CHAPTER EIGHT

AMERICIUM

Wolfgang H. Runde and Wallace W. Schulz

8.1 HISTORICAL

Americium, element 95, was discovered in 1944–45 by Seaborg *et al.* (1950) at the Metallurgical Laboratory of the University of Chicago as a product of the irradiation of plutonium with neutrons:

$$^{239}\mathrm{Pu}(n,\gamma)^{240}\mathrm{Pu}(n,\gamma)^{241}\mathrm{Pu} \xrightarrow{-\beta^-} {}^{241}\mathrm{Am}$$

This reaction is still the best method for the production of pure ^{241}Am. In post-World War II work at the University of Chicago, Cunningham isolated $Am(OH)_3$ and measured the first absorption spectrum of the Am^{3+} aquo ion (Cunningham, 1948). By the 1950s, the major center for americium chemistry research in the world was at Los Alamos. Since the 1970s, the majority of publications on americium have come from researchers in the former USSR and West Germany. Extensive reviews of americium chemistry can be found in Freeman and Keller (1985), Gmelin (1979), Penneman and Asprey (1955), and Schulz (1976).

8.2 NUCLEAR PROPERTIES OF ISOTOPES

To date, 13 americium isotopes with mass numbers 232–247 and half-lives ranging from 55 s to 7370 years are known (Table 8.1). While the isotopes with mass numbers 232, 234, and 237–247 have been known for some time, the neutron-deficient isotopes Am-233, Am-235, and Am-236 have only recently

Table 8.1 *Nuclear properties of americium isotopes.*

Mass number	*Half-life*	*Mode of decay*	*Main radiations* (MeV)	*Method of production*
232	1.4 min	SF isomer		^{230}Th(^{10}B, 8n)
233	3.2 min	α	α 0.00678	^{238}U(^{6}Li, 6n)
234	2.6 min	EC		^{230}Th(^{10}B, 6n)
235	15 min	EC		^{238}Pu(^{1}H, 4n)
236	4.4 min[a]	EC		^{235}U(^{6}Li, 5n)
	3.7 min[b]	EC		^{237}Np(^{6}He, 4n)
237	1.22 h	EC > 99%	α 6.042	^{237}Np(α, 4n)
		α 0.025%	γ 0.280 (47%)	^{237}Np(^{3}He, 3n)
238	1.63 h	EC > 99%	α 5.94	^{237}Np(α, 3n)
		α 1.0×10^{-4}%	γ 0.963 (29%)	
239	11.9 h	EC > 99%	α 5.776 (84%)	^{237}Np(α, 2n)
			5.734 (13.8%)	
		α 0.010%	γ 0.278 (15%)	^{239}Pu(d, 2n)
240	50.8 h	EC > 99%	α 5.378 (87%)	^{237}Np(α, n)
		α 1.9×10^{-4}%	5.337 (12%)	^{239}Pu(d, n)
			γ 0.988 (73%)	
241	432.7 yr	α	α 5.486 (84%)	^{241}Pu daughter
	1.15×10^{14} yr	SF	5.443 (13.1%)	multiple n capture
			γ 0.059 (35.7%)	
242	16.01 h	β^- 82.7%	β^- 0.667	^{241}Am(n, γ)
		EC 17.3%	γ 0.042 weak	
242 m	141 yr	IT 99.5%	α 5.207 (89%)	^{241}Am(n, γ)
	9.5×10^{11} yr	SF α (0.45%)	5.141 (6.0%)	^{241}Am(n, γ)
			γ 0.0493 (41%)	
243	7.38×10^{3} yr	α	α 5.277 (88%)	multiple
	2.0×10^{14} yr	SF	5.234 (10.6%)	n capture
			γ 0.075 (68%)	
244	10.1 h	β^-	β^- 0.387	^{243}Am(n, γ)
			γ 0.746 (67%)	
244 m	26 min	β^- > 99%	β^- 1.50	^{243}Am(n, γ)
		EC 0.041%		
245	2.05 h	β^-	β^- 0.895	^{245}Pu daughter
			γ 0.253 (6.1%)	
246[c]	25.0 min	β^-	β^- 2.38	^{246}Pu daughter
		γ	0.799 (25%)	
246[c]	39 min	β^-	γ 0.679 (52%)	^{244}Pu(α, d)
				^{244}Pu(^{3}He, p)
247	24 min	β^-	γ 0.285 (23%)	^{244}Pu(α, p)

SF, spontaneous fission; EC, electron capture; IT, isomeric transition.

[a] Hall (1989).

[b] Tsukada *et al.* (1998).

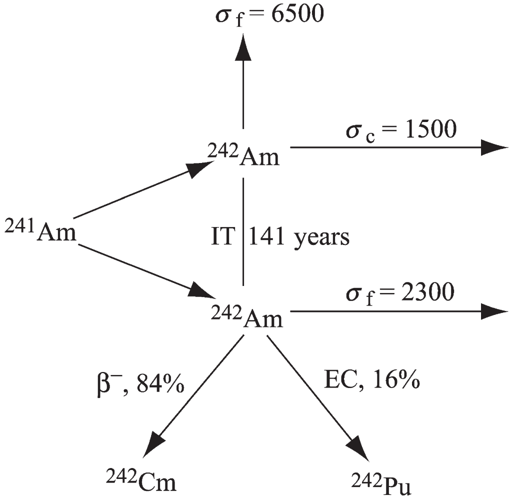
[c] Not known whether ground-state nuclide or isomer.

been produced and characterized (Hall, 1989; Tsukada *et al.*, 1998; Weifan *et al.*, 1999; Sakama *et al.*, 2000). The light isotopes up to ^{243}Am mainly decay by electron capture, emission of alpha particles, and spontaneous fission; the isotopes beyond ^{243}Am are short-lived β^--emitters. Data in Table 8.1 are taken primarily from the comprehensive compilation in Gmelin (1973) and others (Hyde *et al.*, 1971; Wapstra and Gove, 1971; Skobelev, 1972; Natowitz, 1973; Schulz, 1976; Lederer and Shirley, 1978; Kuznetsov and Skobelev, 1966). Although not noted in Table 8.1, literature references (e.g. Schulz, 1976) indicate that some of the identified americium isotopes exist in more than one isomeric energy state.

8.3 PRODUCTION OF PRINCIPAL ISOTOPES

The most important isotopes of americium are ^{241}Am and ^{243}Am due to their long half-lives of 433 and 7380 years, respectively. These isotopes have been made in kilogram quantities with high purity. ^{242}Am ($t_{1/2}$ = 141 years) can be produced to the extent of only a few percent in ^{241}Am by neutron capture.

Americium-241 is superior to all competing radionuclides as a low-energy gamma source because of its cost, convenience, spectral purity, and half-life (Crandall, 1971) and its application as a low-energy gamma source may well be the largest of any actinide nuclide (Seaborg, 1970; LeVert and Helminski, 1973). The major use for ^{241}Am is in smoke-detector alarms and in neutron sources to furnish alpha particles for the (α,n) reaction on beryllium. As a source of nearly monoenergetic alpha (5.44 and 5.49 MeV) and gamma (59.6 keV) radiation, ^{241}Am is also widely used in thickness gauging and density and radiographic measurements, and is utilized to produce ^{242}Cm (up to 0.65 g ^{242}Cm per gram of ^{241}Am (Hennelly, 1972)) by thermal neutron capture. The thermal neutron capture sequence involved in producing ^{242}Cm from ^{241}Am is:



The lower specific activity of ^{243}Am compared to ^{241}Am makes it particularly useful in chemical studies. It is also used in the production of ^{244}Cm, ^{249}Bk/Cf, ^{252}Cf, and other transcurium elements in high neutron-flux reactors.

8.3.1 Production of ^{241}Am by irradiation of ^{239}Pu

Neutron irradiation of ^{239}Pu yields ^{241}Pu, which decays by beta emission with a half-life of 14.4 ± 0.3 years to ^{241}Am. In 1977, more than 1.5 kg of ^{241}Am was isolated from reprocessing aged plutonium at the US Department of Energy (DOE) Rocky Flats site. In 1980, a similar amount was isolated at the DOE Los Alamos site.

8.3.2 Production of ^{243}Am by irradiation of ^{242}Pu

Nearly isotopically pure ^{243}Am results from irradiation of ^{242}Pu with thermal neutrons:

$$^{242}\mathrm{Pu}(\mathrm{n},\gamma)^{243}\mathrm{Pu} \xrightarrow[5\mathrm{h}]{\beta^-} {}^{243}\mathrm{Am}$$

8.3.3 Availability of ^{241}Am and ^{243}Am from power reactor fuel

Commercial nuclear power reactors produce kilogram quantities of both ^{241}Am and ^{243}Am with an isotopic composition dependent on reactor burn-up. The US DOE Savannah River site reactors produced about 9 kg of a ^{243}Am–^{244}Cm mixture over a period of 10 years (Baybarz, 1970). About 1 kg of mixed ^{241}Am and ^{243}Am was recovered at the US DOE Hanford site during reprocessing of the Shippingport reactor blanket fuel (Wheelwright *et al.*, 1968). Approximately 30 kg of americium is reported to remain in the US DOE Hanford site waste tanks (Agnew *et al.*, 1997). But, no industrial reprocessor of commercial nuclear reactor fuel anywhere in the world has opted to pursue systematic recovery of americium. However, a potentially large source of americium is the high-level Purex-process liquid waste from plutonium processing; indeed, future waste storage may require separation of americium.

8.3.4 Critical mass

The calculated minimum critical mass of ^{242}Am in aqueous solution is 23 g at a concentration of 5 g L^{-1} (Bierman and Clayton, 1969). Note that mass separation of ^{242}Am from ^{241}Am is required to obtain pure ^{242}Am.

8.4 SEPARATION AND PURIFICATION OF PRINCIPAL ISOTOPES

Most of the standard methods, aqueous and non-aqueous, for separating and purifying americium from all kinds of sources and materials were developed in the 1950s, 1960s, and 1970s; progress made in this time frame was summarized in the second edition of this work. In contrast to the earlier time period, in the 1980s and 1990s research efforts to develop new or improved technology for recovery and/or purification of americium were largely confined to development and testing of new and improved solvent extraction processes. Worldwide, aside from purely academic investigations mainly in Russia and India, scientists and engineers were motivated by one of two main goals:

(1) In the USA, principally, to find new or modified practicable ways of removing minor amounts of neptunium, plutonium, and americium from various stored defense wastes to convert such wastes from so-called TRU (transuranium) wastes to non-TRU wastes, thus requiring less expensive final disposal procedures and facilities.
(2) To develop and demonstrate practicable technology for removal (partitioning) of long-lived actinides as well as certain long-lived and mobile fission products, e.g. ^{99}Tc, ^{129}I from the high-level aqueous waste (HLW) generated in reprocessing of irradiated commercial nuclear power reactor fuel. Partitioning of these species from the HLW, it is believed, would greatly facilitate and simplify the many current technical and legal obstacles to final geologic disposal of the HLW. Recovered, purified, and concentrated actinides and fission products can, it is further believed, be converted (transmuted) to stable or short-lived radioisotopes by suitable neutron irradiation. Because irradiated commercial nuclear reactor fuel is being reprocessed in Japan, France, and China, investigators in these countries have been active in pursuing partitioning technology options. Several references (ANS, 1993; Prunier *et al.*, 1997; Cohen, 2000; NN, 2002) provide much additional detail concerning the incentives for and status of the development of partitioning and transmutation technology. Particular attention is called to an excellent summary article on actinide partitioning technology (Mathur *et al.*, 2001).

Americium separation technology is presented and discussed here in the same order used in the second edition of this monograph. Significant separation technology developments that have occurred since the second edition was published are incorporated and discussed at appropriate places in the text. (The knowledgeable reader will appreciate that when this text was prepared (early 2002) all the americium separations technologies described in the subsequent parts of Section 8.4 was essentially only of academic and/or historic interest. The present authors are not aware of any current significant effort in any country to actually separate and/or purify americium isotopes from any source.)

8.4.1 Pyrochemical processes

A two-stage, countercurrent molten-salt extraction process was used to extract ^{241}Am from many kilograms of aged plutonium, in which ^{241}Am had grown-in by beta decay of ^{241}Pu. The purification scheme removed about 90% of the americium from plutonium metal, typically containing 200–2000 ppm ^{241}Am (Schulz, 1976).

Mullins and Leary (1969) patented a method of separating americium from plutonium that involves bubbling a mixture of oxygen and argon gas into a molten salt containing both elements. Plutonium precipitates as PuO_2, whereas americium remains in solution.

Ferris *et al.* (1972) 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 of 600–750°C. Some of the americium appeared to be in the divalent state in the $Am/PuCl_3$ system (Mullins and Leary, 1969). The distribution coefficient, $D =$ (g Am per g metal phase)/(g Am per g salt phase), of americium between molten aluminum metal and molten $AlCl_3–KCl$ is 1.96 (Moore and Lyon, 1959). Mills and Reese (1994) demonstrated that ^{241}Am in aged PuF_4 can be cleanly separated from plutonium by low-temperature reaction with O_2F to generate volatile PuF_6. Americium remains in the fluorination residue from which it can be recovered and concentrated by any of the several aqueous methods.

As part of their comprehensive experimental and theoretical studies of the partitioning of actinides from high-level radioactive fuel reprocessing aqueous waste, Japanese scientists, in collaboration with some US investigators, have been developing a pyrometallurgical partition process (Sakamura *et al.*, 1998). The process consists of four main steps: (1) denitration of the HLW; (2) chlorination to convert oxides to chlorides; (3) reductive extraction to reduce actinides in a molten salt by lithium metal and to extract them into liquid cadmium; and (4) electrorefining in LiCl–KCl eutectic to separate actinides from the liquid cadmium anode. Preliminary experimental tests of the entire process show that uranium, plutonium, and neptunium are relatively easily separated from fission product rare earths but that americium is accompanied by some rare earth elements. In related theoretical studies of actinide partitioning technology, Yamana and Moriyama (1996) concluded that it may be feasible to separate americium and curium from lanthanide elements by electrolytic amalgamation techniques.

8.4.2 Precipitation processes

Initially, only precipitation processes were available for recovery and purification of americium. Later, new ion-exchange and solvent extraction processes largely, but not completely, supplanted the early precipitation recovery/purification processes. Because of their insolubility and other special properties precipitation of certain compounds of americium, e.g. AmF_3, $K_8Am_2(SO_4)_7$, $Am_2(C_2O_4)_3$, $K_3AmO_2(CO_3)_3$, is routinely considered for recovery or purification of a batch of americium. The latter two compounds are useful because oxalate ion prevents certain impurities from accompanying americium in the precipitate and, also, because americium oxalate is a convenient starting point for preparation of AmO_2. The insoluble Am(V) carbonate complex is particularly useful for the large-scale separation of americium from curium (Buijs *et al.*, 1973; King *et al.*, 1973).

Hermann (1956) demonstrated that a substantial separation of americium from lanthanum can be obtained by fractional precipitation of americium and lanthanum oxalates. The precipitation is effected in homogeneous solution; the precipitant is generated by slow hydrolysis of dimethyl oxalate. The oxalate precipitate is greatly enriched in americium; about 50% of the lanthanum can be rejected at each stage with only about 4% of the americium.

Stephanou and Penneman (1952) found that Cm(III) could be separated from americium by oxidizing the latter to Am(VI) with potassium persulfate and precipitating CmF_3; Am(VI) is soluble under these conditions. Proctor and Connor (1970) at the US DOE Rocky Flats site used precipitation of cerium peroxide to separate gram quantities of americium from cerium. Proctor (1976) also separated Am(VI) from large quantities of rare earths by precipitation of their trifluorides.

Bhanushali *et al.* (1999) have recently proposed a new application of oxalate precipitation technology for separation of americium. Based on some experimental data, these workers suggest that traces of americium and plutonium remaining in the aqueous waste generated during plant-scale precipitation of plutonium oxalate can be effectively removed by simple coprecipitation with thorium oxalate. It is not known if such a coprecipitation step has been incorporated into routine processing of plutonium in India.

8.4.3 Solvent extraction processes

Solvent extraction processes and systems using amine and organophosphorus compounds are extensively used for the initial recovery and separation of gram to kilogram amounts of americium. Excellent reviews of the solvent extraction chemistry of trivalent americium have been published by Weaver (1974) and Shoun and McDowell (1980). Myasoedov *et al.* (1974a) discussed solvent extraction systems useful for the analysis of americium.

(a) Organophosphorus extractants (Gureev *et al.*, 1970)

(*i*) *Tri*-n-*butyl phosphate* (*TBP*)

TBP is the extractant in widest use for nuclear fuel processing. Extraction of Am^{3+} from nitrate media by TBP conforms to the reaction (Weaver, 1974):

$$\mathrm{Am^{3+}(aq) + 3\,NO_3^-(aq) + 3\,TBP(org) \rightarrow Am(NO_3)_3 + 3\,TBP(org)}$$

The equilibrium constant, $K_{\mathrm{ex}} = [\mathrm{Am(NO_3)_3 \cdot 3TBP}]/[\mathrm{Am^{3+}}][\mathrm{NO_3^+}]^3[\mathrm{TBP}]^3$, has the value of 0.4 at zero ionic strength (Zemlyanukhin *et al.*, 1962). While

TBP, even undiluted, extracts americium only weakly from strong nitric acid solutions, americium is extracted by TBP quite strongly from neutral (or low-acid), highly salted nitrate solutions.

As part of their intensive effort to develop feasible partitioning–transmutation technologies, Kamashida and his coworkers investigated TBP extraction of Am(VI) from nuclear reactor fuel reprocessing solutions (Kamashida and Fukasawa, 1996; Kamashida *et al.*, 1998) as a means of removal of americium while separating it from associated trivalent rare earths (good separation of americium from rare earth elements is desirable/necessary to make efficient use of neutrons in the transmutation process). In these studies, Am(VI) was produced by oxidation of Am(III) with silver-catalyzed peroxydisulfate, both in the presence and absence of $(NH_4)_{10}P_2W_{17}O_{61}$ added to stabilize americium in the hexavalent oxidation state. By use of neat TBP to extract Am(VI) from 1 M HNO_3, an americium distribution ratio as high as 4 was realized; the separation factor from Nd(III) was 50.

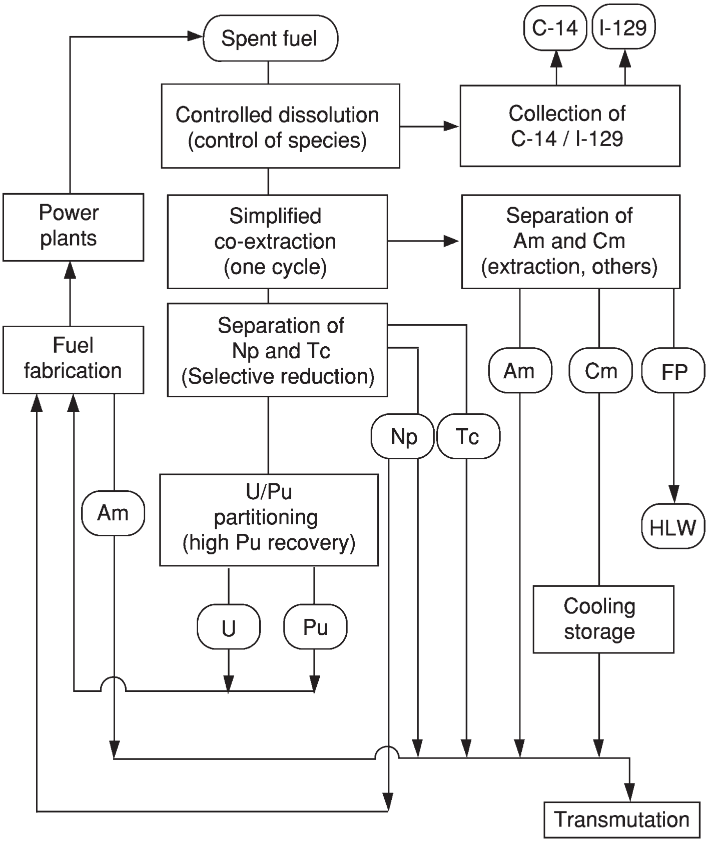


Fig. 8.1 *Schematic of Japanese PARC process* (*Uchiyama* et al., 2000).

In other recent studies, Japanese scientists have developed an advanced Purex process, the PARtitioning Conundrum Key (PARC) process (Uchiyama *et al.*, 2000). Fig. 8.1 shows a schematic diagram of the PARC process concept where americium is not separated in the mainline Purex process, but from HLW generated in the Purex process. The PARC process thus provides for use of certain organic compounds to provide effective Purex process recovery and separation of uranium, neptunium, plutonium, and technetium. Uchiyama *et al.* (2000) conducted tests of parts of the PARC process with aqueous feeds resulting from nitric acid dissolution of highly irradiated (8000 MWD/tU) fuel. Important findings were:

- Np(VI) was reduced to Np(V) by *n*-butyraldehyde selectively in the presence of U(VI), Pu(VI), and Tc(VII);
- high acid scrubbing was effective for separation of technetium;
- isobutyraldehyde reduced Pu(IV) to Pu(III) very effectively;
- *N*-butylamine compounds (carbonate and oxalate) were effective solvent-washing agents.

The French, as stated earlier, are energetically pursuing the partitioning–transmutation alternative for their Purex process HLW. Apparently for proprietary reasons, they have not widely publicized their progress. However, a recent article (NN, 2002) states: "... the Marcoule team have been able to push the current Purex processing technique to enable about 99% of uranium, plutonium, and the minor actinides of most concern, which are neptunium, americium, and curium to be isolated. The separation levels of the main long-lived fission products, which include iodine-129, technetium-99, and cesium-135, are equally impressive. The yields of iodine and technetium extracted are 95 and 90%, respectively. The process for separating cesium is nearing fruition, and technical feasibility is also expected by 2005. These levels of separation provide important benefits as the resulting vitrified waste contains fewer long-lived isotopes. According to the CEA, the radioisotopes of the advanced vitrified product – referred to as 'light glass' – will drop to the level of natural uranium in less than 300 years. This compares to more than 10000 years for the current vitrified HLW and hundreds of thousands for spent fuel." The article in *Nuclear News* does not provide any detail as to the Purex process modifications used to separate americium; it may be, just as in the Japanese PARC process, that the French plan to recover americium from the Purex process HLW by any of several available procedures.

It should be noted that formation constants of complexes formed by Am(III) with aminopolycarboxylic acids are larger than for the comparable complexes of the light lanthanides ($Z = 57$–61). Thus, addition of an aminopolycarboxylic acid to a lithium or aluminum nitrate solution containing Am(III) and rare earth enhances TBP extraction of the lanthanides relative to americium (Koehly and Hoffert, 1967). Americium can be separated from rare earths by TBP extraction from 1 M ammonium thiocyanate solution (Penneman and Keenan, 1960).

The mechanism of Am(iii) and Eu(iii) extraction from 1 m ammonium thiocyanate media by TBP in both the presence and the absence of a quaternary ammonium thiocyanate compound was investigated by Indian scientists (Khopkar and Narayankutty, 1971).

(*ii*) *Dibutyl butylphosphonate* (*DBBP*)

DBBP, $(C_4H_9O)_2(C_4H_9)PO$, extracts Am(iii) from nitrate media more strongly than TBP and was used in a production-scale process at the US DOE Hanford site for several years (Schulz, 1976).

(*iii*) *Trialkylphosphine oxides* (*TRPO*)

It is well known that the basicity of the P–O functionality increases in going from alkyl phosphates (e.g. TBP) to alkyl phosphonates (e.g. DBBP) to alkylphosphine oxides (e.g. TRPO). Corresponding to the increased basicity is increased extractive power for trivalent actinides, e.g. Am(iii) and Cm(iii) from aqueous 1–2 m HNO_3 solutions. Chinese investigators have made use of the extractive power of TRPOs to develop a process for partitioning actinides, including americium and curium, from acidic Purex process HLW (Zhu and Jiao, 1994). Most of the results of Zhu *et al.* have been published in Chinese language journals, which, apparently, have not been translated into readily available English versions. Zhu and Jiao (1994) presented an admirable English language summary of their work up to 1994. They used a 30 vol% TRPO–kerosene solvent to extract trivalent (Am, Cm, lanthanides), tetravalent (Np, Pu), and hexavalent (U) actinides from both synthetic and actual Purex process HLW adjusted to about 1 m HNO_3. These experimenters used a mixture of C_6–C_8 alkylphosphine oxides available commercially (at least in the early 1990s) from operation of a fertilizer manufacturing plant. Zhu and coworkers found their particular 30% TRPO reagent to be very effective in extracting over 99% of all the actinides and lanthanides from the adjusted HLW. Extracted actinides could be stripped successively with 5.5 m HNO_3, 0.6 m oxalic acid, and 5% Na_2CO_3 solution to yield Am + rare earth, Np + Pu, and U fractions, respectively. Auxiliary experiments showed the TRPO solvent to have excellent actinide extraction kinetics and to be quite resistant to radiolytic degradation. Their highly successful batch and continuous countercurrent extraction–stripping tests led the Chinese to believe (at least in 1994) that their TRPO extractant was eminently suited for use in plant-scale partitioning of actinides from Chinese defense HLW. We, the authors, were not able to establish the present status of development/utilization of the Chinese TRPO extraction process.

Very recently, Murali and Mathur in India revisited use of TRPO for partitioning actinides from Purex process HLW (Murali and Mathur, 2001). They used a 30 vol% solution of a commercially available mixture of alkyl TRPOs (Cyanex-923) in dodecane. Cyanex-923 (Cytec Canada, Inc.) is a mixture of four alkylphosphine oxides, $R_3PO, R'_3PO, R_2R'PO, RR'_2PO; R = \text{hexyl}$ and $R' = \text{octyl}$. (Murali and Mathur point out that Cyanex-923 is not the same mixture of alkylphosphine oxides used earlier by the Chinese investigators.) With dodecane as the diluent, the Indian investigators found it necessary to add TBP (5–20 vol%) to the Cyanex-923-dodecane solvent to avoid formation of a third phase even after adjusting the HLW acidity to 1 M HNO_3. Under the latter conditions, Murali and Mathur were able to both successfully extract and strip actinides, including americium, from synthetic Purex process HLW. Despite this successful performance, Murali and Mathur judged, "... the TRUEX solvent (0.2 M CMPO + 1.2 M TBP in dodecane) seems to be a superior extractant for partitioning of minor actinides from HLW solutions as there is no need for any feed adjustment and it tolerates significant amounts of sulfate, fluoride, and oxalate anions." (The TRUEX process is discussed in the later part of Section 8.4.3.)

(*iv*) *Bis*(*2-ethylhexyl*)*phosphoric acid* (*HDEHP*)

HDEHP is an excellent extractant for Am(III) from certain aqueous solutions. This extractant is commercially available in large quantities, can be readily purified, and has been widely used for both analytical purposes and plant-scale recovery and purification of americium (Peppard *et al.*, 1958, 1962; Gureev *et al.*, 1964). A countercurrent HDEHP extraction process was used at the DOE Hanford site in the late 1960s as part of the processing sequence for recovering and purifying 1 kg of americium and 50 g of curium from irradiated Shippingport reactor fuel (Boldt and Ritter, 1969). An HDEHP batch extraction–strip process (Cleanex process) was routinely used in the Transuranium Processing Plant at the DOE Oak Ridge National Laboratory to reclaim americium, curium, and other transuranium elements from rework solution and/or to convert from nitrate to chloride media (Bigelow *et al.*, 1980). The Talspeak HDEHP processes are based upon the results of Weaver and Kappelmann (1964) 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. Lactic acid is used to avoid precipitation of solids when the concentration of lanthanides is high. HDEHP solutions have been used to selectively extract Am(VI) from Cm(III) (Musikas *et al.*, 1980a); in such systems rapid reduction of Am(VI) to lower oxidation states is a problem.

Extraction of Am(III) is very sensitive to the nature of compounds used to dilute the HDEHP (Gureev *et al.*, 1964). The kinetics of Am(III) extraction by HDEHP solutions were studied by Choppin and Nash (1977). In 1998, Indian scientists (Mapara *et al.*, 1998) studied solvent extraction of Am(III) from aqueous 0.1–1.0 M HNO_3 solutions using both HDEHP and 2-ethylhexyl phosphonic acid (PC88a in their notation). Before use, 1 M solutions of both extractants in kerosene were partially neutralized (saponified) to varying degrees with NaOH. In agreement with previously well-known chemistry of

HDEHP and PC88a, Am(III) extraction increased as more and more of the acidic extractant was converted to the sodium form.

(*v*) *Diisodecylphosphoric acid* (*DIDPA*)

Morita, Kubota, and other Japanese scientists (Morita and Kubota, 1988; Morita *et al.*, 1993) closely examined properties of solutions of DIDPA for extraction of actinides from acidic Purex process HLW. DIDPA solutions extract hexavalent (U) and tetravalent (Pu,Np) actinides quite efficiently from 1 to 3 M HNO_3 media. (Before extraction of ^{237}Np, however, it must be first reduced to Np(IV) by reduction of Np(V) and Np(VI) with hydrogen peroxide.) But, a disadvantage of the DIDPA extraction technique is that trivalent americium and curium do not extract well at feed acidities much above about 0.5 M HNO_3. Once extracted, Am(III) and Cm(III) can be selectively stripped with a diethylenetriaminepentaacetic acid (DTPA) solution; lanthanides can be easily stripped with 4 M HNO_3; and plutonium and neptunium can be removed from the organic phase by stripping with an aqueous oxalic acid solution. Japanese tests, both batch and countercurrent, of the DIDPA process with simulated Purex process HLW were generally regarded as successful.

(*vi*) *Neutral multifunctional organophosphorus and carbamoylphosphonate reagents*

Monofunctional organophosphorus extractants, e.g. TBP, DBBP, tri-*n*-octylphosphine oxide (TOPO), do not extract Am(III) from strongly acidic (>1 M HNO_3) aqueous solutions. Such behavior is desirable when the goal decades ago was to separate and purify plutonium and uranium from nitric acid solutions of irradiated nuclear fuel, e.g. the Purex process. But, evolving nuclear waste management strategies and policies have driven an urgent need for liquid–liquid extraction agents and processes capable of effective recovery and/or removal of Am(III) and Cm(III) as well as actinides in the +4 and +6 oxidation states from strong nitric acid medium. Thus, in the USA in the 1970s and 1980s there was an economic incentive to convert so-called transuranic acidic waste solutions containing ^{241}Am and various other actinides, chiefly plutonium, to low-level waste, which could be disposed of inexpensively. And, of course, the emergence of the partitioning–transmutation philosophy for advanced nuclear waste management and disposal places a premium on solvent extraction technology for efficient removal of trivalent actinides from acidic HLW solutions.

In the early 1960s, Siddall (1963, 1964) opened the door to the desired practical solvent extraction schemes for extraction of trivalent americium and curium from concentrated nitric acid solutions. Siddall in his papers noted that certain bifunctional organophosphorus reagents, e.g. diphosphonates and carbamoylmethylphosphonates (CMPs), i.e. compounds of the type $(R_1O)_2P(O)$—$(CH_2)_n$—(O)C—N—$(R_2)_2$, were especially effective in extracting trivalent actinides and lanthanides from strong nitric acid solutions.

Siddall's highly significant work lay buried in the literature until resurrected by Schulz and coworkers (Schulz, 1974, 1975; McIsaac and Schulz, 1976; Schulz and Navratil, 1982) in the early and middle 1970s. Both Schulz at the US DOE Hanford site and McIsaac at the US DOE Idaho site were motivated to develop solvent extraction processes for removing Am(III) and Pu(IV) from certain site acid waste solutions to convert the large volumes of these wastes to more easily managed and disposed of low-level wastes.

Based upon Siddall's data, both Schulz and McIsaac elected to use dihexyl-*N*,*N*-diethylcarbamoylmethyl phosphonate (DHDECMP) as the extractant for Am(III) and 4+ and 6+ actinides. Siddall's results indicated that CMPs were better extracting agents for 3+ actinides than diphosphonates. Another candidate, dibutyl-*N*,*N*-diethylcarbamoylmethylphosphonate, was rejected for use because of its high solubility in aqueous phases. Finally, of considerable significance, DHDECMP was available in liter quantities, albeit in a highly impure state (50–70% DHDECMP), from the Wateree Chemical Co. in South Carolina.

Batch tests with the impure DHDECMP solvent at both the Hanford and the Idaho sites quickly confirmed Siddall's results and demonstrated that this particular reagent would indeed permit efficient removal of all actinides from actual candidate acidic wastes. Auxiliary tests soon showed DHDECMP were sufficiently resistant to radiolysis, both alpha and gamma, to have a long useful life in plant-scale continuous countercurrent operations, especially in short residence time contacting equipment. Kinetics of actinide extraction and stripping were sufficiently rapid for satisfactory operation of continuous countercurrent contactors. The propensity of 20–30 vol% DHDECMP–NPH (normal paraffin hydrocarbon) solvents to form a third phase (second organic phase) when contacted with some acidic (HNO_3) waste solutions was overcome by either changing to an aromatic diluent, e.g. tetrachlorobenzene or decalin, or substituting TBP for a large portion of the NPH diluent. All the batch contact experiments culminated in chemical flowsheets (extraction–scrub–strip) that were very successfully demonstrated with both actual Idaho and Hanford sites acid waste solutions.

The only serious discordant note observed in tests with the impure Wateree Chemical Co. DHDECMP arose in attempts to use very dilute, e.g. ~0.01 M HNO_3 solutions to selectively strip 3+ actinides and lanthanides from pregnant organic phases. With as-received DHDECMP extractant D_{Am} instead of decreasing regularly upon successive strip contacts actually increased, resulting in a certain fraction of unstrippable americium. Such behavior is very symptomatic of the presence of an acidic organic compound in an otherwise neutral extractant. To overcome the deleterious effects of the acidic organic impurity, the 20–30 vol% DHDECMP solvent, before use, was subjected to various empirical chemical treatments designed to remove or at least reduce the concentration of the impurity, e.g. washing with ethylene glycol or alternate washing with HCl and NaOH solutions to hydrolyze the organic impurity. These chemical treatments, although cumbersome, removed enough of the offending impurity to allow successful selective stripping of americium in continuous countercurrent flowsheet tests.

Tetravalent actinides and, if not previously removed, trivalent actinides were easily and effectively stripped from the DHDECMP phase with aqueous solutions containing fluoride or oxalate ions. And, as would be expected, dilute NaOH solutions effectively removed all 3+, 4+, and 6+ actinides from the DHDECMP solvent.

Following publication of the Schulz and McIsaac work, many other investigators, both in and outside the USA, conducted comprehensive experimental studies with DHDECMP and various other CMP-type reagents (Martella and Navratil, 1979; Petrzilova *et al.*, 1979; Horwitz *et al.*, 1981; Kalina *et al.*, 1981b; Hugen *et al.*, 1982; McIsaac, 1982; McIsaac and Baker, 1983; Kalina and Horwitz, 1985; Mathur *et al.*, 1991, 1992b). Indeed, as late as 1994, long after the TRUEX process had been proposed (cf. Section 8.4.3a(vi)), Rapko and Lumetta (1994) were still investigating use of a 0.75 M DHDECMP–1.05 M TBP/NPH solvent for extracting U(VI), Pu(IV), and Am(III), as well as competing metal ions, e.g. Fe(III), Zr(IV), from nitric acid solutions. And, in the late 1980s DHDECMP-based flowsheets were still under consideration for removal of all actinides from the DOE Idaho site sodium-bearing waste. Most of the work with CMP-based reagents after the early Schulz and McIsaac studies were done with DHDECMP; some investigators, however, synthesized various other CMP-type compounds to investigate their capability for extracting 3+ as well as 4+ and 6+ actinides from various acid waste solutions.

As discussed in the next section, CMP processes for efficient extraction of Am(III) and other actinides from acidic media have been supplanted and superseded by advanced organophosphorus reagent technology. Even so, the significance of the pioneering work of Schulz and McIsaac cannot be overstated. Through their efforts, scientists and engineers throughout the world became aware of Siddall's papers and the great potential of multifunctional organophosphorus reagents in actinide separation and recovery from many other sources.

Carbamoylphosphine oxide reagents

"CMPO" is a generic acronym for any carbamoylmethylenephosphine oxide. CMPO is also used here and elsewhere in the literature to denote one particular compound, namely, octylphenyl-*N*,*N*-diisobutylmethylenecarbamoylphosphine oxide, $(C_8H_{17})(C_6H_5)P(O)–CH_2–(O)C–N –N–(iC_4H_9)_2$. The actinide separation community is indebted to Dr E. P. Horwitz and his colleagues for their innovative efforts in initially synthesizing this particular CMPO and in evaluating many of its outstanding properties.

Being familiar with the Schulz and McIsaac results with DHDECMP (Section 8.4.3a(vi)), and having worked with this carbamoylphosphonate, Horwitz was motivated to find an improved trivalent actinide extractant with the following highly desirable attributes:

- Greatly increased capability for extracting 3+ actinides.
- Ease of synthesis of high-purity reagent.
- Increased solubility/compatibility with straight-chain hydrocarbon diluents.
- Excellent chemical and radiolytic stability.
- Suitability of extractant-diluent(s) solution for use in centrifugal contactors.
- Satisfactory selectivity for actinide and lanthanide extraction from aqueous media.

Horwitz's aspirations were essentially realized with the synthesis of the octylphenyl CMPO compound and the many successful tests of this reagent.

Gatrone and coworkers (Gatrone and Rickert, 1987; Gatrone *et al.*, 1987, 1989) published complete details of the synthesis of CMPO via a Grignard reaction. The crude CMPO product from the Grignard synthesis contains one or more acidic organophosphorus impurities that seriously interfere with the use of dilute nitric acid solutions to strip trivalent actinides and lanthanides. After testing various purification schemes, Gatrone and coworkers concluded that the most effective way to remove the offending acidic compounds was to first contact a heptane solution of the CMPO with 50 g L^{-1} of a macroporous cation-exchange resin at 50°C and then, without removing the cation resin, contact the heptane–CMPO solution with 50 g L^{-1} of a macroporous anion-exchange resin. This procedure, which Gatrone and his collaborators believe is generic and applicable to removal of acidic compounds from anyneutral organophosphorus extractant, yields solvent extraction-grade CMPO, i.e. $D_{\mathrm{Am}} = <0.02$ in 0.01 M HNO_3/CMPO.

Many different diluents have been used in bench-scale studies of the extraction properties of solvent extraction-grade CMPO. Candidate diluents used at one time or another include aromatic (decalin), chlorinated (tetrachloroethylene), and aliphatic (dodecane) commercially available mixtures of C_{10}–C_{12} NPHs. For plant-scale application of CMPO a mixture of NPHs is the preferred diluent. However, HNO_3 and metal nitrates, e.g. lanthanide nitrates, have only a very limited solubility in CMPO/NPH solutions; once the solubility limit is exceeded, the organic phase splits into two phases (familiar third-phase formation phenomenon). Horwitz *et al.* (1985b) found that a simple and highly effective way to avoid the complications of a third-phase formation is to dilute the CMPO extractant with Purex process solvent to yield, for example, a 0.2 M CMPO/1.2 M TBP/dodecane solution. This solvent composition allows the CMPO fraction to be loaded to near theoretical capacity with trivalent lanthanides without causing a second organic phase to form. And, of course, an added advantage of the latter solvent composition is that its physical properties are little changed from those of familiar Purex process solvent and, therefore, no mechanical difficulties are encountered in operating centrifugal (or other) contactors with the CMPO/TBP/dodecane (or NPH) solvent. Horwitz and coworkers (Kalina *et al.*, 1981a; Horwitz *et al.*, 1982, 1985b, 1986; Horwitz and Kalina, 1984; Kolarik and Horwitz, 1988), as well as many other investigators (Liansheng *et al.*, 1991; Mathur *et al.*, 1992a; Rapko, 1995), conducted comprehensive bench-scale studies to establish the extractive properties of CMPO/TBP/diluent solvents for many different metal ions over a wide range of conditions. Most of these studies were concerned with the extraction of actinides and other metal ions from nitrate-based aqueous media with CMPO/TBP/dodecane (or NPH) solvent, but some work has been done with aqueous HCl solutions (Horwitz *et al.*, 1987). All these bench-scale studies confirmed that the CMPO/TBP/diluent mixture would efficiently extract trivalent actinides and lanthanides as well as 4+ and 6+ actinides from almost any strong, i.e. ca. 1 M, nitric acid solution. Indeed, the more or less constant distribution ratio values for Am(III), Pu(IV), and U(VI) between 1 and 6 M HNO_3 is a very valuable and unique aspect of the CMPO/TBP system.

While the lanthanides and actinides are extracted almost quantitatively by CMPO/TBP/diluent solutions, with only a few exceptions most common metal ions in nuclear waste solutions are not extracted by the CMPO reagent (Horwitz *et al.*, 1985b). Not unexpectedly, Zr(IV) is significantly extracted ($D_{Zr} = \sim 1$–3) by CMPO/TBP/diluent solution from aqueous 1 M HNO_3. Zirconium is one of the major constituents of the DOE Idaho site waste; this particular waste also contains large concentrations of fluoride ion, which, fortunately, greatly inhibits CMPO extraction of inert zirconium (McIsaac and Baker, 1983). Paralleling known Purex process experience, ^{99}Tc, if present, is also well extracted ($D_{Tc} =$ 1–3) from nitric acid feed solutions as the $HTcO_4$ species. (Technetium largely remains in the CMPO phase during actinide scrubbing and stripping stages and is removed when the CMPO phase is washed with alkaline carbonate solutions to remove degradation and other species.) Other metallic contaminants of some interest ($D_M = 0.1$–0.6) include Mo, Ru, Pd, Ag, and Fe; these constituents are present in nearly all nuclear waste solutions that contain Am and other actinides. Adequate separation of actinides from the latter metal ions in CMPO extraction systems can be controlled by adding oxalic acid to the feed solution and/or by scrubbing the CMPO extract with a dilute oxalic solution before stripping of actinides.

To strip actinides from the CMPO/diluent or, more commonly, CMPO/TBP/NPH phase, conventional practice is to selectively strip, in order, 3+ actinides and lanthanides, 4+, and, if present, 6+ actinides. For this order of actinide stripping, preferred reagents (Mathur *et al.*, 2001) are, respectively, dilute nitric acid, e.g. <0.05 M HNO_3; a dilute oxalic acid, dilute ammonium oxalate, or a mixture of HF and HNO_3, e.g. 0.05 M HNO_3/0.05 M HF; and dilute sodium carbonate, e.g. 0.25 M Na_2CO_3. Sodium carbonate solutions do double duty and also act as a solvent cleanup reagent to remove solvent degradation products. But, in the case where it is desired to strip all the 3+, 4+, and 6+ actinides and lanthanides into a single aqueous phase, Horwitz and Schulz (1990) recommended use of a solution of either vinylidene-1,1-diphosphonic acid (VDPA) or 1-hydroxyethylene-1,1-diphosphonic acid (HEDPA). Also, in a novel approach, Rizvi and Mathur (1997) utilized the ferrocyanide ion to co-strip actinides and lanthanides from CMPO phases. Other stripping agent studies of interest are those of Chitnis *et al.* (1998, 1999) who used a mixture of formic acid, hydrazine hydrate, and citric acid to remove Am(III) and Pu(IV) from CMPO solutions. Finally, Ozawa *et al.* (1998) reported that a mixture of hydrazine oxalate, hydrazine carbonate, and tetramethylammonium hydroxide will selectively strip 3+, 4+, and 6+ actinides from CMPO extractants.

A matter of concern for any liquid–liquid extraction process, especially one dealing with radionuclides, is the resistance of the extractant and its diluents to chemical and radiolytic degradation. Five separate studies (Chiarizia and Horwitz, 1986, 1990; Nash *et al.*, 1988, 1989; Mathur *et al.*, 1998) addressed this concern for CMPO extraction systems. Three of these investigations were concerned only with CMPO/TBP/dodecane solvents while two (Chiarizia and Horwitz, 1986; Nash *et al.*, 1988) also addressed radiolysis of CMPO diluted with decalin or tetrachloroethylene. Test solvents were irradiated both neat and while in contact with aqueous nitric acid solutions. Although results varied to some degree with the reagent used to dilute the CMPO and TBP, the general degradation behavior of CMPO/TBP/diluent solvent was independent of the nature of the diluent. Thus, the general degradation behavior is that chemical hydrolysis produces only acidic degradation products while radiolysis generates both neutral and acidic organophosphorus compounds.

The neutral organophosphorus degradation products of CMPO serve only as diluents for CMPO and TBP. But the acidic radiolytic degradation products are highly troublesome because they seriously interfere with stripping of Am(III) by dilute (<0.05 M HNO_3) solutions. Mathur *et al.* (2001) have published an excellent table, based on data obtained by Mathur *et al.* (1998) that illustrates very markedly the increase in the distribution ratio for Am(III) at 0.04 M nitric acid upon irradiation of a 0.2 M CMPO/1.2 M TBP/dodecane solvent to a total absorbed dose of 26–28 Mrad. According to these data, up to a dose of about 20 Mrad the distribution ratio of Am(III) at 0.04 M nitric acid is less than 1 and, hence, stripping with 0.04 M nitric acid should still be possible. Also, up to a dose of about 20 Mrad washing the spent solvent with a dilute sodium carbonate solution will remove most of the acidic degradation products. But, at higher absorbed radiation doses, in addition to sodium carbonate washing, it is necessary to provide a secondary solvent cleanup step, i.e. treatment with macroporous anion and cation-exchange resins or treatment with basic alumina.

