a composite of aluminum metal; in this case aluminum was first separated by dissolution in an $NaOH–NaNO_3$ solution.

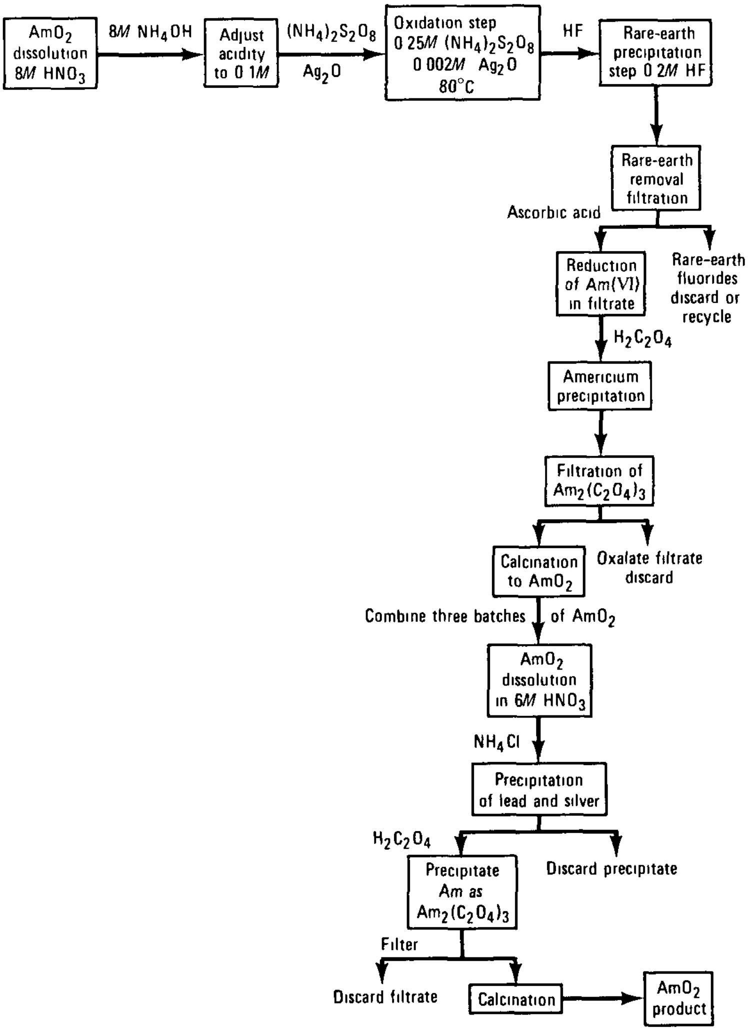


Fig. 5.4 Precipitation process used at Rocky Flats Plant to make high-purity AmO_2.

Precipitation processes still figure prominently in new analytical methods for the determination of trace amounts of americium in process and environmental samples. Iyer and Kamath[84] have developed a novel method of analyzing for americium in urine which involves coprecipitation of Am^{3+} with BiOCl. Sill and Williams[85] carry Am^{3+} and other actinides on $BaSO_4$ to analyze for trace amounts of these elements in various matrices; recent physicochemical studies of coprecipitation of americium with $BaSO_4$ and with BaC_2O_4 have been reported by Ginzburg, Karantsevich, and Maksimov[86] and by Bykhovskii and Petrova,[87] respectively.

SOLVENT EXTRACTION PROCESSES

Introduction

Solvent extraction technology is widely used for the recovery, separation, decontamination, and analysis of both trace and macro amounts of americium. In particular, solvent extraction processes and systems using amine and organophosphorus extractants are extensively used for the initial recovery and separation of gram amounts of americium from a wide variety of aqueous solutions; the discussion here is restricted primarily to their technology. Weaver[88] has recently published an excellent up-to-date general review of the solvent extraction chemistry of trivalent americium; Weaver's paper includes much information previously reviewed earlier by other authors.[89-94] Solvent extraction systems for the analysis of americium have been discussed by Myasoedov et al.[95]

Organophosphorus Extractants

Tri-*n*-Butyl Phosphate. Extraction of Am^{3+} from nitrate media by tri-*n*-butyl phosphate (TBP) conforms to the reaction:[88,96-100]

$$Am^{3+}_{(aq)} + 3NO^-_{(aq)} + 3TBP_{(org)} \rightleftharpoons Am(NO_3)_3 \cdot 3TBP_{(org)} \qquad (5.3)$$

The value of the equilibrium constant, $K_{ex} = [Am(NO_3)_3 \cdot 3TBP]/[Am^{3+}][NO_3^-]^3$ $[TBP]^3$, for Eq. 5.3 at zero ionic strength is[100] 0.4. [Russian investigators[101] have compiled a list of equilibrium constants for the extraction of americium by several neutral organophosphorus compounds; Table 5.2 is abstracted from their compilation.]

Tri-*n*-butylphosphate, even undiluted, extracts americium only weakly from strong HNO_3 solutions (Fig. 5.5). [Throughout this book the americium distribution ratio, $D_{Am} \equiv$ concentration of americium in organic phase/concentration of americium in aqueous phase.] However, TBP extracts americium quite strongly from neutral (or low-acid), highly salted nitrate solutions as shown by results listed in Table 5.3 and the more extensive data tabulated in Refs. 102 and 103. Highly hydrated ions such as Al^{3+} and Li^+ are particularly effective as salting agents. Reflecting its low TBP extractability from HNO_3 solutions, Am^{3+} in Purex-type extraction processes reports to the high-level aqueous waste stream; this latter solution then constitutes a valuable and important feedstock for recovering americium by the various solvent extraction processes described here and elsewhere in this chapter.

Batch TBP solvent extraction procedures have been successfully used recently at both the Hanford and Savannah River plants to recover hundreds of grams of ^{241}Am and ^{243}Am from fuel-reprocessing waste solutions. The Savannah River application involved isolating ~10 kg of ^{243}Am and ^{244}Cm from the aqueous solution remaining after dissolving an irradiated plutonium–aluminum alloy (see Chap. 2, Fig. 2.2) in

Table 5.2

EQUILIBRIUM CONSTANTS FOR THE EXTRACTION OF Am(III) BY SOME NEUTRAL ORGANOPHOSPHORUS COMPOUNDS*

Reagent	K_{ex}†
$(C_4H_9O)_3PO$	0.4‡
$(C_4H_9O)_2(C_4H_9)PO$	7.4
$(C_4H_9O)(C_4H_9)_2PO$	1800.
$(C_4H_9)(C_6H_5)(C_4H_9O)PO$	45
$(C_8H_{17}O)_3PO$	0.3
$(i\text{-}C_8H_{17}O)_3PO$	0.2
$(C_8H_{17}O)_2(C_8H_{17})PO$	4.2
$(C_8H_{17}O)(C_8H_{17})_2PO$	580.
$(C_8H_{17})_3PO$	3000
$(i\text{-}C_8H_{17})_3PO$	100.

*[From F. S. Gureev, V. B. Dedov, S. M. Karpacheva, I. K. Shvetsov, M. N. Ryhzov, P. S. Trukchlayev, G. N. Yakovlev, and I. A. Lebedev,[101] Methods of Recovery and Some Chemical Properties of the Transplutonium Elements, in *Progress in Nuclear Energy, Process Chemistry*, Series III, C. E. Stevenson, F. A. Mason, and A. T. Gresky (Eds.), Vol. 4, p. 631, Pergamon Press, Inc., New York, 1970.]

†$K_{ex} = [Am(NO_3)_3 \cdot 3O]_{org}/[Am^{3+}]_{aq}[NO_3^-]^3_{aq}[O]^3_{org}$, where O is the organophosphorus extractant, values listed are for zero ionic strength.

‡Value from Ref. 100

HNO_3 and recovering the plutonium by TBP extraction. The solution was adjusted to 6.5*M* to 6.8*M* inextractable nitrate [~0.67*M* $Al(NO_3)_3$–4.5*M* $NaNO_3$] and 0.10*M* to 0.35*M* HNO_3 before extracting the americium and curium with two successive equal volume portions of 50 vol.% TBP in a hydrocarbon diluent. Subsequently the americium and curium were stripped into 0.2*M* HNO_3. Recovery was greater than 95% with 5680-liter batches on a plant scale, essentially no aluminum or fission products other than lanthanides, ^{95}Zr, and ^{106}Ru were extracted. Details of the Savannah River experience have been recounted by Henry[74] and others[104-105b]

At Hanford, batch TBP extraction was used to recover about 1100 g of americium, 60 g of curium, and 200 g of promethium from the aqueous waste produced when Shippingport reactor fuel was processed in the Redox plant.[106-109] This waste solution, after concentration, contained, typically, 1.6*M* $Al(NO_3)_3$–1.5*M* $NaNO_3$–0.2*M* $Na_2Cr_2O_7$ and 0.6*M* NaF. Feed (16,500 liters) for the batch TBP extraction step was prepared by reducing Cr(VI) to Cr(III) by adding $NaNO_2$ and adjusting the pH to the range 0.0 to 0.5. The solvent, 50 vol.% TBP in *n*-paraffin hydrocarbon (NPH) diluent, was contacted with successive equal-volume amounts (~2650 to 3800 liters) of feed until excessive aqueous raffinate waste losses indicated the need to reduce the product loading. The loaded organic phase was then contacted with one-half of its

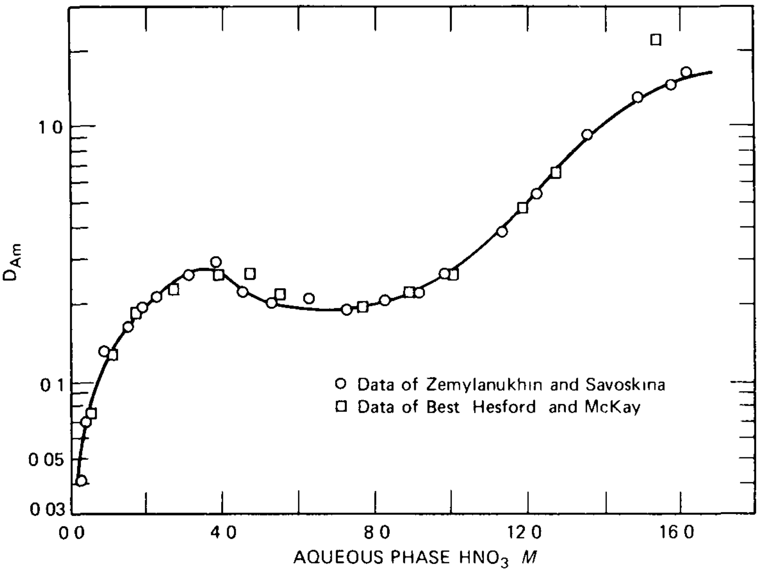


Fig. 5.5 Extraction of Am(III) by undiluted TBP [From V I Zemlyanukhin and G P Savoskina,[99] Extraction of Americium by Tributyl Phosphate, *Radiokhimiya* 3 411 (1961) through *Radiochemistry (USSR) (English Translation)* 3(4) 182 (1961), and G F Best, E Hesford, and H A C McKay,[98] Tri *n* Butyl Phosphate as an Extracting Agent for Inorganic Nitrates VII, The Trivalent Actinide Nitrates *Journal of Inorganic and Nuclear Chemistry,* **12** 136 (1959)]

volume of 1*M* HNO_3 to strip the americium and curium The resulting aqueous product solution (Table 5 4) was scrubbed with NPH diluent to remove entrained TBP, recovery and purification of americium and curium from this crude concentrate by extraction with *bis*(2-ethylhexyl)phosphoric acid is described on pages 208 to 220 The TBP process recovered about 92% of the americium and curium in the Shippingport waste Excessively long phase disengagement times encountered in some extraction contacts were attributed to the high solids content of the Shippingport waste solution These solids were believed to be ZrO_2 fines left in the dissolver vessel after the decladding step and those formed during evaporation of the waste to a high salt concentration

Batch TBP extraction procedures have also been developed and applied in France[71] and Japan[110] to recover small amounts of americium and curium from nuclear fuel-processing waste solutions A continuous counter current TBP extraction process for the recovery of grams of americium from Hanford slag and crucible waste was developed by Rainey [111] Following the dissolution of the slag and crucible in HNO_3–HF media, Pu(IV) was first recovered by extraction with 30% TBP In Rainey's process, excess (5*M*) HNO_3 in the aqueous waste from the plutonium extraction step was neutralized to 0 01*M* with gaseous NH_3 The resulting feed

Table 5.3

DISTRIBUTION OF Am(III) BETWEEN 30 VOL.% TBP-*n*-PARAFFIN AND AQUEOUS $Al(NO_3)_3$–$LiNO_3$–$NaNO_3$ SOLUTIONS*

$Al(NO_3)_3$, *M*	$LiNO_3$, *M*	$NaNO_3$, *M*	HNO_3, *M* Aqueous	HNO_3, *M* Organic	D_{Am}
0.73	3.15	0	0.055	0.355	21.0
0.73	3.15	0	0.135	0.565	7.57
0.73	3.15	0	0.285	0.710	3.05
0.73	3.15	0	0.345	0.745	2.26
1.05	0	3.23	0.050	0.360	10.1
1.05	0	3.23	0.145	0.555	4.07
1.05	0	3.23	0.320	0.675	1.69
1.05	0	3.23	0.375	0.715	1.21
0	3.09	2.99	0.040	0.370	8.49
0	3.09	2.99	0.160	0.540	4.14
0	3.09	2.99	0.345	0.650	1.76
0	3.09	2.99	0.431	0.659	1.38
0.75	2.07	1.93	0.025	0.385	24.8
0.75	2.07	1.93	0.125	0.575	6.55
0.75	2.07	1.93	0.280	0.685	2.66
0.75	2.07	1.93	0.372	0.718	1.95

*From Ref. 103.

solution, which contained large amounts of Ca^{2+}, Mg^{2+}, and Al^{3+}, was contacted with a 30% TBP solution to extract the americium. Subsequently the organic extract was scrubbed with 3*M* NH_4NO_3 solution to remove any extracted calcium and magnesium, and the americium was then stripped into water. This process was satisfactorily tested in pulse column runs with actual slag and crucible waste solution but was never used at Hanford (compare pages 202 to 205).

Reflecting their chemical similarity, Am(III) and trivalent lanthanides extract about equally well from HNO_3 solutions into TBP solvents.[112,113] Thus considerable effort has been expended to devise TBP extraction processes for purifying americium from lanthanum and other rare-earth elements. One such process (Fig. 5.6) developed by Lewis[114] takes advantage of the fact that, in 17*M* HNO_3, D_{Am} is 10-fold higher than D_{La} (Fig. 5.7). In the flow sheet of Lewis, undiluted TBP is used to extract the americium from the 17*M* HNO_3 feed. Small amounts of coextracted lanthanum and cerium are scrubbed with a small volume of 13.5*M* HNO_3, and the americium is then stripped into 6*M* HNO_3. In pilot-plant-scale tests of this flow sheet, americium recoveries were 99.5%, and the recovered americium contained less than 1% of the lanthanum and cerium in the feed. Satisfactory 17*M* HNO_3 feedstock containing only americium and rare earths can be prepared by preliminary TBP extraction from an $Al(NO_3)_3$-salted low-acid feed. A TBP extraction process similar to that shown in

Table 5.4

PRODUCT FROM TBP BATCH EXTRACTION OF AMERICIUM AND CURIUM FROM SHIPPINGPORT REACTOR FUEL-PROCESSING WASTE

(Estimated Volume 1040 liters)

Component	Concentration
HNO_3	2 2M
$Al(NO_3)_3$	0 3M
$NaNO_3$	0 2M
$Cr(NO_3)_3$	0 1M
$Fe(NO_3)_3$	0 08M
F	0 06M
$UO_2(NO_3)_2$	0 06M
Total rare earths*	34 6 g liter ^{1}
^{241}Am	0 87 g liter ^{1}
^{243}Am	0 25 g liter ^{1}
^{242}Cm	0 00045 g liter ^{1}
^{244}Cm	0 061 g liter ^{1}
Np	0 024 g liter ^{1}
Pu	0 016 g liter^{-1}
^{147}Pm	238 Ci liter^{-1}
^{144}Ce ^{144}Pr	235 Ci liter ^{1}
^{154}Lu	12 Ci liter^{-1}
$^{106}Ru-^{106}Rh$	5 5 Ci liter ^{1}
^{137}Cs	2 1 Ci liter ^{1}

*As oxides

Fig 5 6 was proposed by Leuze[115] for the recovery and purification (from rare earths) of americium and curium from irradiated plutonium–aluminum alloy fuel Neither this process nor that of Lewis has been used in routine plant-scale operation

Both French[116] and American workers[117] have studied the effects of aminopoly carboxylic acids on TBP extraction of americium from low-acid $LiNO_3$ and $Al(NO_3)_3$ solutions Formation constants of complexes formed by Am(III) with aminopolycarboxylic acids (compare Table 3 11) are higher than those of complexes of the light lanthanides ($Z = 57$ to 61) with these ligands Thus, addition of an aminopolycarboxylic acid to an $LiNO_3$ [or $Al(NO_3)_3$]–Am(III)–rare earth (RE) solution enhances TBP extraction of the lanthanides relative to that of americium Separation factors (D_{RL}/D_{Am}) measured by Koehly and coworkers[116] for some typical aminopolycarboxylic acids are listed in Table 5 5 McKibben et al [117] at the Savannah River Plant devised a TBP extraction process (Fig 5 8) for separating americium and curium from large amounts of light lanthanides Feedstock for this process is prepared by adding $LiNO_3$ and diethylenetriaminepentaacetic acid (DTPA) to the product solution obtained, as described earlier, by batch TBP extraction of americium and

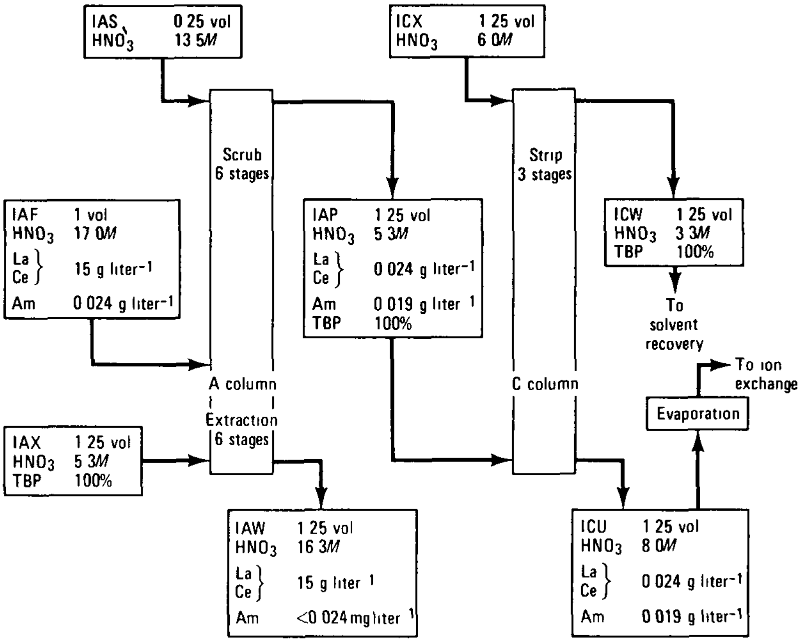


Fig. 5.6 TBP extraction flow sheet for the separation of americium from lanthanum and cerium (From W H Lewis,[114] Americium and Neptunium Recovery Processes, in *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy Geneva, 1958,* Vol 17, page 236, United Nations, New York, 1958)

curium from the waste solution resulting from the processing of irradiated ^{239}Pu fuel Maleic acid is added to the extraction column via a scrub stream to buffer the aqueous phase and thereby decrease the sensitivity of the process to changes in aqueous acidity The aqueous raffinate containing the actinides and residual lanthanides can be further processed by extraction with 30% TBP solvent to remove interfering salts ($LiNO_3$ and DTPA) prior to final separation and purification of ^{243}Am and ^{244}Cm by high-pressure ion-exchange procedures (compare pages 245 to 252) The lanthanide rejection process (Fig 5 8) has been satisfactorily demonstrated in miniature mixer–settler runs, but so far no production-scale use has been made of it

An intensive effort was mounted at the Oak Ridge site in the 1960s to develop and demonstrate processes for separating and purifying transplutonium elements from highly irradiated HFIR (compare Chap 2) fuel elements Various methods of separating americium and curium from lanthanides were investigated as part of this activity One such scheme which provided reasonably good separation of the two actinides from europium and other rare earths involved preferential extraction of americium and curium from a 10*M* LiCl–0 1*M* HCl solution into 30% TBP solvent[118] Subsequent tests led, as described on pages 220 to 222, to the development of a more

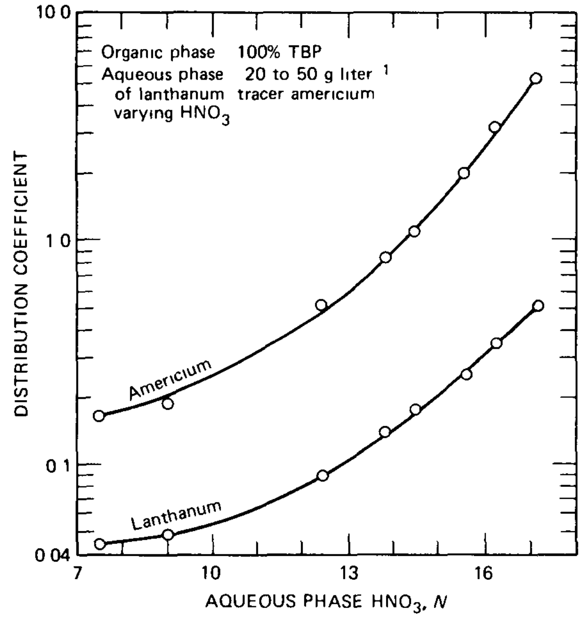


Fig. 5.7 TBP extraction of americium and lanthanum from concentrated HNO_3 solutions (From W H Lewis,[114] Americium and Neptunium Recovery Processes, in *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958,* Vol 17, page 236, United Nations, New York, 1958)

efficient amine extraction process (Tramex process) for purifying americium and curium from rare earths

Penneman and Keenan[32] report that Am(III) can be separated from rare earths by TBP extraction from 1*M* NH_4SCN solutions The mechanism of extraction of Am(III) and Eu(III) from 1*M* NH_4SCN media by TBP both in the presence and in the absence of a quaternary ammonium thiocyanate was recently investigated by Indian scientists[119] Thiocyanate–TBP systems have not been used in production-scale recovery or purification of americium, thiocyanate solutions have been much used, however, in large-scale ion-exchange purification of americium from lanthanides and other contaminants (compare pages 234 to 237)

Chemistry involved in TBP extraction of Am(III) from molten (120°C) KNO_3-LiNO_3 mixtures has been studied by Foos and Guillaumont,[25, 27] Isaak, Fields, and Gruen,[120] and Borkowska, Mielcarski, and Taube[121], some of their results are discussed on pages 187 to 189 No large-scale application of this separation technology has been made

Conflicting evidence has been obtained for TBP extraction of Am(VI) from HNO_3 solutions Zangen[122] found that TBP–CCl_4 solutions extract Am(VI) much more

Table 5.5

EFFECT OF COMPLEXANTS ON TBP EXTRACTION OF AMERICIUM AND RARE EARTHS*

(Aqueous Phase: 4M $LiNO_3$–0.1M $Al(NO_3)_3$–0.1M Complexant, pH 2.5 to 3.0; Organic Phase: 40% TBP in Dodecane)

Lanthanide	Separation factor D_{RE}/D_{Am} In absence of complexant	With complexant† present EDTA	DTPA	TTHA	DACTA	HPDTA
La		20.5	1200	52	45	
Ce	0.9	10.3	51	26	15	
Pr	1.07	3.81	12.5	7.8	3.5	
Pm	1.15	3.1	5.8	6.4	2.3	
Eu	1.35	2.9	1.96	3.1		1.44
Tb	1.55	0.62	1.03	1.5	0.80	
Er	1.03	0.04	1.00	0.62	0.55	
Tm	0.93	0.037	1.01	0.36	0.41	
Yb	0.73	0.006	1.07	0.23	0.32	

*[From G. Koehly and E. Hoffert,[116] Separation of the Actinide Group from That of the Lanthanides in Nitric Medium, in Semiannual Report of the Chemistry Department, Center for Nuclear Studies at Fontenay-Aux-Roses, December 1966–May 1967, French Report CEA-N-856, through USAEC Report ANL-Trans-628, Argonne National Laboratory, 1967.]