In 1985, Horwitz and his collaborators (Horwitz and Schulz, 1985, 1986, 1990, 1999; Horwitz *et al.*, 1985a,b; Schulz and Horwitz, 1988) proposed a generic actinide solvent extraction process, the TRUEX process (Table 8.2) based on the superior properties of CMPO to remove all 3+, 4+, and 6+ actinides from any nitrate-based aqueous nuclear waste solution. The generic

Table 8.2 *Applications of the TRUEX process.*

Year	*Country*	*References*	*TRUEX process application/demonstration*
1985	USA	[1]	Removal of Am and Pu from Hanford complexant concentrate waste
1985	USA	[1]	Removal of Am and other actinides from Hanford single-shell tank sludges
1985–1991	USA	[2]	Removal of Am and other actinides from Hanford neutralized cladding removal waste
1988	USA	[3]	Removal Am and Pu from Hanford plutonium finishing plant waste
1988–1989	Italy	[4]	Removal of actinides from MOX fuel fabrication waste and waste from analytical laboratories
1992–1998	Japan	[5]	Removal of actinides from actual Purex process high-level waste
1993–1998	India	[6]	Removal of actinides (Am, Cm, Pu, Np, U) from synthetic pressurized water reactor reprocessing Purex process waste
1993–1998	India	[6]	Removal of actinides (Am, Cm, Pu, Np, U) from synthetic Purex process sulfate-bearing high-level waste (SBHLW)
1994–2000	India	[7]	Recovery of Pu and U from oxalate precipitation process waste
1997	USA	[8]	Removal of actinides from actual Argonne National Laboratory analytical wastes
1998	USA	[9]	Removal of actinides from Idaho site actual sodium-bearing waste
1998	USA	[10]	Removal of actinides from actual dissolved Idaho site calcine waste

[1] (Horwitz *et al.*, 1985b); [2] (Swanson, 1991; Lumetta and Swanson, 1993a,b); [3] (Schulz and Horwitz, 1988); [4] (Casarci *et al.*, 1988, 1989); [5] (Ozawa *et al.*, 1992, 1998); [6] (Deshingkar *et al.*, 1993, 1994; Chitnis *et al.*, 1998); [7] (Mathur *et al.*, 1994; Michael *et al.*, 2000); [8] (Chamberlain *et al.*, 1997); [9] (Law *et al.*, 1998a); [10] (Law *et al.*, 1998b).

TRUEX process, which utilizes a nominal 0.2 M CMPO/1.05 M TBP/dodecane (or other NPH-type diluent) solvent, is intended for use in short residence time centrifugal contactors. It typically comprises four separate operations: extraction, scrubbing of the organic phase, one or more stripping steps, and solvent cleanup. The users of the TRUEX process are free to specify whatever the number of extraction stages and organic-to-aqueous phase flow ratios are required to provide the required degree of removal of Am(III) and other actinides. Similarly, the TRUEX process operator is responsible for choosing the number of scrub stages (if any) and the composition of scrub solution(s) needed to adequately remove any co-extracted impurities, e.g. Zr(IV). The generic TRUEX process allows, by choosing particular aqueous phase strip compositions, either selective stripping of 3+, 4+, and 6+ actinides or stripping of combinations of actinides, e.g. 3+ and 4+ or 4+ and 6+. One or two contactor stages for washing the stripped TRUEX process solvent with a dilute sodium carbonate solution are typically included to remove solvent degradation products and any traces of metal ions. Investigators in several countries have conducted continuous countercurrent demonstrations of variations of the TRUEX process with actual radioactive waste solutions of interest to them: references cited in the following list should be consulted for further details:

For various reasons, including the prolonged Cold War syndrome, Russian scientists, largely independent of Western world progress, conducted extensive studies of the actinide extraction properties of multifunctional organophosphorus reagents (Myasoedov *et al.*, 1980, 1986; Chmutova *et al.*, 1983, 1989; Myasoedov and Lebedev, 1991). A recent review paper by Myasoedov (1994) is of special interest. The Russian version of the American TRUEX process utilizes diphenyl-*N*,*N*-dibutylcarbamoylmethylenephosphine oxide dissolved in a commercially available (at least in Russia) fluoroether diluent (Fluoropol 732). According to Russian investigators, use of the fluoroether diluent eliminates any need to dilute the diphenyl CMPO with TBP to avoid third-phase formation; but others (Horwitz and Schulz, 1999) have expressed concern that diluent degradation under plant-scale conditions could lead to undue formation of corrosive HF. The Russian transuranium element extraction process behaves very similarly (Myasoedov, 1994) to the TRUEX process in its efficiency for extracting trivalent americium; in continuous countercurrent tests of the process in centrifugal extractors greater than 99.5% of the actinide elements in the aqueous feed were removed. In addition to the possibility of excessive generation of HF, other possible limitations to the Russian process include difficult americium stripping because of the need to use a very low concentration of nitric acid in the aqueous strip solution and complex solvent cleanup before reuse of the solvent (Horwitz and Schulz, 1999). In addition to the americium extraction results discussed earlier in Section 8.4.3a, certain other, more academically oriented studies of the extraction characteristics of novel phosphate-based reagents are of interest. For example, Paine and his research group (Bond *et al.*, 1997, 1998) investigated the extraction of Am(III) by 1,6-bis(diphenylphosphino)methyl-pyridine-*N*,*P*,*P*′-trioxide solutions from both hydrochloric and nitric acid media. And, Mishra *et al.* (1996) investigated the synergistic extraction of Am(III) by a mixture of Aliquat 336 and TOPO from acidic nitrate medium.

Rais and Tachimori (1994) studied the synergism in extraction and separation of Am(III) and Eu(III) in two systems: (1) dicarbollide anion and dibutyldiethylcarbamoylmethylenephosphonate (DBDECMP) and (2) dicarbollide anion and CMPO. Synergism was observed in both systems at low aqueous phase acidities but the effect was lower with CMPO than with DBDECMP.

Mohapatra and Manchanda (1995, 1999) reported on the unusual extraction behavior of Am(III) and UO_2^{2+} from aqueous picric acid solutions by TBP and TOPO extractants. Surprisingly, under these conditions, the organophosphorus compounds extract Am(III) better than the uranyl ion. Of course, from aqueous nitrate media, TBP and TOPO both extract U(VI) much better than Am(III). Mohapatra and Manchanda attribute the different extraction order from picric acid media to the formation of outer sphere rather than inner-sphere coordination complexes.

(b) Amine extractants

Nitrogen-based extractants, especially tertiary amines and quaternary ammonium compounds, are particularly effective in separating and recovering americium and other actinide elements from aqueous media.

(*i*) *Tertiary amine salts*

Tertiary amine salts extract Am^{3+} poorly from concentrated nitric or hydrochloric acids but extract it very strongly from concentrated nitrate or chloride solutions of low acidity (Myasoedov *et al.*, 1974a). Marcus *et al.* (1963) and Horwitz *et al.* (1966) found that Am^{3+} is extracted from nitrate media as complex $(R_3NH)_2Am(NO_3)_5$. A much more detailed account of the application of tertiary amine salts to extract americium is provided in Schulz (1976); indeed, essentially all the reported results obtained with tertiary amine salts in extraction of americium have been summarized in Schulz (1976).

(*ii*) *Quaternary ammonium salts*

Quaternary alkylammonium nitrate salts were shown by Horwitz *et al.* (1966) to extract Am^{3+} considerably more efficiently from low-acid, highly salted aqueous nitrate solutions than do tertiary alkylamines. The extraction sequence for trivalent actinides into either Aliquat 336 (a mixture of trioctylmethylammonium and tridecylmethylammonium salts made by General Mills, Inc.) nitrate or trilaurylmethylammonium nitrate is $Cm<Cf<Am<Es$. Horwitz *et al.* (1969) included an extraction step with Aliquat 336 in the preparation of 20–30 Ci of high-purity ^{242}Cm. Koch and Schoen (Koch and Schoen, 1968; Koch, 1969) devised and tested on a laboratory scale a quaternary ammonium extraction process for the isolation of ^{241}Am from aged plutonium scrap. Advantages of a quaternary ammonium nitrate extraction process over other schemes, e.g. Tramex process, for isolating trivalent lanthanides and actinides were discussed by Moore (1966a). Finally, Moore (1964, 1966b) and later Gerontopulos *et al.* (1965) found that the thiocyanate salt of Aliquat 336 preferentially extracts actinides over lanthanides in moderately concentrated NH_4SCN solutions.

(c) Amide extraction reagents

Diamide extractants are generally organic compounds with the generic formula $(R_1,R_2)N–C(O)–CR_3H–C(O)–N(R_1,R_2)$ where R_1, R_2, and R_3 are (typically) alkyl substituents. For various reasons, including doubtlessly their well-recognized nationalistic pride, French investigators have chosen to focus on diamides for possible application in partitioning of americium and other actinides from aqueous Purex process HLW vis-à-vis one of the more well-known and tested carbamoylphosphonates or phosphine oxides. Interestingly, various researchers including the French repeatedly extol the virtues of the carbon, hydrogen, oxygen, nitrogen (CHON) principle, i.e. design and use of liquid–liquid extraction reagents that contain neither sulfur nor phosphorus. Supposedly, degraded CHON-type extractants would be easier to dispose of, e.g. incinerate, than spent extractants that contain phosphorus or sulfur; there are no economic or technical data and/or experience to support the latter claim.

Between 1987 and 2002, numerous diamide compounds have been synthesized and examined for their ability to extract actinides in various oxidation states from aqueous nitric acid solutions. Details and results of these studies were reported (Musikas and Hubert, 1983; Musikas, 1987, 1995; Charbonnel and Musikas, 1988; Cuillerdier *et al.*, 1991a,b, 1993; Musikas *et al.*, 1991; Baudin *et al.*, 1993; Madic *et al.*, 1994; Nigond *et al.*, 1994; Shen *et al.*, 1996; Tan *et al.*, 1999).

Currently, one diamide, namely, *N*,*N*′-dimethyl-*N*,*N*′-dibutyl-2-tetradecylmalonamide (DMDBTDMA) appears particularly suitable for use in plant-scale removal of actinides from Purex process HLW. In France DMDBTDMA has been chosen as the extractant in their DIAMEX process for partitioning of actinides from Purex process HLW. Experiments show that DMDBTDMA is soluble in dodecane and does not produce a third phase when dodecane solutions are contacted with 3–4 M HNO_3. Indian scientists (Mahajan *et al.*, 1998) have also studied DMDBTDMA extraction of Am(III), U(VI), Np(IV), Fe(III), Sr(II), and Cs(I) from various nitric acid solutions and also from a simulated HLW, which would result from reprocessing of commercial pressurized water reactor fuel. These latter experiments confirm that DMDBTDMA is very promising for extraction of Am(III) and other actinides from 3 to 4 M HNO_3, particularly under high solvent loadings of neodymium or neodymium plus uranium.

Even after two decades, diamide extraction of actinides from nitric acid media is a continuing fertile research area. For example, Spjuth *et al.* (2000) have recently prepared seven new malonamide extractants by placing phenyl substituents on the nitrogen atoms in the malonamide or an ether oxygen into the bridging chain. The basicity of such compounds is reported to be less than that of DMDBTDMA, which makes them slightly better extractants for Am(III).

Sasaki and Tachimori (2002) have recently synthesized diamide extractants that they term 'structurally tailored diamides.' The diamides investigated include $(CH_2)_n$–$(CONR_1R_2)_2$ ($n = 0, 1, 2,$ and 3); O–$((CH_2)_{n'}$–$CONR_1R_2)_2$; S–$((CH_2)_{n''}$–$CONR_1R_2)_2$; and SS–$((CH_2)_{n'''}$–$CONR_1R_2)_2$, (n', n'', $n''' = 1, 2$). The diglycolamide introducing an ether oxygen into the main structure, O–$(CH_2$–$CONR_1R_2)_2$, exhibits the highest extractability for An(III), An(IV), and An(VI) compared with the other bidentate diamides. The results of Sasaki and Tachimori also demonstrated that the thiaglycolamide, which substitutes an ether sulfur atom or oxygen in the molecule also enhances the extraction of actinides.

(d) Separation of americium from lanthanides

The challenge of separating Am(III) from trivalent lanthanides was first addressed and resolved by Weaver and Kappelmann (1964) as early as 1964. These investigators devised the Talspeak process that is based upon the fact that HDEHP solutions extract trivalent lanthanides much more strongly than trivalent actinides from aqueous carboxylic acid solutions containing an aminopolycarboxylic acid chelating agent.

A reverse Talspeak process involves, naturally, using an aqueous solution of an aminopolycarboxylic acid (e.g. DTPA) to preferentially strip Am(III) (and Cm(III) also if present) from an organic phase containing both trivalent actinides and lanthanides. In the DIDPA extraction process (Section 8.4.3a(v)) an aqueous lactic acid solution containing DTPA is used to strip trivalent americium and curium (Persson *et al.*, 1984); lanthanides remaining in the DIDPA phase are subsequently stripped with 4 M HNO_3.

In yet another application of the Talspeak process technology, the Japanese SETFICS (Solvent Extraction for Trivalent f elements Intragroup separation in CMPO-complexant System), a typical TRUEX process extraction stage, utilizes an aqueous 0.4 M $NaNO_3$ solution containing DTPA (Koma *et al.*, 1998). In a countercurrent test of the SETFICS process with radioactive feed, the reported $^{144}Ce/^{241}Am$ decontamination factor was 72.

The renewed focus on partitioning–transmutation technology that began in the 1980s (and continues unabated to this day) prompted many new studies of technology for separation of trivalent actinides from trivalent lanthanides. (See the review of the subject of lanthanide/actinide separations (Nash, 1994).) The breakthrough to more efficient lanthanide/actinide separation technology originated with Musikas in France who pointed out that soft-donor extractant molecules containing nitrogen or sulfur functionalities offered great potential to achieve the desired separation (Musikas *et al.*, 1980b; Musikas, 1984). In work published in the late 1970s and mid-1980s, Musikas reported that an extractant consisting of tripyridyltriazene (TPTZ) and dinonylnapthalene sulfonic acid (HDNNS) in carbon tetrachloride preferentially extracted Am(III) from a dilute nitric acid solution containing Am(III) and trivalent lanthanides. In 1985, Musikas in his paper noted that the HDNNS could be replaced by bromocapric acid in an aliphatic hydrocarbon diluent.

Musikas' seminal work in the mid-1980s has triggered a cascade of studies of the ability of other nitrogen (and also sulfur)-containing extractants to provide separation of trivalent actinides from trivalent lanthanides. Noteworthy examples of such research efforts, not in chronological order, include work by Ensor and coworkers (Ensor *et al.*, 1988; Smith *et al.*, 1989), who used the synergistic combination of 4-benzoyl-2,3-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-thione and 4,7-diphenyl-1,10-phenanthroline as an extractant to separate trivalent americium and europium, in the USA; Ensor *et al.* reported Am/Eu separation factors of greater than 10 with this synergistic combination of reagents. In Germany, Kolarik *et al.* (1999) investigated an extraction system based on polyaza ligands, e.g. 2,6-di-(5,6-dipropyl-1,2,4-triazin-3-yl) pyridenes for selective extraction of trivalent actinides from 1.9 M NH_4NO_3/HNO_3 solutions. Kolarik *et al.* reported Am/Eu separation factors in the range 100–120. And, of course Madic and Hudson (1998) as late as 1998 were still investigating TPTZ extraction systems for separating trivalent actinides from associated lanthanides in France. Madic's latest efforts center around attempts to suppress the solubility of TPTZ in aqueous phases by placing alkyl substituents at the 2-pyridyl rings and in replacing bromocapric acid by other anion sources.

An effective nitrogen-based soft-donor extractant for separation of trivalent actinides and lanthanides clearly would adhere to the CHON principle. But, unfortunately, to date at least, research efforts from 1987 to 2002 do not appear to have yielded a nitrogen-based 3+ actinide extractant suitably effective and stable for use on a plant scale with radioactive aqueous nitrate media. Conversely, because of recent breakthrough research results obtained by Zhu and his coworkers, prospects for developing a sulfur-based soft-donor extractant (non-CHON-type) suitable for plant-scale application appear to be reasonably good. In 1996, Zhu and coworkers reported that the compound bis(2,3,4-trimethylpentyl)-dithiophosphinic acid dissolved in a suitable diluent, e.g. heptane, preferentially extracted Am(III) from Eu(III) in aqueous nitrate media (Zhu, 1995; Zhu *et al.*, 1996b, 1998); Zhu and his collaborators found a separation factor as high as 5900 in favor of Am(III). Of particular interest and advantage, bis(2,3,4-trimethylpentyl)-dithiophosphinic acid is marketed commercially by Cyanamide Canada, Inc. under the trade name Cyanex 301; Cyanex 301 contains 77.2% of the dithiophosphinic acid compound. The primary impurities in Cyanex 301 are 14.6% R_3PS, 3.5% R_2POOH, and 0.8% R_2PSOH (Zhu *et al.*, 1996b). Chen *et al.* (1996) developed a scheme for upgrading commercially supplied Cyanex 301 to >99% bis(2,3,4-trimethylpentyl)-dithiophosphinic acid.

The excellent results obtained by Zhu and his coworkers with as-received Cyanex 301 were quickly confirmed in work at Florida State University by Zhu *et al.* (1996a). Data in Fig. 8.2 clearly illustrate the propensity of Cyanex 301 solutions to provide clean separation of Am(III) from trivalent lanthanides in

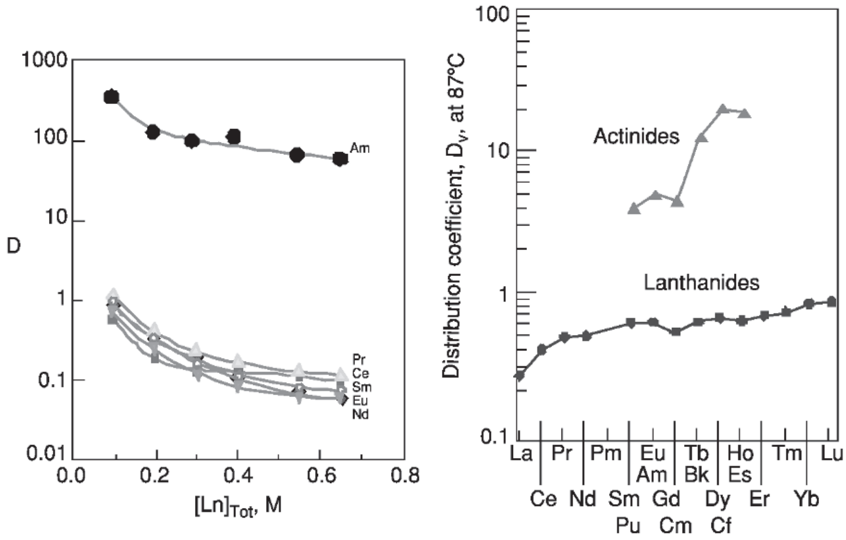


Fig. 8.2 *Distribution ratios of Am*(*III*) *and Ln*(*III*) *in* 1.0 M *Cyanex* 301-*heptane* (16 mol% *of Cyanex* 301 *neutralized before extraction contacts*) (*left*) (*Zhu* et al., 1996a). *Distribution coefficients of actinides and lanthanides into Dowex* 1 × 8 *resin from* 10 M *LiCl* (*right*) (*Hulet* et al., 1961).

pH 3 aqueous media. In later work, Modolo and Odoj (1998) also confirmed the initial results of Zhu and his collaborators with Cyanex 301. One very successful continuous countercurrent test of a Cyanex 301-based trivalent actinide/lanthanide separation flowsheet was made; using three extraction and two scrub stages >99.9% of Am(III) was separated from a trace amount of Eu with <0.1% extraction of Eu (Modolo and Odoj, 1998).

An immediate and continuing concern about plant-scale use of Cyanex 301 (or for that matter, any sulfur-based extractant) in a rather hostile environment, e.g. high nitrate concentration–high radiation zone, is its chemical and radiolytic stability. With respect to chemical stability, Sole *et al.* (1993) found that Cyanex 301 exhibits satisfactory resistance to chemical degradation when in contact with aqueous sulfuric acid, hydrochloric acid, and nitric acid solutions provided that the nitric acid concentration is maintained at (or less) than 2 M. With respect to radiolytic stability, one study found that irradiation of Cyanex 301 produces dialkylmonothiophosphonic acid, dialkylphosphinic acid, and other phosphorus compounds (Chen *et al.*, 1996). Purified Cyanex 301 separates tracer amounts of Am(III) from tracer amounts of Eu(III) even after irradiation to a cumulative dose of 10^5 gray; commercially available Cyanex 301 only performs satisfactorily at radiation doses up to 10^4 gray. The practical plant-scale consequences of the relatively poor resistance of Cyanex 301, even purified, to radiolysis would be reflected in the need to conduct countercurrent extraction operations in short residence time equipment, e.g. centrifugal contactors, and, likely, frequent extractant inventory change-outs.

In addition to its relatively poor resistance to radiolytic degradation, Modolo and Odoj (1999) note another serious disadvantage to the use of Cyanex 301 to separate trivalent lanthanides and actinides, namely, the need to conduct extraction operations at an aqueous feed pH of 3 or higher. This latter need derives directly from the mechanism whereby Cyanex 301 humic acid (HA) extracts Am(III) and Eu(III):

$$\mathrm{M}^{3+}_{\mathrm{aq}} + 2(\mathrm{HA})_{2\ \mathrm{org}} \rightarrow \mathrm{MA}_3(\mathrm{HA})_{\mathrm{org}} + 3\mathrm{H}^{+}_{\mathrm{aq}} \text{ where } \mathrm{M} = \mathrm{Am, Eu}$$

Three protons are released during the extraction operation; thus, Cyanex 301 only becomes an effective extractant at aqueous phase pH of 3 or more.

Modolo and Odoj (1999) recently synthesized and tested a new class of aromatic dithiophosphinic acids as separating agents for trivalent actinides and lanthanides. These compounds are conveniently represented as R_2PSSH with $R = C_6H_5$, ClC_6H_4, FC_6H_4, and $CH_3C_6H_4$. Modolo and Odoj achieved high separation factors (>20) with $D_{\mathrm{Am}} > 1$ in the range 0.1–1.0 M HNO_3 by means of synergistic mixtures of $(C_6H_4Cl)_2PSSH$ with either TBP, TOPO, or tributylphosphine oxide. (Interestingly, none of the R_2PSSH compounds by itself has any capacity to extract trivalent actinides.) Not only do the aromatic dithiophosphinic acids achieve satisfactory separation of trivalent actinides from trivalent lanthanides from low pH (0.1–1.0 M HNO_3) aqueous solutions but they are also reported to be considerably more resistant to radiation degradation than is Cyanex 301. Thus, Modolo and Odoj demonstrated that the selectivity and capacity of all the R_2PSSH–synergist combinations remained intact even at an absorbed dose as high as 10^6 gray. The capability of aromatic compounds to act as radiation 'sinks' is, of course, well known. Finally, it should be noted that none of the R_2PSSH compounds synthesized and studied by Modolo and Odoj are commercially available in large amounts.

Hence, when and if any country commits to plant-scale execution of a partitioning–transmutation approach to nuclear waste management and disposal, it seems quite likely that past and ongoing research and development efforts by many investigators will have culminated in a new solvent extraction process for separation of Am(III) and Cm(III) from lanthanides that operates satisfactorily under plant-scale conditions. The usable fallback technology, even though it may be considered cumbersome, is the Talspeak process.

8.4.4 Ion-exchange processes

The combination of chromatographic elution techniques with cation-exchange resins provides a powerful and sophisticated tool to purify 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 (1974) points out that displacement-development chromatography is capable of separating macroquantities only, whereas, unless very large columns are used, elution-development chromatography is applicable only to the separation of tracer amounts. Jenkins and Wain (1972) listed publications covering the use of ion exchange to recover and purify ^{241}Am and ^{243}Am.

(a) Cation-exchange resin systems

Cation-exchange resins sorb Am^{3+} very strongly from dilute nitric acid solutions. An important application is to concentrate Am^{3+} and other trivalent and tetravalent ions from dilute acid solutions to separate them, at least partially, from many impurities (Hale and Lowe, 1969; Gmelin, 1979). Before production operations ceased at the US DOE Rocky Flats site, a cation–anion exchange process had replaced the hydroxide precipitation and thiocyanate ion-exchange system formerly used for recovering ^{241}Am from solutions of spent NaCl–KCl–$MgCl_2$ salt residues generated at the site (Proctor, 1975).

(*i*) *Distribution coefficients: separation factors*

Data for the distribution of Am^{3+} between cation-exchange resins and many aqueous solutions were analyzed in a comprehensive review by Ryan (1974). Solutions of α-hydroxycarboxylic acid and aminopolycarboxylic acids are commonly used to elute americium from cation-exchange resins. When these reagents are used in a displacement elution system, they provide excellent separation of americium from trivalent lanthanides and other trivalent actinides. For example, the separation factor for americium from curium ranges from 1.2 to 1.4 for α-hydroxycarboxylic acids and from 1.2 to 2 for aminopolycarboxylic acids (Schulz, 1976).

(*ii*) *Chromatographic elution schemes*

Although citric acid has found use, both lactic and α-hydroxyisobutyric acids provide better separation of americium from curium. Using chromatographic elution from Dowex 50-X12 resin with α-hydroxyisobutyric acid, Campbell (1970) demonstrated the effective use of high-pressure ion-exchange methods for the rapid separation of americium from curium. Highly efficient displacement chromatographic separation schemes that use nitrilotriacetic acid (NTA) and/or DTPA as eluents have been applied at the US DOE Hanford and at Savannah River sites to purify kilogram amounts of americium from curium and lanthanides (Wheelwright *et al.*, 1968; Harbour *et al.*, 1972). Wheelwright *et al.* (1968) successfully used a two-cycle cation-exchange process to separate and purify 1 kg of ^{241}Am and ^{243}Am, about 60 g of ^{244}Cm, and 140 g of ^{147}Pm extracted from 13.5 tons of blanket fuel elements from the Shippingport nuclear reactor. 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 resins beds with a 0.105 M NTA solution buffered to pH 6.5 with NH_4OH. Harbour *et al.* (1972) adapted the displacement elution scheme to pressurized columns at the Savannah River site.

Nearly 20 years after Wheelwright's work, Chuveleva and some of his colleagues at the Institute of Physical Chemistry in Moscow revisited, as recently as 1999, displacement chromatography for separation of traces of americium and curium (Chuveleva *et al.*, 1999) (interestingly, in these papers Chuveleva *et al.* did not make any reference to Wheelwright's earlier work). The basic system used by the Russian scientists in 1999 utilized their KU-2 cation-exchange resin previously converted to the Ni- (or Zn) form; a NTA solution for elution, and Cd^{2+} as the separating ion. Performance of the Russian system was quite satisfactory; indeed, their results appeared to be in full accord with expectations from Wheelwright's earlier studies.

(b) Anion-exchange resin systems

For routine, large-scale purification of americium, application of anion-exchange resins is limited to sorption from thiocyanate, chloride, and, to a limited extent, nitrate solutions (Hermann, 1956).

(*i*) *Thiocyanate solutions*

Am(III) forms relatively strong complexes, e.g. $AmSCN^{2+}$, $Am(SCN)_2^+$, and $Am(SCN)_3$ in concentrated aqueous thiocyanate solutions, and its thiocyanate species are sorbed on anion-exchange resins considerably more strongly than are the corresponding lanthanide thiocyanate complexes (Coleman *et al.*, 1955, 1957; Surls and Choppin, 1957). Thiocyanate anion-exchange systems have been used to purify americium from rare earths. For example, a plant-scale thiocyanate ion-exchange process has long been used (1960–75) at the US DOE Rocky Flats plant for routine purification of ^{241}Am recovered from aged plutonium metal (Schulz, 1976).

(*ii*) *Chloride solutions*

Am(III) is sorbed much more strongly onto anion-exchange resins from concentrated lithium chloride solutions than are the lanthanides (Hulet *et al.*, 1961). Americium distribution ratios increase with increased lithium chloride concentration whereas increased temperature enhances the separation of americium from rare earths. A lithium chloride-based anion-exchange process for separating milligram amounts of americium and curium from lanthanide fission products and to isolate an Am–Cm fraction free of heavier actinides was routinely operated at the US DOE Oak Ridge facility (Baybarz, 1970).

(c) Inorganic exchangers

Most studies concerned with sorption of Am^{3+} from aqueous solutions have used zirconium phosphate. The order of the distribution coefficients of trivalent actinides and lanthanides on zirconium phosphate is the reverse of the order observed with a typical strong-base cation-exchange resin (Horwitz, 1966). Both American (Moore, 1973) and Russian (Shafiev *et al.*, 1971) scientists utilized the fact that the singly charged AmO_2^+ is not sorbed by zirconium phosphate from dilute acid media to separate americium from curium and other metal ions.

Inorganic exchangers formed by hydrolysis of the alkoxides of titanium, niobium, or zirconium were developed for actinide/lanthanide separation (Lynch *et al.*, 1975) and possible disposal. Schulz *et al.* (1980) investigated the use of sodium titanate [$Na(Ti_2O_5H)$] and bone char (a form of calcium hydroxyapatite) to decontaminate alkaline nuclear waste streams containing minor amounts of americium and other actinides and to separate trivalent curium from trivalent americium.

More recently, as part of the overall Japanese partitioning–transmutation program, Yamagishi *et al.* (1996) reported results of experiments to use the inorganic cation exchanger titanium antimonate ‘TiSb’ to separate Am(III) from trivalent lanthanides. Before Yamagishi *et al.*’s work the TiSb exchanger had been reported (Kaneko *et al.*, 1992, 1993) to have a high selectivity for Pu^{4+} and trivalent americium and a low selectivity for trivalent lanthanides from concentrated HNO_3 solutions. Yamagishi *et al.* prepared TiSb according to conditions reported by Abe and coworkers (Abe and Tsujii, 1983; Abe *et al.*, 1985) and found that the TiSb exchanger exhibited superior selectivity toward trivalent americium over trivalent europium and other rare earths. The Japanese investigators concluded that TiSb is a promising material particularly for preconcentration of Am^{3+} from HNO_3 solutions containing Am^{3+} and large amounts of La^{3+} without the need for complexing or oxidizing agents.

Ritter (Ebner *et al.*, 1999) and his coworkers synthesized a new magnetic adsorbent material that combines the properties of both organic resin and inorganic material for use in actinide removal from nuclear waste solutions. This new material is called magnetic polyamine–epichlorohydrin (MPE) resin. MPE resin consists of spherical beads of polyamine–epichlorohydrin that have activated iron ferrite (magnetite) particles attached to their outer surfaces. Ferrites have been shown in previous work (Boyd *et al.*, 1986; Kochen, 1987; Kochen and Navratil, 1987; Boyd and Kochen, 1993) to be excellent adsorbents for actinide elements (including Am^{3+}) in wastewaters at relatively low alkaline conditions ($pH > 9$) and independent of a magnetic field. Results obtained by Ritter and his colleagues demonstrated that MPE resin has a significantly enhanced capacity for actinides over conventional-based ferrite surface complexation adsorption processes (where no field is applied) and over traditional high-gradient magnetic separation processes that remove suspended particles.

8.4.5 Extraction chromatographic processes

Extraction chromatography combines the best features of liquid–liquid solvent extraction and chromatographic separation techniques. Extraction chromatographic systems consist of 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.

Many systems using either HDEHP or Aliquat 336 as the stationary phase have been studied for extraction chromatographic separation of americium at tracer-level concentrations. An Aliquat 336 (nitrate-form)–kieselguhr system was used both in the USA and in Europe to separate milligram to gram amounts of americium from curium (Horwitz *et al.*, 1967; Müller, 1971).

In the two decades since the publication of the second edition of this monograph extraction chromatographic techniques for separating Am(iii) and small amounts of other actinides from various aqueous media have been pursued for routine analytical purposes and for specialized process purposes. Thus far, the analytical applications have met with much greater acceptance and success than the proposed process applications.

Horwitz and his colleagues at the U.S. Argonne National Laboratory have been the prime movers in developing practical extraction chromatographic materials and procedures for analytical-scale separations and determination of Am(iii) and other actinides. (Materials developed by Horwitz *et al.* are commercially manufactured and marketed by Eichrom Industries, Darien, Illinois.) Horwitz *et al.* (1990, 1993) initially developed an extraction chromatographic material, which was marketed under the name TRU^{TM} resin; the TRU^{TM} resin, which consisted of a solution of CMPO adsorbed on Amberchrom-CG 71 (Rohm & Haas Co.), had a number of attractive features including offering the possibility of sequential elution of individual sorbed actinide elements. However, a major weakness of the TRU^{TM} resin was that it would not effectively sorb actinides from solutions containing significant concentrations of complexing anions such as fluoride, oxalate, or phosphate. Extraction chromatographic analytical applications of the TRU^{TM} resin for the separation and determination of Th, U, Pu, Am, and Cm have been described in a series of papers (PilvVo and Bichel, 1998, 2000; PilvVo *et al.*, 1999).

In follow-on development work by Horwitz *et al.* the Diphonix^{TM} resin, containing geminally substituted diphosphonic acid groups chemically bonded to a styrene-based polymer matrix, was shown to exhibit extraordinarily strong affinity for the actinides particularly the 4+ and 6+ ions. Because of its strong retention of actinides, the Diphonix^{TM} resin found application in the characterization of mixed and transuranic waste (Chiarizia *et al.*, 1997) and in analytical pre-concentration of actinides from a variety of biological and environmental samples (Smith *et al.*, 1995). Further tests revealed two important weaknesses of the Diphonix^{TM} resin in extraction chromatographic applications, namely (i) insufficient uptake and retention of trivalent actinides and (ii) difficult stripping/recovery of actinides from the loaded resin.

The final important contribution to actinide element extraction chromatography of the Horwitz group at the Argonne National Laboratory was the development and introduction of the DIPEX^{TM} resin (Horwitz *et al.*, 1997). The DIPEX^{TM} resin consists of a new compound, bis(2-ethylhexyl)methanediphosphonic acid (H_2DEH[MDP]) supported on an inert polymeric substrate. Horwitz and his coworkers state that this compound contains the same diphosphonic acid functional group as the Diphonix^{TM} resin but two of the four ionizable hydrogen atoms have been replaced by a C_8 alkyl group to make the molecule more lipophilic. According to the experimental evidence of Horwitz and colleagues, the DIPEX^{TM} resin exhibits stronger affinity for 3+, 4+, and 6+ actinides from acidic chloride media and superior selectivity for Am(III) over Al(III) and Fe(III) than the Diphonix^{TM} resin. Indeed, so strongly does the DIPEX material sorb actinides that the only convenient way to strip sorbed actinides appears to be to wash the resin with isopropanol to completely solubilize the H_2DEH[MDP] for subsequent wet oxidation to liberate the actinides for further treatment and analysis. Despite what appears to be a cumbersome procedure for stripping sorbed actinides, the DIPEX^{TM} resin is considered to be eminently suited for separation and pre-concentration of actinides from complex soil and bioassay matrices.

Nowadays, extraction chromatographic materials and techniques are generally considered to be most suited for analytical aims. But, some process-scale applications of such materials and techniques continue to be proposed from time to time. For example, Akatsu and Kimura (1990) reported on the use of extraction chromatography in the DHDECMP–(XAD-4) HNO_3 system. Also, several investigators (Barney and Cowan, 1992; Lumetta *et al.*, 1993) studied the feasibility of using TRU^{TM} resin and other types of extraction chromatographic supports impregnated with CMPO to separate actinide elements from stored US DOE Hanford site tank wastes including actual neutralized decladding waste and also other acidic waste solutions. Scientists in India (Gopalakrishnan *et al.*, 1995; Mathur *et al.*, 1995) have reported good success in applying an extraction chromatographic material consisting of CMPO adsorbed on Chromosorb-102 to selectively take up U(VI), Pu(IV), and Am(III) from neat nitric acid media, from synthetic sulfate-bearing high-level waste (SBHLW) and actual Purex process oxalate supernatant liquors.

Two other extraction chromatographic process-scale applications for separation of americium and other actinides are noteworthy. Mohapatra *et al.* (2000) found that the diamide DMDBTDMA adsorbed on an inert support was very efficient in taking up tracer concentrations of Am(III) and other actinide ions from 3 to 5 M HNO_3 solutions. Wei and his coworkers (Wei, 2000a,b) prepared and investigated the actinide sorption properties of several novel silica-based extraction chromatographic resins by impregnating organic extractants such as CMPO, HDEHP, and Cyanex 301 into a styrene–divinylbenzene copolymer, which is immobilized in porous silica particles. Recently, these scientists have synthesized 2,6-bis-((5,6-dialkyl)-1,2–4-triazene-3-yl)-pyridine and impregnated such compounds into styrene–divinylbenzene copolymers immobilized in porous silica particles (Wei *et al.*, 2000a,b). The resulting extraction chromatographic material preferentially sorbed Am(iii) over trivalent lanthanides.

A most unusual and intriguing type of extraction chromatographic separation scheme for Am(iii) and other actinides was prepared by Nunez *et al.* (1996). These researchers adsorbed a layer of CMPO/TBP onto polymeric-coated ferromagnetic particles. The CMPO/TBP was very efficient in taking up actinides from 0.01 to 6 M HNO_3 nuclear waste solutions as expected from the results with the TRUEX process (see Section 8.4.3a(vi)). Once loaded with actinides, the ferromagnetic particles could be readily recovered from the waste solutions with a magnet.

8.5 ATOMIC PROPERTIES

8.5.1 Electron configuration

Americium is the sixth member of the actinide series, with electron configurations in its ground and ionized states analogous to those of its lanthanide homolog, europium. Note, however, that the solution chemistries of these two elements show substantial differences, with the major ones being the difficulties in preparing Am(ii) and the absence of Eu(iv), Eu(v), and Eu(vi). Electronic configurations of gaseous americium species as determined from spectroscopic and atomic-beam experiments showed a $5f^77s^2$ ground state for Am(g) and $(5f^7)^{2+}$ state for Am^{2+} (Tomkins and Fred, 1949).

8.5.2 Atomic and ionic radii

Metallic, covalent, and ionic radii of americium in various oxidation states were first calculated by Zachariasen (1948a, 1954). The radius of americium metal with a coordination number (CN) of 12 was reported to be 1.73 Å (McWhan *et al.*, 1960). On the basis of a refined single-crystal structure for $AmCl_3$, Burns and Peterson (1970, 1971) calculated the ionic radius of Am^{3+} (CN 6) in $AmCl_3$ to be 0.984 ± 0.003 Å. Zachariasen (1978) has also deduced some highly useful bond length–bond strength relationships that provide, as a function of americium valence and coordination number, a condensation of many americium–oxygen and americium–halogen distances derived from the best-known structures. For the Am^{3+} and Am^{4+} ions, Zachariasen (1948a) reported crystal radii of 1.00 and 0.85 Å, respectively. Shannon (1976) provided a list of revised effective ionic radii and reported 1.21 Å (CN 6) and 1.26 Å (CN 8) for Am^{2+}, 0.975 Å (CN 6) and 1.09 Å (CN 8) for Am^{3+}, 0.85 Å (CN 6) and 0.95 Å (CN 8) for Am^{4+}. No data are available on Am(v) and Am(vi). David (1986) reported an ionic radius for Am^{3+} of 0.980 Å (CN 6) and 1.106 Å (CN 8).

8.5.3 Ionization potentials

Trautmann and colleagues (Trautmann, 1994; Deissenberger *et al.*, 1995) experimentally determined the first ionization potential of americium to be 5.9738 (2) eV. This determination was made with only 10^{12} atoms of americium using a newly developed method based on resonance ionization mass spectroscopy in the presence of an external electric field. Before the work of Trautmann and colleagues, Carlson *et al.* (1970) calculated the ionization potential values for Am^0 (5.66 eV), Am^+ (12.15 eV), and Am^{2+} (18.8 eV). Penneman and Mann (1976) also estimated the same potentials based on *jj* coupling; these investigators underestimated the first ionization potential but were in good agreement on the potentials for higher ionizations.

8.5.4 Emission spectra

Studies of the arc and spark spectra of americium have been summarized by Carnall (1973a) in *Gmelin's Handbook of Inorganic Chemistry*. Corresponding to the absolute term value (48767 cm^{-1}) of the ground state, the ionization potential of Am(i) is 6.0 eV (Carlson *et al.*, 1970). As noted above Deissenberger *et al.* (1995) refined the ionization potential to 5.9738(2) eV.

8.5.5 X-ray spectrum

Atomic energy levels (binding energies) of americium have been calculated from experimental measurements of X-ray emission wavelengths; for example, the value for $K–M_{III}$ is 120.319 and 102.041 keV for the $K–L_{II}$ transition (Carnall, 1973b). All K X-ray energies of americium correspond to electric dipole transitions. A critical literature evaluation and a listing of atomic energy levels of americium are given in Bearden (1967).

8.5.6 Photoelectron spectrum

In a highly important experimental measurement, Naegele and coworkers (Naegele *et al.*, 1984) at the European Institute for Transuranium Elements were able in 1984 to directly conduct X-ray and high-resolution ultraviolet photoemission spectroscopy of the conduction band of americium metal. These measurements, parallel to those successfully performed earlier with uranium metal, directly revealed that the 5f electrons in americium metal are localized. Naegele *et al.* state that the final-state multiplet structure arises from a trivalent $5f^6$ Am ground state. In later work, Naegele *et al.* (Martensson *et al.*, 1987) attempted an interpretation of the valence band photoelectron spectrum for americium metal.

8.5.7 Mössbauer spectrum

Beta decay of ^{243}Pu ($t_{1/2} = 4.98$ h) to the 83.9 keV level of ^{243}Am produces an excited nuclear state ($t_{1/2} = 2.34$ ns) of ^{243}Am that is suitable for Mössbauer spectroscopy (Kalvius *et al.*, 1969; Bode *et al.*, 1976). Data obtained with a $^{243}PuO_2$ source at 4.2 K showed the shift of the $^{243}AmF_3$ resonance line relative to $^{243}AmO_2$ to have an unusually large value of 55 mm s^{-1} (Kalvius *et al.*, 1969; Bode *et al.*, 1976).

8.6 METAL AND ALLOYS

8.6.1 Metal preparation

Americium metal has been prepared by the following methods: (1) reduction of AmF_3 with barium (or lithium) metal; (2) reduction of AmO_2 with lanthanum metal; (3) bomb reduction of AmF_4 with calcium metal; and (4) thermal decomposition of Pt_5Am. Lanthanum metal (or thorium metal) reduction of AmO_2 in tantalum equipment and subsequent distillation of the americium metal from the reaction mixture yields americium of very high (>99.9%) purity. Americium is about a factor of 10^4 more volatile than lanthanum. Extensive applications of this technique by the Euratom group led to important new measurements of the physical and thermodynamic properties of americium metal (Oetting *et al.*, 1976). Workers at the U.S. DOE Rocky Flats site also reported similar success with vacuum distillation techniques (Berry *et al.*, 1982).

Preparation of americium metal by thermal decomposition of the intermetallic compound Pt_5Am is a more recent development. Müller *et al.* (1972) produced high-purity americium metal by thermal decomposition of the intermetallic compound at 1550°C and 10^{-6} Torr, followed by further distillation.

8.6.2 Properties

Americium metal is silvery, ductile, non-magnetic, and very malleable. Selected physical properties are listed in Table 8.3. There are two well-established crystalline forms of americium metal, a double hexagonal close-packed (dhcp, $P6_3/mmc$) phase, stable at room temperature, and a face-centered cubic (fcc, $Fm3m$) phase (McWhan *et al.*, 1960; Stephens *et al.*, 1968; Oetting *et al.*, 1976). Differential thermal analysis and dilatometric experiments on americium metal have presented (Rose *et al.*, 1979) evidence for at least three phases existing between room temperature and the melting point (1170°C): an alpha phase

Table 8.3 *Selected properties of americium metal* (*adopted from Schulz* (1976) *and Oetting* et al. (1976); *see also Chapter* 19).

Property	*Values*[a]
Crystallographic data	
symmetry	<658°C, dhcp (α) 793–1004°C, fcc (β) ~1050–1173°C, bcc (?)
space group	$P6_3/mmc$ and $Fm3m$
lattice parameters	dhcp: $a = 3.4681$ Å, $c = 11.241$ Å fcc: $a = 4.894$ Å
density	13.671 g cm^{-3} (calc.); 13.671 g cm^{-3} (obs.)[b]
high-pressure structures[c]	0–5 GPa Am (I): dhcp; 5 to 8–10 GPa Am(II): fcc; 8 to 15–23 GPa Am(III): double body-centered monoclinic, or trigonal distortion of fcc, or monoclinic α-Pu; >15–23 GPa Am(IV): orthorhombic α-U or monoclinic (α-U alloys)
metallic radius (CN 12)	1.73 Å
melting point	(1149 ± 5) K
boiling point	2067°C (calc.)
coefficient of thermal expansion	$\alpha_a = 7.5 \pm 0.2 \times 10^{-6}\ K^{-1}$ and $\alpha_c = 6.2 \pm 0.2 \times 10^{-6}\ K^{-1}$
compressibility at 1 atm	0.00277 $kbar^{-1}$ at 23°C
vapor pressure[d]	$\log (p/\text{atm}) = (6.578 \pm 0.046) - (14315 \pm 55)/T$ at 990–1358 K
magnetic susceptibility	$\chi_{20°C} = (881 \pm 46) \times 10^{-6}\ cm^3\ mol^{-1}$
magnetic moment	~0
microhardness (Vickers) at 25°C	800 MN m^{-2}
electrical resistivity	68 μΩ cm (300 K), 71 μΩ cm (298 K)
crystal entropy, $S°298$	55 J K^{-1} mol^{-1}
heat capacity, $(C_P)_{298}$	25.5 J K^{-1} mol^{-1}
heat of vaporization at boiling point	230.2 kJ mol^{-1} (calc.)
entropy of vaporization at boiling point	100.8 J K^{-1} mol^{-1} (calc.)
heat of transformation	5.9 kJ mol^{-1}
heat of fusion	14.4 kJ mol^{-1}
heat of dissolution in aqueous HCl	1 M HCl: −616.3 kJ mol^{-1} 1.5 M HCl: −615.5 kJ mol^{-1} 6 M HCl: −618.0 kJ mol^{-1}

[a] For the dhcp-form unless otherwise indicated.

[b] By immersion in monobromobenzene.

[c] Refer to Section 8.6.2.

[d] Ward *et al.* (1975) give the following equation for americium above its melting point: $\log(p/\text{atm}) = 5.185–13191/T$.

existing up to 658°C; a beta phase existing between 793 and 1004°C; and a gamma phase which forms at 1050°C. In studies with high-purity americium metal, Sari *et al.* (1972/73) concluded that there is no phase transition between 600 and 700°C. But, Russian scientists (Seleznev *et al.*, 1979) put forth evidence that the transition from the dhcp structure to the fcc structure occurs at 771 ± 15°C; their observation is in agreement with the conclusions reached from dilatometric and differential thermal analysis measurements.