†EDTA = ethylenediaminetetraacetic acid
DTPA = diethylenetriaminepentaacetic acid
TTHA = triethylenetetraminehexacetic acid.
DACTA = 1,2-diaminocyclohexanetetraacetic acid.
HPDTA = 2-hydroxypropanediaminetetraacetic acid.

strongly than Am(III) from 0.05M HNO_3. Conversely, other workers[41,123] report that TBP rapidly reduces Am(VI) to inextractable Am(III).

Dibutyl butylphosphonate. Dibutyl butylphosphonate [$DBBP = (C_4H_9O)_2(C_4H_9)PO$] extracts Am(III) from nitrate media according to the reaction:

$$Am^{3+}_{(aq)} + 3NO^-_{3(aq)} + 3DBBP_{(org)} \rightleftharpoons Am(NO_3)_3 \cdot 3DBBP_{(org)} \qquad (5.4)$$

This reaction stoichiometry is similar to that followed by TBP (compare Eq. 5.3) and other monofunctional neutral organophosphorus extractants.

Distribution data plotted in Fig. 5.9 show that DBBP extracts Am(III) more strongly than TBP from nitrate solutions (compare also Table 5.2); DBBP is a powerful extractant for Am(III) from low-acid highly salted nitrate solutions. Distribution ratio data for DBBP extraction of Am(III) from HNO_3–metal nitrate solutions are listed in Refs. 100, 102, 125, and 126.

A production-scale countercurrent DBBP solvent extraction process (Fig. 5.10) is currently operated at Hanford to recover plutonium and americium values from the acid aqueous waste (CAW) solution produced in the operation of the Hanford

Plutonium Reclamation Facility (PRF). [The PRF uses a reflux-type 20% TBP–CCl_4 solvent extraction process to recover and purify plutonium from HNO_3 and HNO_3–HF solutions of a wide variety of metallurgical scrap.[127,128]] The present Hanford DBBP americium–plutonium recovery process evolved from an earlier batch extraction process devised by Kingsley.[129,130] Important contributions to the development of the flow sheet shown in Fig. 5.10 were made by Lorenzen and Speakman,[131] Taylor,[132] and Richardson.[133]

Feed for the Hanford DBBP americium extraction process is prepared by adding NaOH to the PRF aqueous waste to adjust its acidity from ~2*M* to 0.1*M* HNO_3. Americium(III) and Pu(IV) in the adjusted feed are coextracted into the 30% DBBP–CCl_4 solvent. Subsequently the americium is preferentially stripped into dilute 0.1*M* HNO_3; Pu(IV) and residual americium are stripped with an HNO_3–HF solution. The latter solution is recycled to the mainline TBP process in the PRF, whereas the americium is concentrated and purified by the ion-exchange process described on pages 245 to 252.

The Hanford DBBP americium extraction process is performed in three packed pulse columns; for the conditions shown in Fig. 5.10, the extraction column is

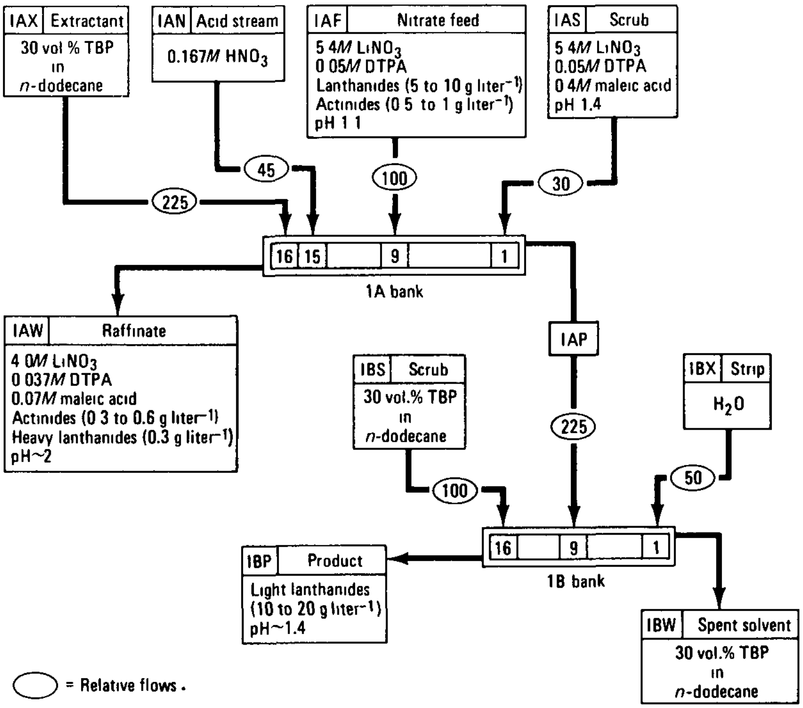


Fig. 5.8 Lanthanide rejection flow sheet–TBP extraction process for separating americium and curium from light rare earths.[117]

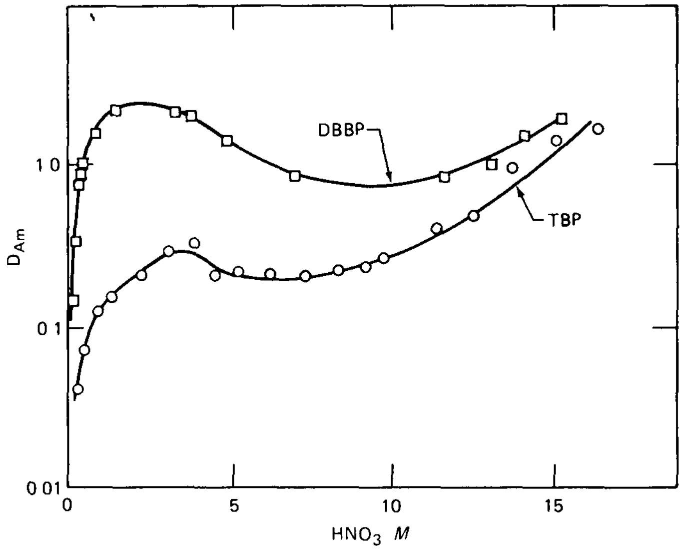
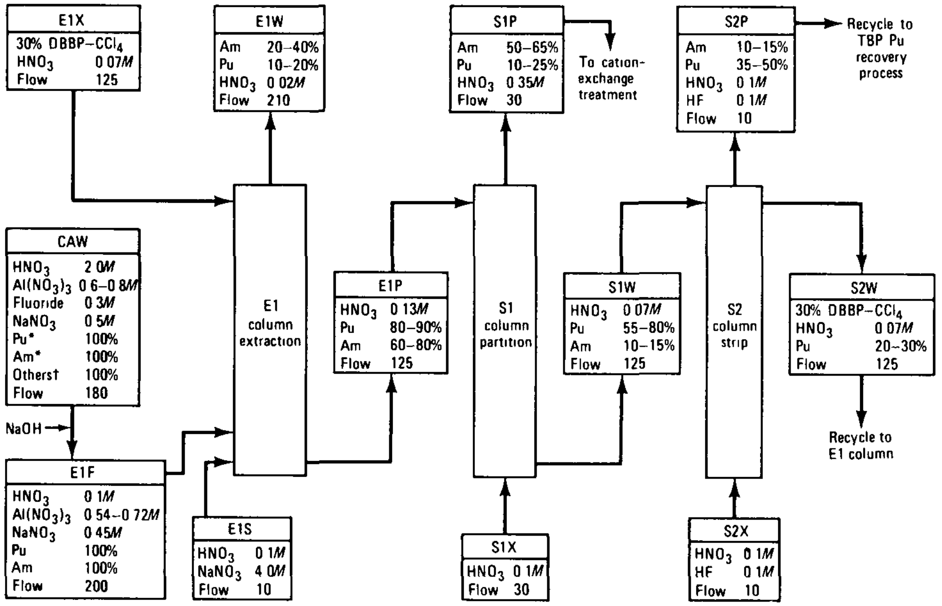


Fig. 5.9 Extraction of Am(III) from HNO_3 by TBP and DBBP [Adapted from V. I. Zemlyanukhin, G P Savoskina, and M I Pushlenkov,[124] Complex Formation of Nitrates of Transuranium Elements with Neutral Organophosphorus Compounds, *Radiokhimiya*, **6**: 714 (1964), through *Soviet Radiochemistry (English Translation)*, **6**: 690 (1964).]

calculated to operate with one to two extraction stages and one scrub stage, and the partition and plutonium strip columns each operate with three stages Overall, americium recovery in typical plant-scale operation with the DBBP extraction process ranges from 60 to 80%, the relatively poor americium recovery is attributed primarily to improper in-line neutralization of HNO_3 in the unbuffered CAW solution and to inadequate extraction-column equipment. The DBBP extraction process recovers essentially all the soluble plutonium in the feed to the process, however, any insoluble plutonium (e g , finely divided PuO_2) is not recovered. The Hanford americium extraction process is operated with a small inventory of 30% DBBP–CCl_4 solvent which is replaced frequently, for this reason the process operates satisfactorily without routine washing of the solvent with Na_2CO_3 or NaOH solutions

Aside from the Hanford application, no other plant-scale use has been made of DBBP (or any other neutral phosphonate) for the recovery of americium. From time to time, however, workers in several countries have proposed conceptual phosphonate solvent extraction processes for the recovery and/or purification of americium. For example, Schulz and Richardson[134] suggested a DBBP solvent extraction process for the recovery of americium and other actinide elements from the high-level aqueous waste stream resulting from the processing of irradiated UO_2–PuO_2 fuel in the Liquid Metal-Cooled Fast Breeder Reactor. The application of DBBP and other phosphonates

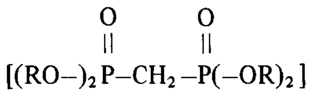


*CAW solution contains, typically, 0 005 to 0 01 g liter^{-1} each of americium and plutonium
†Includes small concentrations of calcium, magnesium, iron, chromium, nickel, etc

Fig. 5.10 Hanford DBBP americium extraction process flow sheet.

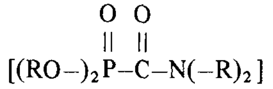
for extracting americium and curium from LiCl–HCl solutions was studied at Oak Ridge National Laboratory.[118] Russian scientists[101,135] have studied the extraction of Am(III) from HNO_3 and LiCl solutions by diisoamyl methylphosphonate, and Koehly and Hoffert[116] have investigated the extraction of Am(III) from HNO_3 media by methyldibutylphosphonate.

Neutral Bifunctional Organophosphorus Compounds. Siddall[136,137] in two papers published in the early 1960s reported that certain neutral bifunctional organophosphorus compounds effectively extract trivalent lanthanides and actinides from strong HNO_3 solutions. [This behavior contrasts sharply (Fig. 5.11) with that of such neutral monofunctional organophosphorus reagents as TBP and DBBP, which, as already noted, extract Am(III) only weakly from strong HNO_3 media.] In particular, Siddall synthesized various methylenediphosphonates



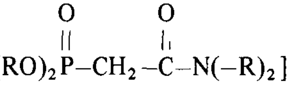
$$[(RO-)_2\overset{\overset{\displaystyle O}{\|}}{P}-CH_2-\overset{\overset{\displaystyle O}{\|}}{P}(-OR)_2]$$

carbamyl phosphonates



$$[(RO-)_2\overset{\overset{O}{\|}}{P}-\overset{\overset{O}{\|}}{C}-N(-R)_2]$$

and carbamyl methylenephosphonates



$$[(RO)_2\overset{\overset{O}{\|}}{P}-CH_2-\overset{\overset{O}{\|}}{C}-N(-R)_2]$$

and determined their ability to extract Am^{3+}, Ce^{3+}, and Pm^{3+} from 0.1*M* to 12*M* HNO_3 solutions. On the basis of the favorable results of his exploratory studies, Siddall suggested such bidentate extractants could be used to remove trivalent lanthanides and actinides from high-level Purex process waste, this idea was eventually patented.[138]

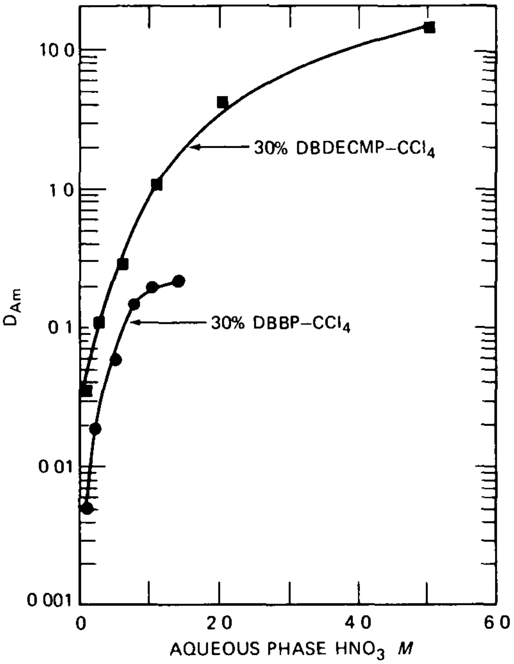
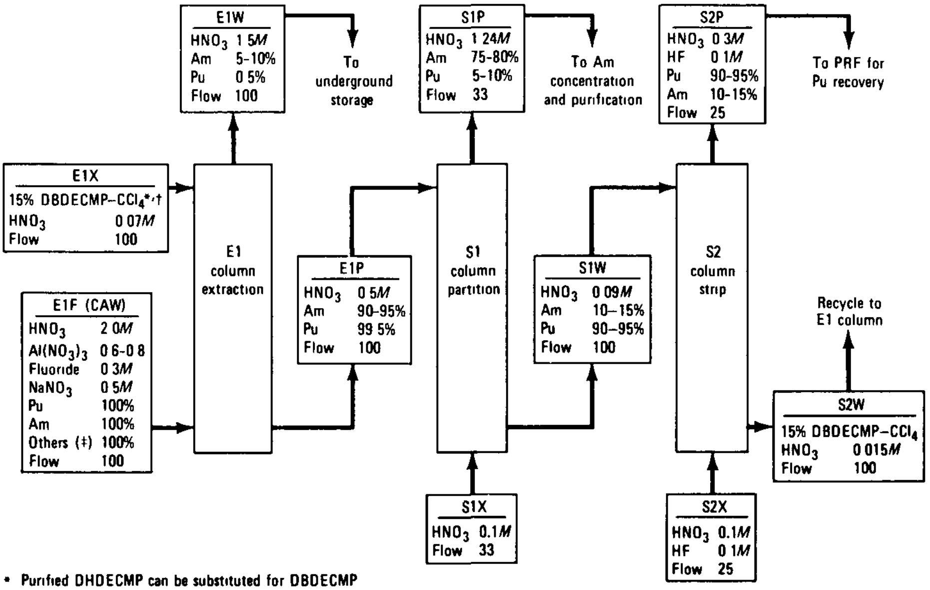


Fig. 5.11 Extraction of Am(III) by typical neutral monodentate and bidentate extractants. DBBP = dibutyl butylphosphonate, DBDECMP = dibutyl-*N*,*N*-diethylcarbamyl methylenephosphonate

Schulz[139] and McIsaac[140] at the Hanford and Idaho Falls sites, respectively, have recently revived interest in plant-scale application of neutral bidentate organophosphorus extractants, particularly dihexyl-*N*,*N*-diethylcarbamyl methylenephosphonate (DHDECMP) and dibutyl-*N*,*N*-diethylcarbamyl methylenephosphonate (DBDECMP). McIsaac and coworkers are concerned with developing a bidentate solvent extraction scheme to remove small amounts of neptunium, plutonium, americium, and other actinides from the high-level waste resulting from processing of irradiated ^{235}U-enriched fuels at the Idaho Chemical Processing Plant.

At Hanford, work is in progress to develop a solvent extraction process to replace the DBBP process (pages 202 to 205) presently used to recover americium and plutonium from neutralized (pH 1) aqueous waste (CAW solution) produced in operation of the Hanford Plutonium Reclamation Facility. A conceptual flow sheet for DBDECMP (or DHDECMP) extraction of Am(III) and Pu(IV) directly from the acid (~2*M* HNO_3) CAW stream is presented in Fig. 5.12; this flow sheet has been successfully demonstrated in miniature mixer–settler runs with an actual CAW solution.

Major deterrents to large-scale applications of carbamyl methylenephosphonate extractants include their current limited availability and high cost ($50 to $100 per liter) and the need to purify them before use. As prepared by the Arbuzov or Michaelis reactions,[136,137] both commercially available DHDECMP and DBDECMP contain an



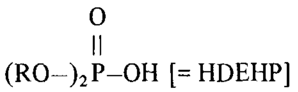
* Purified DHDECMP can be substituted for DBDECMP
† Trichlorobenzene can be substituted for CCl_4.
‡ Includes small concentrations of calcium, magnesium, iron, chromium, nickel, etc.

Fig. 5.12 A conceptual bidentate organophosphorus extraction process for the recovery and separation of americium and plutonium from Hanford CAW solution.[140]

unidentified impurity with a very strong affinity for Am^{3+} at low aqueous-phase HNO_3 *concentrations* (Fig. 5.13); *this impurity must be removed to permit the use of* dilute aqueous acid solutions to strip americium and partition it from coextracted Pu(IV). Pure DBDECMP (Fig. 5.13) can be prepared by vacuum distillation of the technical-grade material at ~180°C and 0.1 torr. Schulz[139] claims that a satisfactorily pure DHDECMP extractant can be prepared from the commercially available material by contacting DHDECMP–CCl_4 solutions for 24 hr at 60°C with 6*M* HCl and subsequent washing of the organic solvent with NaOH and HNO_3 solutions.

Butler and Hall[141] recommend the bidentate extractant, dibutyl-*N,N*-diethylcarbamyl phosphonate for use in determination of americium and other actinides in biological samples.

***Bis*(2-ethylhexyl)phosphoric Acid.** Chemistry involved in the extraction of Am^{3+} by *bis*(2-ethylhexyl)phosphoric acid



$$(RO\text{—})_2\overset{\overset{\displaystyle O}{\|}}{P}\text{—}OH \; [= \text{HDEHP}]$$

has been intensively studied by scientists in many countries. This extractant is commercially available in large quantities, can be readily purified, and has been much used for both analytical and plant-scale recovery and purification of americium.

Ferraro, Mason, and Peppard[142,143] at ANL have established that HDEHP, like other organophosphorus acids, exists as a dimer in nonpolar solvents and predominantly as the monomer in polar diluents. Extraction of small concentrations of trivalent americium by monomeric and dimeric HDEHP, respectively, conforms to the following equations:[144,145]

$$Am^{3+}_{(aq)} + 3HDEHP_{(org)} \rightleftharpoons Am(DEHP)_{3(org)} + 3H^{+}_{(aq)} \tag{5.6}$$

$$Am^{3+}_{(aq)} + 3(HDEHP)_{2(org)} \rightleftharpoons Am[H(DEHP)_2]_{3(org)} + 3H^{+}_{(aq)} \tag{5.7}$$

Mason, Lewey, and Peppard[146] state that monomeric HDEHP may also extract Am^{3+} in the form of the species $[Am(DEHP)_3(HDEHP)_3]_{(org)}$. Letting HX stand for HDEHP, the equilibrium constants for Eqs. 5.6 and 5.7 can be written as

$$K_{ex} = \frac{[AmX_3] \cdot [H^+]^3}{[Am^{3+}] \cdot [HX]^3} \text{ and } K_{ex} \frac{[Am(HX_2)_3] \cdot [H^+]^3}{[Am^{3+}] \cdot [(HX)_2]^3}$$

respectively. For Eq. 5.6, $K_{ex} = 0.27$ (Ref. 144), whereas for Eq. 5.7, $K_{ex} = 0.033$ (Ref. 112).

Data in Table 5.6 illustrate the profound effect of the nature of the carrier solvent on HDEHP extraction of Am(III). Corresponding to the inverse third-power

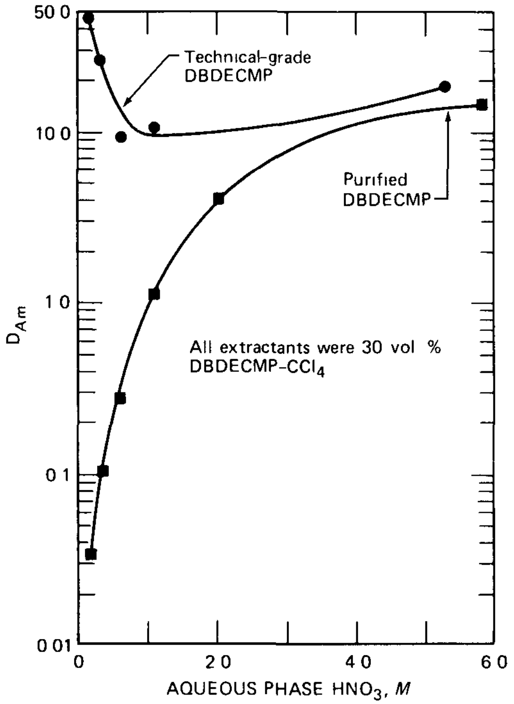


Fig. 5.13 Extraction of Am(III) by purified and unpurified DBDECMP [140]

Table 5.6

EFFECT OF DILUENT TYPE ON HDEHP EXTRACTION OF Am(III)*

(Organic Phase: 0.5*M* HDEHP; Aqueous Phase: 0.5*M* HNO_3)

Diluent	D_{Am}
Isooctane	21.1
Decane	17.7
Cyclohexane	4.5
CCl_4	0.49
Toluene	0.15
Benzene	0.092
Chloroform	0.0167

*[From E. S. Gureev, V. N. Kosyakov, and G N Yakovlev,[144] Extraction of Actinide Elements of Dialkylphosphoric Acids, *Radiokhimiya*, 6: 655 (1964), through *Soviet Radiochemistry (English Translation)*, 6: 639 (1964).]

dependency on hydrogen concentration (Eqs. 5.6 and 5.7), relatively dilute (1*M* to 2*M*) HNO_3 solutions readily strip Am^{3+} from HDEHP extractants (Fig. 5.14).

Kinetics of extraction of Am^{3+} from $HClO_4$ solutions by HEDHP-*n*-decane solutions follow the rate law:

$$\frac{d[Am^{3+}]}{dt} = \frac{k\,[Am^{3+}]_{(aq)} \cdot [HDEHP]^{1.5}_{(org)}}{[H^+]^2_{(aq)}} \tag{5.8}$$

At 25°C and $\mu = 0.2M$, $k = 0.137 \pm 0.02\ (mol)^{0.5}\ sec^{-1}$. According to Karpacheva and Ilozheva,[147] the limiting step in the extraction process is

$$AmDEHP_2^+ + HDEHP \rightarrow Am(DEHP)_3 + H^+ \tag{5.9}$$

which most likely takes place in the aqueous phase.

A countercurrent HDEHP extraction process was used at Hanford in the late 1960s as part of the processing sequence for recovering and purifying some 1000 g of Am and 50 g of Cu from irradiated Shippingport reactor fuel.[106-109,148] This is by far the largest plant-scale application of HDEHP extraction technology for americium recovery and purification yet reported. Feed for the HDEHP extraction process used at Hanford was the crude concentrate (Table 5.4) obtained in prior TBP batch extractions. The crude concentrate was adjusted to pH 4 by the addition of NaOH. Hydroxyacetic acid and sodium nitrilotriacetate were added to complex aluminum, iron, and various other metallic impurities and to provide buffering capacity. Americium, curium, and lanthanides were extracted into a 0.4*M* HDEHP–0.2*M* TBP–NPH (Normal Paraffin Hydrocarbon, a mixture of C_{10}–C_{14} normal paraffins) solvent using countercurrent equipment (pulse columns installed in the Hanford Semiworks). The actinide–lanthanide mixture was stripped into 2*M* HNO_3; the strip product was adjusted to 0.5*M* H^+ by destruction of HNO_3 by reaction with sugar and thermally concentrated to a volume of about 570 liters. [Follow-on chromatographic ion-exchange procedures used to separate the americium from lanthanides and curium are described on pages 245 to 252.] This HDEHP extraction process proceeded extremely well; americium and curium recoveries exceeded 95%. A chemical flow sheet for the recovery–purification scheme is given in Fig. 5.15.