Smith and Haire (1978) found that americium metal with the dhcp structure became superconducting between 0.55 and 0.75 K; observation of the onset of superconductivity in americium metal confirmed an earlier prediction made from theoretical considerations. In later work, Link *et al.* (1994) found that the superconductivity transition temperature of dhcp americium increases considerably with pressure, reaching a maximum value of 2.3 K at 6.6 GPa. Müller *et al.* (1978), at several laboratories in Europe and in USA, recently measured the electrical resistivity and specific heat of americium metal. These latter investigators observed binding in americium metal to be reduced compared to that in lighter actinide metals and attributed this result to the importance of 5f electrons in electrical conduction. In a later paper, Hall *et al.* (1980) used their data to generate 'best values' for the heat capacity, crystal entropy, and electrical resistivity of americium metal; these 'best values' are shown in Table 8.3.

Owing to its unique position and properties in the actinide series of elements, americium metal has proven to be, over the last quarter of a century, a material of great interest to both theoreticians and experimentalists. In the light actinide metals (Ac–Pu) the 5f electrons are known to be itinerant and not localized. But, there is much evidence, e.g. cohesive properties, magnetic properties, atomic volume, etc. to indicate that the 5f electrons in americium metal at atmospheric pressure are localized and chemically inert. (Indeed, results of recent photoemission spectral studies cited in Section 8.4 essentially prove that 5f electrons in americium metal are localized.) Once the 5f electron localization behavior was noted for americium metal, Johannson (1978) also posited that americium metal under compression will transform to a dense phase where the 5f electrons are itinerant and not localized.

The first experimental study of the behavior and some properties of americium metal above atmospheric pressure was conducted by Stephens *et al.* (1968). These investigators determined the compressibility and electrical resistance of americium metal at room temperature over the range 3.5–12 GPa. They also made an attempt to determine the phase diagram of americium metal over this range of pressures.

Following Johannson's 1978 paper several groups of scientists in the early 1980s determined structural properties from X-ray diffraction data for americium metal at various pressures. The overall goal of these studies was to determine the number and type of different crystalline structures formed as a function of applied pressure and, thereby, obtain experimental evidence for delocalization of the 5f electrons. Thus, Akella and coworkers (Akella *et al.*, 1980;

Roof *et al.*, 1980; Smith *et al.*, 1981; Roof, 1982) established four different crystalline structures in americium metal over the pressure range from 100 kPa (1 atm) to 18 GPa: Am(I)-dhcp; Am(II)-fcc (at 5 ± 1 GPa); Am(III)-not indexed (10 ± 1 GPa); and Am(IV)-not indexed (15 ± 1 GPa). Later Roof (1982) repeated and extended the pressure experiments of Akella and coworkers up to 20 GPa. Roof and his collaborators noted the same four crystalline phases as observed by Akella and coworkers. But, Roof and his collaborators indexed the Am(III) phase (10–15 GPa) as a double-body centered monoclinic structure and the Am(IV) phase (10–20 GPa) as an orthorhombic structure similar to that of alpha uranium metal.

The latest experimental studies of delocalization of 5f electrons in americium metal under pressure were performed by Benedict and colleagues (Benedict *et al.*, 1985, 1986). Benedict *et al.* conducted their experiments over the pressure range 3 to 52 GPa, and, under these conditions, also noted the Am(I)–Am(II)–Am(III)–Am(IV) phase transformation sequence. Benedict *et al.* however, state that the transitions between phases occur at higher pressures than noted by previous workers; in particular, Benedict and his fellow authors state that the Am(III) to Am(IV) transition occurs at 23 GPa, not at 15 GPa. Benedict *et al.* claim that the Am(III) phase is not a monoclinic structure, as previously indexed, but is really a trigonal distortion of the Am(II) fcc structure. Finally Benedict *et al.* state that according to their results, 5f electron delocalization occurs only at a pressure of 23 GPa or above. Lindbaum *et al.* (2001) observed the transition of the normal-pressure double hexagonal close packed ($P6_3/mmc$) structure transforms at 6.1 GPa to the face centered cubic (*Fm3m*) form, which converts at 10.0 GPa to a face centered orthorhombic (*Fddd*) structure. This orthorhombic form converts at 16 GPa to a primitive orthorhombic (*Pnma*) form, which is stable up to at least 100 GPa. Based on the data of americium's pressure behavior the authors concluded that Am f-electrons are involved in the metallic bonding of the AmIII and IV phases.

Coincident with experiments conducted to ascertain the response of americium metal to increasing pressure, theoreticians in several countries have mounted a sustained effort to apply first-principles calculations to deduce the state of 5f electrons both in the presence and absence of applied pressure (Skriver *et al.*, 1980; Johannson, 1984; Nikolaev and Ionova, 1991; Eriksson and Wills, 1992; Eriksson *et al.*, 1993, 1995, 2000; Soderland *et al.*, 2000). The present state of the theoretical calculations is best discussed in a recent paper by Soderland *et al.* (2000). The latter investigators used density functional electronic calculations to study the high-pressure behavior of americium metal. At about 8 GPa, such calculations revealed a phase transition from the fcc structure Am(II) to a dense phase of lower symmetry that Johannson *et al.* were convinced is a monoclinic form similar to the structure of α-plutonium (Fig. 8.3); they state emphatically that it does not have the orthorhombic structure called out by Roof and Benedict *et al.* According to Johannson and collaborators, their calculation results are consistent with a Mott transition;

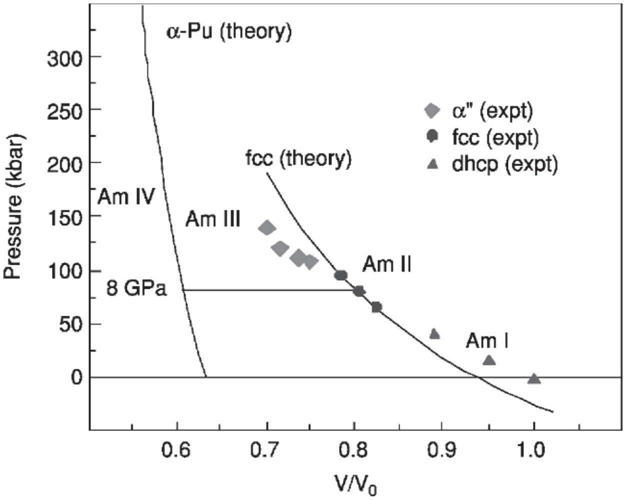


Fig. 8.3 *Calculated equations of state for americium metal from fits to total energies* (*Soderland* et al., 2000)*; equations indicate a volume decrease of* 25% *at* 8 GPa.

the 5f electrons are delocalized and bonding on the high-density side of the transition and chemically inert and non-bonding (localized) on the low-density (fcc phase) side of the transition.

Even at this advanced time in the chemistry of americium, there are still some serious disagreements between experimentally determined and calculated (from theoretical considerations) effects of compression of americium metal. To be sure, both approaches offer strong support for the contention that upon compression the 5f electrons in americium delocalize. Both the experimentalists and the theoreticians concur that at moderate applied pressure, the dhcp structure converts to the fcc phase. And, both groups concur that at some threshold applied pressure the fcc structure transforms to a more dense phase, i.e. Am(III) and, possibly, Am(IV), in which the 5f electrons are delocalized. But, certainly the parties involved do not agree on exactly how many different dense phases (one or two) eventually form on further application of pressure or on the exact pressure of phase transformations and certainly not on the crystal structure of the new dense phase(s). (The data shown in Table 8.3 are listed so as to capture much of the present uncertainty concerning transition pressures and crystalline structures.) Another important point of disagreement and uncertainty, long known and troublesome to theoreticians, is that the experimentally observed volume decreases when the 5f electrons in americium metal are delocalized only to about 6% compared to the 30–35% decrease predicted from theory. The present disagreement between experimental and calculated results point to flaws and deficiencies in both approaches, e.g. difficulties in obtaining and accurately deciphering X-ray diffraction data from a pressurized radioactive system and inadequacies of present calculational tools. It is hoped that future research will resolve the discrepancies between calculation and experiment.

8.6.3 Alloys and intermetallic compounds

Presently, alloy systems involving interaction of americium metal with some 23 different elements have been investigated. One or more intermetallic compounds of definite composition are known to exist in 16 of these systems; Table 8.4 summarizes the significant stoichiometry, structure, and synthesis information for these 16 systems and also provides relevant literature references.

No definite compounds have been observed in the Am–Ce, Am–Hg, Am–La, Am–Np, Am–Pu, Am–Th, or Am–U systems. Phase diagrams for the Am–Np, Am–Pu, and Am–U systems have recently been summarized and published by Okamoto (1998). Okamoto took careful note of the phase diagram for the Am–Pu system constructed earlier by Ellinger *et al.* (1966). Gibson and Haire (1992a) have reported phase relations in the Am–Np system while Adair (1970) prepared alloys of thorium with 0.54–5.0 wt% americium by both levitation and arc melting of prepared mixtures of americium and thorium metal.

Interaction of americium metal with two rare earth metals, lanthanum and cerium, has been investigated, respectively, by Hill and coworkers (Hill and Ellinger, 1971; Hill *et al.*, 1971) and by Connor (1982). Lanthanum–americium alloys containing 0.92–2.37 at% americium dissolved in fcc-beta lanthanum were produced by arc melting the constituent elements. Connor used both co-melting (arc) and co-reduction techniques in his studies of the Am–Ce system. Co-reduction alloy preparation involved calcium metal reduction of an appropriate mixture of AmF_4 and CeF_3 in a sealed vessel.

The Am–Hg system has been studied by Bouissières and Legoux (1965), David and Bouissières (1968), Maly (1969), and Tikhonov *et al.* (1988). A dilute americium amalgam may be prepared either by reduction of Am(III) ions with a sodium amalgam or by electroreduction of Am(III) ions on a mercury electrode. Tikhonov *et al.* also investigated some properties of a concentrated americium amalgam that was prepared electrolytically; their results indicated the formation of an Am–Hg intermetallic compound but no information on the stoichiometry or structure of such a compound was reported. Guminski (1995) recently reviewed and evaluated the equilibrium and thermodynamics of the Am–Hg system.

8.7 IMPORTANT COMPOUNDS

Inorganic compounds containing halides or oxygen-donor ligands are far more numerous than simple oxides, hydroxides, or other binary or ternary compounds. The structures and references to the preparation of about 180 compounds of americium with anionic inorganic ligands are listed in alphabetical order in Table 8.5; compounds of americium with organic ligand coordination are listed in Table 8.6. A group of compounds in which americium could be considered as part of the anionic constituent appears under the heading oxides, ternary.

8.7.1 Inorganic compounds

(a) Oxides and hydroxides

The binary americium oxides are limited to AmO, Am_2O_3, AmO_2, and non-stoichiometric phases between Am_2O_3 and AmO_2. Although the AmO (fcc) phase has been reported twice (Zachariasen, 1949a,c; Akimoto, 1967), the corresponding lattice parameters, 4.95 Å (Zachariasen, 1949a,c) and 5.045 Å (Akimoto, 1967), are not consistent. Accidental exposure of AmH_{2+x} to air at 300°C yielded a fcc phase (Roddy, 1973), which agrees with Akimoto's AmO (Akimoto, 1967) but may in fact be an oxynitride similar to the corresponding 'PuO' (Larson and Haschke, 1981). The difficulty in achieving Am(II) in solution and in solid compounds makes it likely that the monoxide can only be synthesized under high pressure by conproportionation of Am metal and Am_2O_3, analogous to the preparation of the lanthanide monoxide SmO (Leger *et al.*, 1981). Recent evidence that PuO and surface-layer lanthanide monoxides are really oxycarbides or nitrides (Larson and Haschke, 1981) reinforces the uncertainty of whether any claim for AmO is valid.

Phase relationships and thermodynamic data in the $AmO_{1.5}$–AmO_2 systems are well established. The red-brown ('persimmon') sesquioxide, Am_2O_3, is easily prepared in H_2 at temperatures as low as 600°C but it oxidizes very readily in air, even at room temperature. Baybarz (1973a) summarized the transition temperatures of the low-temperature (body-centered cubic (bcc), C-phase) to medium-temperature (monoclinic, B-phase) to high-temperature (hexagonal, A-phase) sesquioxides. The C→B transition temperature appears to be sluggish, occurring between 460 and 650°C and the B→A transition occurs between 800 and 900°C (Chikalla and Eyring, 1968; Hurtgen and Fuger, 1977). The pale tan hexagonal sesquioxide phase undergoes slight swelling with time and self-irradiation causes cubic Am_2O_3 to transform to the hexagonal phase at room temperature within about 3 years (Hurtgen and Fuger, 1977). It is possible that the monoclinic Am_2O_3 is stabilized by small amounts of rare earth impurities (Berndt *et al.*, 1974; Keller and Berndt, 1975) and that pure Am_2O_3 passes directly from the C- to the A-phase; it is also possible that the C→B transition occurs well below 650°C. The hexagonal sesquioxide is stoichiometric but the cubic form may have a lower oxygen limit of $AmO_{1.513}$ (Chikalla and Eyring, 1968). Studies on americium oxides include the measurement of the melting point of Am_2O_3, 2205 ± 15°C (Chikalla *et al.*, 1973), and the enthalpy of formation of AmO_2, -932.2 ± 3.0 kJ mol^{-1} (Morss and Fuger, 1981).

The dioxide AmO_2 was the first reported compound of americium (Zachariasen, 1949a,c). It can be prepared by heating a variety of americium compounds, e.g. hydroxides, carbonates, oxalate, or nitrate, in air or oxygen at

Table 8.4 *Intermetallic compounds in the americium alloy system.*

				Lattice constants			
Class	*Formula*	*Symmetry*	*Structure type*	a_0 (Å)	c_0 (Å)	*Comments*	*References*
aluminide	$AmAl_2$	cubic	$MgCu_2$	7.861		arc melt	[1]
antimonides	AmSb	fcc		6.239		Am/Sb/heat	[2]
	$AmSb_2$		$LaSb_2$				
	Am_4Sb_3	bcc	anti-Th_3	9.239		AmH_3/Sb/heat	[3]
arsenide	AmS	fcc	F$m3m$	5.880		Am/As/heat	[4]
				5.875		AmH_3/As/heat	
beryllide	$AmBe_{13}$	fcc	F$m3c$	10.283		AmF_3/Be/vac/heat	[6]
						AmO_2/Be/vac/heat	[7]
bismuthide	AmBi	fcc	F$m3c$	6.338		Am/Bi/heat	[8]
						AmH_3/Bi/heat	[8]
cobaltide	$AmCo_2$	$MgCu_2$				arc melt	[9]
iridium	Ir_2Am	cubic	F$d3m$, Cu_2Mg	7.55		AmO_2/H_2/Ir/1550°C	[10]
iron	Fe_2Am	cubic	Cu_2Mg	7.30		arc melt, ferromagnetic	[9]
lead	Pb_3Am	not reported				PbF_2/AmF_3/Ca/heat	[11]
nickel	Ni_2Am	cubic	F$d3m$,Cu_2Mg	6.99		Am/Ni/arc melt	[12]
osmium	Os_2Am	hexagonal	P6_3/mmc	5.320	8.849	Am/Os/arc melt	[12]
palladium	Pd_3Am	cubic	Pm/3m	4.158		Am_2O_3/Pd/H_2/heat	[13]
platinum	Pt_2Am	cubic	F$d3m$	7.615		AmO_2/Pt/H_2/heat	[13]
	Pt_5Am		$CaCu_5$	5.312	4.411	Am_2O_3/Pt/H_2/heat	[13]
rhodium	Rh_2Am	cubic	F$d3m$,Cu_2Mg	7.548		AmO_2/Rh/H_2/heat	[13]
	Rh_3Am	cubic	P$m3m$,Cu_3A	4.098		Am_2O_3/Rh/H_2/heat	[14]
ruthenium	Ru_2Am	hexagonal	$MgZn_2$	5.26	8.73	arc melt	[9]
tin	Am_2Ni_2Sn	tetragonal	P4/mbm,U_3Si_2				[15]
	Am_2Pd_2Sn	tetragonal					[15]

[1] (Hyde *et al.*, 1971; Aldred *et al.*, 1975); [2] (Mitchell and Lam, 1970a; Roddy, 1974; Charvillat *et al.*, 1975a, 1977); [3] (Charvillat *et al.*, 1975b); [4] (Roddy, 1974); [5] (Charvillat and Damien, 1973); [6] (Runnals and Boucher, 1955, 1956; Benedict *et al.*, 1975); [7] (Brachet and Vasseur, 1969); [8] (Roddy, 1974); [9] (Hyde *et al.*, 1971; Aldred *et al.*, 1975); [10] (Erdmann, 1971; Erdmann and Keller, 1971, 1973; Rebizant and Benedikt, 1978); [11] (Connor, 1982); [12] (Lam and Mitchell, 1972); [13] (Erdmann, 1971; Rebizant and Benedikt, 1978); [14] (Erdmann and Keller, 1971); [15] (Pereira *et al.*, 1997).

Table 8.5 *Inorganic compounds of americium.*

Class	*Structural formula*	*Symmetry*	*Type*	*Lattice constants*			*Angle* (deg)	*Comments*	*References*
				a_0 (Å)	b_0 (Å)	c_0 (Å)			
Aluminates									
	$AmAlO_3$	hexagonal	$R\bar{3}m$, $LaAlO_3$	5.336		12.91		$Am(OH)_3/Al(OH)_3/H_2$/heat	[1,2]
Arsenates									
	$AmAsO_4$	monoclinic	$P2_1/n$	6.89	7.06	6.62	$\beta = 105.5$		[2]
	$NH_4AmO_2AsO_4 \cdot nH_2O$	tetragonal	$P4/nmn$ or $I4/mmm$	7.11		8.93		Am(VI)/0.1 M H_3AsO_4/pH 3.5, lemon yellow	[3]
	$KAmO_2AsO_4 \cdot nH_2O$	tetragonal	$P4/nmn$ or $I4/mmm$	7.10		9.09		Am(VI)/0.1 M H_3AsO_4/pH 3.5, lemon yellow	[3]
	$RbAmO_2AsO_4 \cdot nH_2O$	tetragonal	$P4/nmn$ or $I4/mmm$	7.15		17.73		Am(VI)/0.1 M H_3AsO_4/pH 3.5, lemon yellow	[3]
	$CsAmO_2AsO_4 \cdot \mathrm{v}nH_2O$	tetragonal	$P4/nmn$ or $I4/mmm$	7.09		17.72		Am(VI)/0.1 M H_3AsO_4/pH 3.5, lemon yellow	[3]
Borates									
	$AmBO_3$	orthorhombic	$Pnam$	5.053	8.092	5.738		AmO_2/B_2O_3/heat	[1,2]
Borides									
	AmB_4	tetragonal	$P4/mbm$	7.105		4.006		vac. heat Am/B 1:2	[4]
	AmB_6	simple cubic	$Pm3m$	4.115				arc melt Am/B	[4]
Bromides									
	$AmBr_2$	*tetragonal*	$P4/n$, $EuBr_2$	11.59		7.121		Am/$HgBr_2$/vac./heat	[5,6]
	$AmBr_3$	orthorhombic	$Cmcm$, $PuBr_3$	4.064	12.66	9.144			[7,8,9]
	$AmBr_3 \cdot 6H_2O$	monoclinic	$P2/n$	9.955	6.783	8.166	$\beta = 91.75$	$AmBr_3$, H_2O vapor	[9]
	$[(C_6H_5)_3PH]_3AmBr_6$							ethanol pptn.	[10]
	$AmOBr$	tetragonal	$P4/nmm$	3.982		7.644			[11]
Carbides									
	Am_2C_3	bcc	$I\bar{4}3d$	8.276				Am/C arc melt	[12]
Carbonates									
	$AmOHCO_3$	orthorhombic						Am(III)/$NaHCO_3$/0.03% CO_2	[13]
	$Am_2(CO_3)_3 \cdot 2H_2O$							Am(III)/trichloroacetate	[14]
	$Am_2(CO_3)_3 \cdot 4H_2O$							Am(III)/$NaHCO_3/CO_2$	[15]
	$NaAm(CO_3)_2 \cdot nH_2O$	tetragonal	$NaNdO_2CO_3$	13.07		9.93		Am(III)/Na_2CO_3/5 M NaCl	[16]

Table 8.5 (*Contd.*)

Class	Structural formula	Symmetry	Type	Lattice constants			Angle (deg)	Comments	References
				a_0 (Å)	b_0 (Å)	c_0 (Å)			
	$NH_4AmO_2CO_3$	hexagonal	*C6/mmc*					Am(iii)/$(NH_4)_2CO_3/O_3$	[17]
	$Na_{2x+1}AmO_2(CO_3)_{1+x}$							Am(vi)/Na_2CO_3/heat	[17,18]
	$KAmO_2CO_3 \cdot nH_2O$	hexagonal	*C6/mmc*	5.112		9.740		*n* is variable with H_2O	[18–20]
	$RbAmO_2CO_3$	hexagonal	*C6/mmc*	5.12		10.46		Am(iii)/10 M Rb_2CO_3/O_3	[17,21]
	$CsAmO_2CO_3$	hexagonal	*C6/mmc*	5.123		11.538		Am(iii)/$CsHCO_3/O_3$	[22]
	$K_3AmO_2(CO_3)_2 \cdot nH_2O$	rhombic (a,b)	*C6/mmc*	5.32	9.21	8.76		(a) 4.7 M, (b) 2.3 M K_2CO_3	[20]
				5.29	9.11	8.83		Am(iii)/3.5 M K_2CO_3	[23]
	$K_5AmO_2(CO_3)_3$	orthorhombic						Am(iii)/>5 M K_2CO_3/O_3	[17,24]
	$(NH_4)_5AmO_2(CO_3)_3$							Am(vi)/NH_4CO_3	[3]
	$(NH_4)_4AmO_2(CO_3)_3$							Am(vi)/$NaHCO_3/(NH_4)_2CO_3$	[25]
	$Cs_4AmO_2(CO_3)_3$							Am(vi)/$NaHCO_3/Cs_2CO_3$	[25]
Chlorides									
	$AmCl_2$	orthorhombic	*Pbnm*	8.963	7.573	4.532		Am/$HgCl_2$/heat	[5,6]
	$AmCl_3$	hexagonal	$P6_3/m$	7.382		4.214		AmO_2/HCl	[7–9,26]
	$AmCl_3 \cdot 6H_2O$	monoclinic	*P2/n*	9.702	6.567	8.009	$\beta = 93.62$		[26,27]
	$AmOCl$	tetragonal	*P4/nmm*	4.00		6.78			[28]
	$CsAmCl_4$							Am(iii)/HCl/CsCl	[29]
	$CsAmCl_4 \cdot 4H_2O$							Am(iii)/HCl/CsCl	[29,30]
	Cs_3AmCl_6							Am(iii)/HCl/CsCl	[31]
	$Cs_2NaAmCl_6$	fcc	*Fm3m*	10.8548(8)				Am(v)/HCl/CsCl/NaCl	[29,30,32]
	$[(C_6H_5)_3PH]_3 AmCl_6$		$Cs_3NpO_2Cl_4$					ethanol pptn.	[10,33]
	$Rb_2AmO_2Cl_4$	monoclinic	*C2/c*	11.53	7.48	5.65	$\beta = 99.19$	Am(v)/HCl/RbCl	[3]
	$Cs_2AmO_2Cl_4$	monoclinic	*C2/c*	11.92	7.61	1167	$\beta = 99.56$	Am(v)/HCl/CsCl	[3]
Chromate									
	$(AmO_2)_2CrO_4 \cdot nH_2O$							20–80°C	[34]
Fluorides									
	AmF_3	hexagonal	$P\bar{3}c1$, LaF_3	7.044		7.225		m.p. 1400°C/v.p.	[35]
	AmF_4	monoclinic	*C2/c*, UF_4	12.538	10.516	8.204	$\beta = 126.8$	AmF_3/F_2/v.p.	[36,37]
	AmO_2F_2	hexagonal	*R3m*	4.136		15.85			[38]
	AmF_6							KrF_2/HF(li); dark brown	[39]

	$NaAmF_4$	hexagonal	*P*6	6.109		3.731		$AmO_2/HF–H_2/NaF$	[40,41]
	$KAmF_4$	orthorhombic	*Pnma*	6.13	3.71	15.2			[42]
	K_3AmF_6	hexagonal	K_3LaF_6	22.75		7.56		$AmO_2/HF–H_2/KF/$ 650°C	[42]
	K_2AmF_5		K_2PrF_5						[42]
	KAm_2F_7	cubic	KEu_2F_7	5.857					[41,42]
	$(NH_4)_4AmF_8$	monoclinic	$C2/c$, $(NH_4)_4UF_8$					$Am(OH)_4/NH_4F$	[43]
	$LiAmF_5$	tetragonal	$I4_1/a$	14.63		6.449			[44]
	$K_7Am_6F_{31}$	hexagonal	*R*3	14.938		10.293		Am(III)/KF	[44,45]
	$Na_7Am_6F_{31}$	hexagonal	*R*3	14.48		9.665			[45]
	$RbAmF_4$	orthorhombic	*Pnma*	6.43	3.76	16.0			[42]
	Rb_2AmF_6	orthorhombic	*Cmcm*	6.962	12.001	7.579			[45,46]
	$KAmO_2F_2$	rhombohedral	$R3m$,$CaUO_4$	6.78			$\alpha = 36.25$	$AmO_2{}^+/KF$	[47]
	$RbAmO_2F_2$	rhombohedral	$R3m$	6.789			$\alpha = 36.25$	$AmO_2{}^+/RbF$	[48]
Germanate									
	$AmGeO_4$	Tetragonal	$I4_1/a$	5.04		11.03			[49]
Hydrides									
	AmH_2	fcc	*Fm*3*m*	5.348				AmH_{2+x}, $x = 0–0.7$	[50,51]
	AmH_3	trigonal	*P*3*c*1	6.68		6.75			[51]
Hydroxide									
	$Am(OH)_3(am)$	hexagonal	$Nd(OH)_3$	6.426		3.745		Am(III)/NaOH, $Ksp \sim 3 \times 10^{-18}$	[52]
	$Am(OH)_3(cr)$							$Am_2O_3(s)/H_2O(g)$	[53]
	$Am(OH)_4$							$Am(OH)_3/NaOCl$	[54]
	$LiAmO_2(OH)_2 \cdot xH_2O$							Am(V)/0.1–2 M LiOH	[55]
	$NaAmO_2(OH)_2 \cdot xH_2O$							Am(V)/0.1–0.5 M NaOH	[55]
	$KAmO_2(OH)_2 \cdot xH_2O$							Am(V)/0.1–0.5 M KOH	[55]
	$RbAmO_2(OH)_2 \cdot xH_2O$							Am(V)/0.1–0.5 M RbOH	[56]
	$CsAmO_2(OH)_2 \cdot xH_2O$							Am(V)/0.1–0.5 M CsOH	[56]
	$Na_2AmO_2(OH)_3 \cdot xH_2O$							Am(V)/2 M NaOH	[55]
	$K_2AmO_2(OH)_3 \cdot xH_2O$							Am(V)/2 M KOH	[55]
	$Rb_2AmO_2(OH)_3 \cdot xH_2O$							Am(V)/>2 M RbOH	[56]
	$Cs_2AmO_2(OH)_3 \cdot xH_2O$							Am(V)/>2 M CsOH	[56]
Iodides									
	AmI_2	monoclinic		7.677	8.311	7.925	$\beta = 98.46$	$Am/H_2/I_2$/vac.	[57]
	α-AmI_3	orthorhombic	*Ccmm*	4.31	14.03	9.92		AmO_2/AlI_3	[8,58]
	β-AmI_3	hexagonal	*R*3	7.42		20.55			[8,58]
	AmOI	tetragonal		4.011		9.204			[8,58]
Iodates									
	$Am(IO_3)_3$	monoclinic	$P2_1/c$	7.243	8.538	13.513	$\beta = 100.123$	$Am/HCl/KIO_4$/180°C	[59]
	$K_3Am_3(IO_3)_{12} \cdot HIO_3$	triclinic		22.096	22.096	13.436	$\gamma = 120$	Am/KIO_4/180°C	[59]

Table 8.5 (*Contd.*)

Class	*Structural formula*	*Symmetry*	*Type*	*Lattice constants* a_0 (Å)	b_0 (Å)	c_0 (Å)	*Angle* (deg)	*Comments*	*References*
Molybdates									
	α-$Am_2(MoO_4)_3$	tetragonal	$I4_1/a$	5.24		11.52		$AmO_2/MoO_3/\sim825°C$	[60,61]
	β-$Am_2(MoO_4)_3$	orthorhombic		9.095	10.527	10.820		$AmO_2/MoO_3/>850°C$	[60,61]
	$LiAm(MoO_4)_2$	tetragonal	$I4_1/a$, $LiGd(MoO_4)_2$	5.20		11.39		$Am_2(MoO_4)_3/Li_2MoO_4$	[61]
	$Am_2(MoO_4)_3$	tetragonal	scheelite						[60]
	$NaAm(MoO_4)_2$	tetragonal	scheelite	5.25		11.55			[61]
	$Na_5Am(MoO_4)_4$		$Na_5La(WoO_4)_4$	11.515		11.429		solid-state reaction	[61]
	$K_2Am(MoO_4)_4$							solid-state reaction	[61]
	$K_{10}Am(MoO_4)_8$							solid-state reaction	[61]
	$K_3AmO_2(Mo_2O_7)_2 \cdot nH_2O$							$AmO_2NO_3/K_6Mo_7O_{24}$	[62]
	$(NH_4)_3AmO_2(Mo_2O_7)_2 \cdot nH_2O$							$AmO_2NO_3/(NH_4)_6Mo_7O_{24}$	[62]
	$AmO_2Mo_2O_7$							AmO_2SO_4/Na_2MoO_4, <100°C	[62]
Nitride									
	AmN	fcc	$Fm3m$,NaCl	5.000				$Am(AmH_3)/N_2$	[63,64]
Nitrate									
	$CsAmO_2(NO_3)_3$							$Cs_4AmO_2(CO_3)_3$/2M HNO_3/O_3; evap	[25]
Oxides									
	AmO(?)	fcc	$Fm3m$	5.045				Am/Ag_2O	[63,65]
	A-Am_2O_3	hexagonal	$P3m1$	3.817		5.971		$AmO_2/H_2/800°C$	[66,70]
	B-Am_2O_3	monoclinic	$C2/m$	14.38	3.52	8.92	$\beta = 100.4$		[67,68]
	C-Am_2O_3	cubic	$Ia3$	11.03				600°C	[66,69,70]
	AmO_2	fcc	$Fm3m$	5.374				$^{241}AmO_2$, $^{243}AmO_2$	[70,71]
	AmO_{2-x}								[67,74]
	$LiAmO_2$								[1,72,73]
	Li_2AmO_3								[1,72,73]
	Li_8AmO_6	hexagonal	Li_8PbO_6	5.62		15.96			[1,72,73]
	Li_3AmO_4	tetragonal	Li_3UO4	4.459		8.355			[1,72,73]

Li_7AmO_6	hexagonal	*R*3	5.54		15.65			[1,72,73]
Li_4AmO_5	tetragonal	*I*4/*m*	6.666		4.415			[1,72,73]
Li_6AmO_6	hexagonal	Li_6ReO_6	5.174		14.59			[1,72,73]
K_2AmO_4	tetragonal	*I*4/*mmm*	4.286		13.05			[73]
Na_2AmO_3	monoclinic	*C*2/*c*	5.92	10.26	11.23	$\beta = 100.12$		[1,72,73]
Na_3AmO_4	fcc	*Fm*3*m*	4.757					[1,72,73]
Na_4AmO_5	fcc	*Fm*3*m*	4.70					[1,72,73]
Na_6AmO_6	hexagonal	Li_6ReO_6	4.76		16.10			[1,72,73]
$BaAm_2O_4$								[1,75]
$BaAmO_3$	cubic	perovskite	4.356					[1,75]
Ba_3AmO_6	cubic	*F*43*m*	8.81					[1,75]
$SrAm_2O_4$								[1,75]
$SrAmO_3$	cubic	perovskite	4.23					[1,75]
Sr_3AmO_6	cubic	Ba_3WO_6						[1,75]
Cs_2AmO_4	tetragonal	*I*4/*mmm*	4.364		14.65		$AmO_2/CsOH/O_2/$ 250°C	[76]
Rb_2AmO_4	tetragonal	*I*4/*mmm*	4.316		13.71		$AmO_2/RbOH/O_2/$ 250°C	[76]
$(Am_{0.30},Cm_{0.70})O_{2.00}$	fcc		5.368				350°C in O_2	[77]
$(Am_{0.30},Cm_{0.70})O_{1.83}$	fcc		5.433				550°C in O_2	[77]
$(Am_{0.30},Cm_{0.70})O_{1.685}$	rhombohedral		6.687			$\alpha = 99.47$	760°C in He	[77]
$(Am_{0.30},Cm_{0.70})O_x$	bcc		10.935				900°C in He	[77]
$(Am_{0.64},Cm_{0.36})O_{1.5}$	monoclinic		14.321	3.665	8.926	$\beta = 100.17$	1100°C in H_2/He	[77]
$(Am_{0.64},Cm_{0.36})O_{1.5}$	hexagonal		3.812		5.980		1500°C in H_2/He	[77]
AmO–ZrO_2	cubic	fluorite					18–100% AmO_2/ZrO_2, SS	[1,78]
AmO–HfO_2							SS, extent unknown	[1,78]
AmO–ThO_2	cubic	fluorite					ThO_2/AmO_2, complete SS	[1]
α-$AmNbO_4$	monoclinic	I2	5.444	11.25	5.141	$\beta = 94.95$	AmO_2/Nb_2O_5	[1,2]
β-$AmNbO_4$	tetragonal	*I*4$_1$/*a*	5.30		11.34		α→β ~ 600°C	[1,2]
$Am_{0.33}NbO_3$	pseudo-tetragonal	*P*4/*mm*, $La_{0.33}TaO_3$	3.819		7.835			[1,2]
Ba_2AmNbO_6	cubic	*F*43*m*	8.520				$AmNbO_4/BaO$	[1,2]
$AmNbTiO_6$	orthorhombic	*Pnam*	5.34	11.00	7.53		$AmNbO_4/TiO_2$	[1,2]
$AmTaO_4$	monoclinic	*I*2	5.489	11.21	5.115	95.37	AmO_2/Ta_2O_5	[1,2]
$Am_{0.33}TaO_3$	tetragonal	*I*41/*a*	3.889		7.820		AmO_2/Ta_2O_5	[1,2]
Ba_2AmTaO_6	cubic	*F*43*m*	8.518					[1,2]
$AmTaTiO_6$	orthorhombic	*Pnam*	5.33	10.95	7.49			[2]
$AmPaO_4$	fcc	*Fm*3*m*	5.458				AmO_2/Pa_2O_5	[1,2]
Ba_2AmPaO_6	cubic	*F*43*m*	8.793				$(Am_{0.5}Pa_{0.5})O_2/BaO$	[1,2,79]

Table 8.5 (*Contd.*)

Class	*Structural formula*	*Symmetry*	*Type*	*Lattice constants* a_0 (Å)	b_0 (Å)	c_0 (Å)	*Angle* (deg)	*Comments*	*References*
Phosphates									
	$AmPO_4$	monoclinic	$P2_1/n$	6.73	6.93	6.41	103.5	stable to 1000°C	[2]
	$AmPO_4 \cdot 0.5H_2O$	Hexagonal		6.99		6.39		pptn. dried at 200°C	[2]
	$NH_4AmO_2PO_4 \cdot 3H_2O$							Am(vi)/$NaHCO_3$/$NH_4H_2PO_4$	[25]
	$NH_4AmO_2PO_4 \cdot zH_2O$	tetragonal	*P*4/*nmm* or *I*4/*mmm*	6.99		9.06		Am(vi)/0.1 M H_3PO_4/pH 3.5, lemon yellow	[3]
	$KAmO_2PO_4 \cdot zH_2O$	tetragonal	*P*4/*nmm* or *I*4/*mmm*	6.91		9.00		Am(vi)/0.1 M H_3PO_4/pH 3.5, lemon yellow	[3]
	$RbAmO_2PO_4 \cdot zH_2O$	tetragonal	*P*4/*nmm* or *I*4/*mmm*	6.94		9.02		Am(vi)/0.1 M H_3PO_4/pH 3.5, lemon yellow	[3]
	$CsAmO_2PO_4 \cdot zH_2O$	tetragonal	*P*4/*nmm* or *I*4/*mmm*	6.94		8.82		Am(vi)/0.1 M H_3PO_4/pH 3.5, lemon yellow	[3]
Phosphide									
	AmP	cubic	NaCl	5.711				AmH_3/P/580°C	[63,80]
Rhenate									
	$Am(ReO_4)_3$	hexagonal		10.11		6.26		AmO_2/aq $HReO_4$	[81]
								AmO_2/Re_2O_7/850°C	[81]
Scandate									
	$AmScO_3$	orthorhombic	*P6mm*, $GdFeO_3$	5.540	5.785	8.005		AmO_2/H_2/Sc_2O_3	[82]
								oxidation yields fluorite	[68]
Selenates									
	AmSe	cubic	NaCl	5.821				AmH_3/Se	[63]
	$AmSe_{2-x}$	tetragonal		4.096		8.347			[83]
	Am_3Se_4	bcc	*I*43*d*, Th_3P_4	8.799					[63,80,86]
Silicate									
	$AmSiO_4$	tetragonal	zircon	6.87		6.20		hydrothermal	[49]
Silicide									
	Am_5Si_3			11.419		5.538		AmF_3/Si/1050°C	[84]
	AmSi	orthorhombic		8.39	4.09	6.01		AmF_3/Si/1050°C	[85]
	$Am_3Si_5 \ldots Am_2Si_3$	hexagonal	Pu_3Si_5	3.871		4.120		AmF_3/Si/1050°C	[84]
	$AmSi_x$ $(x < 2)$	tetragonal	α-$ThSi_2$	4.02		13.7			[85]

Sulfates									
	$Am_2(SO_4)_3 \cdot 8H_2O$								[37]
	$Am_2O_2SO_4$								[37]
	$Am_2(SO_4)_3 \cdot 5H_2O$								[37]
	$KAm(SO_4)_2$								[37]
	$NaAm(SO_4)_2 \cdot H_2O$								[37]
	$KAm(SO_4)_2 \cdot 2H_2O$								[37]
	$RbAm(SO_4)_2 \cdot 4H_2O$								[37]
	$CsAm(SO_4)_2 \cdot 4H_2O$								[37]
	$TlAm(SO_4)_2 \cdot 4H_2O$								[37]
	$K_3Am(SO_4)_3 \cdot H_2O$								[37]
	$K_8Am_2(SO_4)_7$								[37]
	$Cs_8Am_2(SO_4)_7$								[37]
	$Tl_8Am(SO_4)_7$								[37]
	$\{[Co(NH_3)_6](HSO_4)_2 [AmO_2(SO_4)_3]\} \cdot nH_2O$	cubic							[87]
	$(AmO_2)_2SO_4 \cdot nH_2O$							AmO_2OH/aqH_2SO_4/evap	[88]
	$CsAmO_2SO_4 \cdot nH_2O$							aq. $Cs_2SO_4/(AmO_2)_2SO_4$/evap	[88]
	$Co(NH_3)_6AmO_2(SO_4)_2 \cdot 2H_2O$								[88]
Sulfides									
	AmS	fcc	*Fm*3*m*	5.592					[89]
	Am_2O_2S	trigonal	*P*3*m*	3.91		6.772			[52]
	$AmS_{1.9}$	tetragonal		3.938		7.981			[52]
	α-Am_2S_3	orthorhombic	*Pnma*	3.98	6.39	15.36		$\alpha \rightarrow \gamma \sim 1300°C$	[89,90]
	β-Am_2S_3								[91]
	γ-Am_2S_3	bcc	*I*43*m*	8.434					[91]
	$Am_{10}S_{14}O_3$								[91]
Tellurides									
	$AmTe_2$	tetragonal		4.366		8.969		AmH_3/Te/heat	[63,92]
	$AmTe_3$	orthorhombic	*Bmmb*	4.399	4.339	25.57			[92]
	Am_2Te_3	orthorhombic	*Pbnm*	11.93	12.12	4.33			[93]
	Am_3Te_4	bcc	I43*d*	9.394					[93,96]
Titanates									
	$Am_2Ti_2O_7$	monoclinic		13.07		7.69		AmO_2/TiO_2/1200–1300°C	[94]
	$SrAm_2Ti_4O_{12}$	tetragonal		3.89		7.75		$SrCO_3/AmO_2/TiO_2$/1215°C	[94]
Tungstate									
	$Am_2(WO_4)_3$	tetragonal	*I*4$_1$/*a*						[60]

Table 8.5 (*Contd.*)

Class	*Structural formula*	*Symmetry*	*Type*	*Lattice constants*			*Angle* (deg)	*Comments*	*References*
				a_0 (Å)	b_0 (Å)	c_0 (Å)			
Vanadates									
	$AmVO_3$	orthorhombic	*Pbnm*, $GdFeO_3$	5.45	5.58	7.76		AmO_2/V_2O_5	[1,2]
	$AmVO_4$	tetragonal	zircon	7.31		6.42			[1,2]
Xenate									
	$Am_4(XeO_6)_3 \cdot 40H_2O$								[95]

[1] (Keller and Walter, 1965); [2] (Keller, 1967); [3] (Lawaldt *et al.*, 1982); [4] (Eick and Mulford, 1969); [5] (Peterson, 1973); [6] (Baybarz, 1973b); [7] (Zachariasen, 1948b; Fried, 1951; Brown *et al.*, 1968; Pappalardo *et al.*, 1969b); [8] (Asprey *et al.*, 1965); [9] (Brown *et al.*, 1968); [10] (Ryan, 1967); [11] (Weigel *et al.*, 1979); [12] (Mitchell and Lam, 1970b); [13] (Runde *et al.*, 1992); [14] (Weigel and ter Meer, 1967); [15] (Fang and Keller, 1969); [16] (Runde and Kim, 1994); [17] (Nigon *et al.*, 1954); [18] (Coleman *et al.*, 1963); [19] (Keenan and Kruse, 1964); [20] (Volkov *et al.*, 1974); [21] (Ellinger and Zachariasen, 1954); [22] (Keenan, 1965); [23] (Burney, 1968); [24] (Yakovlev and Gorbenko-Germanov, 1955); [25] (Fedoseev and Perminov, 1983); [26] (Burns and Peterson, 1970, 1971); [27] (Lohr and Cunningham, 1951; Fuger and Cunningham, 1963); [28] (Weigel *et al.*, 1975); [29] (Bagnall *et al.*, 1968; Morss *et al.*, 1970); [30] (Bagnall *et al.*, 1967); [31] (Marcus and Shiloh, 1969); [32] (Schoebrechts *et al.*, 1989); [33] (Marcus and Bomse, 1970); [34] (Fedoseev *et al.*, 1991); [35] (Jones, 1951; Carniglia and Cunningham, 1955; Burnett, 1965, 1966); [36] (Asprey, 1954; Asprey and Keenan, 1958; Chudinov and Choporov, 1970; Connor, 1971); [37] (Yakovlev and Kosyakov, 1958a,b); [38] (Keenan, 1968); [39] (Drobyshevskii *et al.*, 1980); [40] (Keller and Schmutz, 1964); [41] (Schmutz, 1966); [42] (Jove and Pages, 1977); [43] (Asprey and Penneman, 1962); [44] (Keenan, 1966); [45] (Keenan, 1967); [46] (Kruse and Asprey, 1962); [47] (Asprey *et al.*, 1954a); [48] (Keenan, 1965); [49] (Keller, 1963); [50] (Katz and Seaborg, 1957); [51] (Olson and Mulford, 1966); [52] (Weaver and Shoun, 1971; Haire *et al.*, 1977); [53] (Morss and Williams, 1994); [54] (Cunningham, 1949; Penneman *et al.*, 1961); [55] (Tananaev, 1990b); [56] (Tananaev, 1991); [57] (Baybarz and Asprey, 1972); [58] (Asprey *et al.*, 1964); [59] (Bean *et al.*, 2003b); [60] (Freundlich and Pages, 1969; Tabuteau and Pages, 1978); [61] (Tabuteau *et al.*, 1972); [62] (Fedoseev and Budantseva, 1990); [63] (UCRL, 1959; Akimoto, 1967); [63] (Charvillat *et al.*, 1975a); [64] (Charvillat and Zachariasen, 1977); [65] (Zachariasen, 1949a); [66] (Templeton and Dauben, 1953); [67] (Chikalla and Eyring, 1968; Chikalla *et al.*, 1973); [68] (Berndt *et al.*, 1974; Keller and Berndt, 1975); [69] (Eyring *et al.*, 1949, 1952); [70] (Hurtgen and Fuger, 1977); [71] (Fahey *et al.*, 1974); [72] (Keller *et al.*, 1965b); [73] (Hoekstra and Gebert, 1978); [74] (Chikalla and Eyring, 1967); [75] (Keller, 1964); [76] (Hoekstra and Gebert, 1978); [77] (Mosley, 1970); [78] (Radzewitz, 1966); [79] (Keller, 1965); [80] (Charvillat *et al.*, 1975b); [81] (Silvestre *et al.*, 1977); [82] (Keller *et al.*, 1972); [83] (Damien and Jove, 1971); [84] (Wittmann, 1980); [85] (Burns and Baybarz, 1972; Weigel *et al.*, 1977); [86] (Mitchell and Lam, 1970a; Roddy, 1974); [87] (Ueno and Hoshi, 1971); [88] (Fedoseev and Budentseva, 1989); [89] (Damien, 1971); [90] (Zachariasen, 1949d); [91] (Damien *et al.*, 1972, 1975, 1976); [92] (Burns *et al.*, 1979); [93] (Damien and Charvillat, 1972); [94] (Shoup and Bamberger, 1997); [95] (Marcus and Cohen, 1966).

temperatures of 600–800°C (Eyring *et al.*, 1952; Baybarz, 1960; Chikalla and Eyring, 1967; Hurtgen and Fuger, 1977; Morss and Fuger, 1981). This stoichiometry of the black oxide is believed to be $AmO_{2.00}$ (Chikalla and Eyring, 1967, 1968) and is better than $AmO_{1.99}$ even at 1000°C in oxygen (Chikalla and Eyring, 1967). It undergoes an expansion of its fcc lattice constant due to radiation damage, which reversibly broadens the diffraction lines at low temperatures in both $^{241}AmO_2$ and $^{243}AmO_2$ (Hurtgen and Fuger, 1977; Benedict and Dufour, 1980). Benedict and Dufour (1980) studied the variation of the lattice parameter, of the thermal linear expansion, and of the coefficient of thermal linear expansion for AmO_2 in the range 38–300 K. Upon cooling, AmO_2 contracts more strongly than the dioxides of the lower actinides. The lattice parameters quoted in Table 8.3 represent an extrapolation to zero time for both $^{241}AmO_2$ and $^{243}AmO_2$ (Fahey *et al.*, 1974; Hurtgen and Fuger, 1977).

There is no evidence for any binary oxide of americium higher than AmO_2 (Katz and Gruen, 1949; Templeton and Dauben, 1953). However, ternary oxides are known for Am(III) through Am(VI) (Keller, 1964, 1965; Keller *et al.*, 1965b; Radzewitz, 1966; Mosley, 1970; Keller *et al.*, 1972; Keller and Berndt, 1975; Hoekstra and Gebert, 1978). Stabilization of high oxidation states in complex oxides is frequently observed (Keller, 1964, 1967; Morss, 1982); excellent examples are the thermally stable Am(VI) compounds Cs_2AmO_4 and Ba_3AmO_6. Most complex oxides of americium have been prepared by Keller and Hoekstra and their coworkers (Keller, 1964, 1967; Keller *et al.*, 1965b; Hoekstra and Gebert, 1978).

Initially, americium was prepared in significant quantities as $Am(OH)_3$ and to date hydroxide phases are known for the oxidation states III–VI. Isostructural to its chemical analog $Nd(OH)_3$, the Am(III) hydroxide is by far the most important americium hydroxide for separation and purification purposes and its solubility has been widely studied. The pinkish amorphous hydroxide precipitates by addition of dilute hydroxide to Am(III) solutions under ambient conditions. Rod-like microcrystalline $Am(OH)_3$, similar to $Nd(OH)_3$, is obtained in water after heating at 80°C for about 90 min (Milligan and Beasley, 1968). The transformation rate depends on various experimental parameters, such as solution composition, basicity, temperature, radiolysis, and the (pre)treatment of the precipitate. The crystalline phase can also be obtained by boiling a $^{241}Am(OH)_3$ suspension in 5 M NaOH (Silva, 1982) or hydration of Am_2O_3 with steam at 225°C (Morss and Williams, 1994). The destruction of the crystalline phase by its own alpha-radiation depends strongly on the specific activity of the isotope used: complete degradation is obtained within 1 day using $^{244}Cm(III)$ (specific activity 3000 MBq mg^{-1}) and 5 months with $^{241}Am(III)$ (specific activity 120 MBq mg^{-1}) (Haire *et al.*, 1977). The complex aging behavior of $Am(OH)_3$ in aqueous solutions and the changes in particle size result in large differences in its solubility. Nevertheless, two thermodynamic solubility products for the reaction

$$\mathrm{Am(OH)_3 + 3H^+ = Am^{3+} + 3H_2O}$$

have been recommended: $\log K^\circ = 15.2 \pm 0.6$ for crystalline $Am(OH)_3$ and 17.0 ± 0.6 for amorphous $Am(OH)_3$ (Silva *et al.*, 1995).

Few attempts to prepare and characterize $Am(OH)_4$ were reported, probably due to the instability of Am(IV). A black precipitate of $Am(OH)_4$ was obtained by heating $Am(OH)_3$ at 90°C in 0.2 M NaOH with NaOCl or in 7 M KOH with peroxydisulfate (Penneman *et al.*, 1961). The dissolution of this precipitate in sulfuric or nitric acid leads to a mixture of Am(III), Am(V), and Am(VI). Structural and thermodynamic data on $Am(OH)_4$ are not known. $AmO_2(OH)$ has been suggested to precipitate in slightly basic concentrated NaCl solutions under inert atmosphere but the amorphous character of the solid phase inhibited characterization (Magirius *et al.*, 1985; Stadler and Kim, 1988; Giffaut and Vitorge, 1993; Runde and Kim, 1994; Runde *et al.*, 1996). In more concentrated hydroxide solutions ternary Am(V) hydroxides, yellow $MAmO_2(OH)_2 \cdot nH_2O$ at 0.1–0.5 M OH^- and rose-colored $M_2AmO_2(OH)_3 \cdot nH_2O$ (M = Na, K, Rb, Cs) at 0.5–2.0 M OH^- (Tananaev, 1990b, 1991), form, and were characterized by X-ray diffraction. Only the lithium compound appeared to be stable over the entire range of hydroxide concentrations. No information on Am(VI) hydroxides is available.

(b) Hydrides

Olson and Mulford (1966) characterized the ^{241}Am–hydrogen system and found parallels to the lanthanides. The reported AmH_{2+x} (fcc) phase is isostructural with NpH_{2+x}, PuH_{2+x}, and most of the rare earth dihydrides (Roddy, 1973). There is also a phase that approximates hexagonal AmH_3. Although the lattice parameters were reported to be $a_0 = 3.77$ Å and $c_0 = 6.75$ Å (Olson and Mulford, 1966), Keller (1971) has pointed out that recent data on HoD_3 makes the most probable space group $P3c1$ (lattice parameters are given in Table 8.3). A study by Roddy (1973) with ^{243}Am essentially confirms this conclusion.

(c) Halides

A number of americium halides have been synthesized with americium in oxidation states II–VI and the halide systems have been studied extensively. Most remarkable are the halides of americium in extreme oxidation states, i.e. divalent and hexavalent. While solid structures are rare for divalent americium compounds, the black halides, $AmCl_2$ and $AmBr_2$ (Baybarz, 1973b), and AmI_2 (Figure 8.8) (Baybarz and Asprey, 1972) were prepared by reacting metallic americium with the corresponding mercuric halides at 300–400°C. The dihalides cannot be prepared by hydrogen reduction of the Am(III) halides, although hydrogen reduction is successful for the chemical analog lanthanides Sm, Eu, and Yb. Interestingly, all three compounds crystallize in different lattices: orthorhombic $AmCl_2$, tetragonal $AmBr_2$, and monoclinic AmI_2.

(1) Am(III): A number of Am(III) halides have been synthesized and their compositions range from binary AmX_3 adducts such as $AmCl_3 \cdot MCl$ where MCl is LiCl, CsCl, $(C_4H_9)_4NCl$, or $(C_2H_5)_4NCl$, to ternary complexes, i.e. $MAmX_4$, M_2AmX_5, KAm_2F_7, and M_2AmX_6 and M_3AmX_3. In addition, Bagnall *et al.* (1968) and Morss *et al.* (1970) made the cubic derivative $Cs_2NaAmCl_6$, in which the americium atoms are surrounded by six chlorides in an octahedral environment. The iodide AmI_3 is the only actinide triiodide known to be dimorphic; spectrophotometric observations indicate a pressure-induced phase transition from the rhombohedral to the orthorhombic structure (Haire *et al.*, 1985). The compound $(NH_4)_2AmCl_5$ decomposes at 300°C under vacuum to form $AmCl_3$ (Schleid *et al.*, 1987). Crystal structures have been reported for AmF_3 (Templeton and Dauben, 1953), $AmCl_3$ (Burns and Peterson, 1970) and $AmCl_3 \cdot 6H_2O$ (Burns and Peterson, 1971), $AmBr_3$ and AmI_3 (Zachariasen, 1948b; Baybarz and Asprey, 1972), and AmOX (X = Cl Figure 8.8 (Templeton and Dauben, 1953), Br (Weigel *et al.*, 1979) and I (Baybarz and Asprey, 1972)). Octahedral $AmCl_6^{3-}$and $AmBr_6^{3-}$ can be prepared as triphenyl phosphonium salts in anhydrous ethanol (Ryan, 1967; Marcus and Bomse, 1970).

(2) Am(IV): Orange-pink crystals of orthorhombic Rb_2AmF_6 form in concentrated aqueous fluoride solutions with $RbAmO_2F_2$ or $Am(OH)_4$ (Kruse and Asprey, 1962).

(3) Am(V): The ternary Am(V) fluorides, $KAmO_2F_2$ (Asprey *et al.*, 1954a) and $RbAmO_2F_2$, precipitate from concentrated aqueous fluoride solutions of Am(V) and consist of $AmO_2F_2^-$ connected by K^+ or Rb^+ cations. In contact with acidic RbF solution, $RbAmO_2F_2$ reduces overnight to Rb_2AmF_6 (Kruse and Asprey, 1962). The green chloride $Cs_3AmO_2Cl_4$ precipitates with ethanol from 6 M HCl containing Am(V) hydroxide and CsCl (Bagnall *et al.*, 1968) and is isostructural with the analogous Np(V) compound (Bagnall *et al.*, 1967).

(4) Am(VI): The binary Am(VI) fluoride AmO_2F_2 was prepared by reacting solid sodium Am(VI) acetate with anhydrous HF containing a small amount of F_2 at −196°C (Keenan, 1968). The compound is isostructural with other actinyl(VI) fluorides. Dark-red $Cs_2AmO_2Cl_4$ is obtained by the unusual oxidation of $Cs_3AmO_2Cl_4$ in concentrated HCl (Bagnall *et al.*, 1967). The cubic form of $Cs_2AmO_2Cl_4$ appears to transform to a monoclinic form when washed with small volumes of concentrated HCl (Bagnall *et al.*, 1968). It is suggested that the cubic form is probably a mixed oxidation state compound of formula $Cs_7(AmO_2)(AmO_2)_2Cl_{12}$ (Melkaya *et al.*, 1982).

Conflicting claims have been put forth concerning the existence of AmF_6. Drobyshevskii *et al.* (1980) reported generating a solid by reaction of AmF_3

with KrF_2 in anhydrous HF and inferred its composition to be AmF_6 based upon its volatility, IR spectrum, and hydrolysis to AmO_2^{2+}; the IR absorption band at $604 \pm 3\ cm^{-1}$ is expected for the ν_3 mode of AmF_6. Fargeas *et al.* (1986) also inferred the existence of AmF_6 in their experiments from thermochromatography data. Most recently, Gibson and Haire (1992b) report that they were not able to confirm the existence of AmF_6; in their words, "... but have not been able to identify or provide evidence for the elusive and controversial AmF_6 species, despite having invoked several synthetic approaches and the sensitive analytical tool of mass spectrometry." Given these latest results, we have elected not to list AmF_6 among the identified inorganic compounds of americium in Table 8.5. It is interesting to note, however, that the proposed hexachloro compound of Am(VI) appears to be sufficiently stable to permit X-ray crystallographic studies.

(d) Chalcogenides and pnictides

The chalcogenides of americium comprise a number of compounds with the general formula AmX (X = S, Se, Te), $AmTe_2$, Am_3X_4 (X = S, Se, Te), AmX_3 (X = S, Se, Te), Am_2X_3 (X = S, Se, Te), and substoichiometric compounds AmX_{2-n} (X = S, Se). Some structural and synthetic properties of these chalcogenides, insofar as they have been determined, are briefly listed in Table 8.5; additional details concerning these compounds are provided in this section. The authors of this chapter are not aware that the chalcogenides are of any but academic interest.

The reaction of AmH_3 with stoichiometric amounts of selenium or telluride metal at 800°C in a vacuum yields the monochalcogenides AmSe and AmTe, respectively (Charvillat *et al.*, 1975a, 1977). Further heating of the monochalcogenides at 1100–1200°C produces Am_3X_4 and a second phase that was identified as (probably unreacted) AmX (Charvillat *et al.*, 1975a, 1977). In contrast, α-Am_2S_3 and not AmS is obtained when AmH_3 is heated with elemental sulfur at 500°C; it decomposes to γ-Am_2S_3 and AmS when heated in a vacuum above 650°C (Damien, 1971).

Americium sesquisulfide exhibits a complex structural chemistry and apparently exists in three different crystalline forms. α-Am_2S_3 is obtained 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 (Damien, 1971). The quartz end of the tube is heated at 500°C and the Pyrex part is maintained at 300°C to prevent sulfur from condensing. According to Damien *et al.* (1972), α-Am_2S_3 transforms into β-Am_2S_3 when heated at 1100°C. However, the existence of the β-form of americium sesquisulfide is seriously in doubt since the same French scientists believe that β-Am_2S_3 is better considered an oxysulfide, namely $Am_{10}S_{14}O$. When heated in a vacuum at 1300°C, α-Am_2S_3 changes to pure γ-Am_2S_3 (Damien, 1971). The pure γ-Am_2S_3 can also be prepared by passing a mixture of H_2S and CS_2 over heated (1400–1500°C) AmO_2 for 5 min

(Fried, 1951). Zachariasen (1949d) determined the crystal structure of γ-Am_2S_3. Am_2Te_3 is formed by dissociation of $AmTe_2$ at 600°C and is isostructural with the rare earth sesquitellurides (η-form) (Damien and Charvillat, 1972). The Am_2Te_3 phase is stable up to around 850°C and transforms into Am_3Te_4 above 900°C. No sesquiselenide of americium has been reported.

The only americium trichalcogenide yet reported, $AmTe_3$, is prepared by vapor-phase reaction of AmH_3 with excess tellurium for 120 h at 350°C (Damien, 1972; Burns *et al.*, 1979). Orthorhombic $AmTe_3$ is isostructural with the corresponding rare earth tritellurides and is used as a precursor for the synthesis of a number of americium/tellurium compounds. In a high vacuum at 400°C, $AmTe_3$ dissociates to tetragonal $AmTe_2$, which is the only stoichiometric americium dichalcogenide. $AmTe_2$ is isostructural with the rare earth ditellurides and most likely has the Fe_2As-type structure. Roddy (1974) prepared what appeared to be tetragonal $AmSe_2$ by heating ^{243}Am metal or hydride with selenium metal for 24 h at 950°C. However, although two research groups (Charvillat *et al.*, 1977; Burns *et al.*, 1979) reported the preparation and properties of $AmTe_2$, Damien and Jove (1971) state that the $AmTe_2$ prepared as described above is rather a tellurium-deficient compound $AmTe_{2-x}$ with a large homogeneity range between 400 and 600°C. The same homogeneity range seems to exist in the Am–S and Am–Se system and the dichalcogenides actually have a composition near $AmS_{1.9}$ and $AmSe_{1.8}$. The black non-stoichiometric compounds are prepared by heating an excess of sulfur or selenium metal with AmH_3 for 1 week at 400°C under high vacuum (Damien and Jove, 1971).

The americium chalcogenides Am_3Se_4 and Am_3Te_4 are isostructural (bcc) with Th_3P_4 and are without magnetic ordering down to 4.2 K (Dunlap *et al.*, 1972). Both compounds can be prepared by heating ^{243}Am metal with elemental selenium or tellurium for 24 h at 950°C (Roddy, 1974). However, X-ray diffraction measurements show that this synthesis contains at least one other phase (Dunlap *et al.*, 1972). Am_3Se_4 (bcc) is also formed when a mixture of 50 mass% americium metal and 50 mass% elemental selenium is heated for 1 h at 217°C and then for 7 h at 850°C before cooling to room temperature (Mitchell and Lam, 1970a). Am_3Te_4 also forms by decomposition of η-Am_2Te_3 at 900°C (Damien and Charvillat, 1972).

Compounds of americium with all group VB elements N, P, As, Sb, and Bi have been prepared. While AmN is of most interest due to its potential use as nuclear reactor fuel, the americium pnictides are mainly of academic interest. Ogawa *et al.* (1997) note that certain actinide nitrides, e.g. UN, NpN, PuN, can be fabricated by carbothermic reduction of their oxides in a nitrogen atmosphere. Based upon the thermodynamics of the carbothermic synthesis of AmN, calculations indicate that the carbothermic preparation of AmN would be much more difficult than preparation of either UN or PuN.

Americium nitride, AmN, was first prepared by reacting AmH_3 (above 800°C) or americium metal (at 750°C) with nitrogen (Akimoto, 1967; Tagawa, 1971) or in a 99.9% N_2/0.1% H_2 atmosphere (Radchenko *et al.*, 1982). Potter and Tennery (1973) disclosed a cyclic process to prepare finely divided AmN, which consists of incrementally dehydriding AmH_3 and nitriding the metal. Charvillat *et al.* (1975a, 1977) prepared milligram quantities of AmN by heating AmH_3 at 550°C under high-purity nitrogen in a sealed tube. A review of the phase behavior and crystal structure of actinide nitrides has been published (Tagawa, 1971).

The only reported synthesis of AmP was published a quarter of a century ago. Charvillat *et al.* (1975a,b, 1977) synthesized AmP by reacting red phosphorus with AmH_3 in a sealed quartz tube at 580°C.

The product of the vapor-phase reaction of excess elemental arsenic with $^{241}AmH_3$ at 330°C contains both unreacted elemental arsenic and a cubic phase that was assigned as AmAs by analogy with the corresponding NpAs and PuAs (Charvillat and Damien, 1973). Heating ^{243}Am metal and elemental arsenic for 24 h at 675°C and then 7 days at 400°C produces AmAs with slightly higher lattice parameters (Roddy, 1974). However, a slight decrease in the lattice parameters is observed after heating AmAs for 10 h at 1000°C. Weak lines that correspond to AmO are observed in the X-ray diffraction pattern of the resulting product indicating the existence of a solid solution between AmAs and AmO. The slight difference in lattice parameters may have been the result of an isotope effect or may be attributed to other minor americium oxide impurities.

The reaction of ^{243}Am metal with elemental antimony for 23 h at 775–900°C in an evacuated quartz bulb yielded cubic AmSb (Roddy, 1974). Cubic AmSb with almost the same lattice parameters was obtained by heating equimolar amounts of ^{241}Am metal and high-purity elemental antimony under vacuum for 1 h at 630°C (Mitchell and Lam, 1970a). The temperature was gradually raised to 850°C and held at this temperature for 7 h before cooling to room temperature. Finally, the resulting AmSb was heated at 1000°C for 24 h, cooled, and then heated again at 400°C for 10 days. The reaction of a 4:3 stoichiometric ratio of $^{241}AmH_3$: elemental antimony in a Pyrex tube at 550°C produced two phases, AmSb and a second phase with the bcc structure of anti-Th_3P_4-type (Charvillat *et al.*, 1975b).

Like AmP, AmBi has also been investigated. Roddy (1974) produced AmBi by reaction of metallic bismuth vapor with either americium metal or americium hydride in a sealed, evacuated quartz tube for 48 h at 975°C.

The magnetic susceptibilities of actinide chalcogenides and pnictides can be fit by the modified Curie–Weiss law:

$$\chi_{\text{measured}} = \chi_{\text{Curie+Weiss}} + \chi_0 = (C/(T - \theta_{\text{para}})) + \chi_0$$

where C is the Curie constant, θ_{para} is the paramagnetic Curie temperature, and χ_0 is a generally temperature-independent additional term. For the americium compounds, the Curie–Weiss term vanishes and experimentally determined values for χ_0 are reported to be 777 for AmN, 550 for AmAs, 1250 for AmSb, and 500 for AmBi (Kanellakopulos *et al.*, 1975; Vogt *et al.*, 1998).

The effective magnetic moment of AmN is 136 Bohr magnetons (Nellis and Brodsky, 1974; Kanellakopulos *et al.*, 1975) and that of AmAs is 1.14 Bohr magnetons (Kanellakopulos *et al.*, 1975). Kanellakopulos measured the magnetic susceptibility of AmAs between liquid helium and room temperature and observed an antiferromagnetic transition at 13 K. Magnetic susceptibility measurements on AmSb show a temperature-independent value of $\chi_0 = (1250 \pm 100) \times 10^{-6}$ emu mol^{-1} for the range 4.2 K $< T <$ 320 K (Dunlap *et al.*, 1972).

(e) Carbides and carbonates

The binary Am(III) carbide, Am_2C_3, is the only known carbide of americium and is prepared by arc melting americium metal with high-purity graphite in an argon–helium atmosphere (Mitchell and Lam, 1970b). The compound is isostructural with Pu_2C_3.

Carbonate compounds of Am(III) and Am(V) have been synthesized and characterized. They are applied in separation processes and also may form under environmental conditions. No solid carbonates of Am(IV) or Am(VI) are known.

(1) Am(III): The binary Am(III) carbonate, $Am_2(CO_3)_3$, precipitates from a CO_2-saturated solution of $NaHCO_3$ (Meinrath and Kim, 1991b; Runde and Kim, 1994). Thermogravimetric analysis of the precipitated binary compound suggests the formula $Am_2(CO_3)_3 \cdot 2H_2O$ (Weigel and ter Meer, 1967) or $Am_2(CO_3)_3 \cdot 4H_2O$ (Keller and Fang, 1969). The ternary compounds $NaAm(CO_3)_2 \cdot 4H_2O$ and $Na_3Am(CO_3)_3 \cdot 3H_2O$ precipitate from 0.5 M $NaHCO_3$ and 1.5 M Na_2CO_3 solutions, respectively (Keller and Fang, 1969). In analogy to neodymium and europium hydroxycarbonates, orthorhombic $AmOHCO_3$ was characterized by X-ray powder diffraction data (Meinrath and Kim, 1991b; Runde *et al.*, 1992), but the formation of its hexagonal form (Standifer and Nitsche, 1988) could not be confirmed.

(2) Am(V): A number of 'double carbonates' of general formula $MAmO_2CO_3$ where M = K (Nigon *et al.*, 1954; Volkov *et al.*, 1974), Na (Nigon *et al.*, 1954; Runde and Kim, 1994), Rb, Cs, NH_4 (Nigon *et al.*, 1954) have been synthesized by precipitation of Am(V) in dilute bicarbonate solutions of the corresponding cation. The use of large excess of alkali carbonate yields the $K_3AmO_2(CO_3)_2$ and $K_5AmO_2(CO_3)_3$ solids (Yakovlev and Gorbenko-Germanov, 1955; Volkov *et al.*, 1981).

(f) Phosphates and sulfates

Light pink $AmPO_4 \cdot xH_2O$ precipitates by adding dilute solutions of H_3PO_4, Na_2HPO_4, or $(NH_4)_2HPO_4$ to a weakly acidic Am^{3+} solution (Lawaldt *et al.*, 1982; Fedoseev and Perminov, 1983; Rai *et al.*, 1992). Rai and coworkers suggest the precipitation of $AmPO_4 \cdot xH_2O$ from dilute acidic solution but the study lacks characterization of the solid phase. Dehydration of the hydrous precipitate yields hexagonal $AmPO_4 \cdot 0.5H_2O$ at 200°C and $AmPO_4$ at higher temperatures up to 1000°C. The anhydrous compound can also be obtained by reacting AmO_2 with stoichiometric amounts of $(NH_4)_2HPO_4$ at 600–1000°C.

Because of the tendency of Am(VI) towards reduction to Am(V) at near-neutral pH, Am(VI) phosphates can be precipitated only in the narrow pH range of 3.5–4. Four ternary Am(VI) phosphates $MAmPO_4 \cdot xH_2O$ with M = NH_4, K, Rb, Cs have been prepared by Lawaldt *et al.* (1982) by precipitating Am(VI) in 0.1 M H_3PO_4 after adjusting the pH with the corresponding carbonate solution.

Binary sulfate compounds are known for Am(III), Am(V), and Am(VI), especially a large number of double sulfates of Am(III).

(1) Am(III): Evaporation of a neutral solution of ^{243}Am(III) sulfate yields thick, up to 0.5 mm long, tabular, pale yellow-pink crystals of $Am_2(SO_4)_3 \cdot 8H_2O$ (Burns and Baybarz, 1972). Crystals of the octahydrate, after being dried in air, are stable to change in their degree of hydration for several days. On the basis of analyses for americium, sulfate, and water, Yakovlev *et al.* (1958) 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. The white anhydrous Am(III) sulfate, $Am_2(SO_4)_3$, is prepared by heating the hydrate to a temperature of 500–600°C in air (Hall and Markin, 1957). Anhydrous americium sulfate does not take up water when cooled to room temperature in air.

    A number of double sulfates of Am(III) with formulas $MAm(SO_4)_2 \cdot xH_2O$ (M = K, Na, Rb, Cs, Tl; x = 0, 1, 2, 4), $K_3Am(SO_4)_3 \cdot xH_2O$, and $M_8Am_2(SO_4)_7$ (M = K, Cs, Tl) have been prepared by adding a metal sulfate solution to a solution of Am^{3+} in 0.5 M H_2SO_4. The concentration ratios M^+/Am^{3+} for the preparation of the various double sulfates as well as the absorption spectra of some Am(III) double sulfates at 80, 200, and 300 K are given by Yakovlev *et al.* (1958). Surprisingly, no X-ray diffraction data were reported for these double sulfates. Coprecipitation of trace amounts of Am(III) with K_2SO_4 and $La_2(SO_4)_3$ has also been published (Grebenshschikova and Babrova, 1958, 1961; Grebenshschikova and Cheinyavskaya, 1962).

(2) Am(V): Fedoseev and Budentseva (1989) claimed the preparation of three solid sulfates of Am(V). $(AmO_2)_2(SO_4) \cdot xH_2O$ crystallizes upon evaporation of an Am(V)-containing sulfuric acid solution. Am(V) sulfate also crystallizes from an ozonated solution of $Am(OH)_3$ after addition of sulfuric acid and subsequent evaporation. Two double salts have been reported: Large light green crystals of $CsAmO_2SO_4 \cdot xH_2O$ were obtained by evaporating a solution containing $(AmO_2)_2(SO_4)$ and Cs_2SO_4 in a 3:1 ratio. According to Fedoseev and Budentseva $Co(NH_3)_6AmO_2(SO_4)_2 \cdot 2H_2O$ can be easily

made by simply including Am(v) among the reagents used to prepare $Co(NH_3)_6(SO_4)_2$.

(3) Am(vi): Addition of hexamine cobalt(iii) ions to an aqueous sulfate solution containing hexavalent americium yields orange cubic crystals of $Co(NH_3)_6(HSO_4)_2(AmO_2(SO_4)_3) \cdot nH_2O$ (Ueno and Hoshi, 1971). The compound is isostructural with the corresponding uranyl and neptunyl compounds. No precipitate forms, however, in an ammonium sulfate solution containing Am(iii) and hexamine cobalt(iii) ions.

(g) Other inorganic compounds

Shirokova *et al.* (2001) reported the complexation of Am(iii) with *N*,*N*-dimethylacetamide and the Keggin-type heteropolyanion $PW_{12}O_{40}^{3+}$. Lawaldt *et al.* (1982) applied the same procedures as used to prepare Am(vi) phosphates for the precipitation of Am(vi) arsenates. The obtained compounds were isostructural to the analogous Am(vi) phosphates.

Only two phases, AmB_4 and AmB_6, have been reported in the boride system in contrast to the richer Np–B system with four phases (Eick and Mulford, 1969).

Weigel *et al.* (1977, 1984) reported the formation of several silicide phases upon reacting AmF_3 with elemental Si at different temperatures. Up to 950°C, the phases Am_5Si_3, AmSi, Am_2Si_3, and $AmSi_2$ have been characterized by X-ray powder diffraction. Orthorhombic AmSi is also prepared at 1050°C and the substoichiometric tetragonal phase $AmSi_x$ ($1.87 < x < 2.0$) forms at 1150–1200°C.

The only silicate known to date, $AmSiO_4$, is obtained as a brown solid by reacting $Am(OH)_4$ with excess SiO_2 in 1 M $NaHCO_3$ solution at 230°C for 1 week (Katz and Seaborg, 1957). $^{241}AmSiO_4$ is patented for the use in manufactured alpha sources.

Large orange needle-like crystals thought to be $AmO_2CrO_4 \cdot H_2O$ were prepared by slowly evaporating a chromic acid (H_2CrO_4) solution containing Am(v) (Fedoseev *et al.*, 1991). Although there is some spectroscopic evidence for the presence of Am(v) in the solid chromate (electronic absorbances at about 518 and 728 nm) the suggested formula of $AmO_2CrO_4 \cdot H_2O$ appears to be erroneous and should rather be $(AmO_2)_2CrO_4 \cdot H_2O$.

Tabuteau and coworkers (Tabuteau *et al.*, 1972; Tabuteau and Pages, 1978) investigated the Am–molybdate and Am–tungstate systems. The solid state reaction of stoichiometric amounts of AmO_2 and MoO_3 or WO_3 at 1080°C resulted in the formation of monoclinic $Am_2(MoO_4)_3$ and $Am_2(WO_4)_3$. Two ternary phases, $KAm(MoO_4)_2$ and $K_5Am(MoO_4)_4$, were found to form at 650°C in the presence of potassium. Fedoseev and Budantseva (1990) report the synthesis of $AmO_2Mo_2O_7 \cdot 3H_2O$ at 100°C, however, no information on the phase characterization was provided.

8.7.2 Compounds of americium with organic ligands

Relatively few solid compounds of americium with organic ligands have been prepared; these are listed in Table 8.6. For detailed reviews of this chemistry see Kanellakopulos (1979) and also Chapters 23 and 25.

(a) Oxalate

Because of its importance for americium separation chemistry $Am_2(C_2O_4)_3 \cdot xH_2O$ (Weigel and ter Meer, 1967) is the most important organic compound of americium. The pink solid precipitates from slightly acidic or neutral solutions of Am^{3+} on addition of oxalic acid or alkali oxalate solution. The hydration number x was previously thought to vary with conditions of preparation and drying and values of 7 (Markin, 1958), 9 (Yakovlev and Kosyakov, 1958a), and 11 (Staritzky and Truitt, 1954) have been reported. Based on their X-ray diffraction studies and in analogy to Nd(III), Pu(III), and Cm(III), Weigel and ter Meer (1967) concluded that the hydration number x is 10. The decahydrate decomposes to the anhydrous form at 340°C through several hydrates and further decomposes to carbonate $Am_2(CO_3)_3$ at about 430°C. The oxalate complexes with general formula $MAm(C_2O_4)_2 \cdot xH_2O$ have been prepared from Am(III) oxalate and $M_2C_2O_4$ ($M = NH_4$, Na, K, Cs) in neutral solution (Zubarev and Krot, 1982, 1983a,b).

(b) Formate

Pink crystals of hexagonal $Am(HCOO) \cdot 0.2H_2O$ form upon evaporation of a concentrated formic acid solution (Weigel and ter Meer, 1967). The formate decomposes at 300–350°C to AmO(HCOO), and at 400–500°C to the oxycarbonate $Am_2O_3CO_3$, which forms at 520°C the sesquioxide Am_2O_3 (Weigel and ter Meer, 1971).

(c) Acetate

Addition of sodium acetate to an acidic Am(VI) solution precipitates lemon-yellow cubic crystals of $NaAmO_2(OOCCH_3)_3$ (Asprey *et al.*, 1950, 1951). The force constant of the Am–O bond in $NaAmO_2(OOCCH_3)_3$ is determined to be 6.12 megadynes/Å (Jones, 1953). The refractive index is 1.528 ± 0.002 (Asprey *et al.*, 1951).

(d) Acetone derivate compounds

Addition of ammonia to aqueous Am^{3+} solution that contains a small amount of acetylacetone precipitates pale-rose $Am(C_5H_7O_2)_3 \cdot H_2O$ at pH 6. The precipitate can be recrystallized in ethanol and dried in air over silica gel or P_2O_5 (Keller and Schreck, 1969). Dropwise addition of aqueous Am^{3+} (pH 4.5) to warm, slightly less than stoichiometric amounts of ammonium benzoylacetone yields pale-rose $Am(C_{10}H_6F_3O_2)_3 \cdot 3H_2O$. Both compounds decompose in air at

Table 8.6 *Organic compounds of americium.*

Organic ligand	*Formula of compound*	*Comments*	*References*
Acetate	$NaAmO_2(OOCCH_3)_3$	lemon yellow	[1]
acetylacetone	$Am(C_5H_7O_2)_3 \cdot H_2O$	pale rose	[2]
benzoyltrifluoroacetone	$Am(C_{10}H_6F_3O_2)_3 \cdot 3H_2O$	pale rose	[2]
cyclooctatetraene	$KAm(C_8H_8)_2 \cdot 2THF^a$	yellow	[3]
cyclopentadiene	$Am(C_5H_5)_3$	flesh	[4]
dipivalomethane	$Am(C_{11}H_{19}O_2)_3$		[5]
formate	$Am(HCOO)_3 \cdot 0.2H_2O$	pink	[6]
hexafluoroacetylacetone	$CsAm(C_5HF_6O_2)_4 \cdot H_2O$	yellow	[7]
hexafluoroacetyl-acetone/TBP	$Am(C_5HF_6O_2)_3 \cdot 2(C_4H_9O)_3PO$	volatile, 175°C	[8]
8-hydroxyquinoline	$Am(C_9H_6NO)_3$	yellow-green	[9]
5-chloro-8-hydroxyquinoline	$Am(C_9H_5ClNO)_3$	dark green	[9]
5,7-dichloro-8-hydroxyquinoline	$Am(C_9H_4Cl_2NO)_3$	green	[9]
oxalate	$Am_2(C_2O_4)_3 \cdot 10H_2O$	pink	[10]
	$KAmO_2C_2O_4 \cdot xH_2O$	color varies from pink to brick red depending on preparation conditions	[11]
	$CsAmO_2C_2O_4 \cdot xH_2O$	green, cubic ($a = 12.5$ Å)	[11]
	$MAmO_2C_2O_4 \cdot xH_2O$	$M = NH_4$, Na	[11]
phthalocyanine	$Am(C_{32}H_{16}N_2)_2$	dark violet	[12]
pyridine-2-carboxylate	$AmO_2(C_5H_4NCOO)_2$	red-brown	[13]
	$HAmO_2(C_5H_4NCOO)_3$	red-brown	[13]
pyridine-*N*-oxo-carboxylate	$AmO_2[C_5H_4N(O)COO]_2$		[14]
salicylate	$Am(C_7H_5O_3)_3 \cdot H_2O$		[15]
thenoyltrifluoroacetate	$Am(C_5H_4F_3O_2S)_3 \cdot 3H_2O$	pale rose	[2]

[a] THF, tetrahydrofuran.

[1] (Asprey *et al.*, 1950, 1951, 1954b); [2] (Keller and Schreck, 1969); [3] (Karraker, 1975, 1977); [4] (Baumgärtner *et al.*, 1966a, 1977; Kanellakopoulos *et al.*, 1970, 1978; Seaborg, 1972); [5] (Danford *et al.*, 1970; Moore, 1970; Sakanoue and Amano, 1975); [6] (Lebedev *et al.*, 1960b, 1962); [7] (Burns and Danford, 1969; Danford *et al.*, 1970; Bagnall, 1972; Sakanoue and Amano, 1975); [8] (Davydov *et al.*, 1975); [9] (Keller *et al.*, 1965a, 1966); [10] (Eyring *et al.*, 1952; Yakovlev and Kosyakov, 1958b; Lebedev *et al.*, 1960a; Weigel *et al.*, 1966; Burney and Porter, 1967; Chikalla and Eyring, 1967; Weigel and ter Meer, 1967, 1971); [11] (Zubarev and Krot, 1982, 1983a); [12] (Kirin *et al.*, 1967; Lux, 1973); [13] (Eberle and Robel, 1970; Robel, 1970); [14] (Robel, 1970); [15] (Burns and Baldwin, 1977).

above 200°C to AmO_2. Yellow $CsAm(C_5HF_6O_2)_4 \cdot H_2O$ crystallizes from $AmCl_3$ solution after addition of excess cesium hexafluoroacetylacetone in 50 vol% ethanol (Burns and Danford, 1969; Danford *et al.*, 1970).

(e) Cyclooctatetraene and cyclopentadiene

Reaction of $^{241}AmI_3$ with $K_2C_8H_8$ in tetrahydrofuran (THF) solution yields the adduct $KAm(C_8H_8)_2 \cdot 2THF$, which is isostructural with its plutonium analog $KPu(C_8H_8)_2 \cdot 2THF$ (Karraker, 1975). The compound decomposes in water and burns in air. Reacting the halides AmF_3 (Moore, 1970) or $AmCl_3$ (Baumgärtner *et al.*, 1966a,b; Kanellakopoulos *et al.*, 1970; Seaborg, 1972) with molten $Be(C_5H_5)_2$ at 65–70°C produces $Am(C_5H_5)_3$ (Moore, 1970). The pure compound can be obtained by fractional sublimation at 10^{-5} Torr and 160–205°C (Baumgärtner *et al.*, 1966a,b). Unlike $Pu(C_5H_5)_3$, $Am(C_5H_5)_3$ is not pyrophoric and decomposes only slowly in air. The IR and absorption spectra of $Am(C_5H_5)_3$ have been reported (Pappalardo *et al.*, 1969a; Kanellakopoulos *et al.*, 1970).

(f) Others

Reaction of AmI_3 at 200°C with phthalodinitride in 1-chloronaphthalene yields the dark violet phthalocyanine compound $Am(C_{32}H_{16}N_8)_2$, which was the first synthesized Am(IV) compound with an organic ligand (Lux, 1973). There is evidence that americium also forms the monophthalocyaninato complex.

Danford *et al.* (1970) precipitated the dipivaloylmethane compound $Am(C_{11}H_{19}O_2)_3$ by adding aqueous Am(III) sulfate to a solution of dipivaloylmethane and NaOH in 70% aqueous ethanol. Sakanoue and Amano (1975) determined the volatility of $Am(C_{11}H_{19}O_2)_3$ and several lanthanide and actinide analog complexes at 180°C and 10^{-3} torr and observed that $Am(C_{11}H_{19}O_2)_3$ is less volatile than its analog compounds of Th, Pu, Cf, or Eu, Gd, or Sc.

The only recorded aliphatic compounds of americium appear to be the citrates $Am(C_6H_5O_7) \cdot xH_2O$ and $[Co(NH_3)_6][Am(C_6H_5O_7)_2] \cdot xH_2O$ (Bouhlassa, 1983), and the salicylate $Am(C_7H_5O_3)_3 \cdot H_2O$ (Burns and Baldwin, 1976); its structure is described in Section 8.9.2.

Hölgye (1982) studied the coprecipitation of Am(III) with various metal cupferrates. With cupferrates of lanthanides and Sc(III), Am(III) coprecipitated quantitatively. But Am(III) coprecipitated only partially with cupferrates of Fe(III), Cu(II), Al(III), In(III), Pb(II), and Bi(III).

8.8 AQUEOUS SOLUTION CHEMISTRY

8.8.1 Oxidation states

In aqueous solutions, americium exhibits the III, IV, V, and VI oxidation states. All four oxidation states can coexist under certain conditions in carbonate media (Bourges *et al.*, 1983). In dilute acid, only the aquo ions Am^{3+} and

AmO_2^{2+} ions are stable, whereas in alkaline solution, americium can exist in all four valence states. In the III and IV oxidation states, americium forms Am^{3+} and Am^{4+} ions in solution, respectively. The highly charged ions in the V and VI states are unstable and hydrolyze instantly to form the linear *trans*-dioxo americyl cations, AmO_2^+ and AmO_2^{2+}, respectively. Analogous to Np(VII) and Pu(VII), americium reportedly can be oxidized to the VII oxidation state in highly alkaline media (Krot *et al.*, 1974a,b; Myasoedov and Kremliakova, 1985).

(a) Preparation

(1) Am(II): In contrast to its chemical analog of the lanthanide series, europium, the divalent state of Am is unstable in aqueous solution. Conditions that stabilize Yb^{2+}, Eu^{2+}, or Sm^{2+} do not reduce Am^{3+} to Am^{2+} (Keenan, 1959). Milyukova *et al.* (1980) claimed electrochemical evidence for unstable Am(II) in acetonitrile; they found that Am(II) was rapidly oxidized to Am(III) by water in the solvent. Sullivan *et al.* (1976, 1978) formed transient Am(II) by pulse radiolysis with an absorption maximum at 313 nm and $t_{1/2} \sim 5 \times 10^{-6}$ s for disappearance. Am(II) can be accessed in the solid state and as dilute solution in CaF_2 (Zachariasen, 1948b; Fried, 1951; Pappalardo *et al.*, 1969b; Baybarz, 1973b; Peterson, 1973). The solid compounds $AmCl_2$ (Baybarz, 1973b), $AmBr_2$ (Baybarz, 1973b), and AmI_2 (Baybarz and Asprey, 1972) have been prepared and characterized.

(2) Am(III): Trivalent americium is the most common and stable oxidation state in aqueous solution. It can be easily prepared by dissolving the metal in acid, dissolving AmO_2 in hot HCl, or by reducing higher valent americium compounds with most common reducing agents, such as NH_2OH, SO_2, or KI (Coleman *et al.*, 1963). Acidic solutions of Am^{3+} are pink in mineral acids but are yellow in concentrated $HClO_4$ or when the Am^{3+} concentration exceeds 0.1 M. Numerous solid compounds of Am(III) have been prepared and characterized.

(3) Am(IV): Tetravalent americium is unstable in non-complexing solutions and is reduced spontaneously to its more stable III oxidation state. Stable Am(IV) can be prepared by dissolving $Am(OH)_4$ in concentrated NH_4F solutions (Asprey and Penneman, 1962). Yanir *et al.* (1969) demonstrated that Am(IV) remains stable in phosphoric and pyrophosphate media. Myasoedov *et al.* (1977) reported that pure Am(IV) is obtained in 8–15 M phosphoric acid by anodic oxidation, while at lower phosphoric acid concentrations impurities of Am(VI) are formed. Similar stability of Am(IV) was reported in an oxidizing mixture of Ag_3PO_4 and $(NH_4)_2S_2O_8$. Electrolytic oxidation of ^{243}Am(III) (<1 V) in 2–5.5 M carbonate solutions resulted in the formation of a golden-yellow Am(IV) carbonate species, which was slowly reduced to Am(III) (Hobart *et al.*, 1982). At potentials exceeding 1.1 V, Am(IV) is oxidized to Am(V) and Am(VI). Am(IV) can be stabilized with heteropolyanions and reduction to Am(III) is caused solely by radiolytic effects

(Saprykin *et al.*, 1976; Kosyakov *et al.*, 1977; Erin *et al.*, 1979). Transient Am(IV) has been observed by pulse radiolysis (Sullivan *et al.*, 1976, 1978).

(4) Am(V): Am(III) can be oxidized to Am(V) in near-neutral and alkaline solution. In acidic media, oxidation of Am(III) yields only Am(VI) because Am(V) is more easily oxidized to Am(VI) than Am(III) is oxidized to Am(V). Solutions of Am(V) can be prepared by oxidation of Am(III) with ozone (Keenan, 1965), hypochlorite (Yakovlev and Gorbenko-Germanov, 1955), and peroxydisulfate (Nigon *et al.*, 1954), or by reduction of Am(VI) with bromide, or by electrolysis (Hobart *et al.*, 1983b). Solid sodium Am(V) carbonate can be precipitated by heating a 2 M Na_2CO_3 Am(VI) solution for 60 min to 60°C (Coleman *et al.*, 1963). Dissolution of the solid in near-neutral solutions yields pure Am(V) solution free of Am(III) and Am(VI). AmO_2^+ solutions free of Am^{3+} can be prepared by first extracting AmO_2^+ from buffered 1 M acetate (pH 3) solutions into 0.1 M thenoyltrifluoroacetone in isobutanol and back-extraction into an aqueous phase (Hara, 1970). More exotic methods include the dissolution of solid Li_3AmO_4 in dilute perchloric acid or the electrolytic oxidation of Am(III) in 2 M $LiIO_3$/0.7 M HIO_3 solutions (pH 1.5) (Keller, 1971).

(5) Am(VI): Powerful oxidants, i.e. peroxydisulfate or Ag(II), oxidize Am(III) and Am(V) in dilute, non-reducing acidic solution to Am(VI) (Myasoedov and Kremliakova, 1985). At acidities above 0.5 M, peroxydisulfate will not oxidize Am(III) completely to Am(VI) because of the interference of acid hydrolysis of $S_2O_8^{2+}$ (Penneman and Asprey, 1955). Ce(IV) oxidizes Am(V) to Am(VI) but only partially oxidizes Am(III) to Am(VI) (Penneman and Asprey, 1955). Electrolytic oxidation of Am(III) in 2 M H_3PO_4 and 6 M $HClO_4$ leads to Am(VI) (Myasoedov *et al.*, 1977) while ozone does not oxidize Am(III) to Am(VI) in acidic medium. In aqueous 2 M carbonate solutions oxidation of Am(III), Am(IV), or Am(V) with ozone or oxidation with $Na_2S_2O_8$ yields an intensely colored red-brown carbonate complex of Am(VI) (Coleman *et al.*, 1963). This complex is also obtained electrolytically at a potential of 1.3 V vs NHE in sodium carbonate solutions (Hobart *et al.*, 1982) or by dissolution of sodium americyl(VI) acetate in sodium carbonate solutions. Ozone oxidation in carbonate solution yields Am(VI) only at 25°C or below while at 90°C oxidation does not proceed past Am(V). Ozone does not oxidize $Am(OH)_3$ or $KAmO_2CO_3$ in 0.1–0.5 M $KHCO_3$ and $K_2S_2O_8$ does not oxidize $Am(OH)_3$ or $NaAmO_2CO_3$ in 0.1 M $NaHCO_3$ (Coleman *et al.*, 1963). This difference to the easy oxidation by $Na_2S_2O_8$ is attributed to the lower solubility of $KAmO_2CO_3$ compared to $NaAmO_2CO_3$. In 0.1–0.5 M $NaHCO_3$, Am(VI) is stable at 90°C to reduction by H_2O, Cl^-, or Br^-, but is easily reduced by I^-, N_2H_4, H_2O_2, NO_2^-, and NH_2OH. Very slow reduction of Am(VI) occurs in 2 M Na_2CO_3. Yellow-colored solutions of Am(VI) in any alkali hydroxide solutions can be prepared by oxidation of solid $Am(OH)_3$ with ozone (Cohen, 1972). Am(VI) in alkali hydroxide solutions undergoes

gradual reduction to form a light-tan solid, which yields Am(v) when dissolved in mineral acid. It is claimed that Am(vi) disproportionates into Am(vii) and Am(v) in >10 M NaOH (Nikolaevskii *et al.*, 1975).