A simple HDEHP extraction-strip process (Dapex process) was also devised and used in the Curium Recovery Facility at Oak Ridge.[76,149] This process was used to convert nitrate solutions containing americium, curium, and lanthanides to chloride media for subsequent amine extraction separations; it was also used with chloride feeds to separate americium and curium from aluminum. A flow sheet for the latter purpose is shown in Fig. 5.16; this flow sheet features coextraction of the americium, curium, and lanthanides into an 0.7*M* HDEHP solvent, scrubbing out of impurities with dilute HCl, and stripping of the actinides and lanthanides with 2*M* HCl. Leuze and Lloyd[76] state, "Plant operation of this process was satisfactory at a feed power density of 20 W/1; extraction losses were low, and decontamination factors of 540 and 24 were obtained for ^{106}Ru and ^{95}Zr–^{95}Nb, respectively."

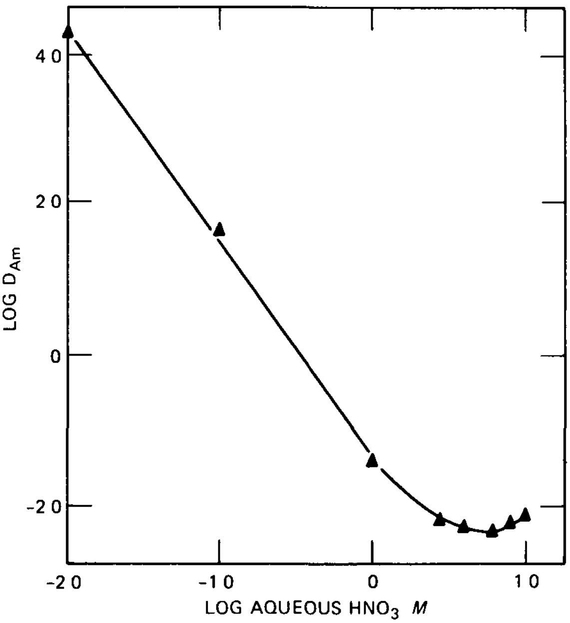


Fig. 5.14 Extraction of Am(III) by 0.5*M* HDEHP in isooctane [From E. S. Gureev, V. N. Kosyakov, and G. N. Yakovlev,[144] Extraction of Actinide Elements by Dialkylphosphoric Acids, *Radiokhimiya,* 6: 655 (1964), through *Soviet Radiochemistry (English Translation),* 6: 639 (1964).]

Another simple HDEHP batch extraction-strip process (Cleanex process) is routinely used in the Transuranium Processing Plant at the Oak Ridge National Laboratory to reclaim americium, curium, and other transplutonium elements from rework solutions and/or to convert from nitrate to chloride media.[150] The Cleanex process is so named because it will clean up transplutonium elements from a great variety of corrosion products, floor sweepings, and other assorted contaminants. It involves extraction of the transplutonium elements from a dilute acid (<0.1*M*) feed into a 1*M* HDEHP–Amsco 125-82 solvent, the metallic impurities are left in the aqueous phase, which is discarded. Subsequently a 6*N* HCl solution is used to strip the actinides from the HDEHP phase. Advantages of the batch Cleanex process have been cited by Bigelow, Chattin, and Vaughen.[150]

Various HDEHP extraction processes have been proposed and, in some instances, used to separate gram amounts of americium (and, usually, associated curium) from large quantities of lanthanides. These processes[151-156] take advantage of the results of Weaver and Kappelmann, who were the first to show that HDEHP extracts lanthanides much more strongly than actinides from aqueous carboxylic acid solutions containing an aminopolycarboxylic acid chelating agent. [Weaver and Kappelmann coined the acronym Talspeak (*T*rivalent *A*ctinide *L*anthanide *S*eparation by *P*hos-

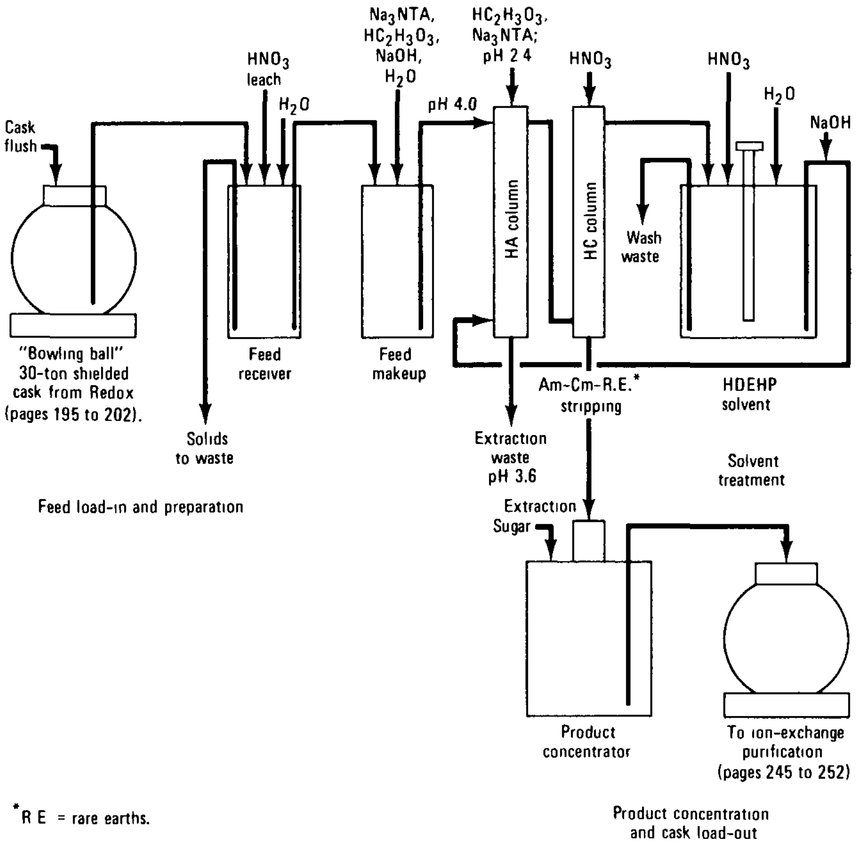


Fig. 5.15 Simplified HDEHP extraction process used at Hanford in recovering americium and curium from Shippingport reactor fuel.[106]

phorus Reagent *E*xtraction from *A*queous *K*omplexes) for this type of separation scheme.] Data in Table 5.7 and Fig. 5.17 are illustrative of the actinide–lanthanide separations that can be achieved by Talspeak-type processes. The actinides are so much more strongly complexed by diethylenetriaminepentaacetic acid (DTPA), the preferred complexing agent, that even the most extractable heavy actinides are only about one-tenth as extractable as the least extractable lanthanides.

Lactic acid is preferred for use in the Talspeak process over the other carboxylic acids listed in Table 5.7 because, of the hydroxyacids, it alone has a high enough solubility of its lanthanide salts to be useful in the separation of actinides from high concentrations of lanthanides. Lunichkina and Renard[157] have recently studied HDEHP extraction of lanthanum and neodymium from 1.0*M* lactic acid–0.5*M* $NaNO_3$ solutions containing 10 g liter^{-1} La or Nd. Their results confirm earlier observations of Weaver and Kappelmann[151] that the HDEHP phase resulting from contact with such

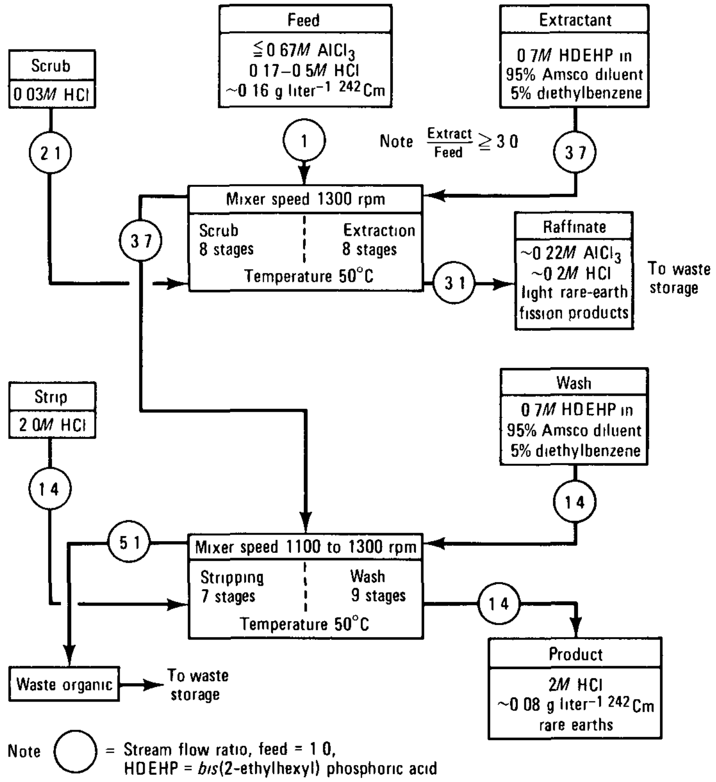


Fig. 5.16 Dapex process used at Oak Ridge to separate americium and curium from aluminum [149]

aqueous solutions contains both metal and lactate species. Lunichkina and Renard suggest that HDEHP extraction of lanthanides (Ln) from lactate (L) media probably proceeds by the reaction:

$$\mathrm{LnL^{2+} + (HDEHP)_2 \rightleftharpoons Ln(DEHP)_2L + 2H^+} \qquad (5.10)$$

Fardy and Pearson[158] found that the purity of HDEHP markedly influences the separation of cerium from americium in a lactic acid–DTPA solution but does not significantly affect separation of americium from europium or promethium. No explanation for this different behavior has been advanced.

No plant-scale application of the Talspeak process in the form originally devised by Weaver and Kappelmann has yet been made. The Tramex process (compare pages 224 to 230) is currently used at Oak Ridge in the processing of HFIR targets for the separation of americium and curium from fission-product lanthanides. In this respect, Weaver[88] believes that the Talspeak process, although it gives a smaller intergroup separation factor than the Tramex process, has a distinct advantage in that its aqueous

Table 5.7

HDEHP EXTRACTION OF AMERICIUM AND LANTHANIDES FROM MIXTURES OF DTPA AND CARBOXYLIC ACIDS*

(Organic Phase: 0.2*M* HDEHP in Diisopropylbenzene; Aqueous Phase: 1*M* Carboxylic Acid–0.05*M* DTPA, pH 3.0)

Acid	Distribution coefficient for americium	Separation factor		
		La/Am	Ce/Am	Eu/Am
Formic	0.0102	270	147	19
Acetic	0.0086	430	163	24
Propionic	0.0052	770	190	29
Butyric	0.0009		190	10
Glycolic	0.0124	145	97	84
Lactic	0.0085	380	140	91
Citric	0.0102	73	84	105
Malonic	0.0087	290	184	57
α-Hydroxyisobutyric	0.0132	370	144	62
Glycine–HNO_3	0.0111	270	144	16

*[From B. Weaver and F. A. Kappelmann,[151] Preferential Extraction of Lanthanides over Trivalent Actinides by Monoacidic Organophosphates from Carboxylic Acids and from Mixtures of Carboxylic and Aminopolyacetic Acids, *Journal of Inorganic and Nuclear Chemistry,* **30:** 263 (1968).]

medium is sufficiently noncorrosive that it does not require special construction materials.

Berger et al.,[159] and other French investigators have applied a Talspeak-like process as part of a scheme for recovering milligrams of americium and curium from highly irradiated Al–10 wt.% Pu alloys. Following dissolution of the irradiated targets, two trilaurylamine extraction cycles were used to recover plutonium from an HNO_3 solution. The plutonium-free raffinate was adjusted to 1.5*M* $Al(NO_3)_3$ and 1*M* to 2*M* HNO_3 and batch contacted with 0.25*M* DHEHP-*n*-dodecane to extract fission-product zirconium and ruthenium. Finally, two HDEHP extraction cycles (Fig. 5.18) were used to recover the americium and curium and to purify them from fission-product lanthanides. A distinguishing feature of the French flow sheet is the use of a concentrated $LiNO_3$ solution containing DTPA to selectively strip americium and curium from the HDEHP extract. Weaver[88] points out that 3*M* $LiNO_3$–0.05*M* DTPA solutions are less effective than carboxylic acid–DTPA solutions in separating transplutonium elements from rare earths. Anion-exchange procedures used for the final purification and separation of americium from curium are described on pages 239 to 243

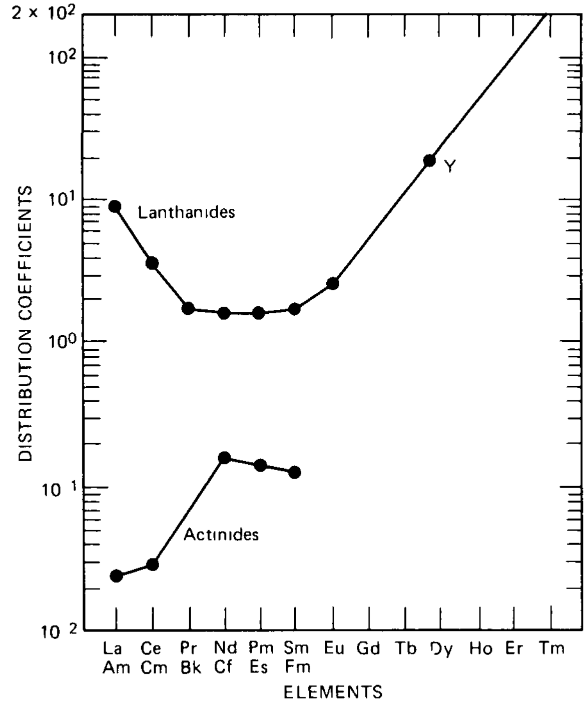
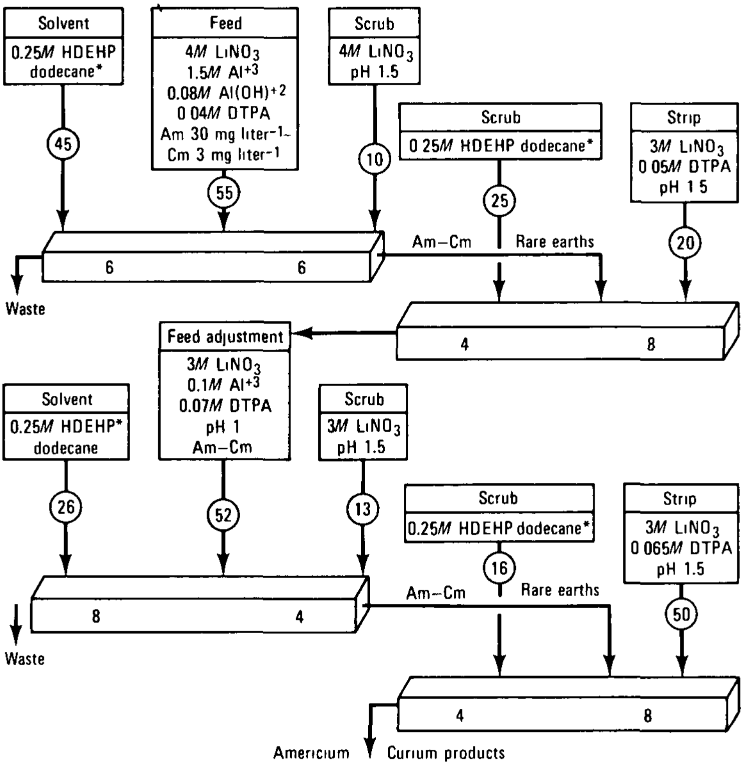


Fig. 5.17 Separation of actinides and lanthanides in the Talspeak process Organic phase, 0 3*M* HDEHP in diisopropylbenzene, aqueous phase, 1*M* lactic acid–0 005*M* DTPA at pH 2 0 [From B Weaver and F A Kappelmann,[151] Preferential Extraction of Lanthanides over Trivalent Actinides by Monoacidic Organophosphates from Carboxylic Acids and from Mixtures of Carboxylic and Aminopolyacetic Acids, *Journal of Inorganic and Nuclear Chemistry*, **30**: 263 (1968)]

Koch, Kolarik, and coworkers in West Germany have been developing for some time now an HDEHP extraction scheme for the removal and separation of americium and curium from Purex-process high-level waste that incorporates both normal and "reverse" Talspeak processes[160–163] A simplified schematic of their current flow sheet is presented in Fig 5 19, with pertinent stream compositions listed in Table 5 8 [An earlier HDEHP solvent extraction flow sheet[164 165] had to be abandoned since it produced a citrate-complexed waste in which vigorous and potentially explosive exothermic reactions occurred on calcination] The initial process step involves denitration of the high-level waste (1WW solution) by reaction with formic acid Conditions are maintained in this step under which americium and curium remain in solution while part of the fission and corrosion products are coprecipitated The denitrated waste solution, which contains the americium, curium, fission-product rare earths, strontium, and cesium, is adjusted to extraction conditions

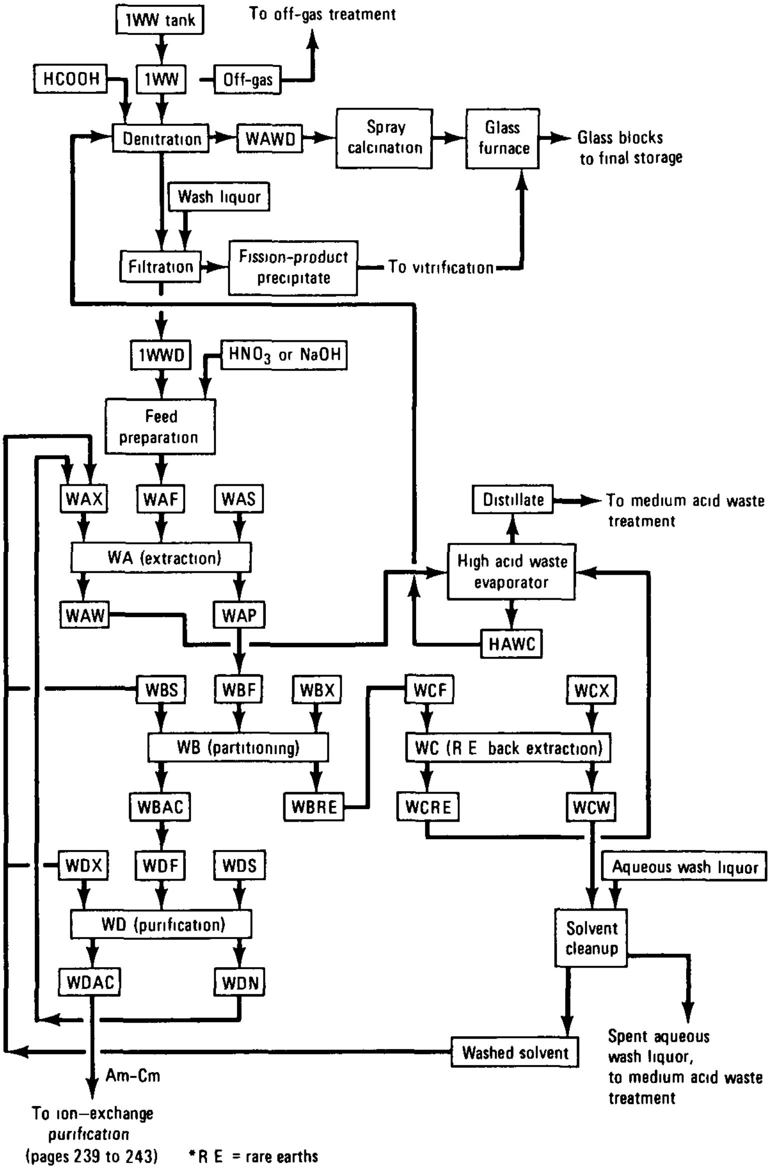


Note Numbers in circles represent the flow rate in milliliters per hour.

* Solvent was mixed with 4M $LiNO_3$–pH 3 before being used

Fig. 5.18 HDEHP extraction process used in France in the recovery and purification of americium and curium from irradiated plutonium–aluminum alloy. [From R. Berger, G. Koehly, C. Musikas, R. Pottier, and R. Sontag,[159] Processing of Highly Irradiated Al–Pu Alloy, *Nuclear Applications and Technology*, 8: 371 (1970).]

The extraction cycle (Fig. 5.19) in the German process involves (1) coextraction of the americium, curium, and rare earths into an 0.3*M* HDEHP–0.2*M* TBP–NPH solvent (WA mixer–settler bank); (2) partitioning of americium and curium from rare earths (WB bank) using a 1*M* lactic acid–0.05*M* DTPA solution to preferentially strip the actinides (reverse Talspeak-type process); (3) stripping of rare earths with 5*M* HNO_3 (WC bank); and (4) further purification of the americium and curium by a normal Talspeak process (WD bank). The rare-earth-loaded solvent (WDW solution) from the WD bank is recycled to the WA bank. The spent solvent (WCW solution) from the WC bank after cleanup is recycled as extractant to the WA and WD banks and as organic scrub solution to the WB bank. The dilute americium and curium product from the WD bank is a 1*M* lactic acid–0.05*M* DTPA solution that is concentrated and purified further by the cation-exchange resin process discussed on pages 245 to 252.



*R E = rare earths

Fig. 5.19 German HDEHP extraction process for recovering americium and curium from high-level Purex-process waste (Stream compositions are listed in Table 5.8.) [From G. Koch, Z. Kolarik, H Haug, W. Hild, and S. Drobnik,[161] Recovery of Transplutonium Elements from Fuel Reprocessing High-Level Waste Solutions, in Symposium on the Management of Radioactive Wastes from Fuel Reprocessing, Paris, France, November 27–December 1, 1972 (CONF-721107, pp. 1081-1110), also, German Report KFK-1651, November 1972.]

Table 5.8

GERMAN HDEHP AMERICIUM–CURIUM RECOVERY PROCESS: STREAM FLOWS AND COMPOSITION*

Stream designation†	Composition													
	Am g liter^{-1}	Cm g liter^{-1}	HNO_3 *M*	RE‡ g liter^{-1}	FP§ g liter^{-1}	$NaNO_3$ *M*	$Ni(NO_3)_2$ *M*	CP¶ g liter^{-1}	H_5DTPA** *M*	HLAC†† *M*	HDEHP‡‡ *M*	TBP§§ *M*	pH	Flow
1WWD	0.12	0.01	4		27	0.22		4						100
WAF	0.06	0.005		5	3¶¶	0.11	0.004						2	200
WAX				0.002							0.3	0.2		500
WAS			0.22											134
WAW					1 8	0.07	0.002						1.1	334
WBF	0.024	0.002		2							0.3	0.2		500
WBX									0.05	1			3.0	166
WBS											0.3	0.2		166
WDF	0.072	0.006		0.006					0.05	1			3.0	166
WCF				1.5							0.3	0.2		666
WCX			5											166
WCRE			4.9	6										166
WCW											0.3	0.2		166
WDX											0.3	0.2		125
WDS									0.05	1			3.0	42
WDAC	0.058	0.0048							0.05	1			3.0	208
WDW				0.008							0.3	0.2		125

*[From G. Koch, Z. Kolarik, H. Haug, W. Hild, and S. Drobnik,[161] Recovery of Transplutonium Elements from Fuel Reprocessing High-Level Waste Solutions, in Symposium on the Management of Radioactive Wastes from Fuel Reprocessing, Paris, France, November 27–December 1, 1972 (CONF-721107, pp. 1081-1110), also, German Report KFK-1651, November 1971.]

†See Fig. 5.19.

‡Rare-earth fission products.

§Other fission products.

¶Corrosion products.

**Diethylenetriaminepentaacetic acid.

††Lactic acid.

‡‡*Bis*(2-ethylhexyl)phosphoric acid

§§*Tri-n*-butyl phosphate.

¶¶Essentially rubidium, strontium, cesium, and barium.

Thus far the German HDEHP americium–curium extraction process has been demonstrated only on a laboratory-scale with simulated Purex-process waste containing added radioisotopes. Although process performance was excellent under such conditions, it is clear, as Koch[161] notes, that pilot-plant-scale tests with actual high-level waste are needed to determine fully the utility of this americium–curium recovery scheme.