The reaction of KrF_2 with AmF_3 in anhydrous HF yields a dark-brown solid of AmF_6 with a vapor pressure that is similar to that of UF_6 (Drobyshevskii *et al.*, 1980).

(6) Am(vii): While attempts to synthesize Am(vii) from Li_2O–AmO_2 mixtures at 300–400°C failed, oxidation of 3–4 M NaOH solutions containing 0.001–0.002 M Am(vi) with ozone at 0–7°C yields a green-colored solution of Am(vii) (Krot *et al.*, 1974a,b; Myasoedov and Kremliakova, 1985). A similar green-colored solution can be obtained by ^{60}Co gamma irradiation at 0°C of a N_2O-saturated 3 M NaOH solution. (N_2O scavenges hydrated electrons by the reaction $N_2O + e^-\ (aq) \rightarrow N_2 + O^-$; $S_2O_8^{2-}$ may be substituted for N_2O.) Spectrophotometric studies showed the oxidation of Np(vi) to Np(vii) and Pu(vi) to Pu(vii) under similar conditions, which provides strong evidence that the green solutions indeed contain a powerful oxidant such as Am(vii) (Krot *et al.*, 1974a,b).

(b) Hydration and coordination numbers

Information on the structure of the Am^{3+}(aq) ion has been obtained indirectly from a variety of spectroscopic techniques. From the similar absorption spectra of Am^{3+} in aqueous solution, $AmCl_3$, and Am^{3+} doped into $LaCl_3$, Carnall (1989) concluded that there were nine inner-sphere water molecules associated in Am^{3+}(aq). Horrocks and Sudnick (1979, 1981) and Choppin and coworkers (Barthelemy and Choppin, 1989; Choppin and Peterman, 1998) developed a linear relationship between the decay rate of the lanthanide(iii) and the Am(iii) fluorescence and the number of inner-sphere water molecules: $n_{H_2O} = (x/\tau) - y$. Kimura and Kato (Kimura and Kato, 1998) determined $x = 2.56 \times 10^{-7}$ s and $y = 1.43$ for Am(iii) by measuring the fluorescence lifetime of Am^{3+} in H_2O and D_2O and using Carnall's proposed nine hydration waters. Runde *et al.* (2000) used Kimura's parameters and calculated from the fluorescence lifetime 11 coordinated water molecules for the Am^{3+} ion. Allen *et al.* (2000) determined ten coordinated water molecules around the Am^{3+} aquo ion in dilute aqueous chloride solution using X-ray absorption fine structure (XAFS) spectroscopy. Recently, Matonic *et al.* (2001) crystallized the isostructural Am(iii) and Pu(iii) triflate (trifluoromethanesulfonic acid) salts where the Am^{3+} ion bonds to nine water molecules in a tricapped, trigonal prismatic geometry (Fig. 8.4).

Shilov and Yusov (1999) analyzed reported variations in the Am(v)/Am(vi) potentials and the stability constants of the actinyl(v) oxalate complexes and proposed that the NpO_2^+(aq) and AmO_2^+(aq) ions are coordinated with five water molecules in the equatorial plane, in contrast to the coordination of four waters by PuO_2^+(aq) and UO_2^+(aq).

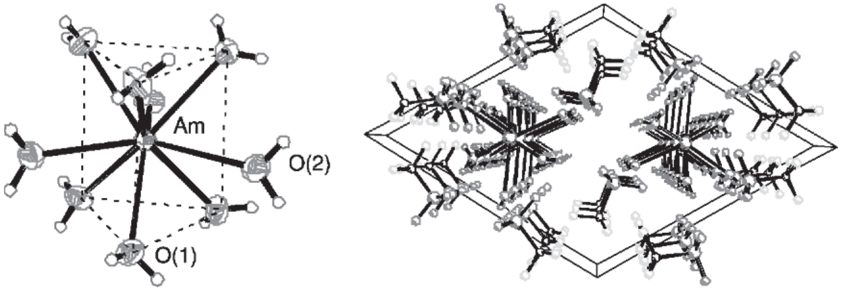


Fig. 8.4 *Coordination environment of* Am^{3+} *and crystal packing in* $[Am(H_2O)_9][CF_3SO_3]$ (*Matonic* et al., 2001).

(c) Electrode potentials and thermodynamic properties

A critical evaluation of available enthalpy and electromotive force (EMF) data were reported (Musikas, 1973b; Fuger and Oetting, 1976; Schulz, 1976; Fuger *et al.*, 1992; Silva *et al.*, 1995). Table 8.7 lists the electrode potentials for americium couples in various aqueous media. The diagram reflects the latest values and data evaluation of Martinot and Fuger (1985), which were accepted with minor changes by the recent Nuclear Energy Agency (NEA) review (Silva *et al.*, 1995). Except for the standard electrode potential ($E°$) of the Am(VI/V) couple, the electrode potentials of all redox couples were measured indirectly.

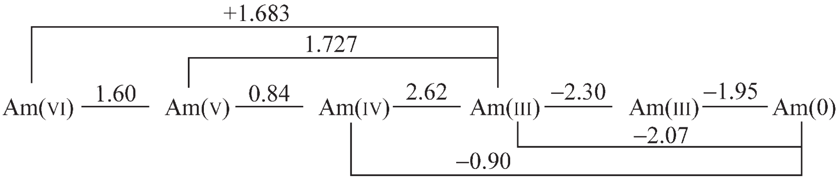
(1) Am(III)/(0): Fuger *et al.* (1972) measured the enthalpy of dissolution of Am metal (dhcp) in hydrogen-saturated HCl solutions and, using the estimated entropy of $Am^{3+}(aq)$, estimated $E°$ to be -2.06 ± 0.01 V in 1 M $HClO_4$; later Martinot and Fuger (1985) recommended -2.07 V.

(2) Am(III)/(II): Nugent *et al.* (1973a) estimated the potential to be -2.3 V as a best value by comparing the properties of lanthanide and actinide chloro complexes in relation to their M(II)/M(III) potentials. The estimated value is close to the -2.4 V estimated by Bratsch and Lagowski (1986).

(3) Am(IV)/(III): Due to the difficulties in preparing Am(IV) in appreciable amounts, estimating its thermodynamic properties is difficult. The originally estimated 2.44 V in 1 M $HClO_4$ appeared to be too small compared to data on the reduction of $Am(OH)_4$ to $Am(OH)_3$ (Penneman *et al.*, 1961). While the reported electrode potentials in concentrated H_3PO_4 are in agreement, 1.75 ± 0.03 V (Marcus *et al.*, 1972) and 1.78 V in 10 M H_3PO_4 (Nugent *et al.*, 1971a), their extrapolated values, $E° = 2.50 \pm 0.06$ and 2.34 ± 0.22 V, respectively, differ significantly, most likely due to uncertainties in solution speciation. A value of 2.6 ± 0.09 V has been calculated from enthalpy measurements (Morss and Fuger, 1981), and has been confirmed by electrochemical data in carbonate solutions (Hobart *et al.*, 1982). Stabilization by carbonate and phosphotungstate decreases the electrode

Table 8.7 *Electrode potentials of americium redox couples.*

(a) 1 M $HClO_4$ (Schulz, 1976; Silva *et al.*, 1995):



(b) Phosphoric Acid (Yanir *et al.*, 1959; Nugent *et al.*, 1971a; Myasoedov *et al.*, 1977):

$$\mathrm{Am(VI)} \xrightarrow[0.54\ \mathrm{M}\ H_3PO_4]{1.43} \mathrm{Am(V)} \text{ and } \mathrm{Am(VI)} \xrightarrow[4.34\ \mathrm{M}\ H_3PO_4]{1.32} \mathrm{Am(V)}$$

$$\mathrm{Am(IV)} \xrightarrow[10\text{–}14.5\ \mathrm{M}\ H_3PO_4]{1.75\text{–}1.78} \mathrm{Am(III)}$$

(c) 1 M NaOH (Standard potentials were calculated based on the solubility products of $K_{sp}(Am(OH)_3) = 10^{23.3}$ and $K_{sp}(Am(OH)_4) = 10^{64}$) (Penneman *et al.*, 1961; Musikas, 1973b; Schulz, 1976):

$$\mathrm{Am(VI)} \xrightarrow{0.9} \mathrm{Am(V)} \xrightarrow{0.7} \mathrm{Am(IV)} \xrightarrow{0.5} \mathrm{Am(III)} \xrightarrow{-2.5} \mathrm{Am(0)}$$

(d) Carbonate media (Bourges *et al.*, 1983; Hobart *et al.*, 1983b; Berger *et al.*, 1988):

$$\mathrm{Am(VI)} \xrightarrow[2\ \mathrm{M}\ Na_2CO_3]{0.975} \mathrm{Am(V)} \text{ and } \mathrm{Am(IV)} \xrightarrow[2\ \mathrm{M}\ Na_2CO_3]{0.92} \mathrm{Am(III)}$$

potential to 0.92 V (Hobart *et al.*, 1982; Bourges *et al.*, 1983) and 1.52 V (Kosyakov *et al.*, 1977), respectively.

(4) Am(VI)/(V): Penneman and Asprey (1950) measured directly the potential of the AmO_2^{2+}/AmO_2^+ couple to be 1.600 ± 0.0005 V in 1 M $HClO_4$ and 1.614 ± 0.001 V in 0.3 M $HClO_4$. From studies of Am(VI) with Pu(VI) in NaOH, Nikolaevskii *et al.* (1974) estimated that the potential for the Am(IV)/Am(V) couple is about 0.65 V rather than 1.1 V.

(5) Am(VII)/(VI): Shilov (1976) reported a value of 1.05 V for the Am(VII)/Am(VI) couple in 1 M NaOH, while Peretrukhin and Spitsyn (1982) reported 0.78 V for this couple in 10 M hydroxide.

The heat of dissolution of americium metal in HCl at 298 ± 0.05 K was redetermined by Fuger *et al.* (1972) with pure americium metal prepared by distillation. Combined with earlier results, Fuger and Oetting (1976) calculated a standard enthalpy of formation of $Am^{3+}(aq)$ at 198 K of -616.7 ± 1.3 kJ mol^{-1}.

The following enthalpies of formation, free Gibbs energies of formation, and standard entropies for the americium aquo ions have been accepted by the NEA review (Silva *et al.*, 1995):

	$\Delta_f H^\circ_m$(298.15 K) (kJ mol^{-1})	$\Delta_f G^\circ_m$(298.15 K) (kJ mol^{-1})	S°_m(298.15 K) (kJ mol^{-1})
Am^{2+}(aq)	-355 ± 16	-377 ± 15	-1 ± 15
Am^{3+}(aq)	-616.7 ± 1.5	-598.7 ± 4.8	-201 ± 15
Am^{4+}(aq)	-406 ± 6	-346 ± 9	-406 ± 21
AmO_2^+(aq)	-804.3 ± 5.4	-739.8 ± 6.2	-21 ± 10
AmO_2^{2+}(aq)	-650.8 ± 4.8	-585 ± 5.7	-88 ± 10

A correlation function of *P*(M) that connects the trivalent gaseous lanthanide atoms with their aqueous ions changes systematically as a function of atomic number (Nugent *et al.*, 1973b). The same property is moderately well-behaved for trivalent actinides (Nugent *et al.*, 1973b; David *et al.*, 1978; Morss, 1983). The calculated *P*(Am) is about 20 kJ greater than expected from neighboring actinides. This anomaly was attributed to the large positive change in entropy of vaporization of Am (Ward and Hill, 1976).

(d) Autoreduction

Radiolytically produced species in aqueous solution, e.g. H_2O_2 and HO_2 radicals, reduce the higher oxidation states of americium to Am(III). Because of its lower specific activity, the rates of autoreduction of ^{243}Am species are much less than those of ^{241}Am. Zaitsev *et al.* (1960b) account for the autoreduction kinetics of aqueous AmO_2^{2+} and AmO_2^+ ions by assuming that H_2O_2 is consumed only in reducing Am(VI) and Am(V) is reduced only by HO_2 radicals, but that Am(V) may be oxidized to Am(VI) by OH radicals.

All investigators concur that autoreduction is kinetically zero order with respect to the AmO_2^{2+} ion and first order with respect to the total americium concentration:

$$-\mathrm{d}[\mathrm{Am(VI)}]/\mathrm{d}t = \mathrm{d}[\mathrm{Am(V)}]/\mathrm{d}t = k_1[\mathrm{Am_{total}}]$$

In both perchloric and sulfuric acid media, the value of the rate constant k_1 decreases with increasing acid concentration, 0.04 h^{-1} in dilute acid to zero in 12 M $HClO_4$ (Zaitsev *et al.*, 1960b). The autoreduction rate of ^{241}Am(VI) approaches 10% per hour in 9 M HNO_3 (Zaitsev *et al.*, 1960b); a slower rate was found in a later study (Myasoedov *et al.*, 1974b). The rate of autoreduction of ^{243}Am(VI) in 2 M $HClO_4$ solution at 76°C is about six times greater than that at room temperature (Zaitsev *et al.*, 1960b).

The autoreduction of Am(V) to Am(III) is usually stated to depend only on the total americium concentration but to be independent of the Am(V) concentration.

Zaitsev *et al.* (1960b) disagreed and found that under some conditions the rate of autoreduction of Am(v) to Am(iii) does depend on the Am(v) concentration. The autoreduction of $^{241}AmO_2^+$ proceeds more slowly in 0.5 M HCl than in 0.2 M $HClO_4$. The maximum reduction rate of AmO_2^+ is about 1% per hour in 0.5 M HNO_3 and 0.8% per hour in 3 M HNO_3 (Zaitsev *et al.*, 1960b).

In 13 M NH_4F, ^{241}Am(iv) is autoreduced at a rate of about 4% per hour (Asprey and Penneman, 1962), increasing to 10% per hour in 3 M fluoride solution (Yanir *et al.*, 1969). Self-reduction of Am(iv) to Am(iii) in phosphoric acid solution follows first-order reaction kinetics (Yanir *et al.*, 1969; Myasoedov *et al.*, 1973, 1975;). In acidic peroxydisulfate solution, no Am(iii) is observed until all Am(vi) is reduced to Am(v). In the presence of $S_2O_8^{2-}$ ions, the radiolytic reduction of Am(v) proceeds more slowly than that of Am(vi) (Rykov *et al.*, 1970).

(e) Disproportionation

1. Am(iv): Tetravalent americium rapidly disproportionates in nitric and perchloric acid solutions according to the following reaction (Penneman *et al.*, 1961):

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

Assuming a reaction that is second order in Am(iv) concentration, Penneman *et al.* (1961) estimated k_1 in the equation

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

to be greater than $3.7 \times 10^{+4}$ L mol^{-1} h^{-1} in 0.05 M HNO_3 at 0°C. The dissolution of $Am(OH)_4$ in 0.05–2 M H_2SO_4 at either 0 or 25°C or of AmO_2 in 1 M H_2SO_4 yields solutions containing Am^{3+} and AmO_2^{2+} (Yakovlev and Kosyakov, 1958b; Penneman *et al.*, 1961). These results are explained by the following mechanism:

$$\text{Disproportionation of Am(IV)}:\ 2\mathrm{Am(IV)} \rightarrow \mathrm{Am(III)} + \mathrm{Am(V)}$$

and

$$\text{Redox Reaction}:\ Am^{4+} + AmO_2^+ \rightarrow Am^{3+} + AmO_2^{2+}$$

The AmO_2^{2+} fraction increases with SO_4^{2-} and HSO_4^- concentrations at constant H^+ concentration, possibly as a result of SO_4^{2-} (or HSO_4^-) stabilization of an Am(iv) complex. Am(iv) is stable only in concentrated H_3PO_4, $K_4P_2O_7$, phosphotungstate, and fluoride (NH_4F, KF) solutions. The average oxidation number of americium remains iv when $Am(OH)_4$ is dissolved in either perchloric, nitric, or sulfuric acids (Penneman *et al.*, 1961), indicating no significant reduction by water, in contrast to the reduction of Cm(iv) (Kosyakov *et al.*, 1977).

2. Am(v): The most thorough study of the disproportionation kinetics of Am(v) was performed by Coleman (1963), who used ^{243}Am to minimize the radiolytically induced redox reactions associated with ^{241}Am. Coleman investigated the disproportionation of Am(v) in 3–8 M $HClO_4$ at 25°C, in 1–2 M $HClO_4$ at 75.7°C, and in about 2 M HCl, H_2SO_4, and HNO_3 solutions at 75.7°C. The disproportionation of Am(v) in 5 M $HClO_4$ and 5 M HCl at 25°C is shown in Fig. 8.5. The disproportionation of Am(v) in all media except HCl follows the reaction

$$3\ \mathrm{AmO_2^+} +\ 4\mathrm{H^+} \rightarrow \mathrm{Am^{3+}} + 2\mathrm{AmO_2^{2+}} + 2\mathrm{H_2O},$$

reflecting the fourth power dependence on the H^+ concentration. The rate law for this disproportionation reaction is

$$-\mathrm{d}[\mathrm{Am(v)}]/\mathrm{d}t = k_1\ [\mathrm{AmO_2^+}]^2[\mathrm{H^+}]^4 = k_2\ [\mathrm{AmO_2^+}]^2[\mathrm{H^+}]^2 + k_3\ [\mathrm{AmO_2^+}]^2[\mathrm{H^+}]^3,$$

with $k_2 = (6.94 \pm 1.01) \times 10^{-4}\ \mathrm{L^3\,mol^{-3}\,s^{-1}}$ and $k_3 = (4.63 \pm 0.71) \times 10^{-4}\ \mathrm{L^3 mol^{-3} s^{-1}}$. The disproportionation rates at 75.7°C in 2 M HNO_3, HCl, and H_2SO_4 are, respectively, 4.0, 4.6, and 24 times greater than in 1 M $HClO_4$, whereas at 25°C the reaction rate increased 450 times in going from 3 to 8 M $HClO_4$. Using the temperature-dependence data from Coleman, Newton (1975) estimated thermodynamic quantities of activation for the disproportionation of Am(v). Note that the formation of Am(vi) in $HClO_4$ reaches a maximum after 5–6 h and then decreases successively with the main end product being Am(iii). In 0.5 and 5 M HCl, Am(v) disappears much faster than in the non-complexing perchlorate medium. The formation of Am(vi) has not been observed in HCl media, indicating a fast reduction of Am(vi) by chloride (Hall and Herniman, 1954; Runde and Kim, 1994).

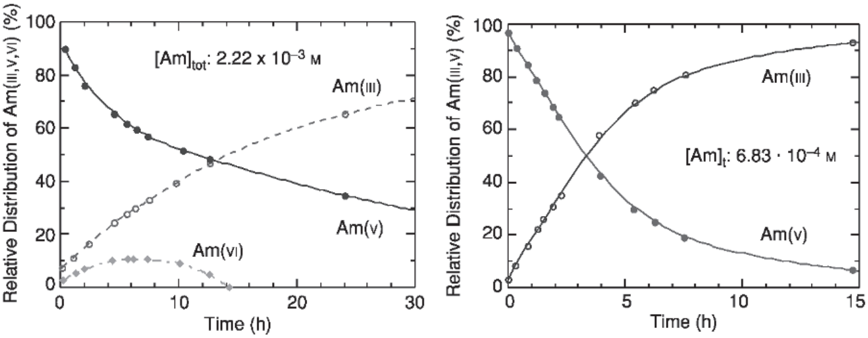


Fig. 8.5 *Disproportionation of Am*(v) *in* 5 M $HClO_4$ (*left*) *and* 5 M *HCl* (*right*) (*Runde and Kim*, 1994).

(f) Kinetics of oxidation–reduction reactions

Data for the few oxidation–reduction reactions that have been studied in detail can now be summarized. This summary supplements information presented by Hindman (1958), Newton and Baker (1967), and Gourisse (1966). An important recent reference on this subject is the critical review by Newton (1975).

(*i*) *Peroxydisulfate oxidation of Am*(III) *in acid media*

Early exploratory work by Asprey *et al.* (1950), the discoverers of the reaction between $S_2O_8^{2-}$ and Am(III) that produces Am(VI), established that the reaction proceeded in the concentration range from 10^{-8} to 10^{-1} M Am(III), implying a low-order dependence of the rate on Am(III) concentration. They further found that acidities greater than a few tenths molar were deleterious, presumably due to the acid-catalyzed decomposition path of $S_2O_8^{2-}$ (Penneman and Asprey, 1955). The general pattern of the oxidation (Fig. 8.6) represents an induction period and a linear region of constant rate followed by a region of gradually decreasing rate at high nitric acid concentrations. Reaction rates are dependent on temperature and on the concentration of HNO_3, $S_2O_8^{2-}$, and, when present, Ag^+. Newton (1975) states that the stoichiometry of the oxidation reaction is

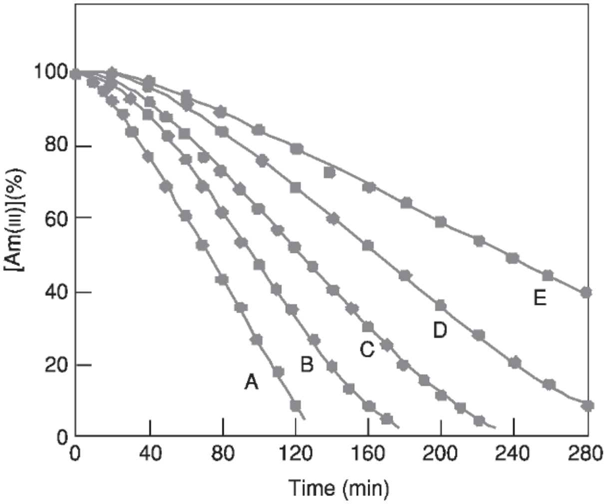


Fig. 8.6 *Kinetics of Am*(III) *oxidation by peroxydisulfate in nitric acid at* 50.6°C ($[S_2O_8^{2+}]_0 = 0.40$ M (*Ermakov* et al., 1971a, 1973, 1974)). *HNO_3 concentrations: A,* 0.09 M*; B,* 0.14 M*; C,* 0.19 M*; D,* 0.24 M*; E,* 0.28 M.

$$3/2\mathrm{S_2O_8^{2-}} + \mathrm{Am^{3+}} + 2\mathrm{H_2O} \rightarrow 3\mathrm{SO_4^{2-}} + \mathrm{AmO_2^{2+}} + 4\mathrm{H^+}$$

All researchers concur that the oxidizing agent is not the $S_2O_8^{2-}$ ion itself but its thermal decomposition products (e.g. $SO_4^{\bullet-}$ or $HS_2O_8^-$).

In contrast to conclusions from studies using micromolar Am(III), Ermakov *et al.* (1971a, 1973, 1974), on the basis of studies with millimolar amounts of ^{243}Am(III), claim that (in the absence of Ag^+) the rate of oxidation of Am(III) in the linear portion of kinetic curves does not depend on the Am(III) concentration and that the rate is given by:

$$\begin{aligned}-\mathrm{d[Am(III)]}/\mathrm{d}t &= (a + b[\mathrm{H^+}])[\mathrm{S_2O_8^{2-}}][\mathrm{Am(III)}]_0\\ &= 2/3k_1 - (k_4[\mathrm{H^+}]/(1+x))[\mathrm{S_2O_8^{2-}}]_0 = k_{\mathrm{III}}\end{aligned}$$

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

$$\mathrm{S_2O_8^{2-}} \xrightarrow{k_1} 2\mathrm{SO_4^{\bullet-}}$$

$$\mathrm{S_2O_8^{2-}} + \mathrm{H^+} \xrightarrow{k_4} \mathrm{HSO_4^-} + \mathrm{SO_4^{\bullet}}$$

$$\mathrm{SO_4^{\bullet}} \xrightarrow{k_5} \mathrm{SO_3} + \mathrm{O}$$

$$\mathrm{SO_4^{\bullet}} + \mathrm{H_2O} \xrightarrow{k_6} \mathrm{H_2O_2} + \mathrm{SO_3}$$

(*ii*) *Peroxydisulfate oxidation of Am*(*V*) *in* HNO_3

Ermakov *et al.* (1971a, 1973, 1974) also investigated the kinetics of the oxidation of Am(V) by $S_2O_8^{2-}$ ion in 0.09–0.6 M HNO_3 media at 45.6–60°C. According to Newton (1975) the stoichiometry of this reaction is

$$1/2\ \mathrm{S_2O_8^{2-}} + \mathrm{AmO_2^+} \rightarrow \mathrm{SO_4^{2-}} + \mathrm{AmO_2^{2+}}$$

Ermakov gives the law:

$$-\mathrm{d[Am(V)]}/\mathrm{d}t = (a' + b'[\mathrm{H^+}])[\mathrm{S_2O_8^{2-}}][\mathrm{Am(V)}]_0$$

At 50.6°C, $a' = 15 \times 10^{-5}\ \mathrm{min^{-1}}$ and $b' = 2.7 \times 10^{-4}\ \mathrm{L\ mol^{-1}\ min^{-1}}$. It follows from this result and the rate data given in the preceding section that

$$-\mathrm{d[Am(III)]}/\mathrm{d}t = -(1/3)\mathrm{d[Am(V)]}/\mathrm{d}t$$

The results of Rykov *et al.* (1970) indicate that the mechanism of reduction of Am(VI) in the presence of $S_2O_8^{2-}$ ions is identical with that proposed for the oxidation of Am(V).

(*iii*) *Peroxydisulfate oxidation of Am*(III) *in carbonate media*

Peroxydisulfate oxidation of Am(III) in carbonate solutions proceeds through the intermediate formation of Am(V). Ermakov *et al.* (1971a, 1973, 1974) found that the rate of oxidation of Am(III) to Am(V) is independent of the total Am and K_2CO_3 concentrations and is equal to the rate of decomposition of $S_2O_8^{2-}$ ions. However, 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 the $S_2O_8^{2-}$ oxidation of Am(III) to Am(V) in K_2CO_3 solutions is close to the activation energy (140 kJ mol^{-1}) of the thermal decomposition of $S_2O_8^{2-}$ ions. Recall that $Na_2S_2O_8$ will oxidize either Am(III) or Am(V) to Am(VI) in Na_2CO_3 or $NaHCO_3$.

(*iv*) *Reduction of Am*(VI) *by hydrogen peroxide*

Using ^{243}Am in $LiClO_4$–$HClO_4$ media, Woods *et al.* (1974) studied the kinetics of the reaction of AmO_2^{2+} with H_2O_2 and found the reduction of Am(VI) to be first order in both Am(VI) and H_2O_2 concentrations:

$$2AmO_2^{2+} + H_2O_2 \rightarrow 2AmO_2^{+} + 2H_2$$

(*v*) *Reduction of Am*(VI) *by other reductants*

Woods and Sullivan (1974) studied the reaction between AmO_2^{2+} and NpO_2^{+} in 1 M (H,Li)ClO_4. The rate law is:

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

At 25°C, k is $(2.45 \pm 0.4) \times 10^4$ L mol^{-1} s^{-1}; for this reaction, $\Delta H^* = 27.87 \pm 0.33$ kJ mol^{-1} and $\Delta S^* = -67.8 \pm 1.3$ J K^{-1} mol^{-1}. Oxalic acid reduces Am(VI) rapidly to approximately equal mixtures of Am(III) and Am(V), whereas reagents such as H_2O_2, HCl, HCOOH, HCHO, etc., reduce Am(VI) initially only to Am(V). The reduction of Am(VI) by nitrous acid is first order in each (Woods *et al.*, 1976).

(*vi*) *Reduction of Am*(V) *by H_2O_2*

From studies of the reduction of AmO_2^{+} to Am^{3+} by H_2O_2 in 0.1 M $HClO_4$, Zaitsev *et al.* (1960a) deduced the rate law:

$$-d[AmO_2^{+}]/dt = k[AmO_2^{+}][H_2O_2]$$

where $k = 14.8 \pm 1.5, 21.6 \pm 2.2$, and 30.3 ± 3.01 mol^{-1} h^{-1} at 25, 30, and 35°C, respectively. The activation energy deduced for the reduction reaction is 55.2 kJ 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 (1969, 1970). They reported that the rate at which AmO_2^+ is reduced is inversely proportional to the perchloric acid concentration and is also strongly dependent on the initial $[Am^{3+}]_0/[AmO_2^+]_0$ and $[H_2O_2]_0/[AmO_2^+]_0$ concentration ratios.

(*vii*) *Reduction of Am*(v) *in NaOH solutions*

Shilov *et al.* (1997) investigated the reduction rate of Am(v) in 1.5 and 3 M NaOH at room temperature. Slow reduction of Am(v) is observed in the presence of 0.005–0.4 M of dithionite ($Na_2S_2O_4$), sulfite (Na_2SO_3), or thiourea dioxide $(NH_2)_2CSO_2$) with a half-reduction time ranging between 0.2 and 9 h. The reduction of Am(v) in 3–14 M NaOH with about 0.01 M hydrazinium nitrate or hydroxylamine is accelerated with reductant concentration and temperature.

(*viii*) *Reduction of Am*(v) *by Np*(iv) *in perchloric acid media*

Blokhin *et al.* (1973) used spectrophotometry to study the kinetics of the Np(iv)–Am(v) reaction in 0.23–1.97 M $HClO_4$ at temperatures in the range 35.0–54.6°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:

$$d[Am^{3+}]/dt - k'1[Np^{4+}][AmO_2^+] + k'2[NpO_2^+][AmO_2^+]$$

The authors report the following thermodynamic activation parameters: $\Delta H^* = 126 \pm 4$ kJ mol^{-1}, $\Delta G^* = 87 \pm 4$ kJ mol^{-1}, and $\Delta S^* = 130 \pm 13$ J K^{-1} mol^{-1}.

(*ix*) *Reduction of Am*(v) *by Np*(v) *in perchloric acid*

Rykov *et al.* (1973) determined spectrophotometrically the rate of the reaction:

$$2NpO_2^+ + AmO_2^+ + 4H^+ \rightarrow 2NpO_2^{2+} + Am^{3+} + 2H_2O$$

Kinetic data were collected in perchlorate ($\mu = 2.0$ M) at temperatures in the range 24.7–44.1°C. These researchers claim that reduction of Am(v) by Np(v) is an irreversible second-order reaction.

(*x*) *Reduction of Am*(v) *by Np*(v) *in Na_2CO_3*

Kinetics of the reduction of Am(v) by Np(v) in Na_2CO_3 solutions were investigated spectrophotometrically (Chistyakov *et al.*, 1974). The stoichiometry of the reduction is

$$4H^+ + AmO_2^+ + 2NpO_2^+ \rightarrow Am^{3+} + 2NpO_2^{2+} + 2H_2O$$

The kinetics of the Am(v) reactions in aqueous Na_2CO_3 follow the same rate law as in $HClO_4$ media.

(*xi*) *Reduction of Am*(*V*) *by U*(*IV*) *in perchloric acid*

At 11.2 and 3.60°C in 0.51–2.60 M $HClO_4$, the reaction between Am(v) and U(IV) proceeds according to the equation:

$$AmO_2^+ + U^{4+} \rightarrow Am^{3+} + UO_2^{2+}$$

Blokhin *et al.* (1974) derived the following rate law:

$$d[Am^{3+}]/dt = k[AmO_2^{2+}][U^{4+}]$$

In 2.0 M $HClO_4$ at 9.5°C, $k = 725 \pm 30$ L mol^{-1} min^{-1}. Standard thermodynamic activation parameters are $\Delta H^* = 75 \pm 4$ kJ mol^{-1}, $\Delta G^* = 63.6 \pm 0.8$ kJ mol^{-1}, and $\Delta S^* = 37.7 \pm 12.5$ J K^{-1} mol^{-1}.

(*xii*) *Oxidation of Am*(*II*) *by water*

In an elegant experiment carried out at the U.S. Argonne National Laboratory, the absorption spectra of both divalent americium and tetravalent americium were obtained (Sullivan *et al.*, 1976, 1978). This technique involved irradiation of Am(III) solutions with single electron pulses and recording the spectra with a streak camera at postirradiation times of 50 μs for Am(II) and 100 μs for Am(IV). Am(II) disappeared via reaction with water, while the Am(IV) species disproportionated to yield Am(III) and Am(v).

(g) Radiolysis

The most commonly used americium isotopes, ^{241}Am and ^{243}Am, decay primarily by emitting high-energy alpha particles of about 5.4 and 5.2 MeV, respectively (see Table 8.1). In solution, the energy (1 mg ^{241}Am releases about 7×10^{14} eV s^{-1}) is released in dense tracks producing radicals, ions, and electrons; thus can impact the stability of americium oxidation states in aqueous solutions. There are numerous reports on the effect of the intense alpha radiation of transuranium elements on their chemical behavior in acidic, basic, and highly concentrated chloride solutions. In acidic media, Am(III) is the most stable oxidation state and Am(v) and Am(VI) are rather rapidly reduced (Vladimirova *et al.*, 1977; Kornilov *et al.*, 1986). The reduction rate is closely related to the dose rate and electrolyte concentration. Vladimirova and coworkers (Vladimirova *et al.*, 1977; Vladimirova, 1986) suggested that Am(v) and Am(VI) reduction in nitric acid solutions cannot be explained by involving only radiolytically produced radicals but also require consideration of chemical reactions with radiolytically produced H_2O_2 and HNO_2:

$$2AmO_2^{2+} + HNO_2 + H_2O \rightarrow 2AmO_2^+ + 3H^+ + NO_3^-$$

$$2AmO_2^+ + HNO_2 + 6H^+ \rightarrow 2Am^{4+} + 3H_2O + HNO_3$$

In perchlorate solutions, alpha-radiolysis produces multiple species, such as Cl_2, ClO_2, or Cl^- that are effective reductants for Am(VI) (Kornilov *et al.*, 1986). A radiolytically enhanced chemical oxidation of Am(III) to Am(V) and Am(VI) (at large gamma doses) is observed in perchlorate solutions at pH 3–6 in the presence of excess of N_2O, $S_2O_8^{2-}$, or XeO_3 (Pikaev *et al.*, 1977). As expected the stability of higher oxidation states increases with pH and Am(III) is radiolytically oxidized to Am(V) in carbonate solutions under the exposure of intense alpha-radiation from ^{244}Cm (3–8 KCi L^{-1}) (Osipov *et al.*, 1977). The formation of oxidizing species in concentrated chloride solutions, i.e. Cl_2 and ClO^-, leads to the autoradiolytical oxidation of Am(III) to Am(V) (Magirius *et al.*, 1985; Runde and Kim, 1994). The radiolytical formation of hypochlorite in basic 5 M NaCl is directly correlated with the alpha-specific activity of ^{241}Am.

8.8.2 Complexation reactions

A critical review of the chemical thermodynamics of experimental data and chemical thermodynamics for americium inorganic compounds was recently published by the NEA (Silva *et al.*, 1995). Nearly all formation constants listed in Table 8.8 are for complexes formed by Am(III), as little work has been done on complexes with Am in higher oxidations states. Color changes of Am(III)-containing solutions indicate existence of Am(VI) nitrate, sulfate, and fluoride complexes. Some spectroscopic evidence exists for a Am(V) peroxide complex in 1 M NaOH (Musikas, 1973a). In agreement with the behavior of other actinide (III) and (IV) ions, the stability of Am(III) complexes with monovalent inorganic ligands follows the sequence:

$$F^- > H_2PO_4^- > SCN^- > NO_3^- > Cl^- > ClO_4^-.$$

As a Chatt–Ahrland ‘A’ type or Pearson ‘hard’ cation, Am^{3+} association with inorganic ligands proceeds initially through electrostatic interactions to form outer-sphere complexes, such as chlorides or perchlorates. Spectrophotometric results suggested the inner-sphere formation of chloride and nitrate ions in concentrated Na/LiCl and $LiNO_3$ solutions (Marcus and Shiloh, 1969; Allen *et al.*, 2000). Inner-sphere complexes are also found to form with harder ligands, such as fluoride or sulfate. In most cases, the stability of Am(III) complexes is similar to those that contain lanthanide ions with similar ionic radii, e.g. Nd(III) and Eu(III). In some cases, the stability of the Am(III) complex is slightly greater than that of the corresponding lanthanide complex presumably because of the participation of f-electrons in the bonding (Moskvin, 1967, 1971, 1973). As discussed earlier, this difference in stability can be used to separate Am(III) effectively from lanthanide elements.

Table 8.8 *Selected formation constants and solubility products of inorganic americium complexes* (*Silva* et al., 1995).

Complex	*log* β° *or* *log* K°_{sp}	$\Delta_f G^o_m$(298.15K) (kJ mol^{-1})	$\Delta_f H^o_m$(298.15K) (kJ mol^{-1})
Solution species			
$AmOH^{2+}$	–6.4 ± 0.7	–799.31 ± 6.21	
$Am(OH)_2^+$	–14.1 ± 0.6	–992.49 ± 5.86	
$Am(OH)_3$(aq)	–25.7 ± 0.5	–1163.42 ± 5.55	
$Am(CO_3)^+$	7.8 ± 0.3	–1171.12 ± 5.07	
$Am(CO_3)_2^-$	12.3 ± 0.4	–1724.71 ± 5.33	
$Am(CO_3)_3^{3-}$	15.2 ± 0.6	–2269.16 ± 5.98	
$AmSCN^{2+}$	1.3 ± 0.3	–513.42 ± 6.45	
AmF^{2+}	3.4 ± 0.4	–899.63 ± 5.32	
AmF_2^+	5.8 ± 0.2	–1194.85 ± 5.08	
$AmCl^{2+}$	1.05 ± 0.1	–735.91 ± 4.77	
$AmSO_4^+$	3.85 ± 0.03	–1364.68 ± 4.78	
$Am(SO_4)_2^-$	5.4 ± 0.8	–2117.53 ± 6.27	
$AmNO_3^{2+}$	1.33 ± 0.2	–717.08 ± 4.91	
$AmH_2PO_4^{2+}$		–1752.97 ± 5.76	
Solid phases			
$Am(OH)_3$(am)	–17.0 ± 0.6		
$Am(OH)_3$(cr)	–15.2 ± 0.6		
AmO_2(cr)		–874.49 ± 4.27	–932.20 ± 3.00
Am_2O_3 (cr)		–1613.32 ± 9.24	–1690.40 ± 8.00
AmF_3 (cr)		–1518.83 ± 13.10	–1588.00 ± 13.00
AmF_4 (cr)		–1616.83 ± 20.06	–1710 ± 20.00
$Am_2(CO_3)_3$ (cr)	16.7 ± 1.1	–2971.74 ± 15.79	
$Am(OH)CO_3$ (cr)	21.2 ± 1.4	–1404.83 ± 9.31	
$AmPO_4$ (am)	24.8 ± 0.6	–1752.97 ± 5.76	

(a) Hydrolysis

(1) Am(III): The hydrolysis of Am(III) has been studied extensively, partly because the hydrolysis reactions are strongly favored in aqueous systems. It is established that Am(III) is complexed by hydroxide above pH 5 to form complexes of general formula $Am(OH)_n^{3-n}$ where $n = 1$–3. Thermodynamic stabilities of these complexes were calculated from data obtained by a variety of methods, such as solubility studies, solvent extraction, and potentiometric and electromigration measurements. Spectroscopic characterization or structural information of these complexes is absent because of their low solubilities. The existence of the anionic species $Am(OH)_4^-$ has been postulated, which would increase the Am(III) solubility at high pH. However, an increase in solubility is not observed at pH > 13 and contamination of the solution by carbonate may have produced anionic carbonate complexes that increase

the overall Am(III) solubility. There is substantial uncertainty about the formation of polynuclear complexes, as common in the U(VI) hydrolysis system.

(2) Am(V): Kim and coworkers (Magirius *et al.*, 1985; Stadler and Kim, 1988) measured the solubility of autoradiolytically formed $^{241}AmO_2(OH)$(s) in 3 and 5 M NaCl. Runde and coworkers (Runde and Kim, 1994; Runde *et al.*, 1996) reported an increased solubility of $^{241}AmO_2(OH)$(s) over $^{237}NpO_2(OH)$(s) in 5 M NaCl. Slope analysis of the solubility data indicated formation of only two americyl(V) hydrolysis products in solution, $AmO_2(OH)$(aq) and $AmO_2(OH)_2^-$. Tananaev (1990a) suggested the formation of $AmO_2(OH)_3^{2-}$ (with an absorption peak at 750 nm) and $AmO_2(OH)_4^{3-}$ in highly alkaline media based on spectroscopic measurements of Am(V) in 0.001–1 M LiOH solutions. Because of the radiolytic formation of oxidizing species (such as OCl^-) and the subsequently increased stability of Am(V), the few solubility studies of Am(V) were performed in concentrated chloride solutions. The reported apparent stability constants for $AmO_2(OH)$(aq) and $AmO_2(OH)_2^-$ are close to those for the analogous Np(V) species (Runde *et al.*, 1996). However, the solubility of $^{241}AmO_2OH$ appears to be higher than that of $^{237}NpO_2OH$, probably due to higher alpha-radiation damage of the Am(V) solid.

(3) Am(IV) and Am(VI): The hydrolysis of Am(IV) and Am(VI) remains rather unexplored because of the instabilities of these oxidation states in aqueous solutions under ambient conditions. There is spectroscopic evidence for the formation of Am(VI) hydrolysis species of general formula $AmO_2(OH)_n^{2-n}$ where $n = 1$–4.

(b) Carbonate complexation

(1) Am(III): The carbonate complexation of Am(III) has been widely investigated using a variety of methods, such as solvent extraction, spectrophotometry, electromigration, and solubility. Meinrath and Kim (1991a) monitored the solubility and complexation reactions of Am(III) in carbonate-containing solutions spectroscopically. Three solution species, $Am(CO_3)_n^{3-2n}$ with $n = 1$–3, were characterized by their distinct absorbances at 505.4 nm ($\varepsilon = 385$ L mol^{-1} cm^{-1}), 506.5 nm ($\varepsilon = 350$ L mol^{-1} cm^{-1}), and 507.8 nm ($\varepsilon = 330$ L mol^{-1} cm^{-1}), respectively. Wruck *et al.* (1999) determined the formation constant of the monocarbonato complex, $Am(CO_3)^+$, at 25, 50, and 75°C at 0.1 m ionic strength using laser-induced photoacoustic spectroscopy. There is no experimental or spectroscopic proof for the proposed formation of bicarbonato complexes, $Am(HCO_3)_n^{3-2n}$, and mixed hydroxocarbonato species, $Am(OH)_m(CO_3)_n^{3-m-2n}$ (Bernkopf and Kim, 1984). These complexes were used to explain extraction and solubility data although the experimental data can be explained by pure carbonato

and hydroxo species. The solid phases $AmOHCO_3$ and $Am_2(CO_3)_3$ were found as solubility-controlling phases in aqueous carbonate solutions (Meinrath and Kim, 1991b; Runde *et al.*, 1992). The double carbonate $NaAm(CO_3)_2 \cdot nH_2O$ was identified by X-ray diffraction to form at increased NaCl concentrations (Runde and Kim, 1994; Rao *et al.*, 1996).

(2) Am(IV): There is only one carbonato complex of Am(IV) discussed in the literature. From combined spectroscopy and cyclic voltammetry data in bicarbonate/carbonate solutions (Bourges *et al.*, 1983), it was concluded that $Am(CO_3)_5^{6-}$ is the limiting carbonate complex of Am(IV). Its logarithmic stability constant, $\log \beta_5^o = 39.3 \pm 2.1$ (Silva *et al.*, 1995), is comparable to those of the analogous U(IV) (34.0 ± 0.9 (Grenthe *et al.*, 1992)) and Np(IV) complexes (33.9 ± 2.6 (Kaszuba and Runde, 1999)).

(3) Am(V): Giffaut and Vitorge (1993) studied the solubility of $NaAmO_2CO_3$ in carbonate-containing 4 M NaCl solution and claimed the formation of two Am(V) carbonate complexes, $AmO_2(CO_3)^-$ and $AmO_2(CO_3)_2^{3-}$. Runde and coworkers (Runde and Kim, 1994; Runde *et al.*, 1996) reported identical solubility and speciation behavior of Am(V) and Np(V) in carbonated 3 and 5 M NaCl solutions. In analogy to the well-characterized Np(V) system in 5 M NaCl, the solubility data were interpreted with the formation of $AmO_2(CO_3)_n^{1-2n}$ ($n = 1$–3) in solution and $NaAmO_2CO_3 \cdot nH_2O$ as the solid equilibrium phases.

Spectroscopic evidence suggests that an Am(V) carbonate complex in $NaHCO_3$, presumably the triscarbonato complex $AmO_2(CO_3)_3^{5-}$, has an absorbance at 727 nm (Tananaev, 1990a).

(4) Am(VI): The appearance of a burgundy-red color upon introducing Am(VI) into carbonate-containing solutions indicates the coordination of AmO_2^{2+} with carbonate ions. However, spectroscopic studies of the carbonate complexation of Am(VI) are few. Based on electrochemical measurements, it is assumed that the limiting complex is the $AmO_2(CO_3)_3^{4-}$ anion (Bourges *et al.*, 1983; Silva *et al.*, 1995).

(c) Organic ligands

With few exceptions, the data in Table 8.9 are for complexes of Am(III). Generally, the higher oxidation states of americium are reduced by organic complexing agents. Aminopolycarboxylic acids complex Am(III) more strongly than either hydroxycarboxylic or aminoalkylpolyphosphoric acids (e.g. ethylenediamine bis(methylene)phosphonic acid). Keller (1971) observed that in the series of α-hydroxycarboxylic acids (e.g. glycolic and lactic), the stability of the Am(III) complex decreases with increasing number of carbon atoms. The logarithm of the stability constant of the Am(III) complexes with aminopolycarboxylic acids increases linearly (Fig. 8.7) with the number of bound donor atoms of the ligand.

Table 8.9 *Complexes of Am(III) with organic ligands (unless otherwise noted, see the compilation by Schulz (1976) and references therein).*

Ligand	Method	Temp. (°C)	Ionic strength, medium μ (mol L^{-1})	Log of formation constants		Other constants	References
				β$_1$	β$_2$		
acetic acid (HAc)	IX	20	9.0 M HAc	2.28 ($AmAc^{2+}$)	3.84($AmAc_2^+$)	$\beta_3 = 4.78$ ($AmAc_3$)	[1]
						$\beta_4 = 5.7$ ($AmAc_4^+$)	[1]
						$\beta_5 = 6.66$ ($AmAc_5^{2+}$)	[1]
						$\beta_6 = 7.62$ ($AmAc_3^{6+}$)	[1]
	PT	20	1.0 M NH_4ClO_4	1.81	3.20	$\beta_3 = 4.57$; $\beta_4 = 5.7$	[1]
						$\beta_5 = 6.73$; $\beta_6 = 7.73$	[1]
	SX	25 ± 0.1	2.0 M NH_4ClO_4	1.95 ± 0.11			[2]
	IX	20	0.5 M NaClO4	1.99 ± 0.01	3.27 ± 0.07	$\beta_3 = 3.9$	[3]
	IX	25	$\mu = 0.2$	2.15	3.83		[4]
		25	$\mu = 0.5$	2.30	3.81		[4]
		25	$\mu = 1.0$	2.08	3.62		[4]
	SX	~25	0.1–1.0 M Ac	1.40 (AmO_2Ac)	2.51($AmO_2Ac_2^-$)		[5]
	SX	25 ± 0.5	0.5 M NH_4ClO_4	2.39 ± 0.05			[6]
α-alanine (Ala)	SX	25	2.0 M $NaClO_4$	0.79 ($AmAla^{2+}$)			[7]
	Spec	18 ± 2	1.0 M KCl	3.9 ± 0.2			[8]
anthranil-*N*,*N*-diacetic acid (H_3ADA)	IX	25	0.1 M NH_4ClO_4	8.92 (AmADA)	14.5(Am(ADA)$_2^{3-}$		[26,52]
arginine				3.8 ± 0.3			[8]
aspartic acid	Spec	18 ± 2	1.0 M KCl	5.1 ± 0.02			[8]
Benzoyltrifluoroacetone (HBTA)	SX	25	0.1 M NH_4ClO_4			$\beta_3 = 14.84$ ($Am(BTA)_3$)	[9]
citric acid (H_3Cit)	Spec	25	1.0 M $NaClO_4$	6.96 (AmCit)	10.3($Am(Cit)_2^{3-}$)	$\beta'_1 = 4.53$ ($AmHCit^+$)	[10,11]
	SX	25	0.1 M(H,Li)ClO_4		12.15	$\Delta G^\circ = 44.98$ kJ mol^{-1} ($AmHCit^{2-}$)	[12]
	IX	25	0.1 M $NaClO_4$	9.16 ± 0.03		$\beta'_1 = 7.00$	[11]
			0.5 M $NaClO_4$	8.73 ± 0.066		$\beta'_1 = 6.29$	[11]
			1.0 M $NaClO_4$	6.72 ± 0.05		$\beta'_1 = 4.24$	[11]
	IX	25	0.1 M NaH_2 Cit	6.74	11.55	$\beta'_1 = 5.31$	[13]
						$\beta'_2 = 8.23$ ($Am(HCit)_2^-$)	[13]
	IX		1.0 M NH_4Cl	7.11	14.0	$\beta''_3 3 = 8.29$ ($Am(H_2Cit)_3$)	[14]
	PEP		0.04 M		9.66		[15]
	SX		0.1 M $LiClO_4$	10.1 ($Am(HCit)^+$)			[16]

				8.0 (Am(Cit))			[16]
				20 $(\mathrm{Am(HcCit)}_2^-)$			[16]
				16.3 $(\mathrm{Am(HCit)(Cit)^{2-}})$			[16]
				12.1 $(\mathrm{Am(Cit)}_2^{3-})$			[16]
	PT		0.1 M $\mathrm{LiClO_4}$	11.36 $(\mathrm{Am(HCit)^+})$			[16]
				8.69 (Am(Cit))			[16]
				18.97 $(\mathrm{Am(HCit)(Cit)^{2-}})$			[16]
				14.29$(\mathrm{Am(Cit)}_2^{3-})$			[16]
				10.53 $(\mathrm{Am(OH)(Cit)^-})$			[16]
				22.80 $(\mathrm{Am(OH)(Cit)}_2^{2-})$			[16]
	SX	25	0.3 M NaCl	5.9 ± 0.1			[17]
			1.0 M NaCl	5.2 ± 0.1			[17]
			2.0 M NaCl	5.0 ± 0.1			[17]
			3.0 M NaCl	4.84 ± 0.04			[17]
			4.0 M NaCl	5.38 ± 0.06			[17]
			5.0 M NaCl	5.10 ± 0.15			[17]
15-crown-5	SX	25	0.1 M	0.21 ± 0.02			[18]
18-crown-6	SX	25	0.1 M	0.55 ± 0.06			[18]
cysteine	Spec	18 ± 2	1.0 M KCl		4.3 ± 0.3		[8]
1,2-diaminocyclohexanetetraacetic acid $(\mathrm{H_4DCTA})$							
	EM	20 ± 0.5	0.1 M KCl/HCl	18.34 $(\mathrm{AmDCTA^-})$		$\beta_1' = 2.87$ $(\mathrm{AmHDCTA^-})$	[19]
	IX	25 ± 1	0.1 M $\mathrm{NH_4ClO_4}$	18.79			[20]
	IX	80	0.001 M $\mathrm{H_4DCTA}$ +0.02 M ammonium-α-hydroxyisobutyrate	18.79^{e}			[21]
	SX	20	0.1 M $\mathrm{NH_4Cl}$	18.21		$\beta_1''' = 2.85 \pm 0.04$ $(\mathrm{AmO_{22}DTPA})^{2-}$	[22]
1,2-diaminopropanetetraacetic acid $(\mathrm{H_4DTPrA^-})$							
	IX	25	0.1 M $\mathrm{NaClO_4}$	17.69 $(\mathrm{AmDTPrA^-})$		$\beta_1' = 9.79$ (AmHDTPrA)	[11]
1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (diaza-crown ether; kryptofix 22; K22)							
	SX	25	1.0 M NaCl	6.05 ± 0.3			[23]
dibutyl-P,P′-ethane-1,2-diphosphonic acid $(\mathrm{H_2B_2EDP})$							
	SX	25	1.0 M $\mathrm{NaClO_4}$			$\beta_1' = 14.52$ $(\mathrm{Am(HB_2EDP)_3})$	[24]
5,7-dichloro-8-hydroxyquinoline (HDCO)							
	SX	25 ± 0.5	0.1 M $(\mathrm{NH_4, H})\mathrm{ClO_4}$			$\beta_3 = 21.93$ (Am(DCO)3)	[25]

Table 8.9 (*Contd.*)

Ligand	*Method*	*Temp.* (°C)	*Ionic strength, medium* μ (mol L^{-1})	*Log of formation constants*		*Other constants*	*References*
				β_1	β_2		
diethylenetriaminepentaacetic acid (H_5DTPA)							
	IX	25	0.1 M NH_4ClO_4	23.07 ($AmDTPA^{2-}$)		$\beta_1' = 14.06$ ($AmHDTPA^{+}$)	[26]
	IX	25	0.1 M NH_4ClO_4	22.92			[27]
	EM	25 ± 0.2	0.1 M KNO_3	22.74		$\beta_1' = 14.3$	[28]
	SX		$\mu = 0.1$	23.2			[29]
	Spec	25	$\mu = 0.1$	23.2			[30]
	Spec	25	0.1 M NH_4ClO_4	24.03			[31]
	Spec	20 ± 0.1	0.5 M $HClO_4/HNO_3$	22.09			[32]
	IX	25	0.1 M NH_4ClO_4	23.32			[33]
	IX	25	1.0 M NH_4ClO_4	21.3		$\beta_1' = 15.46$	[1]
diethylphosphinylpropionic acid (HDEPP)							
	IX	25	0.5 M NH_4ClO_4; $HClO_4$	1.76 ($AmDEPP^{2+}$)	3.16 ($Am(DEPP)_2^{+}$)		[34]
diglycolic acid (H_2DGA)							
	Spec	25.2	0.1 M NH_4ClO_4	6.47 ($AmDGA^{+}$)	10.96 ($Am(DGA)_2^{-}$)	$\beta_3 = 13.83$ ($Am(DGA)_3^{3-}$)	[35]
dioctyl-P,P′-ethane-1,2-diphosphonic acid (H_2O_2 EDP)							
	SX	25	1.0 M NaClO4			$\beta_1' = 19.53$ ($Am(HO_2EDP)_3$)	[24]
diphosphine dioxides (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=$(C_6H_{11})_2P(O)(CH_2)_5(O)P(C_6H_{11})_2$)							
	SX	2.0	2.0 M $NaNO_3$	1.43 ($Am(NO_3)_3 \cdot$ (1,1-DiPO))			[36]
				6.56 ($Am(NO_3)_3 \cdot$ 2(1,4-DiPO))			[36]
				5.92 ($Am(NO_3)_3 \cdot$ 2(1,5-DiPO))			[36]
ethylenediaminebis(isopropyl)phosphonic acid (H_4EDIP)							
	EM	25	0.1 M KNO_3	18.00 ($AmEDIP^{-}$)		$\beta_1' = 6.26$ (AmH_3EDIP^{2+})	[28]
						$\beta_1' = 8.94$ (AmH_2EDIP^{+})	[28]
						$\beta_1' = 13.95$ ($AmHEDIP$)	[28]

ethylenediaminebis(methyl)phosphonic acid (H_4EDMP)							
	EM	25	0.1 м KNO_3	16.52 ($AmEDMP^-$)		$\beta_1' = 6.3$ (AmH_3EDMP^{2+})	[37]
						$\beta_1' = 8.48$ (AmH_2EDMP^+)	[37]
						$\beta_1' = 12.3$ ($AmHEDMP$)	[37]
	IX	25	0.5 м NH_4ClO_4			$\beta_1' = 6.12$ (AmH_2EDMP^+)	[38]
ethylenediaminetetraacetic acid (H_4EDTA)							
	IX	25	0.1 м $NaClO_4$	18.15 ($AmEDTA^-$)			[11]
			0.5 м $NaClO_4$	16.36		$\beta_1' = 9.68$ ($AmHEDTA$)	[11]
			1.0 м $NaClO_4$	15.72			[11]
	Spec	25 ± 0.2	1.0 м $NaClO_4/HClO_4$	15.33	22.10 ($Am(EDTA)_2^{5+}$	$\beta_1' = 8.94$ ($AmHEDTA$)	[11]
	SX	20	0.1 м NH_4Cl	16.91 ± 0.04			[39]
	Spec	25	0.1 м NH_4ClO_4	18.06			[31]
	IX	25 ± 0.02	0.1 м NH_4ClO_4	18.16 ± 0.10			[40]
	IX		1.0 м NH_4ClO_4	18.03 ± 0.13		$\beta_1' = 10.29$ ($AmHEDTA$)	[41]
	EM	25 ± 0.5	0.1 м HCl/KCl	17.0		$\beta_1' = 9.21$ ($AmHEDTA$)	[42]
	IX	80	0.001 м H_4EDTA + 0.2 м α-hydroxyisobutyrate	17.14			[43]
	EM	25 ± 0.1	0.1 м KNO_3	17.00 ± 0.09		$\beta_1' = 9.21$ ($AmHEDTA$)	[22,44]
	Spec	25	$\mu = 0.1$			$\beta = 19.98$ (AmO_2HEDTA^{2+})	[22,44]
						$\beta_1''' = 4.88 \pm 0.05$ (AmO_2HEDTA^{2+})	[22,44]
ethylenediaminetetramethylphosphonic acid (H_8EDTMP)							
	EM	25 ± 0.1	0.1 м KNO_3	22.47 ± 0.08 ($AmEDTMP^{5-}$)		$\beta_1' = 4.8 \pm 0.6$ (AmH_5EDTMP)	[44]
						$\beta_1'' = 7.33 \pm 0.09$ (AmH_4EDTMP)	[44]
						$\beta_1''' = 11.17 \pm 0.07$ (AmH_3EDTMP)	[44]
						$\beta_1'''' = 14.90 \pm 0.06$ (AmH_2EDTMP)	[44]
						$\beta_1''''' = 18.45 \pm 0.08$ ($AmHEDTMP$)	[44]

Table 8.9 (*Contd.*)

Ligand	*Method*	*Temp*. (°C)	*Ionic strength, medium* μ (mol L^{-1})	*Log of formation constants*		*Other constants*	*References*
				β_1	β_2		
ethylenediaminetetrapropionic acid (H_4EDTP)							
	Spec	25 ± 0.2	1.0 M $NaClO_4/HClO_4$	18.84 ± 0.02 ($AmEDTP^-$)	$\beta'_1 = 12.31$ (AmHEDTP)		[11]
ethyleneglycol*bis*(2-aminoethyl)tetraacetic acid (H_4EGTA)							
	IX	25	0.1 M NH_4ClO_4	18.22 (AmEGTA)			[26]
formate	Sol	25	2.0 M $NaClO_4$	2.54 (lg β_1)	4.02 (lg β_2)	$\log \beta_3 = 4.64$ $\log \beta_4 = 4.5$	[45]
formate (Am(v))	Spec	25	2.0 M $NaClO_4$	1.22 ± 0.3			[46]
fulvic acid	Spec	25	0.1 M $NaClO_4$	5.78 ± 0.07			[22]
	SX	25	3 M NaCl 6 M NaCl	4.7 ± 0.1 6.0 ± 0.7			[13]
glutamic acid	Spec	18 ± 2	1.0 M KCl	5.6 ± 0.1			[8]
glycine (HGlyn)	SX	25	2.0 M $NaClO_4$	0.69 ± 0.02 ($AmGlyn^{2+}$)			[47]
	Spec	18 ± 2	1.0 M KCl	4.1 ± 0.02			[8]
glycolic acid (HGlyc)							
	IX	0.5	0.5 M $NaClO_4$	2.82 ($AmGlyc^{2+}$)	4.85($Am(Glyc)_2^+$)	$\beta_3 = 6.30$ ($Am(Glyc)_3$)	[3]
	SX	25	2.0 M $NaClO_4$	2.59			[48]
	Spec	25 ± 0.2	1.0 M $NaClO_4/HClO_4$	2.44 ± 0.02	4.29 ± 0.2	$\beta_3 = 5.20$	[11]
	IX	25	0.5 M $NaClO_4$	2.57 ± 0.02	4.01 ± 0.1		[11]
histadine	Spec	18 ± 2	1.0 M KCl	4.8 ± 0.2			[8]
hydrazine-*N,N*-diacetic acid (H_2HyDA)							
	IX	25	0.1 M $NaClO_4$	10.74 ($AmHyDA^+$)	20.20 ($Am(HyDA)_2^+$)		[11]
	EM	25	$\mu = 0.1$	11.01	19.78		[37]
hydrazineiminodiacetic acid (H_2HyIDA)							
	EM	25	0.1 M KNO_3	10.98 ($AmHyIDA^+$)	19.97 ($AmHyIDA)_2^-$)	$\beta'_1 = 4.13$ ($AmHHyIDA^{2+}$)	[49]
2-hydroxycyclohexylethlenediaminetriacetic acid ($H_3HCEDTA$)							
	IX	25	0.1 M $NaClO_4$	16.09 (AmHCEDTA)		$\beta'_1 = 7.44$ ($AmHHCEDTA^+$)	[11]

N (2-hydroxyethyl)ethylene-*N,N,N′*-triacetic acid ($H_3NHEDTA$)							
	IX	25	0.1 м $HClO_4/NH_4ClO_4$	15.72 (AmNHEDTA)	22.47 ($Am(NHEDTA)_2^{3-}$)		[26,50]
	Spec	25 ± 0.2	1.0 м $HClO_4/NH_4ClO_4$	14.84	22.18		[13]
	Spec	25	0.1 м NH_4ClO_4	16.18			[31]
	IX	22	0.15 м HCl/KCl	15.34			[51]
N′ (2-hydroxyethyl)iminodiacetic acid (H_2NHIDA)							
	IX	25	0.1 м NH_4ClO_4	9.14 (\rm Am(NHIDA$^+$)	17.04 ($Am(NHIDA)_2^-$)		[26,52]
	Spec	25	0.1 м NH_4ClO_4	9.80	17.01		[31]
	SX			9.3 ± 0.1			[53]
	EM	25	0.1 м KNO_3	9.3 ± 0.13	16.5 ± 0.2		[54]
α-hydroxyisobutyric acid (HIBA)							
	Spec	25 ± 0.2	1.0 м $HClO_4/NaClO_4$	2.68 ($AmIBA^{2+}$)	4.38 ($Am(IBA)_2^+$)		[11]
	IX	25 ± 0.2	0.5 м NH_4ClO_4	2.88 ± 0.01	4.03 ± 0.02		[11]
	IX		0.5 м NH_4ClO_4/NH_4IBA	2.38	4.67	$\beta_3 = 5.12$ (Am(IBA)3)	[55]
	IX			2.72	4.69	$\beta_3 = 5.64$	[56]
	SX					$\beta_3 = 6.1$	[57]
bis(hydroxymethyl)phosphonic acid (HMP′A)							
	IX	25		1.76 ± 0.06 ($AmMPA^{2+}$)	2.48 ± 0.02 ($Am(MPA)_2^+$)		[58]
hydroxymethylphosphonic acid (HMP′A)							
	IX	25	0.2 м NH_4ClO_4	1.55 $AmMP'A^{2+}$)	3.18 ($Am(MP'A)_2^+$)		[59]
o-hydroxyphenyliminodiacetic acid (H_2HPIDA)							
	SX	25 ± 0.1	0.1 м NH_4ClO_4	6.80 ($Am(HPIDA)^{2+}$)	11.9 ($Am(HPIDA_2^+$)		[60]
8-hydroxyquinoline-5-sulfonic acid (H_2OXSA)							
	IX	25 ± 0.2	0.1 м NH_4ClO_4	8.64 ± 0.09 ($AmOXSA^+$)			[61]
iminodiacetic acid (H_2IDA)							
	IX	25	0.1 м NH_4ClO_4	7.37 ($AmIDA^+$)	12.39 ($Am(IDA)_2$)		[26]
	Spec	25 ± 0.2	1.0 м $HClO_4/NaClO_4$	6.14		$\beta_5 = 3.34$ ($Am(IDA)_5^{7-}$)	[11]
	Spec	25	0.1 м NH_4ClO_4	6.94			[31]
7-iodo-8-hydroxyquinoline-5-sulfonic acid (H_2IOXSA)							
	IX	25 ± 0.2	0.1 м NH_4ClO_4	6.92 ($AmIOXSA^+$)			[61]
β-isopropyltropolone (HIPT)							
	IX		0.1 м NH_4ClO_4			$\beta_3 = 22.22 \pm 0.15$ (Am(IPT)3)	[9]
	SX	25	0.1 м NH_4ClO_4			$\beta_3 = 21.37$	[9,62]

Table 8.9 (*Contd.*)

Ligand	*Method*	*Temp*. (°C)	*Ionic strength, medium* μ (mol L^{-1})	*Log of formation constants*		*Other constants*	*References*
				β_1	β_2		
lactic acid (HLact)	SX	25	2.0 м NH_4ClO_4	2.52 ($AmLact^{2+}$)	4.77 ($Am(Lact)_2^+$)	$\beta_3 = 5.98$ (Am(Lact)3)	[63]
	IX		0.5 м NH_4ClO_4	2.77	4.64		[64]
	SX	20	0.5 м NH_4ClO_4			$\beta_3 = 5.71 \pm 0.03$	[65]
	IX	20	0.5 м NH_4ClO_4			$\beta_3 = 5.73$	[65]
	PEP	10	1.5 м KCl/HLact	2.57	4.21		[66]
methionine	Spec	18 ± 2	1.0 м KCl	4.8 ± 0.2			[8]
N-methyliminodiacetic acid (H_2MIDA)	IX	25	0.1 м NH_4ClO_4	7.01 ($AmMIDA^+$)	12.51 ($Am(MIDA)_2^-$)		[26]
6-methyl-2-picoline acid (HMAPS)	IX	25 ± 0.2	0.1 м NH_4ClO_4	4.26 ($AmMAPS^{2+}$)			[61]
6-methyl-2-picolyliminodiacetic acid (H_2MPIDA)	IX	25	0.1 м NH_4ClO_4	8.38 ($AmMPIDA^+$)			[26]
methylolethylphosporic acid (HMEPA)	IX	25	0.2 м NH_4ClO_4	1.79 ± 0.12 ($AmMEPA^{2+}$)			[59]
(methylphenylphosphinyl)methylphenylposphinic acid (HMPPA)	SX	25	0.2 м NH_4ClO_4	3.35 ($AmMPPA^{2+}$)			[59]
methylphosphinic acid (HMPA)	IX	25 ± 0.2	0.5 м NH_4ClO_4	2.79 ($AmMPA^{2+}$, at $\mu = 0$)			[67]
naphthoyltrifluoroacetone (HNTA)	SX	25	0.1 м NH_4ClO_4			$\beta_3 = 18.31$ ($Am(NTA)_3$)	[9]
nitrilodiacetomonobutyric acid (H_3NDMBA)	IX	25	0.1 м NH_4ClO_4			$\beta_1' = 3.53$ (AmHNDMBA)	[68,69]
nitrilodiacetomonopropionic acid (H_3NDAPA)	IX	25	0.1 м NH_4ClO_4	10.54 (AmNDAPA)	17.83 ($Am(NDAPA)_2^{3-}$)	$\beta_1' = 4.02$ (AmHNDAPA)	[68,69]
nitrilodiacetomonovaleric acid (H_3NDAVA)	IX	25	0.1 м NH_4ClO_4			$\beta_1' = 3.47$ (AmHNDAVA)	[68,69]

nitrilotriacetic acid (H_3NTA)							
	IX	25 ± 0.2	0.1 м $NaClO_4$	11.72 ± 0.02 (AmNTA)			[11]
			0.5 м $NaClO_4$	10.84 ± 0.06			[11]
	SX	20	0.1 м NH_4ClO_4	10.70	19.71$(Am(NTA)_2^{3-})$		[39]
	IX	20	1.0 м NH_4ClO_4	10.87			[1]
	IX	25.6	0.1 м NH_4ClO_4	11.91	20.18		[35]
	IX	25	0.1 м NH_4ClO_4–$HClO_4$	11.52	20.24		[68]
	IX	25	0.1 м (NH_4, $HClO_4$)	11.68	20.47		[69]
	Spec	24.6	0.1 м NH_4ClO_4	11.99	21.1		[70]
		20		11.65	19.52	$\beta_3 = 13.56$ $(AmNTA(HNTA)^{2-})$	[71]
oxalic acid (H_2Ox)	SX	20	0.1 м NH_4Cl		8.3 $(Am(Ox)_2^-)$	$\beta_3 = 11.8$ $(Am(Ox)_3^{3-})$	[39]
	IX		1.0 м NH_4Cl		9.95	$\beta_4' = 11.0$ $(Am(HOx)_4^-)$	[41]
	Sol	25	$HClO_4/H_2Ox$	7.10 $(AmOx^+)$	11.2	$\beta_3 = 12.3$	[72]
	IX	20–25	0.2 м NH_4ClO_4	5.99	10.1		[73]
	EM	25	0.1 м NH_4Cl/HCl	6.45	10.5		[73]
	SX	25	1.0 м $NaClO_4$	4.63	8.35	$\beta_3 = 11.2$	[74,75]
	IX	25	0.5 м $NaClO_4$	3.8 ± 0.02	8.61 ± 0.01		[28]
	Spec	25 ± 0.1	$\mu = 0.25$; oxalate,pH1–5	3.27 (AmO_2Ox^+)	2.09 $(AmO_2(Ox)_2^{3-})$		[75]
	SX	21	0.7 м Na NaCl	4.58 ± 0.05 (pH 6.0) 3.95 ± 0.15 (pH 8.05)	7.91 ± 0.10 (pH 6.0) 7.54 ± 0.20 (pH 8.05)		[76]
	Sol	25 ± 0.2	I = 0	6.68	9.94	11.62	[77]
	EM	25	0 м $NaClO_4$		9.6		[78]
			0.01 м $NaClO_4$		9.0		[78]
			0.05 м $NaClO_4$		8.3		[78]
			0.1 м $NaClO_4$		8.2		[78]
	SX	25.0	1.0 м $NaClO_4$	4.61 ± 0.06	8.39 ± 0.12		[79]
			3.0 м $NaClO_4$	4.65 ± 0.04	8.67 ± 0.13		[79]
			5.0 м $NaClO_4$	4.83 ± 0.06	9.24 ± 0.09		[79]
			7.0 м $NaClO_4$	4.93 ± 0.11	9.42 ± 0.06		[79]
			9.0 м $NaClO_4$	4.54 ± 0.06	8.77 ± 0.05		[79]
phenylalanine	Spec	18 ± 2	1.0 м KCl	5.1 ± 0.3			[8]
1-phenyl-3-methyl-4-acetylpyrazolone-5 (HPMAP)							
	SX	25	0.1 м NH_4ClO_4			$\beta_3 = 12.23$ $(Am(PMAP)_3)$	[80]
1-phenyl-3-methyl-4-benzoylpyrazolone-5 (HPMBP)							
	SX	25	0.1 м NH_4ClO_4			$\beta_3 = 16.49$ $(Am(PMBP)_3)$	[80]
1-phenyl-3-methyl-4-trichloroacetylpyrazolone-5 (HPMTCP)							
	SX	25	0.1 м NH_4ClO_4			$\beta_3 = 7.47$ $(Am(PMTCP)_3)$	[80]

Table 8.9 (*Contd.*)

Ligand	*Method*	*Temp.* (°C)	*Ionic strength, medium* μ (mol L^{-1})	*Log of formation constants* β₁	β₂	*Other constants*	*References*
1-phenyl-3-methyl-4-trifluoroacetylpyrazolone-5 (HPMTFP)							
	SX	25	0.1 M NH_4ClO_4			$\beta_3 = 9.70$ ($Am(PMTFP)_3$)	[80]
phosphonoacetic acid (H_3PAA)							
	IX	0.2 M NH_4ClO_4				$\beta_1'' = 2.75$ ($Am(H_2PAA)^2$)	[81]
						$\beta_1''' = 5.15$ ($AmHPAA^+$)	[81]
						$\beta_2''' = 8.5$ ($Am(HPAA)_2^-$)	[81]
pyridine-2-carbonic acid (HAPS)							
	IX	25 ± 0.2	0.1 M NH_4ClO_4	4.28 ± 0.05 ($AmAPS^{2+}$)	7.99 ± 0.03 ($Am(APS)_2^+$)	$\beta_3 = 10.51 \pm 0.05$ (Am(APS)3)	[61]
α-picolinic acid-*N*-oxide (HAPSNO)							
	IX	25 ± 0.2	0.1 M NH_4ClO_4	3.09 ± 0.07 ($AmAPSNO^{2+}$)	5.49 ± 0.07 ($Am(APSNO)_2^+$)		[61]
2-picolyliminodiacetic acid (H_2PIDA)							
	IX	25	0.1 M NH_4ClO_4	8.96 ($Am(PIDA^+)$)	17.71 ($Am(PIDA)_2^+$)		[26,52]
	Spec	25	0.1 M	0.94 ± 0.01 ($Am(PIDA)^+$)			[82]
				1.24 ± 0.001 ($Am(PIDA)_2^-$)			[82]
propanetricarboxylic acid (H_3PTA)							
	Spec	25	1.0 M $NaClO_4$	5.61 ± 0.07 (AmPTA)		$\beta_1' = 4.96 \pm 0.02$ ($AmHPTA^+$)	[10,11]
α-pyridiylacetic acid (HAPAA)							
	IX	25 ± 0.2	0.1 M NH_4ClO_4	3.63 ± 0.07 ($AmAPPA^{2+}$)			[61]
pyridine-3-carboxylic acid (Nicotinic acid) (HNIC)							
	IX	25 ± 0.2	0.1 M NH_4ClO_4	3.18 ± 0.07 ($AmNIC^{2+}$)			[61]
pyridine-2,6-dicarboxylic acid (H_2PDA)							
	IX	25 ± 0.2	0.1 M NH_4ClO_4	9.33 ± 0.09 ($AmPDA^+$)	16.51 ± 0.09 ($Am(PDA)_2^-$)		[61]
pyruvic acid (HPruv)							
	SX	25	2.0 M $NaClO_4$	2.03 ($AmPruv^{2+}$)	3.34 ($Am(Pruv)_2^+$)	$\beta_3 = 3.87$ ($Am(Pruv)_3$)	[63]

bis(3-methoxysalicylidenaldehyde)ethylenediimine (B3MOXSEDI)							
	SX	25	0.3 M KNO_3			$\beta'_2 = 0.59$ (AmH $(B3MoxSEDI)_2$)	[83]
bis(salicylidenaldehyde)ethylenediimine (BSEDI)							
	SX	25	0.3 M KNO_3			$\beta'_2 = 4.94$(AmH $(BSEDI)_2$)	[83]
serine		Spec	18 ± 2	1.0 M KCl	4.3 ± 0.1		[8]
squaric acid (H_2Sq, Diketocyclobutenediol)							
	IX	25	1.0 M $(H,NH_4)ClO_4$	2.17($AmSq^+$)	3.10 ($Am(Sq)_2$)		[84]
5-sulphosalicylic acid							
	PT	25	1.0 M $NaClO_4$	8.06 ± 0.02	15.34 ± 0.02		[85]
tartaric acid (H_2Tart)							
	IX		1.0 M NH_4Cl		10.7 ($Am(Tart)_2^+$)		[14,86]
	SX	20	0.1 M NH_4Cl	3.9 ($AmTart^+$)	6.8		[39]
	PEP	(?)	(?)		7.88		[87]
	SX	25 ± 0.5	0.5 M NH_4ClO_4	4.20 ± 0.06	6.84 ± 0.07		[6]
taurine-*N,N*-diacetic acid (H_3TDA)							
	IX	25	0.1 M NH_4ClO_4	8.08 (AmTDA)		$\beta'_1 = 2.29$ ($AmHTDA^+$)	[26]
	Spec	25	0.1 M	0.89 ± 0.001 ($Am(H_3TDA)$)			[82]
				1.14 ± 0.005 ($Am(H_3TDA)_2^{3-}$)			[82]
N,N,N′,N′-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN)							
	PT	25	0.1 M $NaClO_4$	6.69 ± 0.03 ($Am(TPEN)^{+3}$)			[88]
	Spec	25	0.1 M $NaClO_4$	6.77 ± 0.01 ($Am(TPEN)^{+3}$)			[88]
thenoyltrifluoroacetone (HTTA)							
	SX	25	0.1 M NH_4ClO_4	3.4 ($AmTTA^{2+}$)	8.5($Am(TTA)_2^+$)	$\beta_3 = 13.3$ ($Am(TTA)_3$)	[9]
	SX	10.40	0.1 M $HClO_4/ClO_4$			$\Delta G^\circ = 43.9$ kJ mol^{-1} (Am(TTA)3)	[12]
thiodiglycolic acid (H_2TDGA)							
	Spec	25.6	0.1 M NH_4ClO_4	3.52 ± 0.08 ($AmTDGA^+$)	5.66 ± 0.07 ($Am(TDGA)_2^+$)	$\beta'_1 = 2.06 \pm 0.08$ ($AmHTDGA^{2+}$)	[35]
thioglycolic acid (HTGlyc)							
	IX	20	0.5 M NH_4ClO_4	1.55 ($AmGlyc^{2+}$)	2.60($Am(TGlyc)_2^+$)		[3]
p-toluenesulfonic acid (pTSAH)							
	SX	25	2.0 M $HClO_4$/pTSAH	-0.028 ± 0.028 ($AmpTSA2^+$)			[89]
	SX	25	2.0 M HBF_4/pTSAH	0.075 ± 0.018			[89]

Table 8.9 (*Contd.*)

Ligand	*Method*	*Temp.* (°C)	*Ionic strength, medium* μ (mol L^{-1})	*Log of formation constants*		*Other constants*	*References*
				β_1	β_2		
triethylenetetraaminehexaacetic acid (H_6TTHA)							
	IX	25	0.1 M NH_4ClO_4			$\beta'_1 = 18.13$ ($AmHTTHA^{2+}$)	[26]
						$\beta''_1 = 11.85$ (AmH_2TTHA^-)	[26]
	Spec	25	0.1 M NH_4ClO_4	27.61 ($AmTTHA^{3-}$)		$\beta = 30.97$ (Am2TTHA)	[1,31]
						$\beta = 9.15(Am_2H_2(TTHA)_3^{10-})$	[1,31]
Tropolene	SX	25	0.1 M $HClO_4$			$\beta_3 = 16.17 \pm 0.08$	[62]
Tryptophan	Spec	18 ± 2	1.0 M KCl	4.7 ± 0.2			[8]

[1] (Moskvin, 1967, 1971, 1973); [2] (Choppin, 1965, 1970, 1975); [3] (Grenthe, 1962); [4] (Gureev *et al.*, 1970); [5] (Hara, 1970); [6] (Rao *et al.*, 1987); [7] (Aziz and Lyle, 1971); [8] (Rogozina *et al.*, 1974); [9] (Keller and Schreck, 1969); [10] (Eberle and Moattar, 1972); [11] (Moattar, 1971); [12] (Hubert *et al.*, 1974, 1975); [13] (Ohyoshi and Ohyoshi, 1971); [14] (Moskvin *et al.*, 1962); [15] (Marcu and Samochocka, 1966); [16] (Bouhlassa and Guillaumont, 1984); [17] (Wall *et al.*, 2002); [18] (Mohapatra and Manchanda, 1991); [19] (Stepanov *et al.*, 1967); [20] (Baybarz, 1966); [21] (Elesin and Zaitsev, 1971a); [22] (Shilov *et al.*, 1976); [23] (Mohapatra and Manchanda, 1995); [24] (Zur Nedden, 1969); [25] (Keller *et al.*, 1965a, 1966); [26] (Bayat, 1970); [27] (Baybarz, 1965); [28] (Lebedev and Shalinets, 1968; Lebedev *et al.*, 1968); [29] (Burch, 1964); [30] (Hafez, 1968); [31] (Delle Site and Baybarz, 1969); [32] (Piskunov and Rykov, 1972); [33] (Brandau, 1971); [34] (Elesin and Zaitsev, 1972); [35] (Grigorescu-Sabau, 1972); [36] (Goffart and Kuyckaerts, 1969; Vorob'eva *et al.*, 1973a); [37] (Shalinets and Stepanov, 1971, 1972); [38] (Elesin *et al.*, 1973); [39] (Stary, 1966); [40] (Fuger, 1958); [41] (Moskvin *et al.*, 1959); [42] (Lebedev *et al.*, 1967); [43] (Elesin and Zaitsev, 1971b); [44] (Shalinets, 1972a,c); [45] (Anan'ev and Krot, 1985; Anan'ev and Shilov, 1985); [46] (Buckau *et al.*, 1992); [47] (Tanner and Choppin, 1968); [48] (Choppin and Degischer, 1972); [49] (Levakov and Shalinets, 1971); [50] (Eberle and Bayat, 1967); [51] (Mercing and Duyckaerts, 1967); [52] (Eberle and Bayat, 1969); [53] (Ermakov *et al.*, 1971c); [54] (Shalinets, 1972b); [55] (Dedov *et al.*, 1961); [56] (Graus Odenheimer and Choppin, 1956); [57] (Stary, 1965); [58] (Vorob'eva *et al.*, 1973b); [59] (Elesin *et al.*, 1972a,b); [60] (Ermakov *et al.*, 1971b); [61] (Al Rifai, 1970); [62] (Cilindro and Keller, 1974); [63] (Aziz and Lyle, 1971); [64] (Lebedev and Yakovlev, 1961); [65] (Ermakov and Starπ, 1967); [66] (Sakanque and Nakatani, 1972); [67] (Borisov *et al.*, 1967); [68] (Eberle and Ali, 1968); [69] (Ali, 1968); [70] (Eberle and Sabau, 1972); [71] (Gedeonov *et al.*, 1967); [72] (Lebedev *et al.*, 1960a); [73] (Stepanov and Makarova, 1965; Stepanov, 1971); [74] (Sekine, 1965); [75] (Shilov *et al.*, 1974); [76] (Caceci and Choppin, 1983); [77] (Pazukhin *et al.*, 1987); [78] (Rosch *et al.*, 1989); [79] (Choppin and Chen, 1996); [80] (Backer and Keller, 1973); [81] (Elesin *et al.*, 1972c); [82] (Bayat and Moattar, 1982); [83] (Stronski and Rekas, 1973); [84] (Cilindro *et al.*, 1972); [85] (Nair and Chander, 1983); [86] (Gel'man *et al.*, 1967); [87] (Marcu and Samochocka, 1965); [88] (Jensen *et al.*, 2000); [89] (Baisden *et al.*, 1972).

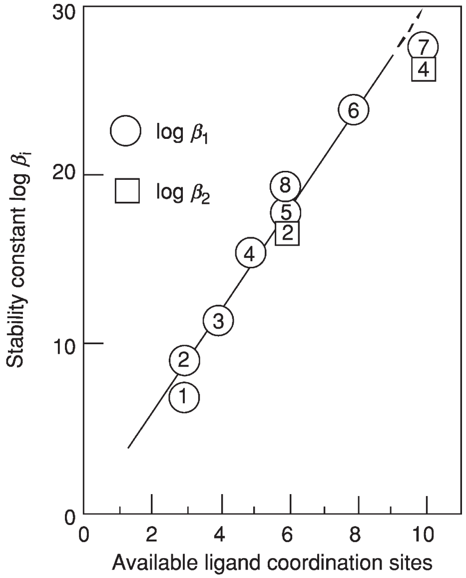


Fig. 8.7 *Correlation of stability constants with number of available coordination sites.* 1, *iminidiacetic acid;* 2, *N-hydroxy-ethyliminodiacetic acid;* 3, *nitrilotriacetic acid;* 4, *N-hydroxyethylenediaminetriacetic acid;* 5, *ethylenediaminetetraacetic acid;* 6, *diethylenetriaminepentaacetic acid;* 7, *triethylenetetraaminehexaacetic acid;* 8, *diaminocyclohexanetetraacetic acid* (*Keller*, 1971).

Methods are being sought to estimate and correlate the strengths of Am(III) complexes and other trivalent actinides and lanthanides with various organic ligands. Shalinets and Stepanov (1971, 1972) suggests a 'rule of additivity of the strength of rings' according to which, under similar conditions, the logarithm of the thermodynamic formation constant of the complex is proportional to the sum of the strengths of the individual rings. In a few cases, formation constants of americium chelates calculated by Shalinets are in good agreement with experimental data. For a more detailed discussion of the nature and stability of organic complexes of americium, refer to Chapters 23 and 25.

It is not surprising that a number of studies focus on the complexation of Am(III) with natural organic substances because of its importance for the assessment of nuclear waste disposal in geologic formations. The majority of naturally occurring organic materials derive from the decomposition of organic matter to soluble polymeric HA and fulvic acid (FA). The surfaces of these substances have a number of hydrophilic functional groups, such as amine, hydroxyl, carboxyl, and phenolic. As a hard cation, Am^{3+} interacts predominantly with the oxygen-donating phenolic and carboxylic groups. A large number of experimental data exist that are usually interpreted by the charge neutralization model or a polyelectrolyte model (Choppin and Labonne-Wall, 1997). The charge neutralization model is based on the cation complexation by a number of carboxylate groups expressed as an experimentally determined loading capacity of the organic substance. The polyelectrolyte model can better accommodate the chemical behavior of the humic/fulvic acids and takes into account the nature of the binding functional group (carboxylate). The concentration of binding sites and the ionization degree is determined experimentally via pH titration. For a more detailed discussion of these two models and of the impact of humate and fulvate complexation on the environmental behavior of americium, refer to Chapters 27 and 29.

Choppin and coworkers (Bertha and Choppin, 1978) performed ion-exchange studies at pH 4.5 to determine $\log \beta_1 = 6.83$ and $\log \beta_2 = 10.58$ for a Lake Bradford, Florida (USA), humic substance. These results agree well with $\log \beta_1 = 6.4$ and $\log \beta_2 = 10.58$ determined for HA from Mount Kanmuri, Japan (Yamamoto and Sakanoue, 1982). Applying a degree of ionization of the HA, Choppin and coworkers (Torres and Choppin, 1984) reported $\log \beta_1 = 6.8–11.6$ and $\log \beta_2 = 11.9–14.3$ for the Am(III)—HA (Lake Bradford) complex determined at pH 3.75–5.7. Using UV–VIS and laser-induced photoacoustic spectroscopy Kim *et al.* (1993) determined $\log \beta_1 = 6.4 \pm 0.1$ at pH = 6 ($I = 0.1$) for HAs obtained from natural water at the German Gorleben (Gohy-573) site and from a commercial HA (Aldrich Chemical Co.). For the calculation of the Am(III)–HA stability constant, Kim *et al.* determined a loading capacity of 62.2% for Gohy-573 HA and of 81.5% for Aldrich HA. The Am(III) absorption band at 506 nm was assigned to an Am(III)–HA complex and was used for data analysis. Moulin *et al.* (1987) spectroscopically monitored the complexation of Am(III) with Aldrich HA at pH 4.65 ($I = 0.1$) and calculated $\log \beta_1 = 7–7.5$.

The stability constants found for Am(III) fulvate are slightly smaller than those found for humate. Buckau *et al.* (1992) determined $\log \beta_1 = 5.9$ for FA extracted from the Gohy-573 groundwater using UV–VIS absorption spectroscopy. This FA is characterized by a proton exchange capacity of 5.7 meq g^{-1} and a loading capacity of 64.9% at pH 6.0. Interestingly, the stability constant of the Am(III)–FA complex is constant in the Am(III) concentration range of 4×10^{-5} to 5×10^{-8} mol L^{-1} at $[HA] = 10^{-6}$ mol L^{-1}.

Complexation of Am(III) with the hexadentate ligand *N*,*N*,*N′*,*N′*-tetrakis (2-pyridylmethyl)ethylenediamine (TPEN) in 0.1 M $NaClO_4$ at 25°C to form $Am(TPEN)^{3+}$ is about two orders of magnitude higher than that of Sm(III), reflecting the stronger bonding of the trivalent actinide cations with softer ligands as compared to lanthanides (Jensen *et al.*, 2000).

(d) Others

The stability constants of Am(III) fluoride complexes are much larger than for the other halides (Silva *et al.*, 1995). Positive enthalpies for the reaction of Am^{3+} with F^- anions indicate that the AmF_n^{3-n} are inner-sphere complexes.

Two Am(III) fluoride solution species have been identified, AmF^{2+} and AmF_2^+, with recommended formation constants of log $\beta_1^o = 3.4 \pm 0.4$ and log $\beta_2^o = 5.8 \pm 0.2$, respectively. In contrast, the recommended formation constant for $AmCl^{2+}$, log $\beta_1^o = 1.05 \pm 0.06$, suggests a very weak bonding of chloride ions.

Few reliable data have been reported for the sulfate complexation of Am(III). Stability constants for two complexes, $AmSO_4^+$(log $\beta_1^o = 3.85 \pm 0.03$) and $Am(SO_4)_2^-$(log $\beta_2^o = 5.4 \pm 0.7$), were recommended (Silva *et al.*, 1995). There is no evidence for the formation of $Am(III) - HSO_4^-$ complexes.

The formation of Am(III) thiocyanate complexes was studied intensively because of the use of such complexes in separation of lanthanide and actinide elements. Three complexes of general formula $Am(SCN)_n^{3-n}$ (n = 1–3) have been identified from spectroscopic and solvent extraction data. The complexation of Am(III) by thiocyanate is quite weak and the accepted thermodynamic constant for the 1:1 complex is log $\beta_1^o = 1.3 \pm 0.3$ (Silva *et al.*, 1995).

Nitrate complexes of Am(III) are weak complexes and two complexes, $AmNO_3^{2+}$ and $Am(NO_3)_2^+$, have been used to interpret solvent extraction data in nitric acid media. The recommended formation constant of the 1:1 complex is log $\beta_1^o = 1.33 \pm 0.20$ (Silva *et al.*, 1995).

A number of studies of Am(III) complexation in phosphate media have been reported with only a few reliable data interpretations and complex characterizations. The system is complicated by the presence of multiple (hydrogen) phosphate species in solution. The solution complexes $AmHPO_4^+$ and $Am(H_2PO_4)_n^{3-n}$ (n = 1–4) have been used to interpret cation exchange, solvent extraction, and spectroscopic data. Lebedev *et al.* (1979) attributed the changes of the characteristic absorption band of Am^{3+} at 503 nm to the formation of $Am(III) - H_2PO_4^-$ complexes. With increasing phosphoric acid concentration (up to 13 M), the absorbance maximum is shifted to about 502 nm and the characteristic shoulder in the Am^{3+} band at 506 nm almost disappears. It remains unclear if these changes are due to inner-sphere complexation with phosphate or to changes in the number of coordinated water molecules in these extreme experimental conditions. The NEA recommends a stability constant only for the complex $AmH_2PO_4^{2+}$, log $\beta_1^o = 3.0 \pm 0.5$ (Silva *et al.*, 1995).

Am(IV) can be stabilized in acidic media by complexation with heteropolyanions. Chartier *et al.* (1999) reported spectroscopic evidence for the formation of $AmP_2W_{17}O_6^{16-}$ and $Am(P_2W_{17}O_{61})_2^{16-}$ via their absorbance bands at 789 and 560 nm, respectively. Chartier *et al.* reported log $\beta_1 = 19.2 \pm 0.2$ and log $\beta_2 = 22.8 \pm 0.2$ in 1 M HNO_3. The rate of autoradiolytic reduction of Am(IV) in these complexes is independent of the complex composition. Th(IV) causes the destruction of the complexes and subsequent disproportionation of free Am(IV) into Am(III) and Am(VI). Complex formation of Am(III) with $W_{10}O_{36}^{12-}$, $PW_{11}O_{39}^{7-}$, and $SiW_{11}O_{39}^{8-}$ was discussed qualitatively by Yusov (1989). Chartier *et al.* (1999) determined the apparent formation constants for $AmSiW_{11}O_{39}^{4-}$ and for $Am(SiW_{11}O_{39})_2^{12-}$ in 1 M HNO_3, log $\beta_1 = 21.3 \pm 0.3$ and log $\beta_2 = 26.2 \pm 0.2$, respectively. In contrast, Williams *et al.* (2000) used extended X-ray absorption fine structure (EXAFS) to determine that the Am center cation is trivalent when integrated in the Preyssler anion, $AmP_5W_{30}O_{110}^{12-}$.