HDEHP extraction processes that make use of the differences in stability of the chloride and thiocyanate complexes of the lanthanides and actinides (compare Chap. 3) have been proposed[95,101,166,167] for separating americium and curium from the rare earths. Such processes use concentrated LiCl (or $CaCl_2$) and NH_4SCN aqueous feedstocks. Gureev et al.[166] have described laboratory-scale mixer–settler tests in which an 0.74*M* HDEHP–dodecane solvent was used with either a 6*M* NH_4SCN or a 11*M* LiCl–0.4*M* HCl aqueous feed to extract rare earths away from americium. Decontamination factors of americium from rare earths of ~10 (Cl^- system) and ~1000 (SCN^- system) were realized in these tests. No industrial-scale application of such processes is anticipated, since they are less efficient than the Talspeak process (or modifications thereof)[101] and involve the use of more corrosive and/or difficult-to-handle aqueous-phase compositions.

Similar to results with TBP (compare pages 201 and 202), there is conflicting evidence regarding HDEHP extraction of Am(VI) from HNO_3 solutions. Zangen[122] states that HDEHP–CCl_4 solutions extract Am(VI) from 0.05*M* HNO_3 ~1000 times better than Am(III). Penneman and Asprey[32] also found that an 0.3*M* HDEHP–toluene solution extracts Am(VI) quantitatively from 0.1*M* HNO_3–0.1*M* $Na_2S_2O_8$ solution and suggest this procedure for separating macro amounts of americium from Cm(III). On the other hand, workers at ORNL observe that HDEHP extracts Am(III) considerably better than Am(VI).[156,168] Myasoedov et al.[95] suggest this latter result may have been obtained because of the reduction of Am(VI) to inextractable Am(V). Penneman and Keenan[32] note tracer concentrations of americium are difficult to maintain in the hexavalent state. Definitive experiments are needed to resolve this conflict.

Watanabe and Sagawa[169] have devised an HDEHP extraction process for separating curium and plutonium from americium. This procedure involves reduction of Am(VI) to Am(V) with H_2O_2 in 0.1*M* HNO_3 solution, and extraction of plutonium and Cm(III) into a 50 vol.% HDEHP–xylene (or dodecane) solvent. A decontamination factor of ^{241}Am from ^{242}Cm of 30 ± 10 is obtained in one cycle of solvent extraction. It is not clear why H_2O_2 does not reduce Am(V) to Am(III), nor is it clear whether plutonium is in the +4 or the +3 state. Lee[170] has reported on a study of the Am(III)–Cm(III) separation factors in HDEHP extraction systems.

Myasoedov et al.[171,172] report that a 3 : 1 mixture of HDEHP and P_2O_5 in cyclohexane extracts Am^{3+} quantitatively from 1*M* to 12*M* HNO_3 solution (Fig. 5.20). Large concentrations of $Al(NO_3)_3$ do not interfere in the extraction of Am^{3+} by an 0.3*M* HDEHP–0.1*M* P_2O_5 solution. The Russian investigators postulate that an entity with a great affinity for trivalent transplutonium elements forms when P_2O_5 is dissolved in HDEHP solutions. Myasoedov and coworkers also report that the

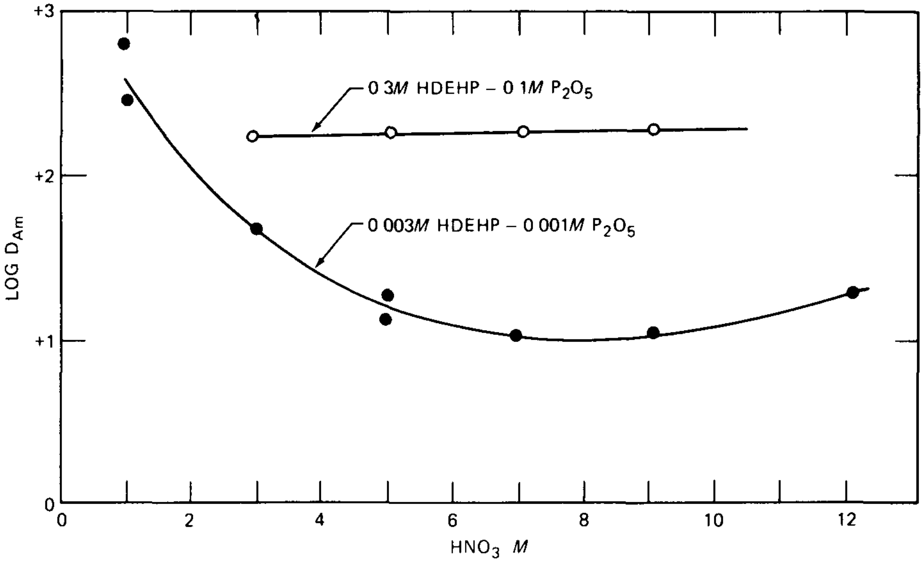


Fig. 5 20 Extraction of Am(III) by HDEHP–P_2O_5 solutions [From B F Myasoedov, M K Chmutova, N E Kochetkova, and G A Pribylova,[171] Solvent Extraction of Trivalent Americium from Acid Media, *Radiochemical and Radioanalytical Letters*, **14:** 63 (1973)]

extractive properties of HDEHP–P_2O_5 mixtures decrease with time A satisfactory way of stripping metal values from the HDEHP–P_2O_5 extractant has not been reported

Synergistic and antagonistic effects in the extraction of Am(VI) and Am(III) by HDEHP–TBP solvents have been reported by Zangen[122,173] and by Kolarik[174] In the system 0 03*M* HDEHP–0 1*M* TBP–CCl_4–0 05*M* HNO_3 Zangen noted a synergistic effect for the extraction of Am(VI) and an antagonistic effect for Am(III) Kolarik notes also that TBP causes only an antagonistic effect in HDEHP extraction of Am(III) from perchlorate, citrate, and nitrilotriacetate solutions

Other Organophosphorus Acid Extractants Only HDEHP has found large-scale use for the recovery and separation of americium, however much laboratory-scale work has been done to evaluate various other organophosphorus acids for their ability to extract americium from different aqueous media and to establish chemistry involved in such extraction systems Several interesting and relevant features of this laboratory work are mentioned here, a more complete description of these studies is provided in Ref 88

Monoacidic phosphonates are obtained by substituting a phosphorus-bound alkyl or aryl group for an ester group of a monoacidic phosphate The former compounds, as shown first by Peppard, Mason, and Hucher,[175,176] are considerably more powerful extractants for the actinides than are the corresponding monoacidic phosphates. Taking advantage of this greater extractive power, Baybarz, Leuze, and Weaver[177,178] devised a countercurrent extraction process using a 1*M* solution of HEHØP [*bis*(2-ethylhexyl) phenylphosphonic acid] in diethylbenzene as an extractant to separate americium and curium from transcurium elements contained in 1*M* HCl. Americium and curium remain in the aqueous phase while the transcurium elements are stripped from the organic phase with 4*M* HCl. Curium losses are about 0.1%, and the decontamination factor of transcurium elements from americium is $\sim 10^3$. Routine use of this process at ORNL in actinide processing operations was precluded by the presence of zirconium in feed solutions because of corrosion of zirconium-based equipment. Zirconium is strongly extracted by HEHØP (Ref. 179); such extraction adversely affects the separation of americium and curium from transcurium elements.

Separation of lanthanides and actinides in the Talspeak process (compare pages 208 to 220) is smaller when HDEHP is replaced by the more powerful HEHØP (Ref. 151). For example, extraction by 0.1*M* HEHØP in diisopropylbenzene from 1*M* lactic solutions 0.04*M* to 0.2*M* in Na_5DTPA gives separation factors of 100 for cerium and europium over americium, but the neodymium/californium separation factor is only about one-half as large as that obtained with HDEHP.

Mason, Bollmeier, and Peppard[180,181] have used *bis*(2,6-dimethyl-4-heptyl) phosphoric acid, $[(i\text{-}C_4H_9)_2CHO]_2PO(OH)$, to preferentially extract Am(VI) and thus partition americium from lanthanides and trivalent actinides. They report that, in the system 0.6*F* $[i\text{-}C_4H_9)_2CHO]_2PO(OH)$-*n*-heptane– 0.025*F* HNO_3–0.025*F* $AgNO_3$–0.185*F* $K_2S_2O_8$, the extraction constant for oxidized americium is greater than 40, whereas that for Cm(III) is $<10^{-5}$. Mason, Bollmeier and Peppard recommend the use of *bis*(2,6-dimethyl-4-heptyl)phosphoric acid as the stationary phase in extraction chromatography systems (compare page 255), but thus far no such application has been reported.

Much interest has been shown in the chemistry and reaction mechanisms involved in the extraction of Am(III) by mono-(2-ethylhexyl)-phosphoric acid $[(H_2)EHP]$.[143,145,166,182-188] This reagent has a much higher tendency to polymerize than HDEHP. In alcohols where (H_2)EHP is monomeric, Am(III) extraction follows the mechanism:[186]

$$Am^{3+}_{(aq)} + 3[(H_2)EHP]_{(org)} \rightleftharpoons Am(HEHP)_{3(org)} + 3H^+_{(aq)} \qquad (5.11)$$

Rao, Mason, and Peppard[183] give the following mechanism for the extraction of Am^{3+} by dimeric (H_2)EHP in hexone:

$$Am^{3+}_{(aq)} + 2.5[(H_2)EHP]_{2(org)} \rightleftharpoons Am(HEHP)[H_3(EHP)_2]_{2(org)} + 3H^+_{(aq)} \qquad (5.12)$$

Finally the extraction of Am(III) by (H_2)EHP in nonpolar diluents (e.g., *n*-hexane) can be represented as:[182,184,185]

$$Am^{3+}_{(aq)} + [(H_2)EHP]_{p(org)} \rightleftharpoons Am[H_{2p-3}(EHP)_p]_{(org)} + 3H^+_{(aq)} \qquad (5.13)$$

Because the extraction capacity of $(H_2)EHP$ is greater than that of HEDHP, considerable effort has been expended in devising $(H_2)EHP$ extraction processes for separating Am(III) from lanthanides. Systems studied in laboratory-scale batch and countercurrent tests involve the extraction of Am(III) from concentrated LiCl solutions[189-191] and from 0.1*M* to 10.3*M* NH_4SCN media.[166,185] Although excellent separations have been obtained in some cases, none of these $(H)_2EHP$ extraction schemes have found any plant-scale use largely because of the required precise control of conditions.

In addition to those already cited, the following organophosphorus acids have also been used in laboratory-scale americium extraction studies: di[*para*(1,1,3,3-tetramethylbutyl)phenyl]-phosphoric acid;[145,146,192] di(hexoxymethyl)phosphoric acid;[193,194] di-*n*-octylphosphoric acid;[195] di-neooctylphosphoric acid;[196] *bis*(2,6-dimethyl-4-heptyl)phosphoric acid;[197] di-*n*-octylphosphinic acid;[198,199] mono-*n*-octylphosphinic acid;[200] 2-ethylhexylphosphinic acid;[200] *n*-octylphenylphosphinic acid;[201] and cyclooctylphenylphosphinic acid.[201]

Amine Extractants. Nitrogen-based extractants, particularly tertiary amines and quaternary ammonium compounds, have been widely studied and used for separating and recovering americium and other actinide elements from aqueous media. General reviews of amine extractants and extraction chemistry have been written by Schmidt,[202] by Coleman, Blake, and Brown,[203,204] and by Müller.[93]

Tertiary Amine Salts. Paralleling the behavior of neutral monodentate organophosphorus extractants, tertiary amine salts extract Am^{3+} only poorly from concentrated HNO_3 or HCl solutions but very strongly from concentrated nitrate or chloride solutions of low acidity (Fig. 5.21). Tertiary amine extraction of tracer amounts of americium from HNO_3–metal nitrate [e.g., $Al(NO_3)_3$, $LiNO_3$, and $Mg(NO_3)_2$] solutions has been investigated in detail as a function of type and concentration of metal nitrate[105,106,113,123] amine type and concentration;[123,206-208] and diluent type.[105,123] Similar studies have been made for tertiary amine extraction of tracer americium from HCl–metal chloride solutions: type and concentration of metal chloride;[93,178,209-215] amine type and concentration;[178,209,214-219a] and diluent effects.[209,215,216] Results and findings of these studies are recounted in Refs. 88 and 95.

In tertiary amine extraction of americium from both nitrate and chloride solutions, D_{Am} varies with the square of the amine concentration.[178,205,206,209,214,216,218] From this extraction dependency, Marcus, Givon, and Choppin[206] and Horwitz et al.[205] assume that Am^{3+} is extracted from nitrate media as the complex $(R_3NH)_2Am(NO_3)_5$. In a similar fashion, Moore[216] postulated that tertiary amines extract Am^{3+} from chloride solutions according to the reaction:

$$2R_3N_{(org)} + 2H^+_{(aq)} + AmCl_5^{2-}{}_{(aq)} \rightleftharpoons (R_3NH)_2AmCl_{5(org)} \qquad (5.14)$$

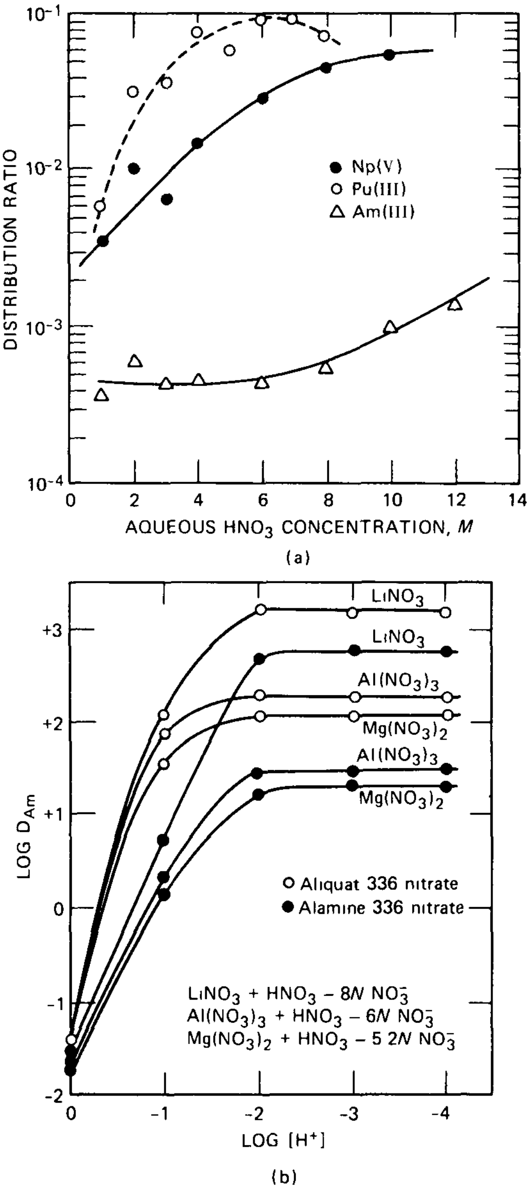


Fig. 5.21 Amine extraction of Am^{3+} from nitrate solutions. (a) Extraction from HNO$_3$ solutions by 10 vol.% tri-*n*-octylamine in xylene. [Adapted from W. E. Keder, J. C. Sheppard, and A. S. Wilson,[207] The Extraction of Actinide Elements from Nitric Acid Solutions by Tri-*n*-Octylamine, *Journal of Inorganic and Nuclear Chemistry,* **12**: 327 (1960).] (b) Extraction from HNO$_3$–metal nitrate solutions by 0.59*M* Alamine 336 · HNO$_3$ in diisopropylbenzene and 0.39*M* Aliquat 336 · NO$_3$· HNO$_3$ in xylene. [From E. P. Horwitz, C. A. A. Bloomquist, L. J. Sauro, and D. J. Henderson,[205] The Liquid–Liquid Extraction of Certain Tripositive Transplutonium Ions from Salted Nitrate Solutions with a Tertiary and Quaternary Amine, *Journal of Inorganic and Nuclear Chemistry,* **28**: 2313 (1966).]

Müller, Duyckaerts, and Fuger[217] postulate that the complex extracted from chloride solutions is formed by association of the $(R_3NH)AmCl_4$ complex with tertiary amine salts R_3NHCl; the resultant ionic quadrupoles

$$\begin{matrix} R_3NH^+ & AmCl_4^- \\ Cl^- & R_3NH^+ \end{matrix}$$

also contain two amine molecules per Am^{3+} ion.

Marcus[219a] has reported on results of studies of tri-*n*-octylamine extraction of macro amounts of Am^{3+} from 0.85*M* HCl–9.45*M* LiCl solutions. He observed coextraction of lithium with americium in a 1 : 1 mol ratio; lithium was not extracted in the absence of americium. To account for his results, Marcus suggested the following extraction mechanism:

$$AmCl_{2(aq)}^+ + 2Cl_{(aq)}^- + Li_{(aq)}^+ + 2(R_3NHCl)_pR_3NH^+Cl_{(org)}^- \rightleftharpoons [(R_3NHCl)_pR_3NH]_2LiAmCl_{6(org)} \quad (5.15)$$

Weaver[88] mentions having heard doubts expressed about the coextraction of lithium and the validity of Eq. 5.15. In some recent related extraction studies, Harmon et al.[219b] observed that 1*M* solutions of Adogen 464 (a quaternary ammonium salt available from Ashland Chemical Company) in xylene extract substantial amounts of lithium from 10*M* LiCl solutions.

Distribution coefficients of Am^{3+} and other trivalent transplutonium elements from concentrated LiCl solutions are 150- to >1000-fold higher than those of trivalent lanthanides (Fig. 5.22). This phenomenon was used by Moore[216,220,221] in various analytical applications; it was also exploited by process chemists at ORNL in the development of the Tramex process[123,178,209,215,222,223] for plant-scale separation of americium, curium, and other transplutonium elements from fission-product lanthanides and other contaminants.

The flow sheet in Fig. 5.23(a) illustrates the essentials of the Tramex process as originally devised,[178] whereas that in Fig. 5.23(b) shows the particular Tramex process used in the Curium Recovery Facility at Oak Ridge to recover 35 g each of ^{243}Am and ^{244}Cm and about 25 g of ^{242}Cm in a highly pure form.[150] The basic Tramex process [Fig. 5.23(a)] involves selective extraction of Am^{3+} and other transplutonium elements from 10*M* to 11*M* LiCl–0.02*M* to 0.25*M* HCl into the hydrogen chloride salt of a tertiary amine in an appropriate diluent. The organic extract is scrubbed with a small volume of 11*M* LiCl–HCl solution, stripped with 8*M* HCl, and discarded to waste without reuse. The strip product is scrubbed with amine extractant containing nitrous acid to improve decontamination from radioruthenium.

The chemistry involved in the Tramex process has been thoroughly worked out by ORNL chemists and engineers.[123,178,209,215,223] Only highlights of this chemistry are mentioned here; much greater detail is provided in an article by Leuze and Lloyd.[76] Distribution coefficients in the Tramex system, in agreement with the earlier

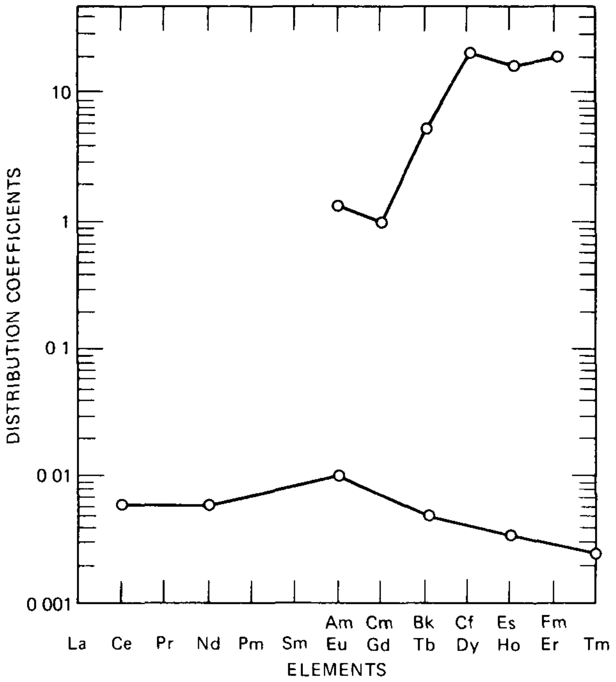


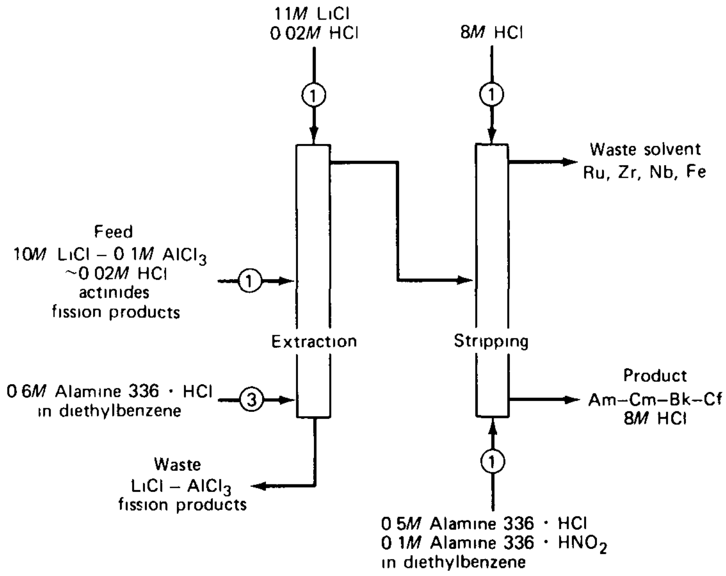
Fig. 5.22 Relative extractability of actinides and lanthanides from 10*M* LiCl solution. Extractant, 0.6*M* Alamine 336 • HCl in diethylbenzene [From R D. Baybarz, B S. Weaver, and H B. Kinser,[209] Isolation of Transplutonium Elements by Tertiary Amine Extraction, *Nuclear Science and Engineering*, **17**: 457 (1963).]

discussion in this chapter, are directly proportional to the second power of the amine concentration and also highly dependent on the type of diluent. Various tertiary amines were tested in laboratory-scale studies, but Alamine 336 (General Mills, Inc.) and Adogen 364HP (Archer Daniels Midland Company), both mixtures of octyl and decyl amines, because they are available in suitably pure form (particularly Adogen 364HP) in commercially available quantities, have been generally used in large-scale Tramex process operation. West and Navarez[224] have published specifications for satisfactory tertiary amine extractants for use in the Tramex process. Because of its ready availability, high flash point, and high distribution coefficients for actinides, diethylbenzene is a preferred diluent.

Extractability of the transplutonium and lanthanide elements into the Tramex process solvent is strongly dependent on the chloride concentrations of the aqueous phase. Distribution coefficients increase with increasing LiCl concentration and decrease with an increasing concentration of free HCl. Mathematical representations for distribution data in the Tramex system have been derived by Roth and Henry[210] and by Agee and Roth.[89] Aluminum chloride is an effective salting agent in the

Tramex process, but its maximum solubility in 10*M* LiCl is 0.2*M* (Ref. 225). At these salt concentrations, $AlCl_3$ will precipitate when the HCl concentration is >0.05*M*. Actinide–lanthanide separation factors in the Tramex process are seriously compromised by the presence of nitrate in the adjusted feed; nearly complete nitrate removal is thus required. The Tramex process provides excellent decontamination from rare earths, aluminum, strontium, and, in general, all those impurities which do not form extractable anionic chloride complexes. Ruthenium, zirconium, niobium, and iron are extracted and remain in the organic. Good ruthenium decontamination is difficult to obtain because of slow conversion of the extracted species to an inextractable one.