Sullivan *et al.* (1961) discovered cation–cation interaction between pentavalent and hexavalent actinides. Subsequently, Guillaume *et al.* (1981) found spectroscopic evidence for the Am(v)–U(vi) interaction in perchlorate medium where the interaction between AmO_2^+ and UO_2^{2+} shifts the main absorbance peak of AmO_2^+ at 716–733 nm and a new band appears at 765 nm. Both bands are close to the absorbances reported for the solid $KAmO_2CO_3$ (733 and 770 nm (Varga *et al.*, 1971)). Upon interaction of Am(v) with U(vi), the symmetrical stretching (Raman) frequency of AmO_2^+ at 732 cm^{-1} is shifted to 719 cm^{-1} (Guillaume *et al.*, 1982). The Am(v)–U(vi) ($K = 0.35 \pm 0.07$ at $I = 10$) and Am(v)–Np(vi) ($K = 0.095 \pm 0.03$ at $I = 6$) (Guillaume *et al.*, 1981, 1982) complexes appeared to be much weaker than the corresponding Np(v) complexes: Np(v)–U(vi) ($K = 3.7 \pm 0.1$ at $I = 7$) and Np(v)–Np(vi) ($K = 3.0 \pm 0.1$ at $I = 7$ (Madic *et al.*, 1979)).

8.9 COORDINATION CHEMISTRY AND COORDINATION COMPLEXES

Although over 250 compounds of americium have been synthesized and characterized, the coordination chemistry of americium is relatively unknown. As of 2001, the crystal structures of 39 americium compounds with inorganic ligands and only seven americium compounds with organic ligands have been structurally characterized. However, the majority of phase identification and characterization relied on X-ray powder diffraction and comparison to isostructural lanthanide, neptunium, or plutonium compounds. Certainly, the application of EXAFS provides useful insight into coordination and bonding of solution complexes and amorphous solid phases. As hard metal ions Am(iii to vi) have a high affinity for hard donor atoms, such as O or N, and the light halides, and their coordination will be discussed in this section. Because of its high redox stability, trivalent americium coordination complexes are the most common. Generally, higher dimensional structures are found containing Am^{2+}, Am^{3+}, or Am^{4+} while the introduction of the linear americyl unit forces Am(v) and Am(vi) to form layered structures.

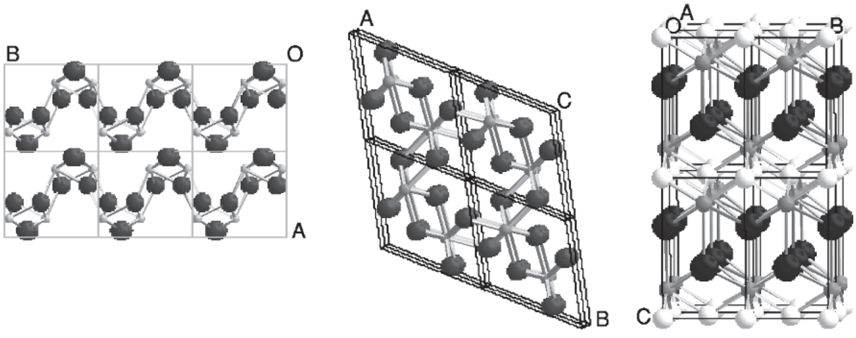
8.9.1 Compounds with inorganic ligands

(a) Halides

Americium exhibits different coordination environments in halide complexes with coordination numbers of 7, 8, 9, and 11. In the orthorhombic M_2AmCl_5 ($M = K$, NH_4, or Rb) trivalent americium is seven-coordinate in $AmCl_5^{2-}$ chains with two of the five chlorides bridging to adjacent Am atoms. In the monoclinic hexahydrate, $AmCl_3 \cdot 6H_2O$, americium is coordinated to two chlorides and six water molecules forming $AmCl_2(H_2O)_6^+$ cations that are linked through chloride anions in the lattice and an extensive hydrogen bond network (Burns and Peterson, 1971). Considering the inner-sphere bonding of the water molecules, the formula of this compound is better represented by $AmCl_2(H_2O)_6 \cdot Cl$. Eight-coordinate americium is also found in the tetrafluoride AmF_4. $AmO_2F_2^-$ layers held together by K^+ ions form the rhombohedral $KAmO_2F_2$, in which americium is eight-coordinate with two axial oxygen atoms (Am–O = 1.936 Å) and six fluorides (Am–F = 2.473 Å) in the equatorial plane (Asprey *et al.*, 1954a). The isostructural oxyhalides AmOCl (Weigel *et al.*, 1975) and AmOI (Asprey *et al.*, 1964, 1965) also contain nine-coordinate americium that is surrounded by four oxygen (2.343 Å) and five iodine atoms (4 Am–I of 2.994 Å and 1 Am–I of 3.0035 Å). Interestingly, AmOBr (Weigel *et al.*, 1979) is reported to be built up from linear Br–Am–O units stacked along the *c*-axis with reported interatomic distances of 2.415 Å for Am–O and 3.21 and 3.36 Å for Am–Br. Using the atomic coordinates reported for AmOBr, we calculate 2.339 and 2.979 Å for Am–O and 3.145 and 3.801 Å for Am–Br bond distances. Considering the discrepancies in the bond distances and the structural anomaly within the AmOX series, there are serious doubts about the reported structure of AmOBr. The trifluoride AmF_3 crystallizes in the 11-coordinate LaF_3 structure (Templeton and Dauben, 1953). In the anhydrous $AmCl_3$, the americium atom is bonded to six chlorine atoms at 2.874 Å and three chlorine atoms at 2.915 Å (Burns and Peterson, 1970) (Fig. 8.8).

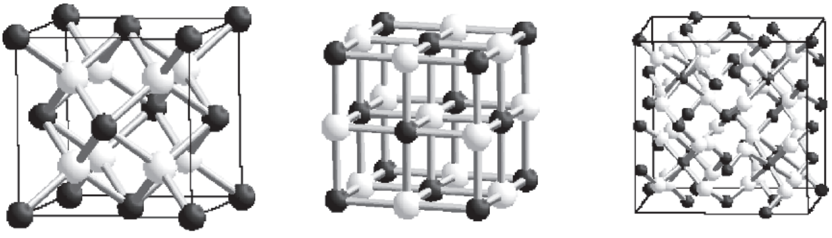
(b) Oxides

Several americium oxides of varying stoichiometry have been prepared and structural data rely principally on X-ray powder diffraction powder data. The binary oxide AmO (CN 6) crystallizes in a cubic structure with octahedral O and Am atoms (Zachariasen, 1949b). Interatomic distances are calculated to be 2.480 Å for Am–O and 3.507 Å for Am–Am. However, AmO may be an oxynitride, as discussed in Section 8.7.1. As discussed in Section 8.7.1, three Am_2O_3 phases are known. Templeton and Dauben (1953) report the lattice parameters $a = 11.03 \pm 0.01$ Å for the low-temperature cubic form and $a = 3.817 \pm 0.005$ Å, $c = 5.971 \pm 0.010$ Å for the high-temperature hexagonal form. In the cubic phase two crystallographically different americium atoms exist: distorted $[Am(1)O_6]$ octahedra with Am(1)–O bond lengths of 2.369 Å are bridged through their oxygens to six Am(2) atoms. The Am(2) atoms are centered within a distorted octahedral environment of six oxygen atoms with Am–O distances of 1.984, 2.678, and 2.774 Å. The Am(2)–O distances of 1.984 Å are unusually short for trivalent actinide–oxygen bonds and only slightly longer than the reported bond lengths of about 1.935 Å for the linear Am=O bonds in Am(v) compounds (Asprey *et al.*, 1954a; Ellinger and Zachariasen, 1954). The intermediate-temperature monoclinic AmO_2 is isostructural with



AmI_2 $AmCl_3$ AmOCl

Fig. 8.8 *Structures of americium halide compounds:* AmI_2 (*Baybarz and Asprey,* 1972), $AmCl_3$ (*Burns and Peterson,* 1970), *and AmOCl* (*Templeton and Dauben,* 1953).



AmO_2 AmO Am_2O_3

Fig. 8.9 *Unit cells of americium oxides:* AmO_2 (*Templeton and Dauben,* 1953; *Chikalla and Eyring* 1967, 1968), *AmO* (*Zachariasen,* 1949a,b), *and* Am_2O_3, (*Templeton and Dauben,* 1953).

PuO_2 with eight Am–Am distances of 3.803 Å and a tetrahedral arrangement of four Am atoms around each oxygen atom (Am–O is 2.480 Å) (Templeton and Dauben, 1953). The three-dimensional ternary oxide $BaAmO_3$ (cubic perovskite structure, $a = 4.35$ Å, although possibly distorted as are $BaPuO_3$ and $BaLnO_3$) is built from edge-sharing [AmO_6] octahedra with large Ba^{2+} cations in 12-coordinated sites (Keller, 1964). Each AmO_6 octahedron shares all oxygen atoms with six adjacent octahedra. The Am–O distances are calculated to be 2.175 Å (Fig. 8.9).

(c) Chalcogenides and pnictides

The americium monochalcogenides AmX (X = S, Se, Te) crystallize in the cubic NaCl-type structure (CN 6) with the lattice parameters increasing with chalcogen atomic number. Early work of Zachariasen (1949d) concluded from powder

X-ray diffraction data that the sesquisulfide Am_2S_3 is isostructural with cubic Ce_2S_3 and contains 16 sulfur atoms and $10^{2/3}$ americium atoms per unit cell. The calculated interatomic Am–S distances of 2.94 Å are indicative of an ionic bonding between Am^{3+} and S^{2-} and compare well with the value of 2.93 Å reported by Damien and Jove (1971) in the substoichiometric compound $AmS_{1.9}$. The substoichiometric ditelluride, $AmTe_{1.73}$ (CN 9), crystallizes in a tetragonal anti-Fe_2As-type structure (Burns *et al.*, 1979). Layers of Te atoms are interleaved with puckered double layers of AmTe. The bond length between Te atoms in the pure Te layer is much shorter than the Te^{2-} interionic distances, suggesting some covalency within the pure Te layer. Random vacancy at sites within the pure Te layers causes the variable stoichiometry in Am–Te_2. The Am–Te bond lengths within the AmTe layers are only slightly shorter (3.258 and 3.208 Å) than the 3.269 Å from the Am atoms to the nearest Te atoms in the pure Te layer.

The structural information on the known pnictides of general formula AmX (X = N, P, Sb, As) was obtained from X-ray powder diffraction data. All binary pnictides crystallize in the cubic NaCl-type structure; both lattice parameters and Am–X bond length increase along the series: in AmN ($a = 5.005$ Å) Am–N is 2.503 Å, in AmP ($a = 5.711$ Å) Am–P is 2.856 Å, in AmAs ($a = 5.875$ Å) Am–As is 2.938 Å, and in AmSb ($a = 5.6.24$ Å) Am–Sb is 3.120 Å.

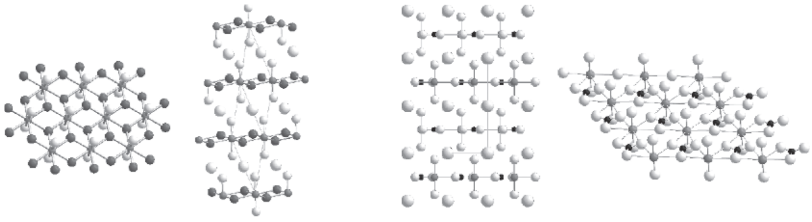
(d) Silicides

Weigel *et al.* (1977, 1984) reported structural information of several silicide phases. The layered structure of the binary AmSi is built up from corner-sharing [$AmSi_3$] pyramids with μ_3-Si atoms and Am–Si distances of 2.56 and 2.66 Å. The tetragonal $AmSi_2$ is isostructural with α-$ThSi_2$ and Am–Si distances range between 2.01 and 2.70 Å. In the sesquisilicide Am_2Si_3 americium atoms are coordinated to Si atoms at Am–Si distances of 3.04 Å.

(e) Oxoanionic ligands

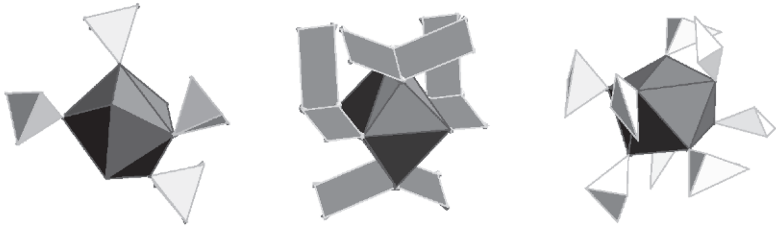
Six oxygen atoms from three bidentately bonded carbonate ligands in the equatorial plane and two axial americyl oxygens form the inner coordination sphere of Am(V) in $RbAmO_2CO_3$ (Ellinger and Zachariasen, 1954) (Fig. 8.10). The Am=O and Am–O_{eq} bond distances are calculated from X-ray powder diffraction data to be 1.935 and 2.568 Å, respectively. Both distances are significantly longer than those in the Np(V) compounds, i.e. 1.75 Å for Np=O and 2.46 Å for Np–O_{eq} in aqueous $NpO_2(CO_3)_n^{1-2n}$ complexes (Clark *et al.*, 1996).

In the pseudotetragonal molybdate $Am_2(MoO_4)_3$ one-third of the Am sites are replaced by ordered vacancies (Tabuteau and Pages, 1978). The molybdate is isostructural to several lanthanide molybdates that crystallize in the pseudoscheelite structure. The Am(III) tungstate, $Am_2(WO_4)_3$, is structurally analogous to $Eu_2(WO_4)_3$ and is built up from [AmO_8] dodecahedra and [WO_4] tetrahedra.



$KAmO_2F_2$ $RbAmO_2CO_3$

Fig. 8.10 *Sheet structures and crystal packing of the Am*(v) *compounds* $KAmO_2F_2$ (*Asprey* et al., 1954a) *and* $RbAmO_2CO_3$ (*Ellinger and Zachariasen*, 1954).



$Am_2(SO_4)_3 \cdot 8H_2O$ $Am_2(MoO_4)_3$ $\alpha\text{-}Am(IO_3)_3$

Fig. 8.11 *Coordination of oxyanions in the Am*(iii) *compounds* $Am_2(SO_4)_3 \cdot 8H_2O$ (*Burns and Baybarz*, 1972), $Am_2(MoO_4)_3$ (*Tabuteau and Pages*, 1978), and α-$Am(IO_3)_3$ (*Bean* et al., 2003).

Burns and Baybarz (1972) reported the synthesis and single-crystal structure analysis of $Am_2(SO_4)_3 \cdot 8H_2O$. Eight-coordinate americium bonded to eight O atoms from four sulfate ligands (Am–O distances range from 2.381 to 2.951 Å) and four water molecules (Am–O range from 2.406 to 2.553 Å). The sulfate tetrahedra share edges and bridge americium atoms within the layers; extensive hydrogen bonding involving the lattice waters occurs between the layers.

Very recently, Bean *et al.* (2003) synthesized the anhydrous Am(iii) iodate, α-$Am(IO_3)_3$, which is isostructural to the Gd(iii) compound (Liminga *et al.*, 1977), and a new f-element iodate of composition $K_3Am_3(IO_3)_{12} \cdot HIO_3$ (Runde *et al.*, 2003) (Fig. 8.11). In both compounds, oxygens from eight iodate pyramids and Am^{3+} ions are located within a distorted $[AmO_8]$ dodecahedron that form a three-dimensional network with Am–O bond distances ranging from 2.34 to 2.60 Å and averaged I–O distances of 1.80 Å. Runde and coworkers also reported the synthesis of β-$Am(IO_3)_3$, that exhibits a novel two-dimensional architecture type within the f-element iodates. The nine-coordinate Am atoms are coordinated with only 7 iodate ligands via a combination of edge-sharing and corner-sharing $[IO_3]$ groups (Bean *et al.*, 2003).

(f) Others

The hydride AmH_3 crystallizes in a cubic structure with eight hydrogen atoms surrounding each Am atom and a tetrahedral arrangement of four Am atoms around each H atom. The bond lengths for Am–H and Am–Am are calculated to be 2.316 and 3.782 Å (Olson and Mulford, 1966).

8.9.2 Compounds with organic ligands

Only seven compounds of americium are listed in the Cambridge Structural Database (version 5.22, October 2001) that compiles complexes of metal cations with organic molecules. However, it is noteworthy that structures obtained from single crystal X-ray diffraction are reported only for two compounds. For the other five compounds, only cell constants and space groups were obtained from X-ray powder patterns and information on bond distances remains unavailable. Information on the overall structure was obtained by analogy to the corresponding compounds of rare earth elements. For a more detailed discussion of the preparation and reactivity of organic americium compounds, refer to Chapters 23 and 29.

(a) Oxygen-donor ligands

A wide variety of oxygen-donor ligands have been used to complex and separate americium. The most synthesized compounds of Am(III) are those with carboxylic acids, because of their applications in separation (Weigel and ter Meer, 1967). However, only the single-crystal structure of the hydrated Am(III) salicylate, $Am(C_7H_5O_3)_3(H_2O)$, has been reported. In this compound, americium is nine-coordinate to one water molecule and six salicylato ligands (Burns and Baldwin, 1976). The six salicylato ligands display three different coordination modes: (i) monodentate binding through the carboxylic oxygens of four ligands; (ii) bidentate binding through its carboxyl group; and (iii) and bidentate binding through a combination of carboxylic and phenolic oxygens. Salicylato complexes have been reported for rare earths and plutonium and are important because the ligands contain carboxylic and hydroxo functional groups, which are typical for the more complex natural humic materials.

The sodium acetate, $NaAmO_2(CH_3CO_2)_3$, is the only characterized complex of americyl(VI) (Jones, 1955). Lychev *et al.* (1980) synthesized the cesium salt of Am(V), $CsAmO_2(CH_3CO_2)_3$, but solved the crystal structure only of the isostructural analogous Np(V) compound. In both americyl acetate compounds, three carboxylates are coordinated bidentately in the equatorial planes of AmO_2^+ and AmO_2^{2+}. Burns and Danford (1969) obtained single crystals of orthorhombic $CsAm(hfa)_4$ (hfa = hexafluoro-acetylacetone) when recrystallizing monoclinic $CsAm(hfa)_4 \cdot H_2O$ (Danford *et al.*, 1970) in 1-butanol. The compound is composed of Am(hfa)-chains that interact with Cs^+ ions. The Am^{3+} ion is chelated by the eight acetone–oxygen atoms of the four hfa ligands with Am–O bond distances between 2.36 and 2.45 Å. $CsAm(hfa)_4$ and $CsAm(hfa)_4 \cdot H_2O$ sublimes at about 135°C. Both hydrated and the anhydrous compounds are metastable and degrade after about 1 week with AmF_3 identified as one of the degradation products (Fig. 8.12).

EXAFS studies of the structure of the solvent-containing $Am(NO_3)_3$ $(TEMA)_2$ complexes (TEMA = *N,N,N,N′*-tetraethylmalonamide) resulted in Am–O distances of 2.52 ± 0.01 Å and a coordination polyhedron similar to that of the corresponding Nd compound, where Nd is ten-coordinate (DenAuwer *et al.*, 2000).

In recent years, the reactions of americium ions with a number of organic molecules were studied in the gas phase. As an example, the gas-phase reaction of laser-ablated americium ions with alcohols yields a mixture of hydroxides and alkoxides, i.e. $Am(OR)^+$ and $Am(OR)^{2+}$ (Gibson, 1999b). The reaction with dimethylether yields the methoxy ion $Am(OCH_3)^+$ as the primary product. Although these reactions do not reveal any structural details, they provide some understanding of potential interaction mechanisms in americium organometallic chemistry. Other products of laser-ablated Am^+ or AmO^+ ions reacting with polyimide, nitriles, or butylamines are AmC_2H^+, $AmC_2H_4^+$, $AmC_2H_2^+$, several cations of general formula $AmC_xH_yN_z^+$, and metal oxide clusters such as Am_2O^+ an $Am_2O_2^+$ (Gibson, 1998a, 1999a). An interesting anomaly was the observation of dimeric Am_2^+ clusters that were not formed by any other actinides studied (Gibson, 1999a).

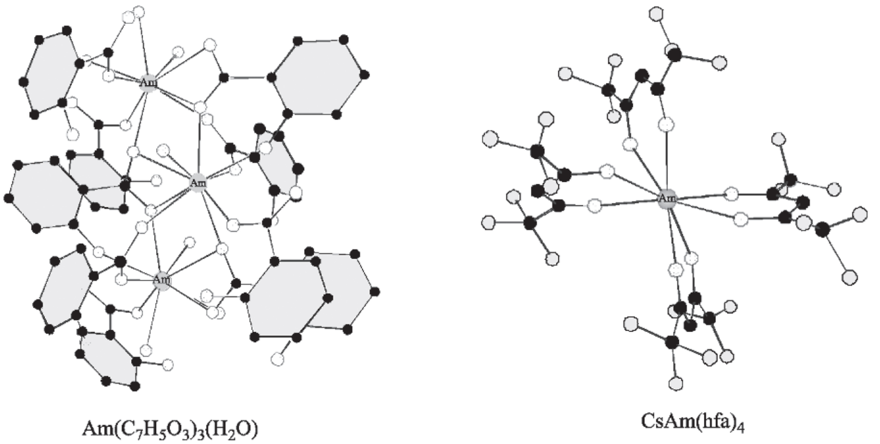


Fig. 8.12 *Nine-fold coordination of Am*(III) *in* $Am(C_7H_5O_3)_3(H_2O)$ (*Burns and Baldwin*, 1976) *and eight-coordinate Am*(III) *in* $CsAm(hfa)_4$ (*Burns and Danford*, 1969).

(b) Nitrogen donors

Only a few complexes of americium with N-donating ligands have been studied yet; structural details are limited. The bis-phthalocyanine complex has been synthesized and displays a sandwich-type complex with eight-coordinate americium (Moskalev *et al.*, 1979). Yaita *et al.* (2001) studied the Am(III) benzimidazole complex using XAFS spectroscopy and found a bidentate coordination of Am through two nitrogen atoms with the bond distance Am–N of 2.63 Å. The overall coordination number of Am(III) is reported to be close to 10.

(c) Sulfur donors

Only few structural studies are reported involving compounds with Am–S bonds. Gibson (1999b) observed SH abstraction from thiols and formation of the hydrosulfide $Am(SH)^+$ in the gas phase. The gas-phase reaction with propanethiol yielded the thiolate $Am(PrS)^+$. Tian *et al.* (2002) used EXAFS to study the structure of extraction complexes of Am(III) with di-*n*-octyldithiophosphinic acid and di(2,4,4-trimethylpentyl)dithiophosphinic acid in kerosene. The two extraction complexes appear to be similar in coordination with eight sulfur atoms in the inner sphere and four phosphorus atoms in the second shell with average Am–S and Am–P bond distances of 2.9 and 3.5 Å, respectively.

(d) Cyclopentadienyl and cyclooctatetraenyl compounds

The organometallic chemistry of americium remains essentially unstudied. The most studied compound is the cyclopentadiene complex, $Am(C_5H_5)_3$, which crystallizes in the orthorhombic *Pbcm* space group and is isostructural with, but not pyrophoric like $Pu(C_5H_5)_3$ (Baumgärtner *et al.*, 1966a). Pappalardo *et al.* (1969a) reported the absorbance spectrum of $Am(C_5H_5)_3$ films from which Nugent *et al.* (1971b) calculated a bond covalency of only 2.8 ± 0.2% (relative to the corresponding bands of $Am(aq)^{3+}$) indicating that the organometallic bonding in $Am(C_5H_5)_3$ is highly ionic. Consequently, Nugent *et al.* suggested that the compound should be designated as a tris-cyclopentadienide rather than a tricyclopentadienyl compound. Bursten and coworkers (Bursten *et al.*, 1989; Li and Bursten, 1997) calculated the electronic structure of $AnCl_3$, $An(C_7H_7)_2$, and $An(C_5H_5)_3$, and discussed the relative role of the 5f and 6d atom orbitals. Karraker (1975, 1977) reported the synthesis of the potassium salt of a bis-cyclooctatetraenyl Am(III) complex, $KAm(C_8H_8)_2$, and obtained the absorbance spectrum in THF. The compound $KAm(C_8H_8)_2 \cdot 2THF$ decomposes in water and burns when exposed to air. The X-ray powder diffraction data show that $Am(C_8H_8)_2$ is isostructural with the analogous Np and Pu compounds and the sandwich complex uranocene. The gas-phase reaction of Am^+ ions with 1.5-cyclooctadiene and cyclooctatetraene produced the dehydrogenation complexes $Am-C_8H_8^+$ and $Am-C_8H_6^+$ that were detected by mass spectrometry

(Gibson, 1998b). The gas-phase reaction of laser-ablated Am^+ with pentamethylcyclopentadiene (HCp^*) yielded the fragments $AmC_8H_{14}^+$, $AmC_9H_{12}^+$, and $AmC_{10}H_{14}^+$ (Gibson, 2000). In contrast to the multiple dehydrogenation reactions observed with Np^+ and Pu^+, the Am^+ ion appeared unreactive and induced exclusively single hydrogen loss. Gibson concludes from this finding that the valence 5f electrons of Am^+ are too inert to form σ-bonds with carbon or hydrogen atoms and therefore do not participate in the Am–HCp interaction.

8.10 ANALYTICAL CHEMISTRY AND SPECTROSCOPY

8.10.1 Radioanalytical chemistry

(a) Alpha spectroscopy

Common analytical procedures include alpha spectrometry for the detection of ^{241}Am and ^{243}Am. The typical alpha-spectrum of ^{241}Am exhibits a peak at 5.49 MeV. The energy of the main alpha particles of ^{243}Am (5.28 MeV) differs by only about 0.2 MeV, which can result in peak broadening and overlap with α-peaks of other radionuclides (Lin *et al.*, 2002). Quantitative analysis by alpha spectrometry requires extensive radiochemical purification, preparation of a high-quality americium source by a skilled radiochemist, and correction for absorption and backscattering from the planchet. Scintillation counting has largely replaced alpha spectrometry in many radioanalytical procedures.

(b) Gamma spectroscopy

Nuclide identification and analysis of biological and environmental samples mainly use high-sensitivity gamma counting in a germanium multichannel detector. ^{241}Am emits two main γ-rays at 59.5 (36%) and 26.3 keV (2.4%). Scintillation counting is also commonly used when only one γ-emitting isotope is in the sample.

8.10.2 Spectroscopy

(a) Solution absorption

(1) Am(III): UV–VIS–NIR absorption spectroscopy has been widely used to characterize americium solution species. The major absorbance that has been measured to speciate Am(III) corresponds to the transition $^7F_0 \rightarrow {}^5L_6$ with its maximum at 503.2 nm ($\varepsilon \sim 410$ L mol cm^{-1}) for Am^{3+}(aq). The molar absorptivity may change with spectral slit widths, temperature, and ionic strength of the solution. Shifts in the position of the absorbance bands

and changes in molar absorbance are evidence of changes in the number of inner-sphere coordinated water molecules and/or coordination of ligands, i.e. carbonate or sulfate. Theoretical calculations of the electronic energy bands in the Am^{3+} ion have been performed by a number of investigators (Conway, 1963, 1964; Carnall and Wybourne, 1964; Carnall *et al.*, 1964; Carnall and Fields, 1967). An unexpected predicted $^7F_0 \rightarrow {}^5D_1$ transition was found in more concentrated Am(III) solution. Carnall (1989) analyzed the energy levels of the Am^{3+} ion by comparing the absorption spectra of $AmCl_3$ and $LaCl_3$ that was doped with Am(III).

Barbanel *et al.* (1997, 2001) studied the transitions in the octahedral complexes AmX_6^{3+} in the Cs_2NaLuX_6 (X = Cl, Br) crystal. The absorption spectra showed excitation to the ground level states $^7F_2$, $^7F_4$, $^7F_6$ and to the exited states $^5L_6$, $^5G_2$, and $^5D_2$. Absorbance spectra have been recorded in H_2SO_4, H_3PO_4, HNO_3, HCl, $HClO_4$, and in carbonate media (Keenan, 1959; Marcus and Shiloh, 1969; Shiloh *et al.*, 1969; Stadler and Kim, 1988; Meinrath and Kim, 1991a; Runde and Kim, 1994) (Fig. 8.13).

(2) Am(IV): The spectrum of Am(IV) in acid media is characterized by broad absorption features and has been measured in 13 M HF (Asprey and Penneman, 1961, 1962), 12 M KF (Varga *et al.*, 1973), 12 M H_3PO_4 (Myasoedov *et al.*, 1977), and in 2 M Na_2CO_3 (Bourges *et al.*, 1983; Hobart *et al.*, 1983b). The spectrum of Am(IV) in concentrated fluoride solution resembles very closely that of solid AmF_4 (Fig. 8.14).

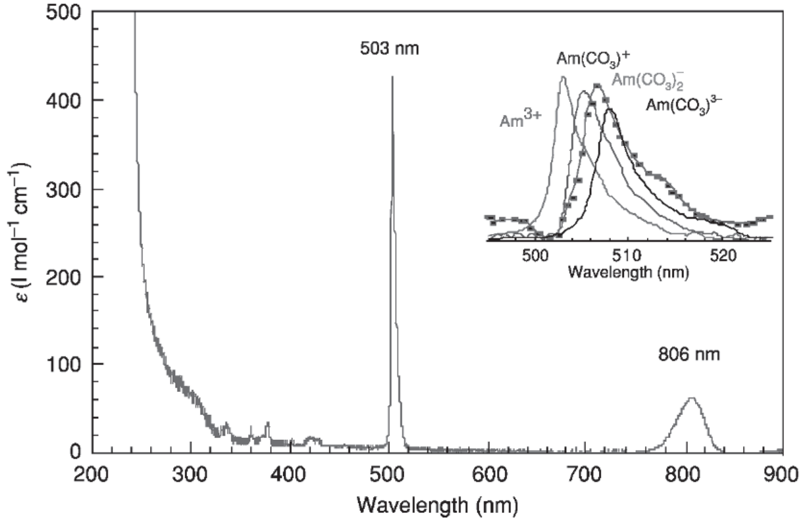


Fig. 8.13 *Electronic absorption spectra of* Am^{3+} *in* 1 M $HClO_4$ *and of the predominant Am*(III) *species in carbonate-containing solutions* (*inset*) (*Meinrath and Kim*, 1991a).

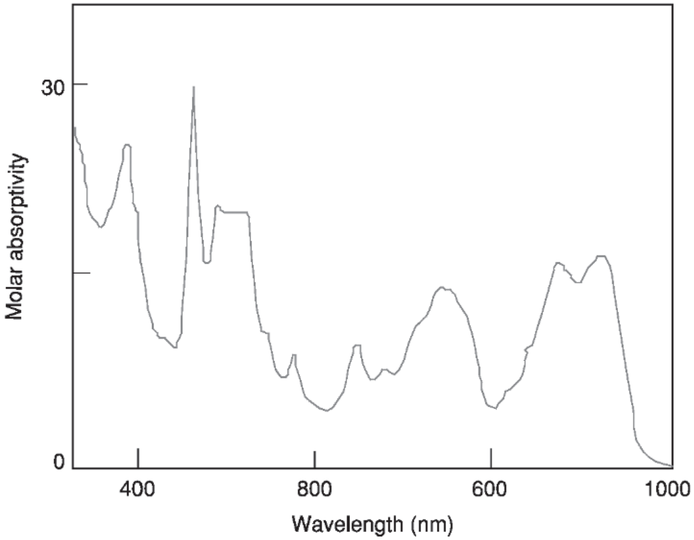


Fig. 8.14 *Absorption spectrum of Am(IV) in* 13 M *NH_4F* (*Asprey and Penneman*, 1962).

(3) Am(V): The Am(V) transitions $^5I_4 \rightarrow {}^3G_5$ and $^5I_4 \rightarrow {}^3I_7$ with their absorbance peaks at 513.7 nm ($\varepsilon \sim 45$ L mol cm^{-1}) and 716.7 nm ($\varepsilon \sim 60$ L mol cm^{-1}), respectively, are the main absorbance bands of the AmO_2^+ ion in aqueous solutions. Absorbance spectra of Am(V) have been recorded in H_2SO_4 (Werner and Perlman, 1950), HCl (Hall and Herniman, 1954; Stadler and Kim, 1988; Runde and Kim, 1994), $HClO_4$ (Asprey *et al.*, 1951; Stephanou *et al.*, 1953), NaCl (Stadler and Kim, 1988; Runde and Kim, 1994), and in 2 M Na_2CO_3 (Bourges *et al.*, 1983; Hobart *et al.*, 1983b) (Fig. 8.15).

(4) Am(VI): The spectrum of Am(VI) in acid media is characterized by the sharp absorption band at about 996 nm with $\varepsilon \sim 100$ L mol cm^{-1} in $HClO_4$ and ~100 L mol cm^{-1} in H_3PO_4. A less intense absorbance appears at 666 nm. Bell (1969) has compared band positions of transuranium actinyl spectra, including those of AmO_2^+ and AmO_2^{2+}, with the spacings between positions of the UO_2^{2+} bands. His results indicate that a single molecular orbital model can represent any of the actinyl ions when the uranyl ion is assumed to have the bonding orbitals exactly filled; the transuranium actinyl ions are represented with the uranyl core and a progressive increase of electrons in the first two lowest unoccupied molecular orbitals (LUMOs). Although the Am(VI) absorbance appears when Am(V) disproportionates in $HClO_4$, the absorbance is absent in HCl media potentially because of the formation of chloride complexes of lower molar absorptivity or due to the instability of Am(VI) in acidic chloride media (Fig. 8.16).

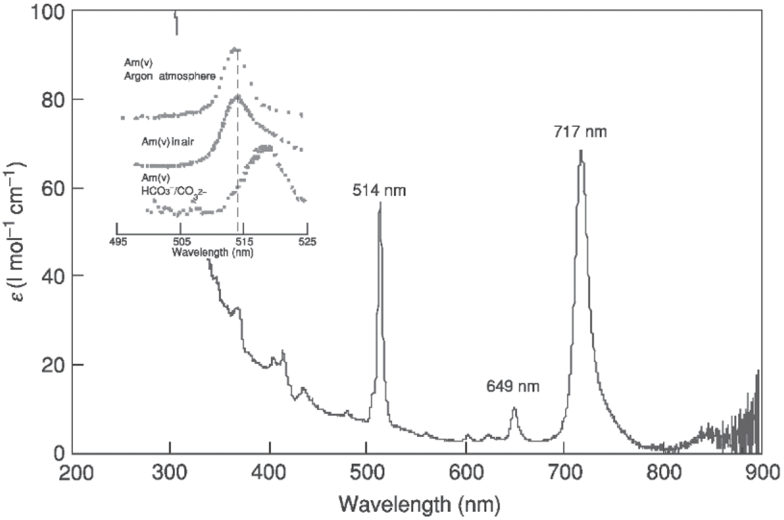


Fig. 8.15 *Electronic absorption spectra of* AmO_2^+ *in* 1 M $HClO_4$ *and in carbonate-containing solutions* (*inset*) (*Stadler and Kim*, 1988).

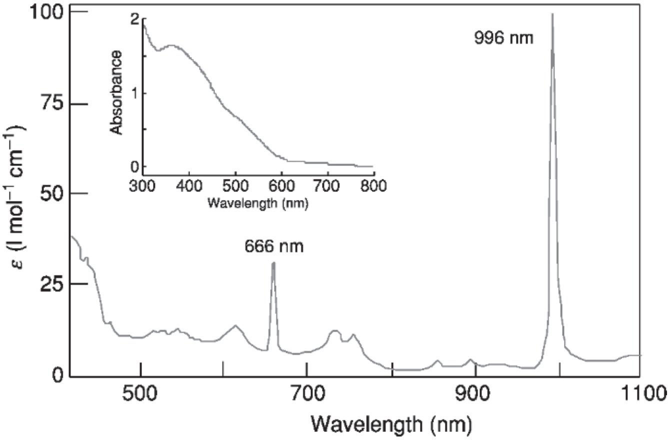


Fig. 8.16 *Absorption spectrum of Am*(*VI*) *in* 1 M $HClO_4$ *and in carbonate solution* (*inset*) (*Penneman and Asprey*, 1955).

(5) Am(VII): Green-colored solutions, believed to be Am(VII), are prepared by oxidation of Am(VI) in 3–5 M NaOH at 0–7°C with either ozone or the O^- radical. The spectrum of Am(VI) and Am(VII) was measured in 3.5 M NaOH solution by Krot *et al.* (1974a,b) and exhibited a broad absorbance

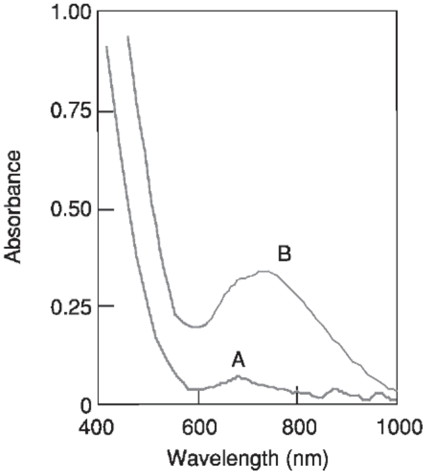


Fig. 8.17 *Absorption spectra of Am*(*vi*) *and Am*(*vii*) *in* 3.5 M *NaOH* (*Krot* et al., 1974a). *A*, 0.0194 M *Am*(*vi*); *B*, 0.0194 M Am_{tot} *with* 50% *Am*(*vi*) *and* 50% *Am*(*vii*).

at 740 nm (Fig. 8.17). Heptavalent americium is unstable and reduces to Am (vi) within minutes. It can be easily reduced by hydrogen peroxide, hydrazine, hydroxylamine, sulfite, and ferrocyanide ions, and Np(vi) and Pu(vi) (Shilov, 1976). A review on the chemistry of heptavalent transplutonium elements can be found in Mikheev and Myasoedov (1985).

(b) Luminescence

Luminescence has been observed only for Am(iii). Reviews of Am(iii) luminescence studies can be found in Beitz (1994) and Yusov (1993). The first study on the luminescence properties of Am(iii) was reported by Beitz *et al.* (1989). Excitation of Am(iii) from the $^7F_0$ ground state to the $^5L_6$ state at 503 nm results in the emission from the lowest luminescent level to the ^7F_J ground-state manifold. From seven expected transitions only two are experimentally accessible. The two most populated transitions are the $^5D_1 \rightarrow {}^7F_1$ band at 685 nm and the $^5D_1 \rightarrow {}^7F_2$ band at 836 nm. These transitions can be used for the determination of trace concentrations of Am(iii) in solution or solid-state matrices (Thouvenot *et al.*, 1993). Beitz and coworkers (Liu *et al.*, 1997) investigated the crystal field splitting and hyperfine energy level structure in the $^5D_1$ level of $^{243}Am^{3+}$ in $LaCl_3$ and $CaWO_4$.

The fluorescence lifetime of the Am^{3+} ion(aq) is reported to be 20.4 ± 2.1 ns (Runde *et al.*, 2000), 24.6 ± 0.6 ns (Kimura and Kato, 1998), and 22 ± 3 ns (Beitz, 1994) in aqueous systems. The lifetime increases dramatically to 155 ± 4 ns (Beitz, 1994) in D_2O. Complexation of the Am^{3+} ion changes the position of the emission bands and the duration of the fluorescence lifetime; e.g. the fluorescence of the triscarbonato complex, $Am(CO_3)_3^{3+}$, is observed at 693 nm with a lifetime of 34.5 ± 2.4 ns (Runde *et al.*, 2000). The luminescence spectra of Am^{3+} have been also measured in Am-doped powdered ThO_2 (Hubert and Thouvenot, 1992), $Cs_2NaLuCl_6$ (Barbanel *et al.*, 1998), $LiYF_4$ (Cavellec *et al.*, 1997), heavy metal fluoride glass containing AmF_3 (Beitz, 1994), and in fluorozirconate glass (Valenzuela and Brundage, 1990; Brundage, 1994) (Fig. 8.18) .

(c) Vibrational (IR and Raman)

There are few data on the IR spectra of americium compounds. Tananaev (1991) reported the antisymmetric vibration frequency of the AmO_2^+ group in $CsAmO_2(OH)_2 \cdot nH_2O$ at 802 cm^{-1}. Hobart *et al.* (1983a) reported the Raman spectra of $AmPO_4$ and $Am(PO_3)_3$ with the most intense Raman frequencies for the symmetric stretching mode of PO_4^{3-} at 973 cm^{-1} and of PO_3^- groups at 1195 cm^{-1}. Jones and Penneman (1953) studied the infrared absorption assigned to the infrared O–An–O asymmetric stretch of actinyl(v) and (vi) ions, concluding that these ions were linear or very nearly so. For the solid $NaAmO_2(CH_3COO)_2$ the vibrational frequencies $\nu_1 = 749$ and $\nu_2 = 914$ cm^{-1} were reported (Jones, 1955). Data on Raman scattering of americyl(v) and (vi) ions have been reported in non-complexing perchloric acid and complexing carbonate solutions (Basile *et al.*, 1974). The values for the polarized symmetric stretching frequencies (ν_1) of AmO_2^+ and AmO_2^{2+} were found to be 730 and 796 cm^{-1}, respectively (Basile *et al.*, 1974). The Raman scattering in carbonate solutions showed a shift of ν_1 to 747 cm^{-1} for Am(v) (Madic *et al.*, 1983) and to 760 cm^{-1} for Am(vi) (Basile *et al.*, 1978). A study of the correlation of the Raman spectra of actinyl(v) and (vi) ions in perchlorate and carbonate

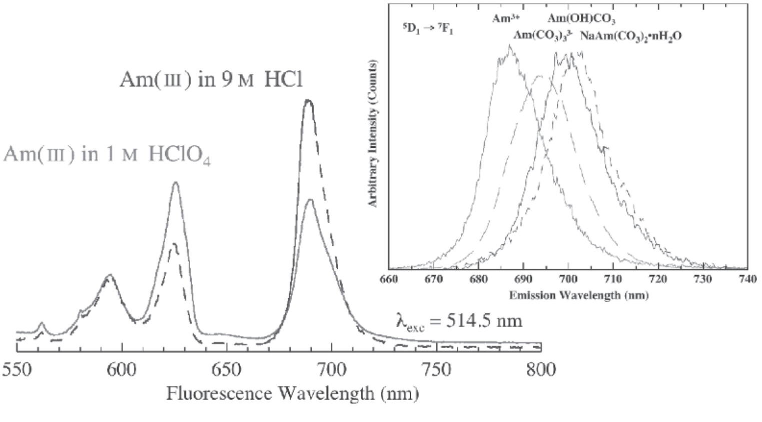


Fig. 8.18 *Luminescence spectrum of* Am^{3+} *in acidic media and of Am*(*III*) *carbonate complexes*. (*Runde* et al., 2000, 2002).

solutions, as well as the spectra of solid actinide(V) double carbonate compounds, $Na_3AnO_2(CO_3)_2 \cdot H_2O$, was published by Madic *et al.* (1983).

(d) X-ray absorption

Although X-ray absorption spectroscopy (XAS, see Chapter 28) has been increasingly used since 1990 to obtain structural information of actinide compounds, only a small number of XAS studies on americium compounds have been reported. Bearden and Burr (1967) reported the edge energy of americium metal at 18 504 eV. Soderholm *et al.* (1996) observed the Am edge energy at 18515 eV in the Am(IV) compound $Pb_2Sr_2AmCu_3O_8$, which is about 4 eV higher in energy compared to the solid Am(III) reference compounds AmF_3 and $Cs_2NaAmCl_6$. EXAFS has been used to study the coordination of americium in organic complexes (DenAuwer *et al.*, 2000; Yaita *et al.*, 2001) and inorganic complexes with $P_5W_{30}O_{110}^{15-}$ (Williams *et al.*, 2000), chloride (Allen *et al.*, 2000), and carbonate (Runde *et al.*, 2002).

REFERENCES

Abe, M. and Tsujii, M. (1983) *Chem. Lett.*, 1561.

Abe, M., Chitrakar, R., Tsujii, M., and Fukumoto, K. (1985) *Solvent Extr. Ion Exch.*, **3**, 149.

Adair, H. L. (1970) *J. Inorg. Nucl. Chem.*, **32**, 1170.

Agnew, S. F., Boyer, J., Corbin, R. A., Duran, T. B., Fitzpatrick, J. R., Jurgensen, K. A., Ortiz, T. P., and Young, B. L. (1997) *Hanford Tank Chemical and Radionuclide Inventories: HDW Model Rev. 4*, Los Alamos National Laboratory.

Akatsu, J. and Kimura, T. (1990) *J. Radioanal. Nucl. Chem.*, **140**, 195.

Akella, J., Johnson, Q., and Schock, R. N. (1980) *J. Geophys. Res.*, **85**, 7056–8.

Akimoto, Y. (1967) *J. Inorg. Nucl. Chem.*, **29**, 2650–2.

Al Rifai, S. (1970) *Complex Formation between Trivalent Transuranium Elements and Ligand which Contain the Pyridinie or Quinoline Ring*. German Report IRCH-10/70-2.

Aldred, A. T., Dunlap, B. D., Lam, D. J., and Shenoy, G. K. *Transplutonium 1975, Proc. 4th Int. Symp.,* Baden-Baden, Germany 1975; Ed. by W. Müller and R. Lindner, North-Holland, Amsterdam; p. 191–5.

Ali, S. (1968) *Chelatbildung der Dreiwertigen Transplutoniumelemente mit Nitrilotriessigsaeure und Ihren Derivaten.*

Allen, P. G., Bucher, J. J., Shuh, D. K., Edelstein, N. M., and Craig, I. (2000) *Inorg. Chem.*, **39**, 505–601.

Anan'ev, A. V. and Krot, N. N. (1985) *Sov. Radiochem.* (*Engl. Transl.*), **26**(6), 716–9.