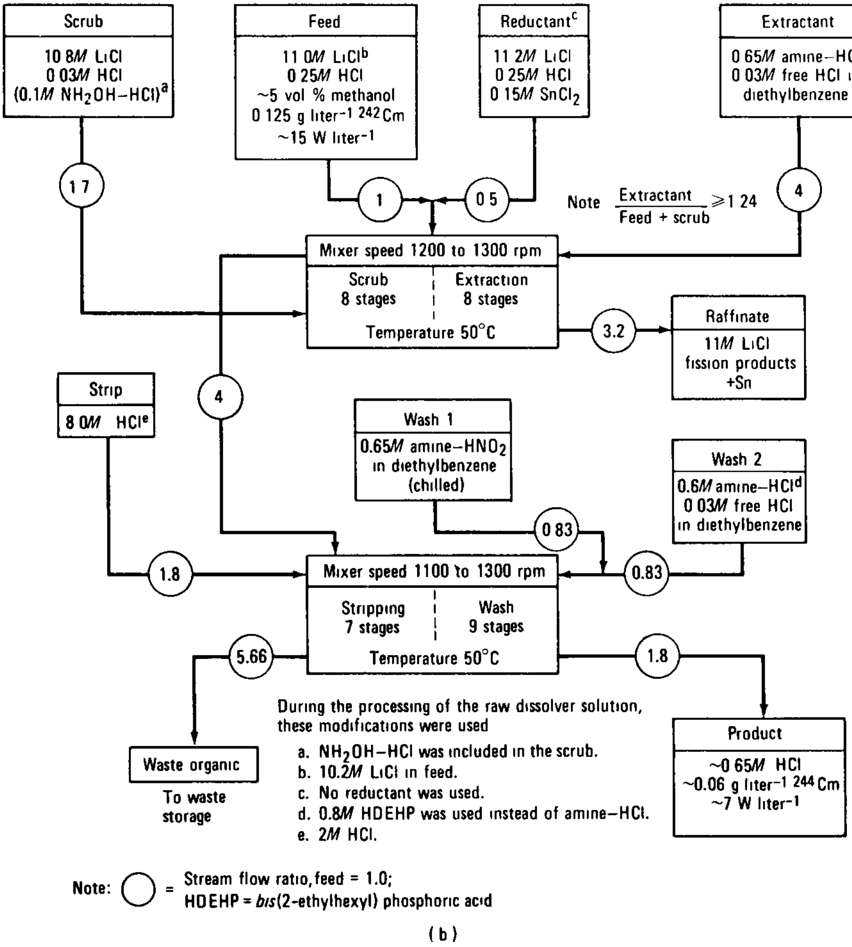
Predominant radiolysis effects in the Tramex process are rapid destruction of HCl and generation of a strong oxidant in LiCl feed solutions which results in poor decontamination from cerium since Ce^{4+} extracts along with the actinides.[76,123,149,150,154,226] To counteract these effects, methanol is added to the feed to suppress the loss of HCl, and 2,5-di-tert-butylhydroquinone (DBHQ), an organic-soluble reductant, is added to the Tramex process solvent to reduce any Ce^{4+} to Ce^{3+} (Ref. 150). In some early Tramex process operation [Fig. 5.23(b)], $SnCl_2$ was added to the feed to insure the presence of trivalent cerium.



(a)

Fig. 5.23 Tramex process flow sheets. (a) As originally devised. (b) As used in the Curium Recovery Facility at Oak Ridge. [From R. E. Leuze and M. H. Lloyd,[76] Processing Methods for the Recovery of Transplutonium Elements, in *Progress in Nuclear Energy, Process Chemistry,* Series III, C. E. Stevenson, E. A. Mason, and A. T. Gresky (Eds.), Vol. 4, page 549, Pergamon Press, Inc., New York, 1970.] See facing page for (b).

The Tramex process has been used routinely since 1967 at the Transuranium Processing Plant (TRU) at ORNL as part of the processing sequence (Fig. 5.24) involved in the recovery and purification of transplutonium elements from highly irradiated (High Flux Isotopes Reactor and/or Savannah River reactors) aluminum-clad ^{242}Pu–Al alloy, $^{242}PuO_2$, and $^{243}AmO_2$–$^{244}CmO_2$ targets. [The Pubex process referred to in Fig. 5.24 involves HDEHP extraction of plutonium and zirconium from the dissolver solution; the Cleanex process (compare pages 208 to 220) is an HDEHP extraction process performed to separate the transplutonides from metallic impurities, and, if necessary, to convert from a nitrate- to a chloride-based system.] At the TRU the Tramex process has been operated satisfactorily in continuous countercurrent



During the processing of the raw dissolver solution, these modifications were used

a. NH_2OH–HCl was included in the scrub.
b. 10.2*M* LiCl in feed.
c. No reductant was used.
d. 0.8*M* HDEHP was used instead of amine–HCl.
e. 2*M* HCl.

Note: ○ = Stream flow ratio, feed = 1.0;
HDEHP = *bis*(2-ethylhexyl) phosphoric acid

Fig. 5.23 (Continued; see facing page for caption.)

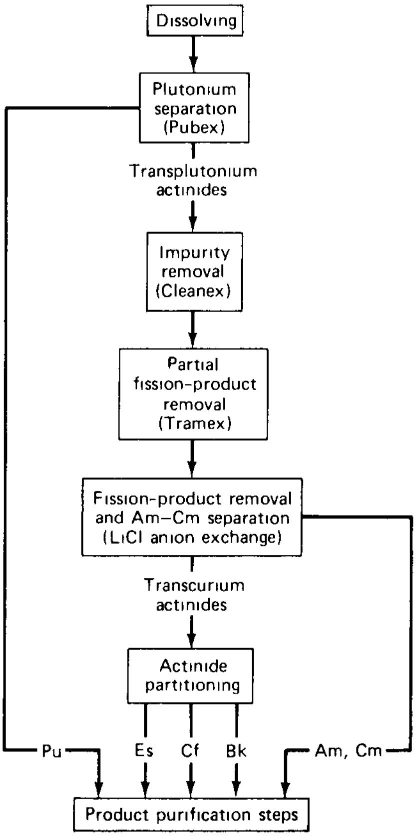


Fig. 5.24 Schematic of processing steps used in the Transuranium Processing Plant at Oak Ridge. Adapted from Ref. 66

equipment (pulse columns) constructed of Zircaloy under flow-sheet conditions very similar to those shown in Fig. 5.23(b) except for the substitution of DHBQ for $SnCl_2$. Design details of the original pulse columns used in Tramex process operations are given in the paper by Leuze and Lloyd;[76] design changes made in second-generation Tramex process pulse columns are mentioned in Ref. 227. Continuous Tramex process operation has been generally satisfactory with feeds derived from PuO_2 and AmO_2–CmO_2 targets. In the initial processing of ^{242}Pu–Al alloy tubes irradiated at Savannah River, extensive carry-over of aluminum to the LiCl feed and attendant solids formation prohibited operation of the continuous Tramex process equipment;[228] batch-type operation was necessary to process such feeds. Other details of the Oak Ridge experience with plant-scale Tramex process operation are provided in a paper by Bigelow, Chattin, and Vaughen.[150]

The Tramex process was also used for a time at the Savannah River Laboratory as part of the process sequence[229] carried out to produce and purify kilograms of

^{244}Cm and ^{243}Am. Savannah River Laboratory experience with continuous Tramex process operation in mixer–settlers has been summarized by Groh et al.[105a] and Prout et al.[230] The two-cycle Tramex process flow sheet shown in Fig. 5.25 was initially satisfactorily demonstrated in laboratory-scale facilities with miniature mixer–settlers. [The actinide–lanthanide concentrate (~2 g liter^{-1} ^{244}Cm, ~0.9 g liter^{-1} ^{243}Am, 6*M* NO_3^-, and 0.4*M* H^+) used as feed to the process derived from the prior batch TBP extraction operations described on pages 195 to 202; the Clanex process described later in this chapter was used as a head-end step to prepare chloride-based feed to the Tramex process.] Subsequently this solvent extraction process (Fig. 5.25) was applied in a large pilot production facility[73] to purify ~1.5 kg of ^{244}Cm and ~0.7 kg of ^{243}Am. Prout et al.[230] state: "The ^{244}Cm produced met the radioactive purity specifications given in the initial report of this series (DP-1009). Although product quality was good, the rate of production was slow. The exacting analysis requirements for process control, and maintenance problems caused by the high concentrations of chloride in the extraction system, made continuous multicycle operation *impractical* . . ." (author's italics). After their unpleasant and frustrating experience with a scaled-up Tramex process, the Savannah River group used a high-pressure displacement chromatographic cation-exchange process (compare pages 245 to 252) to purify the remaining (~3 kg) ^{244}Cm and ^{243}Am.

Nitrate ion in Tramex process chloride feedstock adversely affects the separation of actinides from lanthanides, as previously noted. A HDEHP solvent extraction process (Cleanex process) for converting from nitrate- to chloride-based systems has already been described (compare pages 195 to 202). The Clanex process (Fig. 5.26) is another such nitrate-to-chloride conversion process. In this process, americium, curium, and lanthanides in a 1*M* to 2*M* $Al(NO_3)_3$ or a 7*M* to 8*M* NO_3^- [mixed $Al(NO_3)_3$ and $LiNO_3$] solution are extracted into an 0.6*M* Alamine 336–HNO_3–diethylbenzene solvent, scrubbed with 8*M* $LiNO_3$, and stripped with 3*M* to 8*M* HCl. The strip product is scrubbed with 0.6*M* Alamine 336–HCl–diethylbenzene to remove the last traces of nitrate. The rare earths coextract with the trivalent actinides, but most other contaminants are sufficiently inextractable that they remain in the aqueous raffinate. Applications of the Clanex process have been made both at Oak Ridge[76,231] and at Savannah River.[76,105a,231]

In other laboratory-scale investigations of tertiary amine extractants, Chmutova et al.[232] have studied extraction of Am^{3+} and other trivalent transplutonide elements by mixtures of trioctylamine with TBP, tri-*n*-octylphosphine oxide, and triphenylphosphine oxide. The synergistic effect with such solvents is sufficient according to these Russian scientists to permit quantitative extraction of Am^{3+} from 1*M* HNO_3–7*M* $LiNO_3$ solutions. Conversely Koehly, Madic, and Berger[233] report that extraction of Am^{3+} from $LiNO_3$ solutions by trilaurylamine nitrate solvent decreases when capric acid is added to the organic phase; the antagonistic effect of capric acid is accounted for by these workers on the basis of an addition reaction between one molecule of trilaurylamine nitrate and one capric acid dimer.

Koehly and Berger[234] have studied the effects of aminopolycarboxylic acids (e.g., DTPA and EDTA) on the extraction of Am^{3+} and lanthanides from low-acid $LiNO_3$

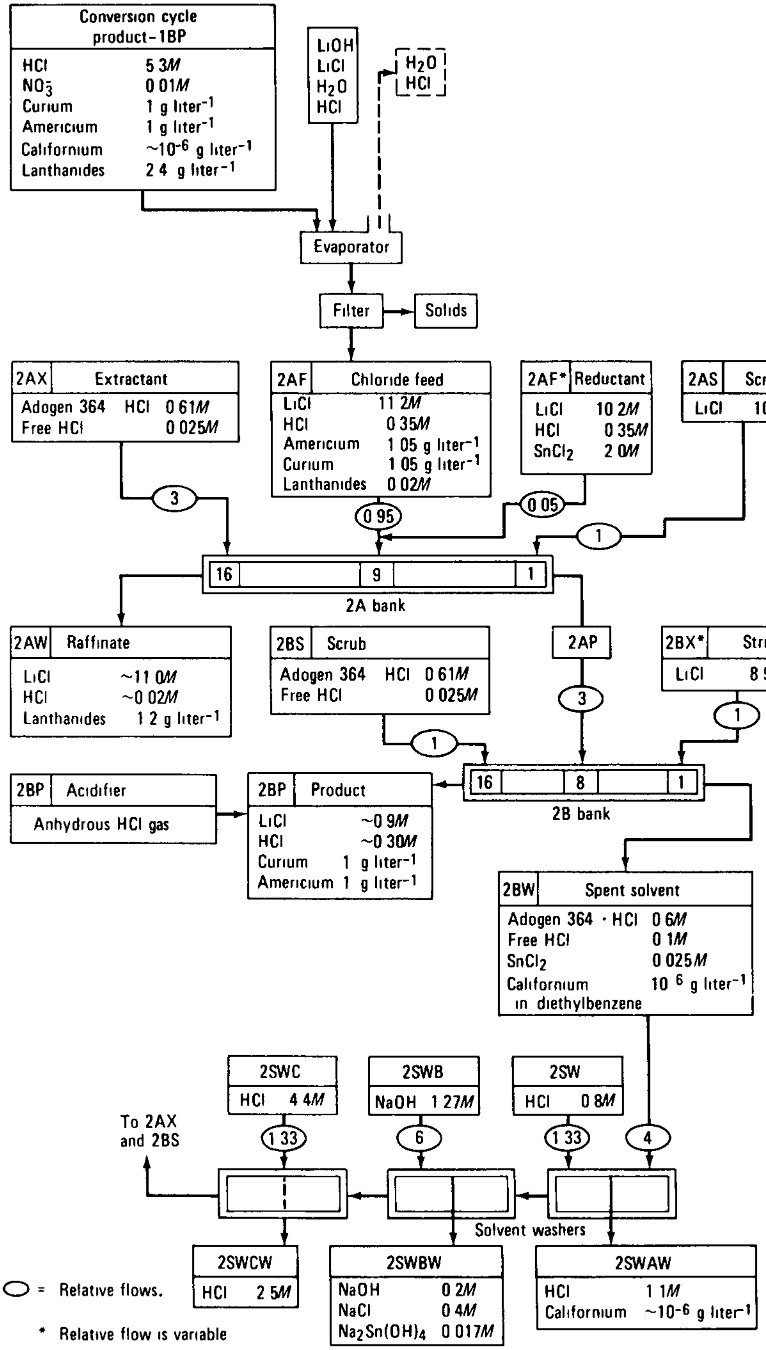


Fig. 5.25 Two-cycle Tramex process flow sheet used to recover americium and curium at the Savannah River Plant.[230]

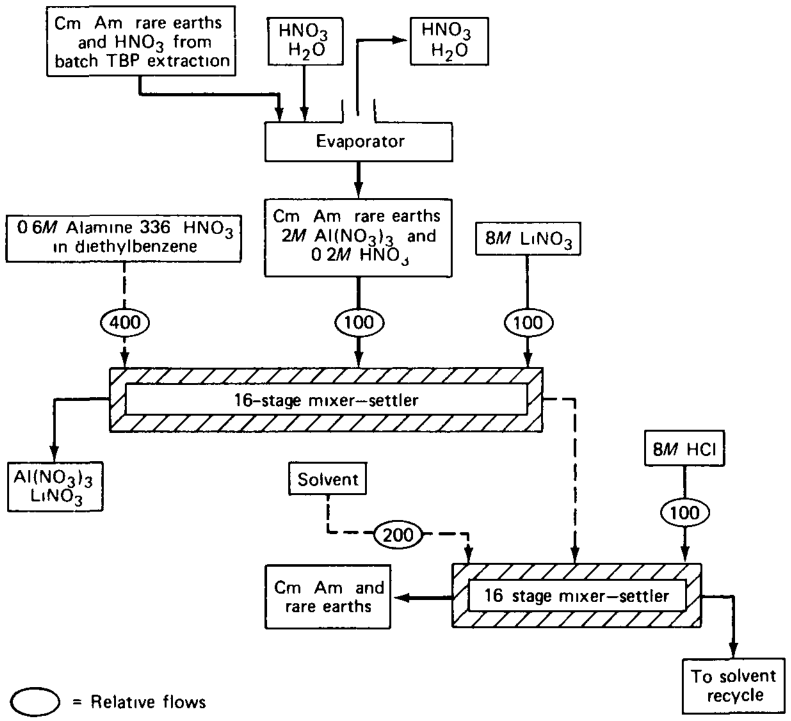


Fig. 5.26 Clanex process used for nitrate to chloride conversion [From H J Groh, R T Huntoon, C S Schlea, J A Smith, and F H Springer,[105a] ^{244}Cm Production and Separation-Status of the Pilot Production Program at Savannah River, *Nuclear Applications* 1· 327 (1965)]

and $Al(NO_3)_3$ solutions by 0 64*M* trilaurylamine in a dodecane–chlorobenzene diluent, separation factors (D_{RE}/D_{Am}) similar to those found (Table 5 5) in TBP extraction from similar solutions were observed Koehly and Berger used their data to devise countercurrent extraction processes for separating Am^{3+} from Pm^{3+} and Cm^{3+}, these processes were subsequently satisfactorily demonstrated in miniature mixer–settler tests with aqueous $LiNO_3$–DTPA solutions containing milligram amounts of ^{241} ^{243}Am and ^{244}Cm (Refs 234 and 235)

Moore[236] reported data for Alamine 336 extraction of Am^{3+} from 0 01*M* HNO_3 solutions containing citric, tartaric, oxalic, acetic, EDTA, or α-hydroxyisobutyric acids

Weaver[237] made a brief comparison of the extraction of Am(VI) and Am(III) from $LiNO_3$ solution by Alamine 336 nitrate in diisopropylbenzene At low nitrate concentrations, Am(III) was less extractable than Am(VI), but a difference in nitrate-concentration dependency reversed the preference at concentrations above 4*M* $LiNO_3$

Quaternary Ammonium Salts Quaternary alkyl ammonium nitrate salts extract Am^{3+} considerably more efficiently from low-acid, highly salted aqueous nitrate solutions than do tertiary alkyl amines, as shown by the data of Horwitz et al [205] [Figure 5 21(b)] [Aliquat 336 is a mixture of trioctylmethyl- and tridecylmethylammonium salts made by General Mills, Inc] Moore[238] also studied the extraction of Am(III) from $LiNO_3$ solutions, whereas Van Ooyen[239 240] studied the extraction of Am^{3+} and other transplutonium elements from $LiNO_3$ solutions with trilaurylmethyl ammonium nitrate–xylene solutions Chudinov and Pirozhkov[241] investigated the effect of the type of metal nitrate salting agent on the extraction of Am(III) by xylene solutions of tetraoctylammonium nitrate Collectively these studies show that D_{Am} decreases rapidly at HNO_3 concentrations much higher than 0 01*M* because of the competition between excess HNO_3 and the americium nitrate complex for the extractant, D_{Am} also varies with diluent type and with the type and concentration of salting agent and appears to be a first-order function of quaternary ammonium extractant concentration The extracted species may be $R_4NAm(NO_3)_4$, but Horwitz et al [205] and others are quick to point out that this empirical formula may well be too simple to account for the extraction process The extraction sequence for trivalent actinides into either Aliquat 336 · nitrate or trilaurylmethylammonium nitrate is $Cm < Cf < Am < Es$

Horwitz, Bloomquist, and Griffin[242] included an extraction step with Aliquat 336 in the preparation of 20 to 30 Ci of high-purity ^{242}Cm Irradiated $^{241}AmO_2$ encapsulated in aluminum was dissolved in an HNO_3–$Hg(NO_3)_2$ solution, a xylene solution of Aliquat 336 was used to extract curium and americium from the $Al(NO_3)_3$ solution and from certain fission products

Koch and Schoen[243 244] devised and tested on a laboratory scale a quaternary ammonium extraction process for the isolation of ^{241}Am from aged plutonium scrap Feed for the extraction process is the americium-containing raffinate resulting from anion-exchange recovery of the plutonium from a strong HNO_3 solution This raffinate is concentrated by evaporation, residual plutonium and, if present, uranium are extracted with Aliquat 336 nitrate in an aromatic diluent The aqueous solution free of plutonium and uranium is adjusted to 7*M* NH_4NO_3 and pH 1 5, and Am^{3+} is extracted with the Aliquat 336 solvent After the organic phase is scrubbed with 7*M* NH_4NO_3, the purified americium is stripped with 3*M* HNO_3 No large-scale application of this process has been reported

Advantages of a quaternary ammonium nitrate extraction process over other schemes (e g , Tramex process) for isolating trivalent actinide–lanthanide elements were discussed by Moore [238] But again, no large-scale use of quaternary amines for the purpose has been made

Moore[245 246] and later Gerontopulos, Rigali, and Barbano[247] found that the thiocyanate salt of Aliquat 336 preferentially extracts actinides over lanthanides from moderately concentrated NH_4SCN solutions Moore[245] gives the order of extractability as $Cf > Bk > Am > Cm \gg Yb \gg Tm > Eu > Pm > Y > Ce > La$ Gerontopulos et al report that distribution coefficients in this system are dependent on temperature, the presence of various contaminant anions, and the type of diluent but that separation factors between americium and rare earths remain relatively constant. Several process-scale applications of the Aliquat 336–NH_4SCN system were suggested by Moore but none have been made.

Polish workers[248] have reported on extraction of Am^{3+}, Cm^{3+}, and rare earths from $LiNO_3$–$0.01M$ HNO_3 solutions by chloroform solutions of cetyltrimethylammonium bromide and cetylpyridinium bromide. Zaman, Merciny, and Duyckaerts[249] investigated the extraction of americium–HEDTA complexes with Aliquat 336 chloride–benzene solution, whereas Moore[250,251] discussed the extraction of americium–HEDTA and americium–DTPA complexes with xylene solutions of Aliquat 336.

ION-EXCHANGE PROCESSES

Introduction

Ion-exchange processes—both cation and anion—are extensively used to concentrate, separate, and purify both micro and macro amounts of americium from a whole host of inert and radioactive contaminants, including, particularly, Cm(III) and lanthanides. A recent innovation for this purpose has been the application of very finely divided resins and high-pressure techniques. Feedstock for the americium ion-exchange processes derives usually from prior solvent extraction (see preceding section), pyrochemical (pages 185 to 187), and even precipitation (pages 190 to 194) schemes.

Ryan[252] has recently completed a comprehensive review of the chemistry and principles involved in the sorption of americium from various aqueous media by both organic and inorganic exchangers. Other authors have reviewed use of ion-exchange materials for the analysis of americium[253] and for studies of americium complexes.[254] Rather than attempting to duplicate this excellent coverage, emphasis here is primarily on an account of the flow sheets, operating details, and performance of the ion-exchange processes used to routinely separate and purify kilograms of americium. Jenkins and Wain[255] have recently authored a list of publications covering the use of ion exchange for recovering and purifying ^{241}Am and ^{243}Am.

Anion-Exchange Resin Systems

Many different aqueous and mixed aqueous–organic media have been used in laboratory-scale studies of the absorption of americium by anion-exchange resins; results of these studies have been reviewed by Ryan.[252] For routine, large-scale purification of americium, however, application of anion-exchange resins is limited to sorption from thiocyanate, chloride, and, to a smaller extent, nitrate solutions.

Thiocyanate Solutions Americium(III) forms relatively strong complexes [$AmSCN^{2+}$, $Am(SCN)_2^+$, $Am(SCN)_3$] in concentrated aqueous thiocyanate solutions (compare Table 3.11). Thiocyanate species are sorbed on anion-exchange resins considerably more strongly[47,256,258] than are the corresponding lanthanide thiocyanate complexes, as illustrated by the distribution data plotted in Fig. 5.27. Distribution coefficients and lanthanide–actinide separation factors decrease with an increase in temperature[256] (Fig. 5.28). Ryan[252] has pointed out that the europium results of Fig. 2 of Ref. 258 are incorrectly plotted a factor of 10 higher than the true values.

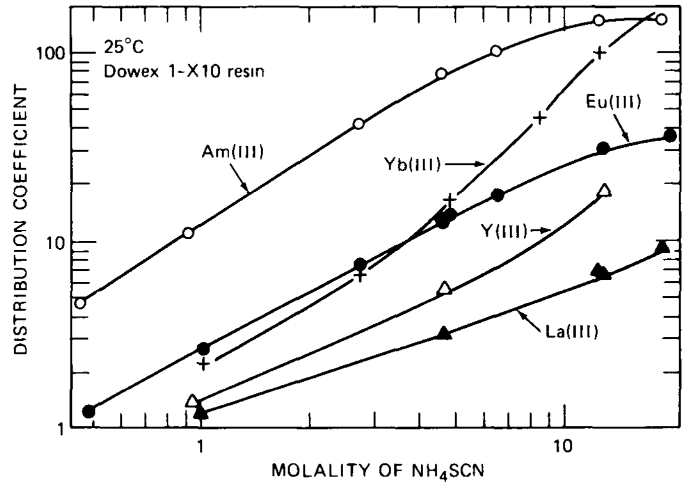


Fig. 5.27 Anion-exchange absorption of Am(III), Eu(III), Yb(III), and La(III) from aqueous NH_4SCN solutions [From J. S. Coleman, L. B. Asprey, and R. C. Chisholm,[258] The Anion-Exchange Absorption of Americium, Yttrium, Lanthanum, Europium, and Ytterbium from Aqueous Ammonium Thiocyanate, *Journal of Inorganic and Nuclear Chemistry* 31: 1167 (1969).]

Much use has been made, particularly in the United States, of thiocyanate anion-exchange systems to purify americium from rare earths and other impurities. Figure 5.29 details in schematic form the thiocyanate ion-exchange process used at the Rocky Flats Plant for about 15 years (1960 to 1975) for routine purification of kilograms of ^{241}Am recovered from aged plutonium metal by the pyrochemical process discussed on pages 185 to 187. This purification scheme was developed originally by Coleman et al.[47,259] and Keenan[260] at the Los Alamos Scientific Laboratory and applied there and also by Naito[261] at the University of California, Lawrence Radiation Laboratory, for purification of milligrams of americium.

Feedstock for the Rocky Flats thiocyanate ion-exchange process is derived from prior aqueous processing of the NaCl–KCl–$MgCl_2$ salt product of the pyrochemical process described on pages 185 to 187. For many years, as discussed on pages 190 to 194, a hydroxide precipitation scheme was used to isolate and concentrate americium from the chloride salt. The hydroxide precipitate was dissolved in nitric acid, and the resulting solution passes through a bed of Dowex 1 anion-exchange resin to remove the bulk of the plutonium. The 7*M* HNO_3 effluent from the anion-exchange column, after dilution to about 0.4*M* HNO_3 constituted feed to the thiocyanate process.

In the thiocyanate process, feedstock was loaded at 25°C and at a rate of about 100 liters hr^{-1} onto a 16.2-liter bed of 50-100 mesh H^+-form Dowex 50-X8 resin (column 1) to sorb and concentrate the americium and plutonium. Feed to this first column contained, typically, 0.02 g Am $liter^{-1}$; 0.003 g Pu $liter^{-1}$; and varying amounts of lanthanum, other rare earths, iron, magnesium, and other metallic impurities. After washing with water and 0.5*M* NH_4SCN to remove the major part of the iron [as the $Fe(SCN)_6^{3-}$ complex], americium, plutonium, and rare earths were eluted with a 6*M* NH_4SCN solution.

The 6*M* NH_4SCN eluate from the cation column, containing at this point approximately 1 g Am $liter^{-1}$ and 0.1 g Pu $liter^{-1}$, was loaded onto a 16.2-liter bed of 50-100 mesh SCN-form Dowex 1-X4 anion-exchange resin (column 2). To provide

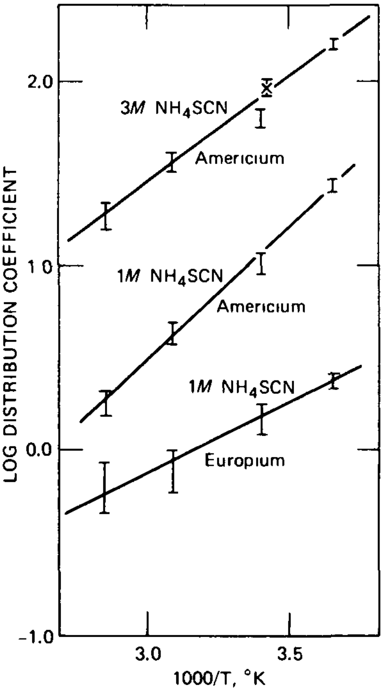


Fig. 5.28 Temperature dependence of distribution coefficients of Am(III) and Eu(III) into Dowex 1-X8 resin from aqueous NH_4SCN solutions. [From J. L. Ryan,[252] Ion Exchange, in *Gmelins Handbuch der Anorganischen Chemie,* Band 21, Transurane, Teil D2, G. Koch (Ed.), Verlag Chemie, G.m.b.H., Weinheim, Germany, 1974.]

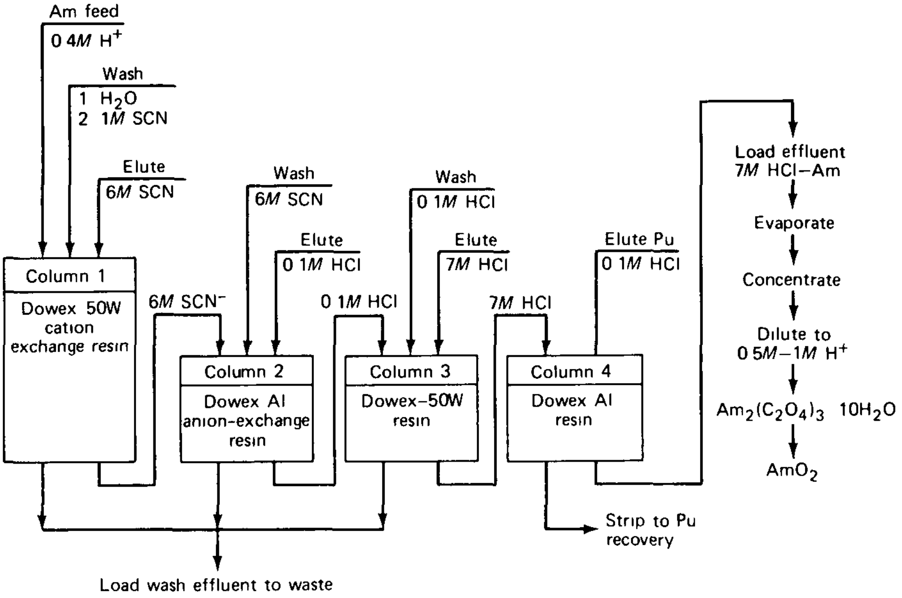


Fig. 5.29 Rocky Flats thiocyanate ion exchange americium recovery process. All columns are 15.2 cm in diameter.

decontamination from cosorbed rare earths, the loaded resin bed was washed with several column volumes of 6*M* NH_4SCN. This sorption–wash sequence was the key element in the overall americium purification scheme, providing separation not only from rare earths but also from iron, magnesium, bismuth, copper, potassium, nickel, and zinc.[262] Naito[261] and also Hagan and Miller[263] have shown that some decontamination from aluminum and manganese is also obtained by washing the resin bed with a limited amount of 2*M* NH_4SCN after the lanthanides are removed.

The amount of resin required to achieve essentially complete separation of americium from rare earths in the thiocyanate ion-exchange process depends on the rare earth/americium ratio. For a lanthanide/americium ratio of 300:1, about 30 ml of resin per gram of lanthanide is required,[47, 259] whereas a loading of about 15 g Am liter^{-1} resin can be used for the satisfactory purification of americium that is already largely free of rare earths.[260]

The final two ion-exchange columns in the Rocky Flats thiocyanate process served to further concentrate the americium and separate it from plutonium. To this end, americium and plutonium in the 0.1*M* HCl solution resulting from elution of the first Dowex 1 resin bed (column 2) were loaded onto a second bed of Dowex 50 resin. Subsequently americium and plutonium were eluted into a 7*M* HCl solution, and the plutonium then preferentially sorbed onto a bed of Dowex 1 resin. The effluent from the latter loading step containing purified americium was evaporated to yield a 6*M* HCl solution containing 25 to 30 g Am liter^{-1} from which the americium was precipitated, after adjustment of the acidity to 0.5*M* to 1*M*, as the oxalate. The oxalate precipitate was calcined to yield high-purity AmO_2.

Some additional details of the Rocky Flats thiocyanate ion-exchange process for purifying americium were given in a paper by Ryan and Pringle.[262] Their report was published in 1960; however, Rocky Flats personnel state that the process was performed, with only minor modifications, much as outlined by Ryan and Pringle. Over 15 years' experience at Rocky Flats shows that the thiocyanate process can be operated successfully on a plant scale to purify americium from rare earths and other metallic impurities. Such experience has also disclosed several process disadvantages, including relatively low (60 to 70%) overall americium recovery, production of troublesome free sulfur from alpha radiolysis of SCN^-, and the general difficulties of handling and disposing of large volumes of viscous concentrated thiocyanate solutions. For these reasons the thiocyanate process has been replaced by a new cation-exchange process (compare pages 244 to 252) to recover and purify americium.

Enhanced anion-exchange resin separation of americium from rare earths can be achieved, according to Russian scientists,[264-266] by adding various alcohols (methanol, ethanol, etc.) to aqueous 0.1*M* to 1.0*M* NH_4SCN solutions. Their results show that distribution coefficients of Am^{3+} increase much more rapidly than do those of lanthanides as the alcohol content of the solution increases. The nature of the resin phase complex in such systems is unknown; no large-scale use of such systems for purifying americium has yet been made.

Chloride Solutions. Distribution of Am(III) into anion-exchange resins is much higher from concentrated LiCl solutions[267,268] than from concentrated HCl solutions.[269,270] Moreover, Am(III) is sorbed much more strongly from concentrated LiCl solutions than are the lanthanides (Fig. 5.30a). Americium distribution ratios increase with increased LiCl concentration (Fig. 5.30b), whereas increased temperature enhances the separation of americium from rare earths (Fig. 5.31). Ryan[252] states that about 10*M* LiCl appears to be optimum for actinide–lanthanide group separations, with poorer separation at lower concentrations and inconveniently long elution times at higher concentrations. Ryan has also questioned the basis for the hypothesis of Marcus[219] that the complex species in the resin is $AmCl_4^-$.

An LiCl-based anion-exchange process (Fig. 5.32) for separating multigram amounts of americium and curium from transuranium elements is routinely and successfully operated at the Oak Ridge TRU facility.[271-273] Feedstock for this process is the chloride solution resulting from the Tramex process (compare pages 222 to 233). Satisfactorily pure actinide products are obtained by controlling the loading step (Fig. 5.32) so that the actinides load only onto the top 20% (~5 to 15 g liter^{-1} of resin average loading) of the resin bed. Following the loading step the resin bed is washed with 5 to 8 column volumes of 10*M* LiCl–0.1*M* $NH_2OH \cdot HCl$–5 vol.% CH_3OH to remove nickel and rare earths; hydroxylamine is used to maintain cerium in the trivalent state, whereas methanol[76,226] is used to suppress the evolution of gas formed by radiolysis. The washed bed is then eluted, as shown in Fig. 5.32, with LiCl–HCl solutions to obtain, sequentially, an americium–curium fraction, a

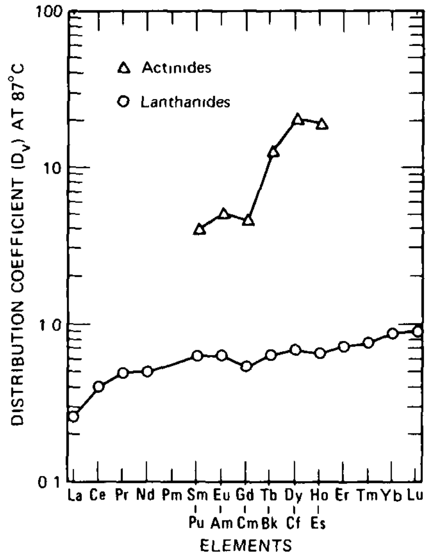


Fig. 5.30a Distribution coefficients of actinides and lanthanides into Dowex 1-X8 resin from 10*M* LiCl. [From E K Hulet, R G. Gutmacher, and M. S Coops,[268] Group Separation of the Actinides from the Lanthanides by Anion Exchange, *Journal of Inorganic and Nuclear Chemistry,* **17**: 350 (1961)]

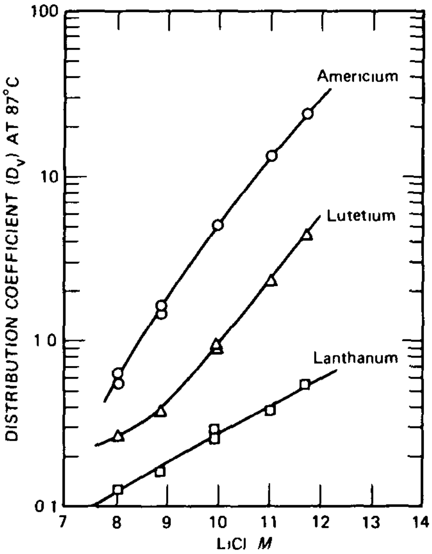


Fig. 5.30b Distribution of americium, lanthanum, and lutetium into Dowex 1-X8 resin as a function of LiCl concentration. [From E. K. Hulet, R G Gutmacher, and M. S. Coops,[268] Group Separation of the Actinides from the Lanthanides by Anion Exchange, *Journal of Inorganic and Nuclear Chemistry,* **17**: 350 (1961).]

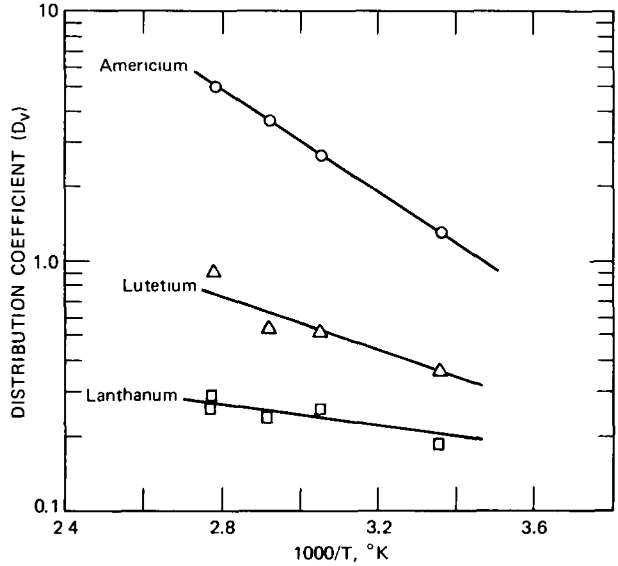


Fig. 5.31 Distribution of americium, lanthanum, and lutetium into Dowex 1-X8 resin from 10*M* LiCl–0.1*M* HCl as a function of temperature. [From E. K. Hulet, R. G. Gutmacher, and M. S. Coops,[268] Group Separation of the Actinides from the Lanthanides by Anion Exchange, *Journal of Inorganic and Nuclear Chemistry*, **17**: 350 (1961).]

curium–berkelium fraction, and a berkelium–californium fraction. Currently in the TRU facility, the LiCl-based process is operated as a conventional low-pressure ion-exchange process.

Chemists[67,68,274] at the European Transuranium Institute in Karlsruhe have successfully applied the LiCl-based anion-exchange process to isolate the americium–curium fraction from irradiated ^{241}Am targets.

Morrow,[275] Guseva and Tikhomirova,[276] Orlandini and Korkisch,[277] and Bochkarev and Lbov[278] have all determined the distribution of Am^{3+} between anion-exchange resins and either HCl or LiCl–HCl aqueous solutions containing varying amounts of ethanol, methanol, acetone and other water-miscible organic components. For several of these mixed solvent systems, americium distribution coefficients were higher than for the corresponding aqueous solutions; better americium–lanthanide separation factors were also observed in some instances. No plant-scale application of these mixed solvent systems to isolate or purify americium has been reported.

Nitrate Solutions. Paralleling behavior in chloride solutions (compare preceding section), Am(III) sorbs only slightly[279] (K_D ~15 at[280] 20*M* HNO_3) onto anion-exchange resins from acidic nitrate solutions but moderately strongly[281-284] from neutral solutions of various metal nitrates. Data for the uptake of americium by

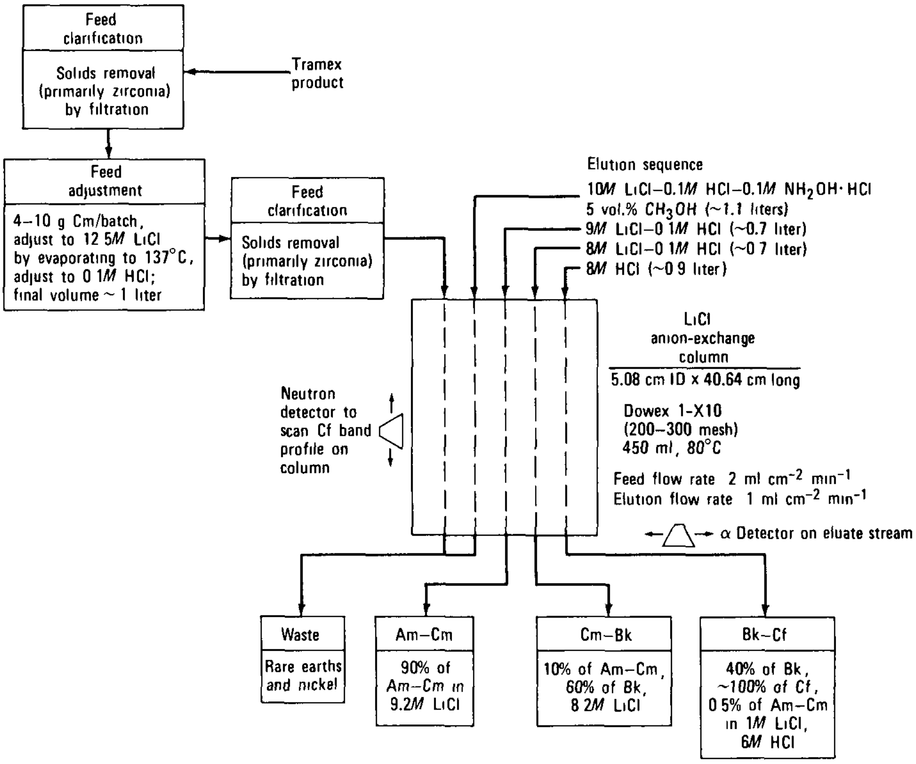


Fig. 5.32 LiCl–anion exchange process flow sheet used in the Transuranium Processing Plant at Oak Ridge. [From R. E. Leuze and M. H. Lloyd,[76] Processing Methods for the Recovery of Transplutonium Elements, in *Progress in Nuclear Energy, Process Chemistry,* Series III, C. E. Stevenson, E. A. Mason, and A. T. Gresky (Eds.), Vol. 4, page 549, Pergamon Press, Inc., New York, 1970.]

Dowex 1 resin from $3M$ to $10M$ $LiNO_3$–$0.05M$ H^+ solutions are[285] shown in Fig. 5.33. Ryan[252] observes that, with due regard to the effects attributable to variations in cross-linkage, Am(III) sorbs about equally well from $LiNO_3$ and $Al(NO_3)_3$ solutions but less strongly from $Ca(NO_3)_2$ solutions. With Dowex 1-X8 resins, distribution coefficients of Am(III) from $LiNO_3$ solutions decrease both with an increase in temperature and an increase in acidity above ~$0.01M$ H^+ (Ref. 285).

Contrary to results obtained with either chloride or thiocyanate solutions, distribution ratios of Am(III) from nitrate solutions onto anion-exchange resins overlap those of the lanthanides. Plant-scale use of nitrate-based anion-exchange systems for purifying americium has been largely precluded by the inability to obtain satisfactory decontamination from rare earths. Lloyd[286] devised an anion-exchange process (Fig. 5.34) for recovering americium, curium, and rare earths from the nitrate waste solution resulting from processing of highly irradiated plutonium–aluminum alloys. Although recoveries of >95% were demonstrated in laboratory tests, only 30 to 40% of the americium–curium was recovered when this process was scaled up for use at Oak Ridge. Solids, mostly aluminum hydroxide, which formed during the feed preparation step, proved difficult to filter and restricted flow rates in the resin column. Lloyd and Leuze[287] state that this anion-exchange process (Fig. 5.34) appears much more difficult to operate than the TBP extraction processes described earlier (compare pages 195 to 202).

Lloyd and Leuze[287] also devised an alternate anion-exchange process for recovering americium and curium from irradiated plutonium–aluminum alloys and for separating them from rare earths. In this scheme (Fig. 5.35), americium, curium, and rare earths are sorbed on Dowex 1-10X resin from an 8*M* $LiNO_3$ solution, followed by selective elution of rare earths with 10*M* LiCl and elution of americium and curium with 1*M* HCl. Subsequently Kingsley[288] modified this process for the purification and concentration of americium recovered at Hanford (compare pages 202 to 205). To date, however, no plant-scale use has been made of the flow sheet shown in Fig. 5.35.

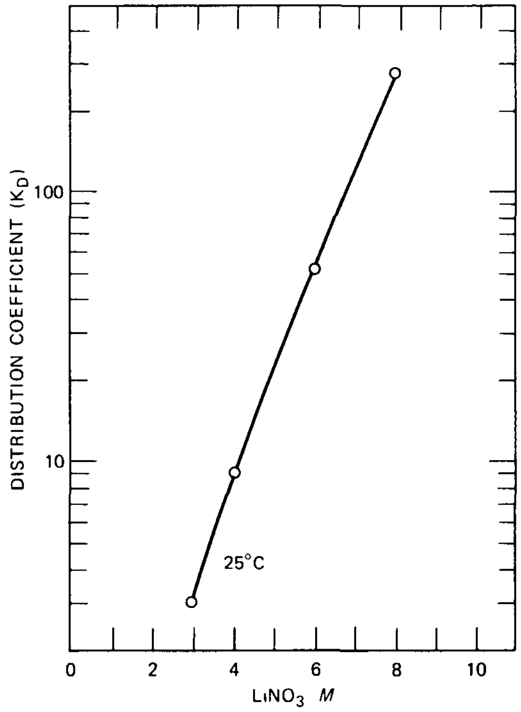
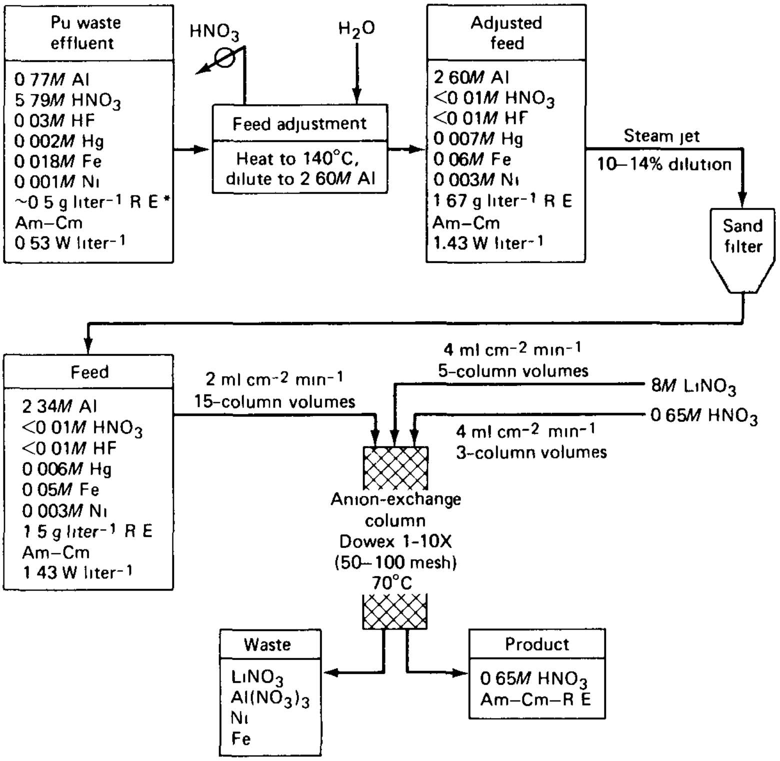


Fig. 5.33 Distribution coefficients of Am(III) between $LiNO_3$ (0.005*M* H^+) solutions and Dowex 1-X8 resin. [From S. Adar, R. K. Sjoblom, R. F. Barnes, P. R. Fields, E. K. Hulet, and H. D. Wilson,[285] Ion-Exchange Behavior of the Transuranium Elements in $LiNO_3$ Solutions, *Journal of Inorganic and Nuclear Chemistry*, **25**: 447 (1963).]



*R.E. = rare earths

Fig. 5.34 Anion-exchange process for recovering americium and curium from NO_3 waste from plutonium–aluminum alloy processing. [From M. H. Lloyd,[286] An Anion Exchange Process for Americium–Curium Recovery from Plutonium Process Waste, *Nuclear Science and Engineering*, 17: 452 (1963).]

Just as with chloride and thiocyanate solutions, anion-exchange resins sorb Am(III) much more strongly from mixtures of HNO_3 or $LiNO_3$ with methanol[283,289,290] and other organic solvents[291] than from aqueous HNO_3 and $LiNO_3$ solutions. Russian scientists[292] have made use of this fact to develop what they claim is a very efficient ion-exchange process for separating and purifying americium from irradiated plutonium targets. In their scheme trivalent actinides and lanthanides are loaded onto a strong base anion-exchange resin from 1*M* HNO_3 in 90% methanol; inert iron and aluminum and fission-product cesium, strontium, zirconium, niobium, and ruthenium are not sorbed from this solution. Separation of rare earths from the americium and curium is accomplished by washing the former off with 0.5*M* NH_4SCN–0.1*M* HCl in 80% methanol (compare page 237). Americium and curium are then sequentially eluted with 0.5*M* HNO_3 in 80% methanol. Lebedev, Myasoedov, and

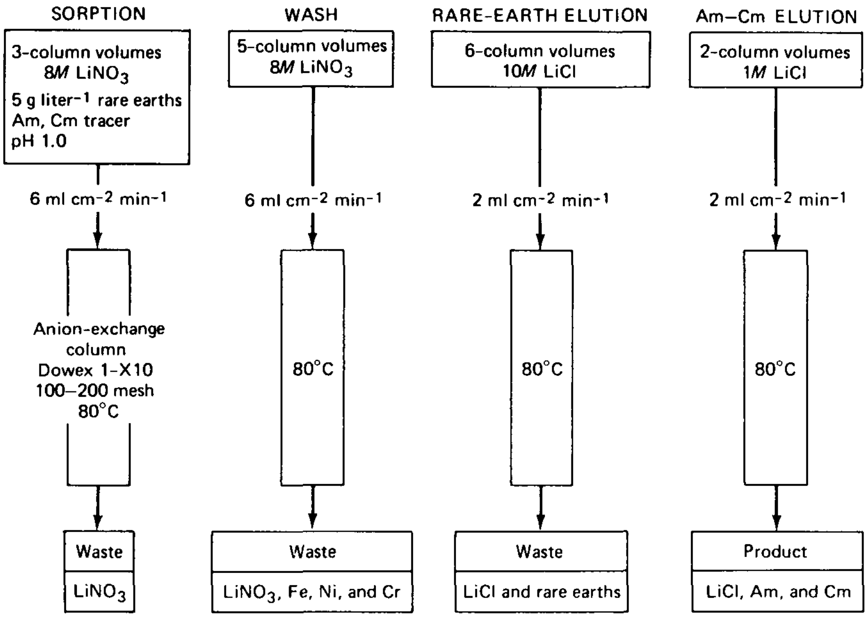


Fig. 5.35 $LiNO_3$–LiCl anion-exchange process for separating americium and curium from rare earths. [From M. H. Lloyd and R. E. Leuze,[287] Anion Exchange Separation of Trivalent Actinides and Lanthanides, *Nuclear Science and Engineering*, 11: 274 (1961).]

Guseva[292] state: "The described process of americium–curium recovery is highly convenient for use in laboratory-scale work. . . . its obvious economic advantages and technological simplicity allow the expectation that the given method may be used on a larger scale."

Berger et al.[159] and his fellow Frenchmen used a nitrate-based anion-exchange system to separate americium and curium previously recovered from irradiated plutonium–aluminum alloy (compare pages 208 to 220) by a Talspeak-type HDEHP extraction process. The 3*M* $LiNO_3$–0.065*M* DTPA strip product (compare Fig. 5.18) from the HDEHP extraction step was adjusted to 6*M* $LiNO_3$ and 0.1*M* $Al(NO_3)_3$, and the americium and curium were batch extracted into a 40% TBP–dodecane solvent. Transplutonium elements were stripped into 1*M* HNO_3; an ethanolic (80 vol.%) solution containing 1.33*M* NH_4NO_3 and 0.05*M* to 0.1*M* HNO_3 was prepared from the strip solution as feed to a bed of 200-400 mesh Dowex 1-X8 resin. Subsequently curium was selectively eluted using an 80 vol.% ethanol solution containing 1.33*M* NH_4NO_3, 0.025*M* DTPA, and 0.08*M* HNO_3. Following removal of the curium, americium was eluted either with 1*M* HNO_3 or a further portion of ethanolic 1.33*M* NH_4NO_3–0.025*M* DTPA–0.08*M* HNO_3 solution. This anion-exchange procedure permitted rapid and clean separation of milligram amounts of americium and curium.

Cation-Exchange Resin Systems

General. Cation exchange resins sorb Am^{3+} very strongly from dilute acid solutions according to the reaction

$$Am^{3+} + 3HR \rightleftharpoons AmR_3 + 3H^+ \qquad (5\ 16)$$

An important application of Eq 5 16 is to simply concentrate Am^{3+} and other trivalent and tetravalent ions from acid solutions obtained in prior solvent extraction or precipitation processes and to separate them, at least partially, from monovalent and divalent impurities that have less affinity for the resin Instances of such use of cation-exchange resins in americium recovery and purification schemes will be discussed later

A combination of chromatographic elution techniques with cation-exchange resins provides a powerful and sophisticated tool for purifying americium from lanthanides and other trivalent actinides Elution chromatography involves the use of organic *chelating agents to produce the largest possible difference in the distribution* coefficients of the metal ions to be separated

Both elution-development and displacement-development (also known as barrier-ion or retaining-ion) chromatography have been used in cation-exchange separation and purification of americium Ryan[252] points out that displacement-development chromatography is only capable of separating macro quantities, whereas, unless very large columns are used, elution-development chromatography is applicable only to the separation of tracer amounts Because of this limitation of the elution-development chromatographic method, its application to purification of americium is not discussed further here Helfferich[293] has presented, in a comprehensive fashion, the theory of both the elution-development and displacement-development procedures

The basic principles of displacement chromatography have been stated by Ryan[252] as follows

> In displacement development chromatography with a chelating agent, a macro-amount of the actinide or lanthanide is loaded onto the upper portion of a column, the rest of which initially contains a restraining or barrier ion This ion is one which in the presence of the complexant exhibits a much lower distribution coefficient than the actinide or lanthanide ion Elution is carried out with a complexant of such strength and concentration of the free ligand that the M^{3+} distribution coefficients are very low This is normally achieved by neutralizing complexants to a higher pH than would be used for elution development with the same complexant Under these conditions the distribution coefficient of the M^{3+} is lower than that of the NH_4^+ or Na^+ ion used in the neutralization, and the M^{3+} is displaced with a self sharpening boundary An eluant concentration such that there is an excess of the trivalent ion in the resin is used. For a mixture of actinides and/or lanthanides the reaction
>
> $$M_a\ (\text{Chelate}) + M_bR_3 \rightleftharpoons M_b\ (\text{Chelate}) + M_aR_3 \qquad 3$$
>
> occurs because of competition for the limited supply of the chelating agent Separation factors are related to complex formation constants in the same manner as discussed in the previous paragraph As the eluant reaches the retaining or barrier ion, it forms a stronger complex with it

> than with the actinide or lanthanide, releasing the latter to be absorbed by the resin Since the complexants are weak acids, H^+ ion is a satisfactory barrier ion unless the complex acid is not sufficiently soluble, in which case an appropriate metal ion is used The actinides and lanthanides develop into discrete bands or zones in direct contact with each other, the resin in the bands being principally in the actinide or lanthanide form The bands become resolved after a certain distance and travel with no further change after that

The effectiveness of chelating agents in cation-exchange displacement elution systems for americium purification is conveniently evaluated in terms of separation factors The separation factor between elements a and b is

$$\alpha_b^a = \frac{(K_D)_a}{(K_D)_b} = \frac{(D_V)_a}{(D_V)_b} \qquad (5\ 17)$$

where K_D = (mg metal/g resin)/(mg metal/ml solution) and D_V = (mg metal/ml resin)/(mg metal/ml solution). Separation factors are commonly referred to one actinide, e g , curium (α_{Cm}^M) or one lanthanide, e g , gadolinium (α_{Gd}^M)

Distribution Coefficients Separation Factors Data for the distribution of Am^{3+} between cation-exchange resins and aqueous $HClO_4$, HNO_3, HCl, HF, HBr, HI, oxalate, acetate, phosphate, and sulfate solutions have been collected and interpreted by Ryan[252] Much of this information was gathered to determine formation constants of complex species (Table 3 11) Not surprisingly, cation-exchange systems for large-scale separation and purification of americium use only HNO_3 solutions as feeds Extensive use has been made of HCl solutions in cation-exchange systems for laboratory- and analytical-scale separation of americium from trivalent lanthanides,[91 269 294 297] but no large-scale use has been made of such systems

Distribution coefficients for Am^{3+} into Dowex-50 resin remain[280] very low and essentially constant over the range 4*M* to 11*M* HNO_3 Even so, the results of Starik and Ginzburg[280] indicate that, from HNO_3 solutions, Am^{3+} sorbs slightly more strongly onto cation-exchange resins than do the lanthanides

Solutions of α-hydroxycarboxylic and aminopolycarboxylic acids are commonly used to elute americium from cation-exchange resin. When these reagents are used in a displacement development elution system, they provide, as detailed on pages 245 to 252, excellent separation of americium from trivalent lanthanides and other trivalent actinides Separation factors, α_{Cm}^{Am} and α_{Pm}^{Am}, provided by some of these compounds are listed in Tables 5.9 and 5 10 Ryan's review[252] furnishes additional information on the use of these organic chelating reagents in eluting transplutonium elements from cation-exchange resins.

Typical Cation-Exchange Americium Purification Processes. *Simple Load-Elution Concentration Processes* Relatively simple load-elute cation-exchange processes still find much use in concentrating (and purifying) americium from dilute feed solutions At Hanford, for example, such a process is used to concentrate americium and plutonium in the dilute product stream from the DBBP solvent extraction process (see pages 205 to 208) After this solution (containing, typically, 10^{-4} to 10^{-3} g $liter^{-1}$ each

Table 5.9

SEPARATION FACTORS IN AMERICIUM CATION-EXCHANGE PURIFICATION SYSTEMS· ELUTION WITH α-HYDROXYCARBOXYLIC ACIDS

Chelating agent	Cation resin	Solution composition	pH	Temp., °C	Separation factors			
					Am/Cm		Am/Pm	
					α	Ref.	α	Ref.
Citrate	Dowex 50 X12	0 25M NH_4 citrate	3.35	25	1.18	295	1.03	295
				87	1 17	269		
Glycolate	Dowex 50-X12	0.25M glycolic acid	4.0	25	1.31	298	0.98	299
			4.0	87	1.24	299	0.92	299
AHIB*	Dowex 50-X4	0.5M NH_4 AHIB		25	1 39	300	1.21	300
	Dowex 50-X12	0.4M NH_4 AHIB	3.8–4.8	78	1 45	301		
	Zeokarb-225	0.4M NH_4 AHIB	4 0	77	1 38	302		
	Dowex 50-X12	1.0M NH_4 AHIB	4 5–5 0	87	1 45	301		
					1.41	303		
Lactate	Dowex 50-X12	0 37M NH_4 lactate	4.1	25	1.21	304	0.97	304
		0.4M NH_4 lactate	4.0	87	1.23	269		
		0 4M NH_4 lactate	4.6	87	1.19	304	0.97	304
		1.0M NH_4 lactate	3 0	87	1.27	305	0.97	305
		0.4M NH_4 lactate	4.0–4.5	87	1.21	269		
		0 27M NH_4 lactate	4 2	87	1.16	303		
Tartrate	Dowex 50-X12	0.1M tartaric acid	4.0	25	1 30	304	0.89	304
		0.1M tartaric acid	4.3	87	1 07	304		
		0 8M tartaric acid	2.8	87	1 20	304		

*AHIB = α-hydroxyisobutyric acid

of americium and plutonium) is diluted with water to about 0 25M HNO_3, it is then loaded at 25°C onto a 14-liter bed (15 cm in diameter) of H^+-form Dowex 50-X8 cation-exchange resin Considerable decontamination from sodium, calcium, magnesium, and other divalent cations is obtained in this step. Subsequently the americium and plutonium are eluted either upflow or downflow with about 6 column volumes of 7M HNO_3, the eluate containing roughly 2 to 4 g liter^{-1} each of americium and plutonium is used as feed to final ion-exchange purification as described subsequently

A new[311] cation–anion exchange process (Fig 5.36) has recently replaced the hydroxide-precipitation (compare pages 190 to 194) and multistage thiocyanate ion-exchange (compare pages 234 to 237) systems formerly used at the Rocky Flats Plant for recovering ^{241}Am from solutions of spent NaCl–KCl–$MgCl_2$ salt residues In this new process, americium and plutonium in an 0 5M H^+ feed solution containing, typically, 4 g Pu liter^{-1} and 0 4 g Am liter^{-1}, are first loaded onto an 11-liter bed of 50-100 mesh Dowex 50-X8 resin. The loaded bed is washed with water and then eluted with 2 5 column volumes of 7M HNO_3 [An earlier version of this separation process developed by Kudera and Guyer[312] involved dissolving the NaCl–KCl–$MgCl_2$ mixture in 0.35M HNO_3 and subsequently loading the americium and plutonium onto a cation-exchange resin]

Table 5.10

SEPARATION FACTORS IN AMERICIUM CATION-EXCHANGE PURIFICATION SYSTEMS: ELUTION WITH AMINOPOLYCARBOXYLIC ACIDS

Chelating agent*	Cation resin	Solution composition	pH	Temp., °C	Separation factor Am/Cm	
					α	Refs.
NTA	Dowex 50-X12	$0.001M$ NTA–$0.1M$ NH_4ClO_4†	2.95	72	1.46	306
EDTA	Dowex 50-X12	$0.001M$ EDTA–$0.1M$ NH_4ClO_4	2–3.5	25	2.04	307, 308
			2.35	80	1.1	308
			2.6	80	1.45	308
NHEDTA	Dowex 50-X12	$0.001M$ NHEDTA–$0.15M$ KCl	2.3	22	1.30	309
			2.3	80	1.30	309
			2.7	22	1.15	309
			2.7	80	1.25	309
			2.9	22	1.70	309
			2.9	80	1.30	309
DCTA	Dowex 50-X12	$0.01M$ DCTA–$0.1M$ NH_4ClO_4	3.0	25	1.18	310

*NTA = nitrilotriacetic acid
EDTA = ethylenediaminetetraacetic acid
NHEDTA = *N*-(2-hydroxyethyl)ethylenediaminetriacetic acid.
DCTA = 1,2-diaminocyclohexanetetraacetic acid
†$0.1M$ glycolic acid also present.

In the anion-exchange portion of the new Rocky Flats americium purification process, the $7M$ HNO_3 solution resulting from elution of the cation-exchange resin is passed through a bed of Dowex 1-X4 resin to sorb plutonium and separate it from americium. Americium in the $7M$ HNO_3 effluent from the anion-exchange load cycle is contaminated with only small amounts of magnesium, potassium, sodium, and plutonium; no chloride ion is present. Double oxalate precipitation of americium from this solution yields, after calcination, AmO_2 of a purity comparable to that obtained by the former thiocyanate ion-exchange process. The oxalate precipitation process involves evaporation of the $7M$ HNO_3 load-cycle effluent to achieve a 10-fold concentration, adjustment of acidity to $0.5M$ HNO_3, precipitation of $Am_2(C_2O_4)_3 \cdot 10H_2O$, dissolution of the precipitate, and a second precipitation of americium oxalate.

Proctor[77] at the Rocky Flats Plant has also devised a cation-exchange procedure to recover and further purify americium from the $7M$ HNO_3 load-cycle effluent stream obtained in the plutonium removal step. In this process, after acidity adjustment, all the metal ions in the feed are absorbed onto a bed of Dowex 50 resin. Following the loading step, the bed is washed with $0.1M$ oxalic acid to remove >99% of any iron, nickel, cobalt, and plutonium and about 60% of any aluminum with minimal (<0.1%) loss of americium. The americium is then eluted with a $0.4M$ citric acid (pH 3) solution; the alkali and alkaline earth elements remain on the resin in this step. Americium can be precipitated directly from the citrate eluant by adding oxalic acid.

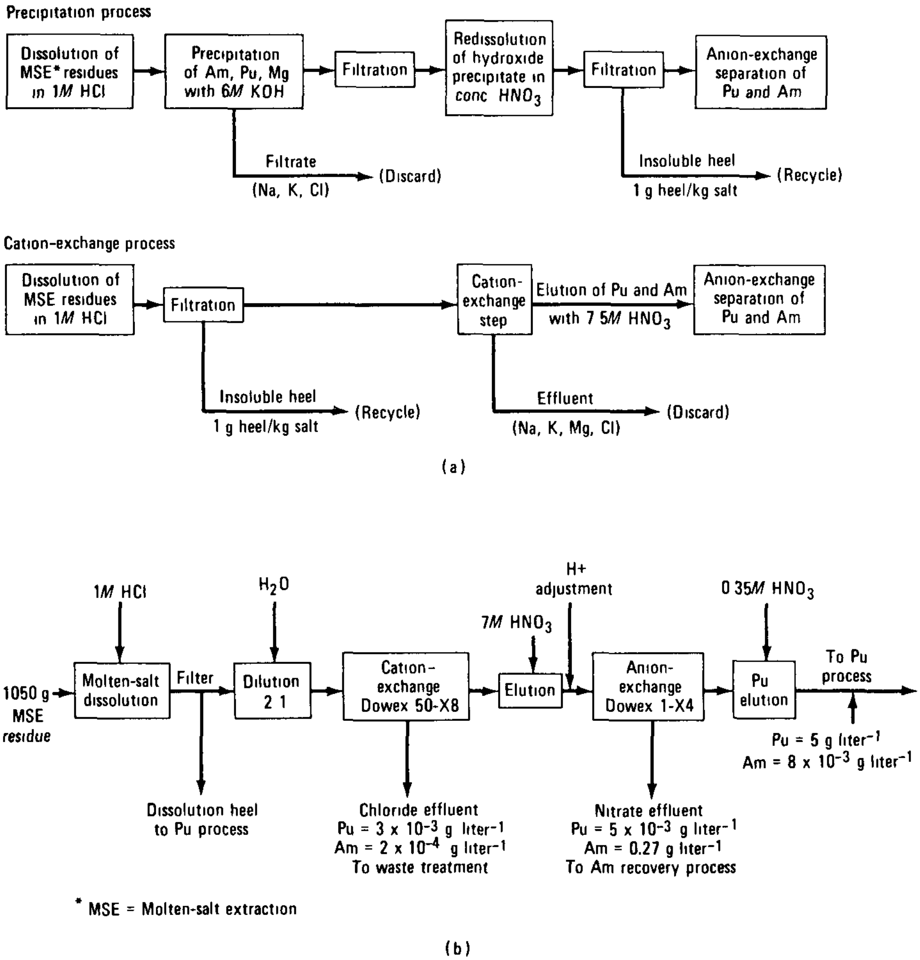


Fig. 5.36 New cation-exchange process used at the Rocky Flats Plant for recovering americium from molten-salt extraction process residues. (a) Ion exchange vs hydroxide precipitation head-end processes. (b) Ion-exchange process flow sheet.[311]

Preliminary laboratory-scale data indicated this cation-exchange process would recover 97% of the americium in the feed while generating only 40% of the waste produced by the thiocyanate process. When it was found that a double oxalate precipitation process could be used to purify the americium directly from the anion-exchange resin load-cycle effluent, this second cation-exchange purification cycle was unnecessary.

Americium recovery by the new cation–anion exchange process presently in use at Rocky Flats is considerably simpler than by the former precipitation–thiocyanate ion-exchange system. It is anticipated that this process simplification will be reflected in greater americium throughput and generation of a substantially smaller volume of aqueous waste more amenable (no thiocyanate) to treatment and disposition.

Haug[313] and others[160,161] in Germany have developed a cation-exchange cycle for the concentration and decontamination of americium and curium present in the 0.05*M* DTPA–1*M* lactic acid product solution resulting from prior HDEHP–TBP solvent extraction of actinides from Purex-process high-level waste (compare pages 208 to 220). Their scheme involves loading the americium and curium from the DTPA–lactic acid solution (adjusted to pH 1.0) onto the Dowex 50-X8 resin, washing the resin with several column volumes of 0.1*M* HNO_3, and then eluting the americium and curium with 3*M* HNO_3. In tracer-level tests, this purification scheme provided excellent decontamination of the americium and curium from DTPA, lactic acid, fission products, and other actinides.

Chromatographic Elution Schemes. In the past, α-hydroxycarboxylic acids were used extensively as eluting agents in cation-exchange processes for the separation and purification of milligram and even gram amounts of americium. For example, Campbell[314] in 1956 purified 9 g Am from kilograms of lanthanum by eluting the americium from a 25% loaded Dowex 50 resin column with 0.15*M* citric acid–0.1*M* diammonium citrate–0.3*M* NH_4NO_3 solution at pH 3.3. Workers at LASL also successfully purified gram quantities of americium from kilograms of lanthanum by displacement elution at 25°C with 0.1% ammonium citrate, pH 8 solution; the retaining ion was H^+.

Both lactic and α-hydroxyisobutyric acids provide better separation (Table 5.9) of americium from curium than does citric acid. Higgins and Crane[267] devised an ion-exchange scheme to isolate and purify thousand-curie quantities of ^{242}Cm from irradiated ^{241}Am targets; one step in this process involved the use of lactic acid solution to selectively elute curium from a cation-exchange resin. Perdue and Hicks[315] separated americium from cerium by selective elution of the former from Dowex 50W resin with 1*M* lactic acid adjusted to pH 2.97 with NH_4OH. Both Russian[257] and German[316-318] workers have used α-hydroxyisobutyric acid in chromatographic cation-exchange separation and purification of ^{242}Cm from solutions of neutron-irradiated ^{241}Am targets. Using chromatographic elution from Dowex 50-X12 resin with α-hydroxyisobutyric acid, Campbell[319] demonstrated the use of high-pressure ion-exchange methods for the rapid separation of americium from curium. Burney and Harbour[320] separated milligram quantities of ^{252}Cf from multigram quantities of ^{244}Cm and ^{243}Am using pressurized cation-exchange elution chromatography and α-hydroxyisobutyric acid as the eluent.

Highly efficient displacement chromatographic separation schemes that use nitrilotriacetic acid and/or diethylenetriaminepentaacetic acid as eluents have been developed and applied in the last 10 years by Wheelwright at Hanford and by Hale, Lowe, and others at Savannah River to purify kilograms of americium from curium and lanthanides. For Dowex 50 resin, Wheelwright et al.[321] report the following elution sequences:

With DTPA,

$$\mathrm{Zn^{2+}, Pb^{2+}, \underline{\underset{\substack{\uparrow \\ Cm^{3+}}}{Er^{3+}}-Ho^{3+}-\underset{\substack{\uparrow \\ Am^{3+}}}{Dy^{3+}}}, Gd^{3+}, Eu^{3+}, Sm^{3+}, Y^{3+}, Pm^{3+}, Nd^{3+}, Pr^{3+}, Ce^{3+}, La^{3+}}$$

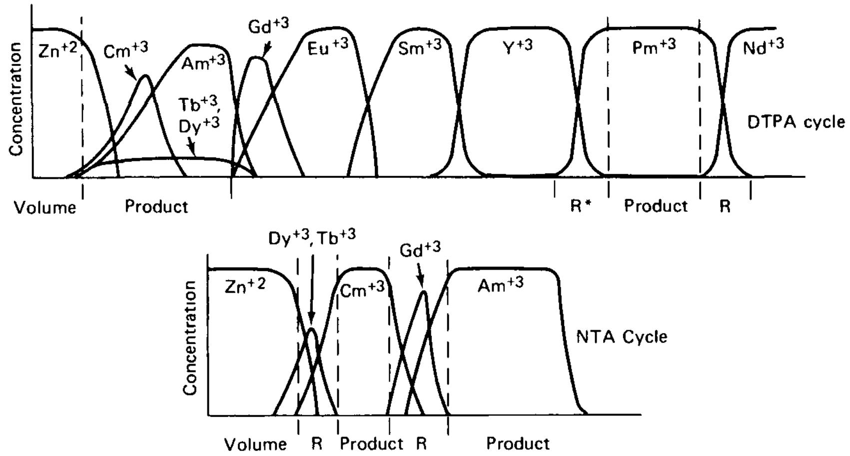
With NTA,

$$\mathrm{Zn^{2+}, (Cm^{3+} - Y^{3+}), Gd^{3+}, (Eu^{3+}, Am^{3+}), Sm^{3+}, Pm^{3+}, Nd^{3+}, Pr^{3+}}$$

On the basis of these elution sequences, Wheelright[321-324] successfully used a two-cycle cation-exchange process in conventional equipment to separate and purify 1 kg ^{241}Am and ^{243}Am, about 60 g ^{244}Cm, and 140 g ^{147}Pm recovered (by solvent extraction techniques, compare pages 202 to 205) from 13.5 tons of blanket fuel elements of the Shippingport reactor. In this process, Am^{3+} and Cm^{3+} (contained in the dilute HNO_3 feed solution) were initially loaded onto a 34.3-cm-diameter bed of H^+-form Dowex 50W-X8 (50-100 mesh) resin. Subsequently the americium and curium were separated from promethium, other lanthanides, and other cosorbed impurities by displacement elution at 60°C through a series of seven Zn^{2+}-form Dowex 50-X8 (50-100 mesh) resin beds with a 0.05*M* DTPA solution buffered to pH 6.5 with NH_4OH; the eluent was pumped through the column system at a flow rate of 4 ml cm^{-2} min^{-1}. The americium–curium product from the DTPA cycle was adjusted to 0.5*M* HNO_3 and loaded onto a 10.8-cm-diameter bed of H^+-form Dowex 50 resin. Separated and highly purified americium and curium fractions were obtained by americium–curium displacement elution at 60°C through a series of four Zn^{2+}-form Dowex 50 resin beds with a 0.105*M* NTA solution buffered to pH 6.5 with NH_4OH. Figure 5.37 illustrates simulated elution curves for Wheelwright's two-cycle americium purification process.

Ion-exchange technology developed by Wheelwright[325] is currently used for the final purification of ^{241}Am recovered at Hanford by reprocessing of aged plutonium metallurgical scrap. Americium and plutonium in the 7*M* HNO_3 solution obtained in prior solvent extraction and ion-exchange (compare pages 202–204 and 245) steps are first separated by sorption of the plutonium on Dowex 1 resin. Subsequently the 7*M* HNO_3 waste stream containing the americium is diluted with water to yield a 1*M* HNO_3 solution containing 0.25 to 0.5 g Am $liter^{-1}$. Americium in this feed is loaded onto a 10.8-cm-diameter bed of H^+-form Dowex 50-X8 (50-100 mesh) resin and then eluted through a series of four Zn^{2+}-form Dowex 50-X8 resin beds with a 0.105*M* NTA solution buffered to pH 6.5 with NH_4OH. Displacement elution is performed at 60°C at a flow rate of 8 ml cm^{-2} min^{-1}. The center product cut from the final column contains 8 to 9 g $liter^{-1}$ of highly purified americium. Oxalic acid is added to this solution, and the resulting oxalate precipitate is calcined to AmO_2. This ion-exchange scheme is used to purify about 1 kg ^{241}Am $year^{-1}$.

Lowe, Hale, Hallman, and others[308,326-328] at the Savannah River Plant adapted Wheelwright's DTPA displacement elution scheme to pilot-scale operation in pressur-



*R denotes recycle solution for further product recovery.

Fig. 5.37 Typical elution curves for two-cycle chromatographic cation-exchange americium purification process. DTPA = diethylenetriaminepentaacetic acid; NTA = nitrilotriacetic acid.[324]

ized equipment. [Pressurization eliminates the bed disruptions caused by radiolytically produced gases in gravity-fed columns, and a severalfold increase in flow rate minimizes radiolytic resin degradation. Pressurization also allows the use of very finely divided resin, thereby improving sorption kinetics.] The pilot-scale system used by the Savannah River workers to successfully purify 3 kg ^{244}Cm and ^{243} Am consisted of four columns constructed of 304L stainless steel, Schedule 80 pipe; column diameters were nominally 10.2, 7.62, 5.08, and 2.54 cm, respectively, and each column was 122 cm long. All columns were filled with Dowex 50W-X8 (25- to 55-μm) resin in the Zn^{2+}-form. A typical batch of feed solution, obtained by prior solvent extraction (compare pages 202 to 205) processing of highly irradiated plutonium, contained 75 g ^{244}Cm, 24 g ^{243}Am, and ~1.6 mol of fission-product lanthanides. After loading this feed onto the top 30 to 40% of the 10.2-cm-diameter column, the americium, curium, and lanthanides were eluted at 70°C with a 0.05*M* DTPA solution adjusted to pH 6.0 with NH_4OH. The desired elution rate of 16 ml cm^{-2} min^{-1} was obtained on each column without exceeding the design pressure of 1000 psig. A typical elution diagram for product fractions collected from the final 2.54-cm-diameter column is shown in Fig. 5.38. Hale and Lowe[308] note that, because the curium/americium ratio in the feed to the pressurized ion-exchange system was ~3 : 1, a large fraction of pure curium could be separated from both americium and lanthanides in a single DTPA ion-exchange cycle.

In further work at the Savannah River Plant, Kelly[329] devised a pressurized cation-exchange system for separating and purifying ^{244}Cm and ^{243}Am from feed solutions with a lanthanide/actinide ratio of ~17 : 1. This process was developed as part of a program to produce gram amounts of ^{252}Cf and was intended for use in the

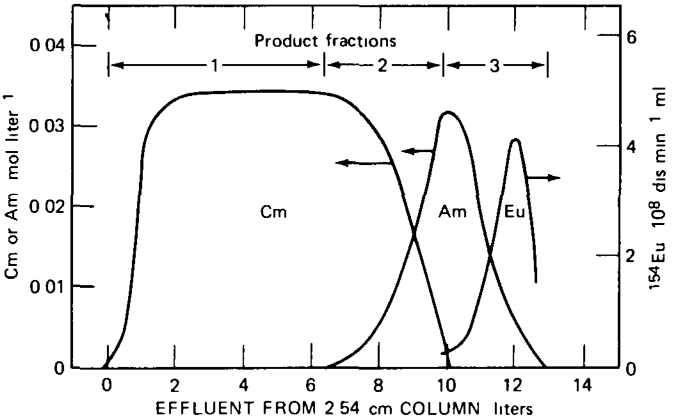


Fig. 5.38 Typical elution diagram for pressurized chromatographic ion-exchange separation of americium from curium Resin, Dowex 50W-X8, Eluent, 0 05*M* DTPA at pH 6 0 [From J T Lowe, W H Hale, Jr , and D F Hallman,[326] Development of a Pressurized Cation Exchange Chromatographic Process for Separation of Transplutonium Actinides, *Industrial and Engineering Chemistry, Process Design and Development,* **10**: 131 (1971)]

Multipurpose Processing Facility constructed at the Savannah River Plant, no large-scale use of this ion exchange process has yet been made Wakat and Peterson[330] have described an on-line radiochemical system for providing control information for pressurized cation-exchange chromatography processes

Specht, Schutz, and Born[331] have reported on a laboratory-scale plant for separating 100 Ci of ^{242}Cm from gram amounts of americium using high-pressure ion-exchange chromatography Schutz, Specht, and Born used an 0 5*M* α-hydroxyisobutyric acid solution adjusted to pH 3 65 as the eluent

Inorganic Exchangers

Several authors have reported results of studies of sorption of Am^{3+} from nitrate and chloride media by various inorganic exchangers (Table 5 11) Studied most intensively has been sorption of Am^{3+} by zirconium phosphate, distribution data for uptake at 75°C of Am^{3+} and other trivalent ions from nitric acid solutions are plotted in Fig 5 39 The order of the distribution coefficients of trivalent actinides and lanthanides into zirconium phosphate is the reverse of the order observed with a typical strong base resin exchanger, indicating that the phosphate groups probably replace part of the water in the hydration sphere of the ions [332] Equilibrium in the zirconium phosphate HNO_3–Am^{3+} system is established very slowly, even for tracer loading at 75°C[332, 335], however, >99% absorption of tracer Am^{3+} occurs in 15 min at 75°C

Table 5.11

SUMMARY OF SORPTION OF Am(III) BY INORGANIC EXCHANGERS

Exchanger	Media	Refs.
Zirconium phosphate	0.01*M*–1.0*M* HNO_3	332–334
Zirconium phosphate	4*M*–11*M* LiCl–0.01*M* HCl	336
Zirconium phosphate–silicate*	0.01*M*–1.0*M* HNO_3	335
Zirconium molybdate	pH 1–5 nitrate solutions	333
Zirconium tungstate	pH 1–5 nitrate solutions	333
Zirconium tungstate	11*M* LiCl–0.01*M* HCl	336
Zirconium oxide†	4*M*- 11*M* LiCl–0.01*M* HCl	333, 336
Ammonium phosphomolybdate	10*M* LiCl–0.01*M* HCl	336
Permutit Decalso M-4‡	11*M* LiCl–0.01*M* HCl	336
Linde Molecular Sieve X-13§	11*M* LiCl–0.01*M* HCl	336
Linde Molecular Sieve AW 500§	11*M* LiCl–0.01*M* HCl	336
Chromatographic Al_2O_3	11*M* LiCl–0.01*M* HCl	336

*Am K_D = 12,400 at 0.01*M* HNO_3, 7.8 at 1.0*M* HNO_3.

†Am K_D = 5.1 at 4*M* LiCl–0.01*M* HCl, 2300 at 11*M* LiCl–0.01*M* HCl.

‡Sodium aluminum silicate made by the Permutit Company.

§Aluminum silicate made by the Linde Division of Union Carbide Company

According to Ryan,[252] several of the eluting agents previously used successfully with resin exchangers have been tested with zirconium phosphate Citrate, tartrate, and oxalate solutions dissolve zirconium phosphate, whereas 2*M* lactate solutions at pH's 3 and 5 and a 1 5*M* α-hydroxyisobutyrate solution at pH 4 2 do not elute trivalent actinides and lanthanides Concentrated mineral acids elute M^{3+} ions without separation Separation of americium from europium or cerium by elution from a zirconium phosphate column with a 10*M* LiCl solution (pH 2 to 3) has been reported by ORNL workers [336]

Uptake of Am^{3+} from nitrate solutions by zirconium molybdate is similar to that by zirconium phosphate With zirconium tungstate, K_D's for Am^{3+} and Cm^{3+} from 10*M* LiCl–0 01*M* HCl are higher by a factor of 2 than for any of the lanthanides Absorption of Am^{3+} from 10*M* LiCl–0 01*M* HCl by ammonium molybdophosphate is fairly similar to that by zirconium phosphate.[336] From the same chloride media, Permutit Decalso M-4 and Linde Molecular Sieves X-13 and AW 500 sorb Am^{3+} only weakly, whereas moderately strong absorption occurs with chromatographic alumina.[336]

Both American[337 338] and Russian[339 340] scientists have recently announced a new way of using a zirconium phosphate exchanger for separating americium from curium and other metal ions This method takes advantage of the fact that the singly charged AmO_2^+ ion is not sorbed by zirconium phosphate from dilute acid media Also, unlike organic exchangers, the inorganic exchanger will not reduce the strongly

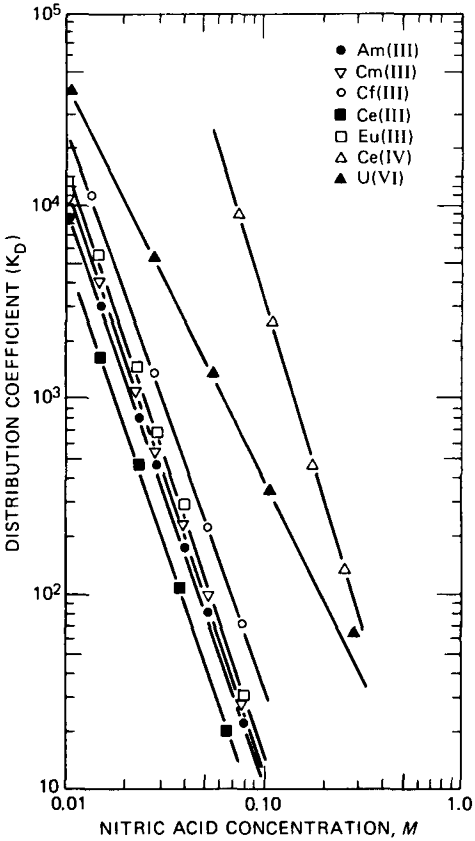


Fig. 5.39 Distribution coefficients (K_D) for several ions onto amorphous zirconium phosphate ($PO_4/Zr = 1.34$) sorbent from HNO_3 solution at 75°C. [From E. P. Horwitz,[332] The Sorption of Certain Transplutonium Ions on Amorphous Zirconium Phosphate, *Journal of Inorganic and Nuclear Chemistry*, 28: 1469 (1966).]

oxidizing AmO_2^+. Shafiev, Efremov, and Andreev[340] have recently separated milligram amounts of americium and curium on zirconium phosphate by sorbing curium preferentially from a pH 2.5 solution containing Am(V) and Cm(III).

In the americium–curium separation scheme patented by Moore,[338] Am^{3+} in a 0.01*M* HNO_3 solution is oxidized to AmO_2^+ by heating at 80 to 90°C with $(NH_4)_2S_2O_8$; the oxidized solution is transferred to the zirconium phosphate exchanger, and the americium is eluted with 0.01*M* HNO_3. If desired, a curium fraction can be eluted with 10*M* HNO_3. The Russian procedure[340] for separating americium from curium is essentially the same as that described by Moore, except for the use of 0.1*M* HNO_3 to elute the AmO_2^+. The Russian scientists note that, in some cases, the oxidized solution may contain some AmO_2^{2+} as well as AmO_2^+; Am(VI) is retained slightly more strongly than Am(V) but can be readily eluted with 0.05*M* to 0.15*M* HNO_3 solutions.

Chelating Resins

Ryan[252] observed that very little work has been done on the reaction of americium and other transuranium elements with chelating exchangers and gives reasons why this is so. Goya and Lai[341] report a value of $K_D = 1.3 \times 10^4$ for sorption of trace amounts of Am^{3+} from seawater into Chelex 100 resin. Myasoedov and Molochnikova[342] have used a chelating resin based on aminopolystyrene and Arsenazo I [2-arsonobenzene-(1-azo-2)-1, 8-dihydroxynaphthalene-3-6-disulfonic acid) to concentrate trace amounts of americium and curium and to separate them from plutonium and fission products. In this analytical procedure, Am^{3+} and Cm^{3+} are sorbed from a mineral acid solution of 0.1*N* to 1*N*; after washing the chelating resin with 0.5*M* oxalic acid and 11*N* H_2SO_4, americium and curium are eluted with 2*M* ammonium citrate solution.

EXTRACTION CHROMATOGRAPHIC PROCESSES

Extraction chromatography (reversed-phase partition chromatography in some of the older literature) combines the best features of solvent extraction and chromatographic separations techniques. Extraction chromatographic systems involve a mobile liquid phase and a stationary liquid phase on an inert support; separations are achieved by taking advantage of the difference in the distribution of ions between the two liquid phases.

Systems that have been studied for extraction chromatographic separation of americium from rare earths, Cm(III), and other transplutonium elements are briefly described in Table 5.12. Not surprisingly, most of the systems investigated have used either HDEHP or Aliquat 336 as the stationary phase. For the most part, the extraction chromatographic procedures listed in Table 5.12 have been tested only with tracer amounts of americium either to investigate americium chemistry in such systems or to develop analytical procedures. A notable exception is the Aliquat 336 (NO_3-form)–kieselguhr system that has been used recently both in the United States[357] and in Europe[359,360] to separate milligram and even gram amounts of americium from curium.

MISCELLANEOUS SEPARATION TECHNIQUES

Many of the solvent extraction, ion exchange, and precipitation processes described earlier in this chapter are used, as noted previously, for large-scale separation and purification of americium in the United States and elsewhere. Various other

Table 5.12

EXTRACTION CHROMATOGRAPHY SYSTEMS FOR AMERICIUM SEPARATION

Carrier	Mesh size	Stationary phase	Eluent	Temp., °C	Application	Refs.
Kieselguhr*	200–400	HDEHP	0.5*M* HCl	87	Separate Am(III) from Bk and Cf	343–345
Silica gel	12–18 μ	HDEHP	0.74*M*–1.02*M* HCl	25	Distribution coefficient data for Am(III)	346
Celite 545†		0.4*M* HDEHP–heptane	0.1*N*–0.6*N* HCl or $\mathrm{HNO_3}$	18–60	Distribution coefficient data for Am(III)	347
Celite 545†	25 μ	8.82 wt.% HDEHP	0.1*N*–0.6*N* HCl or $\mathrm{HNO_3}$	25–75	Separate Am(III) from Cm(III)	348
Kieselguhr*	100–400	HDEHP–xylene	0.1*N*–1*N* $\mathrm{HNO_3}$	20	Separate Am(III) from La and other rare earths	349
Filter Cel	200–400	HDEHP	0.3*N*, 0.5*N*, and 2.1*N* $\mathrm{HNO_3}$		Separate Am(III) from Pm	350
KEL-F‡	170–250	10% HDEHP–heptane	0.97*N*–3.6*N* HCl	20	Separate Am(III) from Eu	351
Tee-Six	70–80	0.45*M* HDEHP–heptane	1*M* monochloroacetic acid–0.025*M* DTPA	25	Separate Am(III) from rare earths	352
Teflon-6§	60–70	1*M* HDEHP–heptane	0.01*M* $\mathrm{HNO_3}$	25	Separate Am(V) from Cm(III)	353
Celite 545†	80–100	1*M* HDEHP	0.1*M*–2*M* $\mathrm{HNO_3}$	0.40	Study behavior of Am(III), (V), and (VI)	354
Celite 545†		0.2*M* HDEHP	0.1*M* $\mathrm{HNO_3}$	25	Study extraction behavior of Am(VI)	355

Kieselguhr*	100–400	Aliquat 336¶ –NO_3-form	3.6*M* $LiNO_3$ –0.01*M* HNO_3	23–24	Separate Am(III) from Cm(III)	68, 70, 239, 240, 356–360
Plaskon–CTFE 2300**		Aliquat 336–SCN-form	0.1*N*–0.6*N* NH_4SCN	25	Separate Am(III) from rare earths	361
Celite	80–120	Aliquat 336–SCN-form	0.1*N*–9*N* NH_4SCN–0.002*N*–0.1*N* H_2SO_4	25	Separate Am(III) from rare earths	362
Paper		0.5*M* tri-*n*-octylamine–xylene	3*M* $LiNO_3$ –0.02*M* HNO_3	25	Separate Am(III) from Cm(III)	363
Paper		0.02*M*–0.18*M* HTTA††–0.02*M* TOP‡‡	0.05*M* HCl	25	Synergistic effect study	364
Kieselguhr*	100–400	0.8*M* TOPO§§–xylene	0.1*M*–1*M* HNO_3	20	Separate Am(III) from Eu	349

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*Commercially available diatomaceous earth.

†Product of the Johns-Manville Company.

‡Polytrifluoro– monochloroethylene.

§Polytetrafluoroethylene.

¶General Mills, Inc.; mixture of trioctylmethyl- and tridecylmethylammonium chloride.

**Trifluorochloroethylene made by the Allied Chemical Company.

††Thenoyltrifluoroacetone.

‡‡Tri-*n*-octylphosphate.

§§Tri-*n*-octylphosphine oxide.

schemes have been proposed and/or used from time to time for recovery, purification, characterization, or analysis of, generally, micro amounts of americium.

Bilal and others[365-368] in Germany, principally at the Hahn-Meitner Institute, suggest that counterflow ion-migration procedures are applicable to the recovery and purification of americium from Purex-process high-level waste as well as irradiated ^{241}Am and ^{243}Am targets. These procedures involve a flow of a solvent counter to that of the ions of a mixture migrating in an electrical field; the velocity of this solvent compensates the mean migration velocity of the ions to be separated. The net result is to set up a stationary distribution of the mixture, within which the more rapid ions are transported upstream and the slower ions downstream. Separations of metal ions provided by counterflow ion-migration processes can be enhanced by the addition of ligands, which form complexes of different strengths with the various metal ions. In the favorable situation, one of the metal ions is converted to a neutral or anionic species, which is then transported out of the separation column by the counterflow liquid and is thus electrolytically extracted from the stationary mixture.

Counterflow ion-migration processes for separating large amounts of material are conveniently performed in troughs.[367,368] Such troughs are divided by permeable diaphragms into compartments to avoid remixing caused by thermal convection and nonuniform flow profiles. Bilal et al.[366] have described the successful application of the counterflow ion-migration technique to recover tracer amounts of ^{241}Am from synthetic denitrated Purex-process waste to which acetic acid had been added. Bilal et al.[365] also applied this technique to cleanly separate americium and plutonium from a $2M$ acetic acid–$0.05M$ HNO_3 electrolyte containing 40 g Pu(IV) liter^{-1} and 0.15 g Am(III) liter^{-1}.

The extraction of americium from dilute acetic acid solutions by sodium amalgam has been reported by Kobayashi and Saito.[369] In their experiments, $0.4M$ to $0.8M$ acetic acid solutions containing about 1 g Am^{3+} liter^{-1} were contacted with sodium amalgam; 98 to 99% of the americium was in the amalgam phase. Most other actinide elements, as well as the lanthanides from lanthanum to europium, also extract under these conditions.

Other reported[370] separation procedures include selective leaching of ^{241}Am from PuO_2 powder by $1.2M$ formic acid at 90°C; ~20% of the available americium extracts into the leach solution. Independent confirmation of this somewhat surprising leach behavior has not yet been reported. Zvarova, Zvára, and coworkers[371-373] have separated microgram amounts of americium, curium, and plutonium by gas chromatography of the volatile chloride complexes formed by the reaction of Al_2Cl_6 vapor with solid actinide chlorides at 250 to 500°C (Fig. 5.40).

Paper electrophoretic procedures using $6M$ to $12M$ HNO_3 (Ref. 374), HNO_3–EDTA solutions (Ref. 375), $0.2M$ citric acid (Ref. 376), and $0.07M$ α-hydroxyisobutyric acid at pH 2.1 (Ref. 377) have been described for separating Am(III) from Cm(III), Ac(III), Pb(II), Th(IV), and Pu(IV). So-called focusing electrophoretic techniques have been used to separate Am(III) and Cm(III) from La(III) and Ce(III) (Ref. 378), and to separate Am(III) from Cm(III) (Ref. 379); the latter separation was

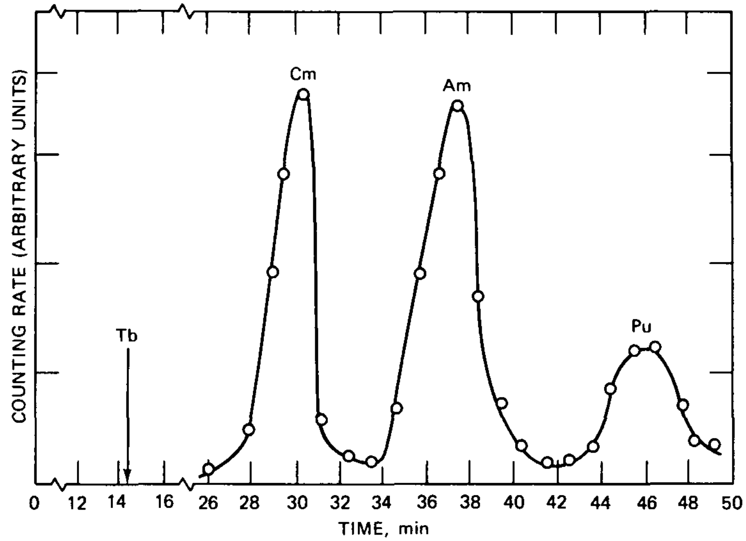

Fig. 5.40 Gas chromatographic separation of a mixture of chlorides of plutonium, americium, and curium. Glass capillary column (2.5 m by 1 mm in inside diameter) at 250°C; Al_2Cl_6 partial pressure, ~100 torrs; helium flow, 8 ml min^{-1}. [From T. S. Zvarova and I. Zvára,[371] Separation of Transuranium Elements by Gas Chromatography of Their Chlorides, *Journal of Chromatography*, **49**: 290 (1970).]

accomplished in a sodium polyphosphate solution at pH 7.0. Details of these electrophoretic methods are given in the text by Myasoedov et al.[95]

Szeglowski and other Polish scientists[380,381] have studied frothless ion flotation of anionic nitrate and citrate complexes of Am(III) from $LiNO_3$ and citric acid solutions, respectively. Cetylpyridynium bromide in isooctyl alcohol was used as a cationic collector. Americium recovery by ion flotation increases with increased $LiNO_3$ concentration but decreases linearly with increased citrate concentration. The Polish workers also studied the flotation of colloidal americium hydroxide from various aqueous solutions using sodium tetradecyl sulfate as an anionic collector; maximum recovery of americium was observed at pH 5.

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