Anan'ev, A. V. and Shilov, V. P. (1985) *Sov. Radiochem.* (*Engl. Transl.*), **26**(6), 768–70.

ANS (1993) *Int. Conf. and Tech. Exposition on Future Nuclear Systems: Emerging Fuel Cycles and Waste Disposal Options*, *Global '93*. Seattle, WA. 1993; Amer. Nucl. Soc., La Grange Park, IL. ISBN 0894481827.

Asprey, L. B., Stephanou, S. E., and Penneman, R. A. (1950) *J. Am. Chem. Soc.*, **72**, 1425–6.

Asprey, L. B., Stephanou, S. E., and Penneman, R. A. (1951) *J. Am. Chem. Soc.*, **73**, 5715–7.

Asprey, L. B. (1954) *J. Am. Chem. Soc.*, **76**, 2019–20.

Asprey, L. B., Ellinger, F. H., and Zachariasen, W. H. (1954a) *J. Am. Chem. Soc.*, **76**, 5235–7.

Asprey, L. B., Stephanou, S. E., and Penneman, R. A.: patent number 2681 923. US, (1954).

Asprey, L. B. and Keenan, T. K. (1958) *J. Inorg. Nucl. Chem.*, **7**, 27–31.

Asprey, L. B. and Penneman, R. A. (1961) *J. Am. Chem. Soc.*, **83**, 2200.

Asprey, L. B. and Penneman, R. A. (1962) *Inorg. Chem.*, **1**, 134–6.

Asprey, L. B., Keenan, T. K., and Kruse, F. H. (1964) *Inorg. Chem.*, **3**, 1137–40.

Asprey, L. B., Keenan, T. K., and Kruse, F. H. (1965) *Inorg. Chem.*, **4**, 985–6.

Aziz, A. and Lyle, S. J. (1971) *J. Inorg. Nucl. Chem.*, **33**, 3407.

Backer, W. and Keller, C. (1973) *J. Inorg. Nucl. Chem.*, **35**, 2945.

Bagnall, K. W., Laidler, J. B., and Stewart, M. A. A. (1967) *Chem. Commun.*, **1**, 24–5.

Bagnall, K. W., Laidler, J. B., and Stewart, M. A. A. (1968) *J. Chem. Soc.* **A**, 133–6.

Bagnall, K. W. (1972) *The Actinide Elements,* Elsevier, New York.

Baisden, P. A., Choppin, G. R., and Kinard, W. K. (1972) *J. Inorg. Nucl. Chem.*, **34**, 2029.

Barbanel, Y. A., Chudnovskaya, G. P., Dushin, R. B., Kolin, V. V., Kotlin, V. P., Nekhoroshkov, S. N., and Pen'kin, M. V. (1997) *Radiochim. Acta*, **78**, 69–72.

Barbanel, Y. A., Chudnovskaya, G. P., Dushin, R. B., Kolin, V. V., Kotlin, V. P., Nekhoroshkov, S. N., and Penkin, M. V. (1998) *J. Alloys Compd.*, **277**, 295–300.

Barbanel, Y. A., Dushin, R. B., Kolin, V. V., Kotlin, V. P., and Nekhoroshkov, S. N. (2001) *Radiochemistry*, **43**, 118–23.

Barney, G. S. and Cowan, R. G. (1992) Separation of actinide ions from radioactive waste solutions using extraction chromatography, *American Chemical Society National Meeting*, San Francisco, CA, USA, April 5–10, p. 77.

Barthelemy, P. and Choppin, G. R. (1989) *Inorg. Chem.*, **28**, 3354–7.

Basile, L. J., Sullivan, J. C., Ferrarro, J. R., and La Bonville, P. (1974) *Appl. Spectrosc.*, **28**, 142–5.

Basile, L. J., Ferrarro, J. R., Mitchell, M. L., and Sullivan, J. C. (1978) *Appl. Spectrosc.*, **32**, 535–7.

Baudin, G., Lefevre, J., Prunier, C., and Salvatore, M. (1993) IAEA Report TECDOC-783, p. 37.

Baumgärtner, F., Fischer, E. O., and Kanellakopulos, B. (1966a) *Angew. Chem. Int. Edn.*, **5**(1), 134–5.

Baumgärtner, F., Fisher, E. O., Kanellakopulos, B., and Laubereau, P. G. (1966b) *Angew. Chem. Int. Edn.*, **78**, 112–3.

Baumgärtner, F., Fisher, E. O., Kanellakopulos, B., and Laubereau, P. G. (1977) *J. Inorg. Nucl. Chem.*, **39**, 87–9.

Bayat, I. (1970) *Über Komplexe dreiwertiger Transurane mit Aminopolykarbonsäuren*, German Report, KFK-1291.

Bayat, I. and Moattar, F. (1982) *Radiochem. Radioanal. Lett.*, **51**(3), 171–9.

Baybarz, R. D. (1960) *Preparation of Americium Dioxide by Thermal Decomposition of Americium Oxalate in Air*, Oak Ridge National Laboratory.

Baybarz, R. D. (1965) *J. Inorg. Nucl. Chem.*, **27**, 1831.

Baybarz, R. D. (1966) *J. Inorg. Nucl. Chem.*, **28**, 1055.

Baybarz, R. D. (1970) *At. Energy Rev.*, **8**, 327–60.

Baybarz, R. D. and Asprey, L. B. (1972) *J. Inorg. Nucl. Chem.*, **34**, 3427–31.

Baybarz, R. D. (1973a) *J. Inorg. Nucl. Chem.*, **35**, 4149–58.

Baybarz, R. D. (1973b) *J. Inorg. Nucl. Chem.*, **35**, 483–7.

Bean, A. C., Scott, B. L., Albrecht- Schmitt, T., and Runde, W. (2003) *Plutonium Futures – the Science, Third Topical Conference on Plutonium and Actinides*, pp. 233–5.

Bearden, J. A. (1967) *Rev. Mod. Phys.*, **39**, 78.

Bearden, J. A. and Burr, A. F. (1967) *Rev. Mod. Phys.*, **39**, 125–42.

Beitz, J. V., Jursich, G., and Sullivan, J. C. (1989) Fluorescence studies of Am3+ in aqueous solution, in *Rare Earth 1988* (eds. L. R. M. H. B. Silber and L. E. Delony), Elsevier Sequoia, Amsterdam.

Beitz, J. V. (1994) *J. Alloys Compd.*, **207/208**, 41–50.

Bell, J. T. (1969) *J. Inorg. Nucl. Chem.*, **31**, 703–10.

Benedict, U., Bujis, K., Dufour, S., and Toussaint, J. C. (1975) *J. Less Common Metals*, **42**, 345–54.

Benedict, U. and Dufour, C. (1980) *Physica*, **102B**, 303–7.

Benedict, U., Itíe, J. P., Dufour, C., Dubos, S., and Spirlet, J. C. (1985) in *Americium and Curium Chemistry and Technology* (eds. N. Edelstein, J. Navratil, and W. Schulz), D. Reidel, The Netherlands.

Benedict, U., Itíe, J. P., Dufour, C., Dubos, S., and Spirlet, J. C. (1986) *Physica*, B&C, **139**, 284.

Berger, P., Blanc, P., and Bourges, J. (1988) *Radiochim. Acta*, **43**, 217–22.

Berndt, U., Tanamas, R., Maier, D., and Keller, C. (1974) *Inorg. Nucl. Chem. Lett.*, **10**, 315–21.

Bernkopf, M. F. and Kim, J. I. (1984) *Hydrolydsereaktionen und Karbonatkomplexierung von dreiwertigem Americium in natürlichen aquatischen Systemen*, Technische Universität München.

Berry, J. W., Knoghton, J. B., and Nannie, C. A. (1982) *Vacuum Distillation of Americium Metal*, US Department of Energy.

Bertha, E. I. and Choppin, G. R. (1978) *J. Inorg. Nucl. Chem.*, **40**, 655–8.

Bhanushali, R. D., Pius, I. C., Muherjee, S. K., and Vaidya, V. N. (1999) *J. Radioanal. Nucl. Chem.*, **240**, 977–9.

Bierman, S. R. and Clayton, E. D. (1969) *Trans. Am. Nucl. Soc.*, **12**, 887–8.

Bigelow, J. E., Collins, E. d., and King, L. J. (1980) *The Cleanex Process: A Versatile Solvent-Extraction Process for Recovery and Purification of Lanthanides, Americium, and Curium, Amer. Chem. Soc.* pp. 147–55.

Blokhin, N. B., Ermakov, V. A., and Rykov, A. G. (1973) *Radiokhimiya*, **16**, 189–92.

Blokhin, N. B., Ermakov, V. A., and Rykov, A. G. (1974) *Radiokhimiya*, **16**, 551–3.

Bode, D. D., Wild, J. F., and Hulet, E. K. (1976) *J. Inorg. Nucl. Chem.*, **38**, 1291–7.

Boldt, A. L. and Ritter, G. L. (1969) *Recovery of Am, Cm, and Pm from Shipping Port Reactor Fuel Reprocessing Wastes by Successive TBP and D2EHPA Extractions*, Atlantic Richfield Hanford Company.

Bond, E. M., Engelhardt, U., Deere, T. P., Rapko, B. M., Paine, R. T., and FitzPatrick, J. R. (1997) *Solvent Extr. Ion Exch.*, **15**, 381.

Bond, E. M., Engelhardt, U., Deere, T. P., Rapko, B. M., Paine, R. T., and Fitz Patrick, J. R. (1998) *Solvent Extr. Ion Exch.*, **16**, 967.

Borisov, M. S., Elesin, A. A., Lebedev, I. A., Piskunov, E. M., Filimonof, V. T., and Yakovlev, G. N. (1967) *Radiokhimiya*, **9**, 166.

Bouhlassa, S. (1983) *Chem. Abstr.*, **98**, 82730.

Bouhlassa, S. and Guillaumont, R. (1984) *J. Less Common Metals*, **99**(1), 157–71.

Bouissières, G. and Legoux, Y. (1965) *Bull. Soc. Chim. Fr.*, **2**, 386.

Bourges, J. Y., Guillaume, B., Koehly, G., Hobart, D. E., and Peterson, J. R. (1983) *Inorg. Chem.*, **22**, 1179–84.

Boyd, T. E., Cusick, M. J., and Navratil, J. D. (1986) *Recent Developments in Separation Science,* CRC Press, Boca Raton, FL.

Boyd, T. E. and Kochen, R. L. (1993) *Ferrite Treatment of Actinide Waste Solutions: Continuous Processing of Rocky Flats Process Waste,* Rockwell International, Golden, CO.

Brachet, G. and Vasseur, C. (1969) *Reduction of Americium Oxide by Beryllium for Neutron-Source Production,* CEA, France.

Brandau, E. (1971) *Inorg. Nucl. Chem. Lett.*, **7**, 1177.

Bratsch, S. G. and Lagowski, J. J. (1986) *J. Phys. Chem.*, **90**, 307–12.

Brown, D., Fletcher, S., and Holah, D. G. (1968) *J. Chem. Soc.* **A**, 1889–94.

Brundage, R. T. (1994) *J. Alloys Compd.*, **213**, 199–206.

Buckau, G., Kim, J. I., klenze, R., Rhee, D. S., and Wimmer, H. (1992) *Radiochim. Acta*, **57**(2–3), 105–11.

Buijs, K., Müller, W., Reul, J., and Toussaint, J. C. (1973) *Separation and Purification of Americium on the Multigram Scale*, Euratom.

Burch, W. D. (1964) *Transuranium Quarterly Progress Report for Period Ending February* 29, 1963, Oak Ridge National Laboratory.

Burnett, J. L. (1965) *Trans. Am. Nucl. Soc.*, **8**, 335.

Burnett, J. L. (1966) *J. Inorg. Nucl. Chem.*, **28**, 2454–6.

Burney, G. A. and Porter, J. A. (1967) *Inorg. Nucl. Chem. Lett.*, **3**, 79–85.

Burney, G. A. (1968) *Nucl. Appl.*, **4**, 217–21.

Burns, J. H. and Danford, M. D. (1969) *Inorg. Chem.*, **8**, 1780–4.

Burns, J. H. and Peterson, J. R. (1970) *Acta Crystallogr. B*, **26**, 1885–7.

Burns, J. H. and Peterson, J. R. (1971) *Inorg. Chem.*, **10**, 147–51.

Burns, J. H. and Baybarz, R. D. (1972) *Inorg. Chem.*, **11**, 2233–7.

Burns, J. H. and Baldwin, W. H. (1976) *Inorg. Chem.*, **16**(2), 289–94.

Burns, J. H. and Baldwin, W. H. (1977) *Inorg. Chem.*, **16**, 289–94.

Burns, J. H., Damien, D., and Haire, R. G. (1979) *Acta Crystallogr. B*, **35**, 143–4.

Bursten, B. E., Rhodes, L. F., and Strittmatter, R. J. (1989) *J. Less Common Metals*, **149**, 207–11.

Caceci, M. and Choppin, G. (1983) *Radiochim. Acta*, **33**(2/3), 101–4.

Campbell, D. O. (1970) *Ind. Eng. Chem. Process Des. Dev.*, **9**, 95–9.

Carlson, T. A., Nestor, C. W. J., Wasserman, N., and McDowell, J. D. (1970) *Comprehensive Calculations of Ionization Potentials and Binding Energies for Multiply-Charged Ions*, Oak Ridge National Laboratory.

Carnall, W. T. and Wybourne, B. G. (1964) *J. Chem. Phys.*, **40**, 3428–33.

Carnall, W. T., Fields, P. R., and Wybourne, B. G. (1964) *J. Chem. Phys.*, **41**, 2195–6.

Carnall, W. T. and Fields, P. R. (1967) in *Lanthanide/Actinide Chemistry* (ed. R. F. Gould), American Chemical Society, Washington, DC, pp. 86–101.

Carnall, W. T. (1979a) Emission Spectra, in *Gmelins Handbuch der Anorganischen Chemie*, Transurane, Teil A2, vol. 8, (ed. G. Koch), Verlag Chemie, Weinheim, Germany, p. 42.

Carnall, W. T. (1979b) X-ray spectra, in *Gmelins Handbuch der Anorganischen Chemie,* Transurane, Teil A2, vol. 8, (ed. G. Koch), Verlag Chemie, Weinheim, p. 80.

Carnall, W. T. (1989) *J. Less Common Metals*, **156**, 221–35.

Carniglia, S. C. and Cunningham, B. B. (1955) *J. Am. Chem. Soc.*, **77**, 1451–3.

Casarci, M., Chiarizia, R., Gasparini, G. M., Puzzuoli, G., and Valeriani, G. (1988) in *Proc. of ISEC '88,* Moscow, USSR.

Casarci, M., Gasparini, G. M., and Grossi, G. (1989) in *Proc. of Actinides – 89*, Tashkent, Russia.

Cavellec, R., Hubert, S., and Simoni, E. (1997) *J. Solid State Chem.*, **129**, 189–95.

Chamberlain, D. B., Conner, C., Hutter, J. C., Leonard, R. A., Wygmans, D. G., and Vandegrift, G. F. (1997) *Sep. Sci. Technol.*, **32**, 303.

Charbonnel, M. C. and Musikas, C. (1988) *Solvent Extr. Ion Exch.*, **6**, 461.

Chartier, D., Donnet, L., and Adnet, J. M. (1999) *Radiochim. Acta*, **85**, 25–31.

Charvillat, J. P., Benedict, U., Damien, D., de Novion, C., Wojakowski, A., and Müller, W. (1975a) in *Transplutonium 1975*, *Proc. 4th Int. Symp.*, pp. 79–93.

Charvillat, J. P., Benedict, U., Damien, D., and Müller, W. (1975b) *Radiochem. Radioanal. Lett.* **20**, 371–381.

Charvillat, J. P. and Damien, D. (1973) *Inorg. Nucl. Chem. Lett.*, **9**, 559–63.

Charvillat, J. P. and Zachariasen, W. H. (1977) *Inorg. Nucl. Chem. Lett.*, **13**, 161–3.

Charvillat, J. P., Benedict, U., Damien, D., de Novion, C., Wojakowski, A., and Müller, W. (1977) *Rev. Chim. Minér.*, **14**, 178–88.

Chen, J., Jiao, R., and Zhu, Y. (1996) *Solvent Extr. Ion Exch.*, **14**, 555.

Chiarizia, R. and Horwitz, E. P. (1986) *Solvent Extr. Ion Exch.*, **4**, 677.

Chiarizia, R. and Horwitz, E. P. (1990) *Solvent Extr. Ion Exch.*, **8**, 907.

Chiarizia, R., Horwitz, E. P., Alexandratos, S. D., and Gula, M. J. (1997) *Separation Science and Technology*, **32**(1–4), 1–35.

Chikalla, T. D. and Eyring, L. (1967) *J. Inorg. Nucl. Chem.*, **29**, 2281–93.

Chikalla, T. D. and Eyring, L. (1968) *J. Inorg. Nucl. Chem.*, **30**, 133–45.

Chikalla, T. D., McNeilly, C. E., Bates, J. L., and Rasmussen, J. J. (1973) in *Proc. Int. Colloq. on High Temp. Phase Transform.*, CNRS Publ. No. 205, pp. 351–60.

Chistyakov, V. M., Ermakov, V. A., and Rykov, A. G. (1974) *Radiokhimiya*, **16**, 553–5.

Chitnis, R. R., Wattal, P. K., Ramanujam, A., Dhami, P. S., Gopalakrishnan, V., Mathur, J. N., and Murali, M. S. (1998) *Sep. Sci. Technol.*, **33**, 1877.

Chitnis, R. R., Wattal, P. K., Ramanujam, A., Dhami, P. S., Gopalalkrishnan, V., Bauri, A. K., and Bannerji, A. (1999) *J. Radioanal. Nucl. Chem.*, **240**, 721.

Chmutova, M. K., Kochetkova, N. E., Koiro, O. E., Myasoedov, B. F., Medved, T. Y., Nesterova, N. P., and Kabachnik, M. I. (1983) *J. Radioanal. Chem.*, **80**, 63.

Chmutova, M. K., Kochetkova, N. E., and Myasoedov, B. G. (1989) *J. Inorg. Nucl. Chem.*, **42**, 897.

Choppin, G. R. (1965) *Inorg. Chem.*, **4**, 1250–4.

Choppin, G. R. (1970) *J. Inorg. Nucl. Chem.*, **32**, 3283–8.

Choppin, G. R. and Degischer, G. (1972) *J. Inorg. Nucl. Chem.*, **34**, 3473–7.

Choppin, G. R. and Unrein, P. J. (1975) in *Transplutonium 1975, Proc. 4th Int. Symp.*, Baden-Baden, Germany, Ed. by W. Müller and R. Lindner, North-Holland, Amsterdam, Netherlands, p. 97–107.

Choppin, G. R. and Nash, K. L. (1977) *Rev. Chim. Minér.*, **14**, 230–6.

Choppin, G. R. and Chen, J. F. (1996) *Radiochim. Acta*, **74**, 105–10.

Choppin, G. R. and Labonne-Wall, N. (1997) *J. Radioanal. Nucl. Chem.*, **221**(1–2), 67–71.

Choppin, G. R. and Peterman, D. R. (1998) *Coord. Chem. Rev.*, **174**, 283–99.

Chudinov, E. G. and Choporov, D. Y. (1970) *At. Energy (USSR)*, **28**, 62–4.

Chuveleva, E. A., Peshkov, A. S., Kharitonov, O. V., and Firosova, L. A. (1999) *Radiochemistry* (*Eng. Transl.*), **41**, 442–4, 445–7, and 465–7.

Cilindro, L. G., Stadlbauer, E., and Keller, C. (1972) *J. Inorg. Nucl. Chem.*, **34**, 2577.

Cilindro, L. G. and Keller, C. (1974) *Radiochim. Acta*, **21**, 29–32.

Clark, D. L., Conradson, S. D., Ekberg, S. A., Hess, N. J., Neu, M. P., Palmer, P. D., Runde, W., and Tait, C. D. (1996) *J. Am. Chem. Soc.*, **118**, 2089–90.

Cohen, D. (1972) *Inorg. Nucl. Chem.*, **8**, 533–5.

Cohen, K. P. (2000) *Nucl. News*, **43** (Nov), 45–6.

Coleman, J. S., Armstrong, D. E., Asprey, L. B., Keenan, T. K., La Mar, L. E., and Penneman, R. A. (1955) *Purification of Gram Amounts of Americium*, Los Alamos Scientific Laboratory.

Coleman, J. S., Armstrong, D. E., Asprey, L. B., Keenan, T. K., La Mar, L. E., and Penneman, R. A. (1957) *J. Inorg. Nucl. Chem.*, **3**, 327–8.

Coleman, J. S. (1963) *Inorg. Chem.*, **2**, 53–7.

Coleman, J. S., Keenan, T. K., Jones, L. H., Carnall, W. T., and Penneman, R. A. (1963) *Inorg. Chem.*, **2**, 58–61.

Conner, W. V. (1971) *J. Less Common Metals*, **25**, 379–84.

Connor, W. V. (1982) *Nucl. Instrum. Methods*, **200**, 55–66.

Conway, J. G. (1963) University of California, Lawrence Laboratory.

Conway, J. G. (1964) *J. Chem. Phys.*, **40**, 2504–7.

Crandall, J. L. (1971) *Applications of Transplutonium Elements*, Savannah River Laboratory.

Cuillerdier, C., Musikas, C., and Hoel, P. (1991a) in *New Separations Technology for Radioactive Waste and Other Specific Applications* (eds. L. Cecille, M. Cesarci, and L. Pietrelli), Elsevier Applied Science, p. 41.

Cuillerdier, C., Musikas, C., Hoel, P., Nigond, L., and Vitart, X. (1991b) *Sep. Sci. Technol.*, **26**, 1229.

Cuillerdier, C., Musikas, C., and Nigond, L. (1993) *Sep. Sci. Technol.*, **28**, 155.

Cunningham, B. B. (1948) *Isolation and Chemistry of Americium*, Argonne National Laboratory.

Cunningham, B. B. (1949) in *The Transuranium Elements* (eds. G. T. Seaborg and J. J. Katz), Natl. Nucl. En. Ser., Div. IV, 14B, McGraw-Hill, New York, pp. 1363–70.

Damien, D. and Pages, M. (1969) in *Rapport Semestriel du Department de Chimie No.* 6, *Juin* 1968–*Novembre*1968, CEA, p. 407.

Damien, D. and Pages, M. (1970) in *Rapport Semestriel du Department de Chimie No.* 8, *Juin* 1969–*Novembre*1969, CEA, p. 472.

Damien, D. (1971) *Inorg. Nucl Chem. Lett.*, **7**, 291–7.

Damien, D. and Jove, J. (1971) *Inorg. Nucl. Chem. Lett.*, **7**, 685–8.

Damien, D. (1972) *Inorg. Nucl Chem. Lett.*, **8**, 501.

Damien, D. and Charvillat, J. P. (1972) *Inorg. Nucl. Chem. Lett.*, **8**, 705–8.

Damien, D., Jove, J., and Marcon, J. P. (1972) *Inorg. Nucl. Chem. Lett.*, **8**, 317–20.

Damien, D., Marcon, J. P., and Jove, J. (1975) *Radiochem. Radioanal. Lett.*, **23**, 145–54.

Damien, D., Marcon, J. P., and Jove, J. (1976) *Bull. D'Inform. Sci. Tech. (fr.)*, **217**, 67–76.

Danford, M. D., Burns, J. H., Higgins, C. E., Stokeley, J. R. J., and Baldwin, W. H. (1970) *Inorg. Chem.*, **9**, 1953–5.

David, F. and Bouisissiéres, G. (1968) *Inorg. Nucl. Chem. Lett.*, **4**, 153–9.

David, F., Samhoun, K., Guillaumont, R., and Edelstein, N. (1978) *J. Inorg. Nucl. Chem.*, **40**, 69–74.

David, F. (1986) *J. Less Common Metals*, **121**, 27.

Davydov, A. V., Myasoedov, B. F., and Travnikov, S. S. (1975) *Dokl. Akad. Nauk SSSR*, **225**, 1075–8.

Dedov, V. B., Lebedev, I. A., Ryzhov, M. N., Trakhlyaev, P. S., and Yakovlev, G. N. (1961) *Radiokhimiya*, **3**, 701.

Deissenberger, R., Kohler, S., Ames, F., Eberhardt, K., Erdmann, N., Funk, H., Herrmann, G., Kluge, H., Nunnemann, M., Passler, G., Riegel, J., Scheerer, F., Trautmann, N., and Urban, F. J. (1995) *Angew. Chem. Int. Edn.*, **34**, 814–5.

Delle Site, A. and Baybarz, R. D. (1969) *J. Inorg. Nucl. Chem.*, **31**, 2201.

Den Auwer, C., Charbonnel, M. C., Drew, M. G. B., Grigoriev, M., Hudson, M. J., Iveson, P. B., Madic, C., Nierlich, M., Presson, M. T., Revel, R., Russell, M. L., and Thuery, P. (2000) *Inorg. Chem.*, **39**, 1487–95.

Deshingkar, D. S., Chitnis, R. R., Theyyunni, T. K., Wattal, P. K., Ramanujam, A., Dhami, P. S., Gopalakrishnan, V., Rao, M. K., Mathur, J. N., Murali, M. S., Iyer, R. H., Badheka, L. P., and Bannerji, A. (1993) Report BARC.

Deshingkar, D. S., Chitnis, R. R., Wattal, P. K., Theyyunni, T. K., Nair, M. K. T., Ramanujam, A., Dhami, P. S., Gopalakrishnan, V., Rao, M. K., Mathur, J. N., Murali, M. S., Iyer, R. H., Badheka, L. P., and Bannerji, A. (1994) Report BARC.

Drobyshevskii, I. V., Prusakov, V. N., Serik, V. F., and Sokolov, V. B. (1980) *Radiokhimiya*, **22**(44), 591–4.

Dunlap, B. D., Lam, D. J., Kalvius, G. M., and Shenoy, G. K. (1972) *J. Appl. Phys.*, **42**, 1419.

Eberle, S. H. and Bayat, I. (1967) *Radiochim. Acta*, **7**, 214.

Eberle, S. H. and Ali, S. (1968) *Z. Anorg. Allg. Chem.*, **361**, 1.

Eberle, S. H. and Bayat, I. (1969) *Inorg. Nucl. Chem. Lett.*, **5**, 229.

Eberle, S. H. and Robel, W. (1970) *Inorg. Nucl. Chem. Lett.*, **6**, 359–65.

Eberle, S. H. and Moattar, F. (1972) *Inorg. Nucl. Chem. Lett.*, **8**, 265.

Eberle, S. H. and Sabau, C. S. (1972) *Radiochem. Radioanal. Lett.*, **11**, 77.

Ebner, A. D., Ritter, J. A., Ploehn, H. J., Kochen, R. L., and Navratil, J. D. (1999) *Sep. Sci. Technol.*, **34**, 1277–300.

Eick, H. A. and Mulford, R. N. R. (1969) *J. Inorg. Nucl. Chem.*, **31**, 371–5.

Elesin, A. A. and Zaitsev, A. A. (1971a) *Radiokhimiya*, **13**, 902.

Elesin, A. A. and Zaitsev, A. A. (1971b) *Radiokhimiya*, **13**, 775.

Elesin, A. A. and Zaitsev, A. A. (1972) *Radiokhimiya*, **14**, 370.

Elesin, A. A., Zaitsev, A. A., Ivanovich, N. A., Karaseva, V. A., and Yakovlev, G. N. (1972a) *Radiokhimiya*, **14**, 546.

Elesin, A. A., Zaitsev, A. A., Karaseva, V. A., Nazarova, I. I., and Petukhova, I. V. (1972b) *Radiokhimiya*, **14**, 374.

Elesin, A. A., Zaitsev, A. A., Kazakova, S. S., and Yakovlev, G. N. (1972c) *Radiokhimiya*, **14**, 541.

Elesin, A. A., Zaitsev, A. A., Sergeev, G. M., and Nazarova, I. I. (1973) *Radiokhimiya*, **15**, 64.

Ellinger, F. H. and Zachariasen, W. H. (1954) *J. Phys. Chem.*, **58**, 405–8.

Ellinger, F. H., Johnson, K. A., and Struebing, V. O. (1966) *J. Nucl. Mater.*, **20**, 83–6.

Ensor, D. D., Jarvinen, G. D., and Smith, B. F. (1988) *Solvent Extr. Ion Exch.*, **6**, 439.

Erdmann, B. (1971) *Darstellung von Actiniden/Lanthaniden-Edelmetall (Pt, Pd, Ir, Rh)-Legierungsphasen durch gekoppelte Reduktion*, Kernforschungszentrum karlsruhe.

Erdmann, B. and Keller, C. (1971) *Inorg. Nucl. Chem. Lett.*, **7**, 675–83.

Erdmann, B. and Keller, C. (1973) *J. Solid State Chem.*, **7**, 40–8.

Eriksson, O. and Wills, J. M. (1992) *Phys. Rev. B*, **45**, 3198–203.

Eriksson, O., Soderland, J. M., Wills, J. M., and Boring, A. M. (1993) *Physica B*, **190**, 5–11.

Erin, E. A., Kopytov, V. V., Rykov, A. G., and Kosyakov, V. N. (1979) *Radiokhimiya*, **21**, 63–7.

Ermakov, V. A. and Star, I. (1967) *Radiokhim.*, **9**, 197.

Ermakov, V. A., Rykov, A. G., Timofeev, G. A., and Yakovlev, G. N. (1971a) *Radiokhimiya*, **13**, 826–32.

Ermakov, V. A., Vorob'eva, V. V., Zaitsev, A. A., and Yakovlev, G. N. (1971b) *Radiokhimiya*, **13**, 692.

Ermakov, V. A., Vorob'eva, V. V., Zaitsev, A. A., and Yakovlev, G. N. (1971c) *Radiokhimiya*, **13**, 840.

Ermakov, V. A., Rykov, A. G., Timofeev, G. A., and Yakovlev, G. N. (1973) *Radiokhimiya*, **15**, 380–5.

Ermakov, V. A., Rykov, A. G., Timofeev, G. A., and Yakovlev, G. N. (1974) *Radiokhimiya*, **16**, 810–17.

Eyring, L., Lohr, H. R., and Cunningham, B. B. (1949) University of California Radiation Laboratory.

Eyring, L., Lohr, H. R., and Cunningham, B. B. (1952) *J. Am. Chem. Soc.*, **74**, 1186–90.

Fahey, J. A., Turcotte, R. P., and Chikalla, T. D. (1974) *Inorg. Nucl. Chem. Lett.*, **10**, 459–65.

Fang, D. and Keller, C. (1969) *Radiochim. Acta*, **11**, 123–7.

Fargeas, M., Fremont- Lamouranne, R., Legoux, Y., and Morini, O. J. (1986) *J. Less Common Metals*, **121**, 439.

Fedoseev, A. M. and Perminov, V. F. (1983) *Sov. Radiochem.* (*Engl. Transl.*), **25**, 522–3.

Fedoseev, A. M. and Budentseva, N. A. (1989) *Sov. Radiochem.* (*Engl. Transl.*), **31**, 525–37.

Fedoseev, A. M. and Budantseva, N. A. (1990) *Radiokhimiya*, **32**, 14–18 and 19–24.

Fedoseev, A. M., Budantseva, N. A., Grigor'ev, M. S., and Perminov, V. P. (1991) *Radiokhimiya*, **33**, 7–19.

Ferris, L. M., Smith, F. J., Mailen, J. C., and Bell, M. J. (1972) *J. Inorg. Nucl. Chem.*, **34**, 2921–33.

Freeman, A. J. and Keller, C. (1985) in *Handbook on the Physics and Chemistry of Actinides*, Elsevier Science Publishers.

Freundlich, W. and Pages, M. (1969) *C. R. Acad. Sci. Ser. C*, **269**, 392–4.

Fried, S. (1951) *J. Am. Chem. Soc.*, **73**, 416–18.

Fuger, J. (1958) *J. Inorg. Nucl. Chem.*, **5**, 332.

Fuger, J. and Cunningham, B. B. (1963) *J. Inorg. Nucl. Chem.*, **25**, 1423–9.

Fuger, J., Spirlet, J. C., and Müller, W. (1972) *Inorg. Nucl. Chem. Lett.*, **8**, 709–23.

Fuger, J. and Oetting, F. L. (1976) *The Chemical Thermodynamics of Actinide Elements and Compounds,* part 2, *The Actinide Aqueous Ions*, IAEA, Vienna.

Fuger, J., Khodakovsky, I. L., Serfeyeva, E. I., Medvedev, V. A., and Navratil, J. D. (1992) *Part 12, The Actinide Aqueous Inorganic Complexes*, IAEA, Vienna.

Gatrone, R. C., Kaplan, L., and Horwitz, E. P. (1987) *Solvent Extr. Ion Exch.*, **5**, 1075.

Gatrone, R. C. and Rickert, P. G. (1987) *Solvent Extr. Ion Exch.*, **5**, 1117.

Gatrone, R. C., Horwitz, E. P., Rickert, P. G., and Diamond, H. (1989) *Solvent Extr. Ion. Exch.*, **7**, 793.

Gedeonov, L. I., Lebedev, I. A., Stepanov, A. V., Shalinets, A. B., and Yakovlev, G. N. (1967) *Chemistry of the Transuranium and Fission Elements*, Izd. Nauka, p. 140.

Gel'man, A. D., Moskvin, A. I., Zaitsev, L. M., and Medfod'eva, M. P. (1967) *Complex Compounds of Transuranides* (*Engl. transl.*), Israel Program for Scientific Translations, Jerusalem.

Gerontopulos, P. T., Rigali, L., and Barbano, P. G. (1965) *Radiochim Acta*, **4**, 75.

Gibson, J. K. and Haire, R. G. (1992a) *J. Nucl. Mater.*, **195**, 156–65.

Gibson, J. K. and Haire, R. G. (1992b) *J. Alloys Compd.*, **181**, 23–32.

Gibson, J. K. (1998a) *J. Phys. Chem. A*, **102**, 4501–8.

Gibson, J. K. (1998b) *Organometallics*, **17**, 2583–9.

Gibson, J. K. (1999a) *Inorg. Chem.*, **38**, 165–73.

Gibson, J. K. (1999b) *J. Mass Spectrom.,* **34**(11), 1166–77.

Gibson, J. K. (2000) *Int. J. Mass Spectrom.*, **202**, 19–29.

Giffaut, E. and Vitorge, P. (1993) *Mat. Res. Soc. Symp. Proc.*, **294**, 747–51.

Gmelin (1973) in *Gmelins Handbuch der Anorganischen Chemie*, Suppl. Work, 8th edition, Verlag Chemie, Weinheim, Germany: Vol. 4, Transurane, Teil C Verbindungen (Compounds); Vol. 7a, Die Elemente (The Elements), Teil A1 (1973); Vol. 8, Teil A2, Die Elemente (The Elements) (1973).

Gmelin (1979) in *Gmelin Handbook of Inorganic Chemistry*, vol. *Transuranium*, Parts A1, A2, B1–3, C, D1, D2, Verlag Chemie, Weinheim.

Goffart, J. and Kuyckaerts, G. (1969) *Anal. Chim. Acta.*, **43**, 99.

Gopalakrishnan, V., Dhami, P. S., Ramanujam, A., Balaramarkishna, M. V., Murali, M. S., Mathur, J. N., Iyer, R. H., Bauri, A. K., and Bannerji, A. (1995) *J. Radioanal. Nucl. Chem. Art.*, **191**, 279.

Gourisse, D. (1966) *Cinetique des Reactions D'Oxydo-Reduction des Elements Transuraniens en Solution*, CEA.

Graus Odenheimer, B. and Choppin, G. R. (1956) *Stability Constants of Alpha hydroxyisobutyric Acid Complexes with Actinide Elements*, University of California Radiation Laboratory, Berkeley.

Grebenshchikova, V. I. and Babrova, V. N. (1958) *Zhur. Neorg. Khim.*, **3**, 400.

Grebenshschikova, V. I. and Babrova, V. N. (1961) *Radiochemistry USSR* **3**, 32.

Grebenshschikova, V. I. and Cheinyavskaya, N. B. (1962) *Sov. Radiochem.* (*Engl. Transl*), **4**, 207.

Grenthe, I. (1962) *Acta. Chem. Scand.*, **16**, 1695.

Grenthe, I., Fuger, J., Konings, R. J. M., Lemire, R. J., Muller, A. B., Nguyen-Trung, C., and Wanner, H. (1992) *Chemical Thermodynamics of Uranium*, Elsevier Science Publishers, North-Holland.

Grigorescu-Sabau, C. S. (1972) *Über die Temperaturabhangigkeit von Komplexgleichgewichten der Transplutone*, Kernforschungszentrum Karlsruhe.

Guillaume, B., Hobart, D. E., and Bourges, J. Y. (1981) *J. Inorg. Nucl. Chem.,* **43**(12), 3295–9.

Guillaume, B., Begun, G. M., and Hahn, R. L. (1982) *Inorg. Chem.*, **21**, 1159–66.

Guminski, C. (1995) *J. Phase Equilib.*, **16**, 333.

Gureev, E. S., Kosyakov, V. N., and Yakovlev, G. N. (1964) *Sov. Radiochem.*, **6**, 639–47.

Gureev, E. S., Dedov, V. B., Karpacheva, S. M., Shvetsov, I. K., Ryzhov, M. N., Trukchlayev, P. S., Yakovlev, G. N., and Lebedev, I. A. (1970) in *Progress in Nuclear Energy, Process Chemistry*, ser. III, vol. 4, (eds. C. E. Stevenson, E. A. Mason, and A.T. Gresky), Pergamon Press, New York, p. 631.

Hafez, M. B. (1968) *Spectrophotometric Study of the Complexes of Cerium and Uranides with Diethylenetriaminepentaacetic Acid* (DTPA).

Haire, R. G., Lloyd, M. H., Milligan, W. O., and Beasley, M. L. (1977) *J. Inorg. Nucl. Chem.*, **39**(5), 837–41 and 843–7.

Haire, R. G., Benedict, U., Young, J. P., Peterson, J. R., and Begun, G. M. (1985) *J. Phys. C: Solid State Phys.*, **18**(24), 4595–601.

Hale, W. H. and Lowe, J. T. (1969) *Inorg. Nucl. Chem. Lett.*, **5**, 363–9.

Hall, G. R. Herniman, and P. D. (1954) *J. Chem. Soc.*, 2214–21.

Hall, G. R. and Markin, T. L. (1957) *J. Inorg. Nucl. Chem.*, **4**, 137–42.

Hall, R. O. A., Lee, J. A., Mortimer, M. J., McElroy, D. L., Müller, W., and Spirlet, J. C. (1980) *J. Low Temp. Phys.*, **41**, 397–403.

Hall, H. L. (1989) Report USDOE LBL-27878, University of California, Berkeley, USA.

Hara, M. (1970) *Bull. Chem. Soc. Jpn.*, **43**, 89–94.

Harbour, R. M., Hale, W. H., Burney, G. A., and Lowe, J. T. (1972) *At. Energy Rev.*, **10**, 379–99.

Hennelly, E. J. (1972) in *Radioisotope Engineering* (ed. G. G. Eichholz), Marcel Dekker, New York, pp. 44–134.

Hermann, J. A. (1956) *Coprecipitation of Am(III) with Lanthanum Oxalate*, Los Alamos Scientific Laboratory.

Hill, H. H. and Ellinger, F. H. (1971) *J. Less Common Metals*, **23**, 92.

Hill, H. H., Lindsey, J. D. G., White, R. W., Asprey, L. B., Streubing, V. O., and Matthias, B. T. (1971) *Physica*, **55**, 615.

Hindman, J. C. (1958) Proc. of the *Second Int. Conf. on the Peaceful Uses of Atomic Energy*, Geneva, United Nations, p. 349–60.

Hobart, D., Samhoun, K., and Peterson, J. R. (1982) *Radiochim. Acta*, **31**, 139–45.

Hobart, D. E., Begun, G. M., Haire, R. G., and Hellwege, H. E. (1983a) *J. Raman Spectrosc.,* **14**(1), 59–62.

Hobart, D. E., Samhoun, K., and Peterson, J. R. (1983b) *Radiochim. Acta*, **31**, 139–45.

Hoekstra, H. and Gebert, E. (1978) *Inorg. Nucl. Chem. Lett.*, **14**, 189–91.

Hölgye, Z. (1982) *Radiochem. Radioanal. Lett.*, **53**, 285–90.

Horrocks, W. D. Jr and Sudnick, D. R. (1979) *Science,* **206**(7), 1194–6.

Horrocks, W. D. Jr and Sudnick, D. R. (1981) *Acc. Chem. Res.*, **14**, 384–92.

Horwitz, E. P. (1966) *J. Inorg. Nucl. Chem.*, **28**, 1469–78.

Horwitz, E. P., Bloomquist, C. A. A., Sauro, L. J., and Henderson, D. J. (1966) *J. Inorg. Nucl. Chem.*, **28**, 2313–24.

Horwitz, E. P., Bloomquist, C. A. A., Orlandini, K. A., and Henderson, D. J. (1967) *Radiochim. Acta*, **8**, 127–32.

Horwitz, E. P., Bloomquist, C. A. A., and Griffin, H. E. (1969) Argonne National Laboratory.

Horwitz, E. P., Kalina, D. G., and Muscatello, A. C. (1981) *Sep. Sci. Technol.*, **16**, 403.

Horwitz, E. P., Kalina, D. G., Kaplan, L., Mason, G. W., and Diamond, H. (1982) *Sep. Sci. Technol.*, **17**, 1261.

Horwitz, E. P. and Kalina, D. G. (1984) *Solvent Extr. Ion Exch.*, **2**, 179.

Horwitz, E. P. and Schulz, W. W. (1985) in *Solvent Extraction and Ion Exchange in the Nuclear Fuel Cycle* (eds. D. H. Logsdail and A. L. Mills), Ellis Horwood, Chichester, p. 137.

Horwitz, E. P., Kalina, D. G., Diamond, H., Kaplan, L., Vandegrift, G. F., Leonard, R. A., Steindler, M. J., and Schulz, W. W. (1985a) in *Actinide/Lanthanide Separations* (eds. G. R. Choppin, J. D. Navratil, and W. W. Schulz), World Scientific, Singapore, p. 43.

Horwitz, E. P., Kalina, D. G., Diamond, H., Vandegrift, G. F., and Schulz, W. W. (1985b) *Solvent Extr. Ion Exch.*, **3**, 75.

Horwitz, E. P. and Schulz, W. W. (1986) in *Proc. ISEC '86.*

Horwitz, E. P., Martin, K. A., Diamond, H., and Kaplan, L. (1986) *Solvent Extr. Ion Exch.*, **4**, 449.

Horwitz, E. P., Diamond, H., Martin, K. A., and Chiarizia, R. (1987) *Solvent Extr. Ion Exch.*, **3**, 419 and 447.

Horwitz, E. P. and Schulz, W. W. (1990) *Symposium on New Separation Chemistry for Radioactive Waste and Other Specific Applications.*

Horwitz, E. P., Dietz, M. L., Nelson, D. M., La Rosa, J. J., and Fairman, W. B. (1990) *Anal. Chim. Acta.*, **238**, 263.

Horwitz, E. P., Chiarizia, R., Dietz, M. L., and Diamond, H. (1993) *Anal. Chem.*, **281**, 361.

Horwitz, E. P., Chiarizia, R., and Dietz, M. L. (1997) *React. Funct. Polym.*, **33**, 25.

Horwitz, E. P. and Schulz, W. W. (1999) in *Metal Ion Separation and Preconcentration: Progress and Opportunities* (eds. A. H. Bond, M. L. Dietz, and R. D. Rogers), American Chemical Society, Washington, DC, p. 20.

Hubert, S., Hussonnois, M., Brillard, L., Goby, G., and Guillaumont, R. (1974) *J. Inorg. Chem.*, **36**, 2361.

Hubert, S., Hussonois, M., Brillard, L., and Guillaumont, R. (1975) in *Transplutonium Elements, Proc. 4th Int. Symp.*, Baden-Baden, Sept. 13–17, Ed. by Müller, W. Lindner, R., North-Holland/Amer. Elsevier, p. 109–118.

Hubert, S. and Thouvenot, P. (1992) *J. Lumin.*, **54**, 103–11.

Hugen, Z., Yuxing, Y., and Xuexian, Y. (1982) *Actinide Recovery from Waste and Low-Grade Source*, Harwood Academic Publishers, New York, USA.

Hulet, E. K., Gutmacher, R. G., and Coops, M. S. (1961) *J. Inorg. Nucl. Chem.*, **17**, 350–60.

Hurtgen, C. and Fuger, J. (1977) *Inorg. Nucl. Chem. Lett.*, **13**, 1186–90.

Hyde, E. K., Perlman, I., and Seaborg, G. T. (1971) *The Nuclear Properties of the Heavy Elements*, Prentice-Hall, New York.

Jenkins, I. L. and Wain, A. G. (1972) *Rep. Prog. Appl. Chem.*, **57**, 308–19.

Jensen, M. P., Morss, L. R., Beitz, J. V., and Ensor, D. D. (2000) *J. Alloys Compd.*, **303**, 137–41.

Johannson, B. (1978) *J. Phys. Chem. Solids*, **39**, 467.

Johannson, B. (1984) *Phys. Rev B*, **30**, 3533–55.

Johannson, B. (1995) *J. Phys. Compds.*, **223**, 211–15.

Johannson, B. (2000) *Physics World*, 26–7.

Jones, M. E. (1951) *The Vapor Pressure of Americium Trifluoride* (Thesis), University of California Radiation Laboratory.

Jones, L. L. (1953) *J. Chem. Phys.*, **23**, 2105.

Jones, L. H. and Penneman, R. A. (1953) *J. Chem. Phys.*, **21**, 542–4.

Jones, L. H. (1955) *J. Chem. Phys.*, **23**, 2105–7.

Jove, J. and Pages, M. (1977) *Inorg. Nucl. Chem.*, **13**, 329–34.

Kalina, D. G., Horwitz, E. P., Kaplan, L., and Muscatello, A. C. (1981a) *Sep. Sci. Technol.*, **16**, 1127.

Kalina, D. G., Mason, G. W., and Horwitz, E. P. (1981b) *J. Inorg. Nucl. Chem.*, **43**, 159.

Kalina, D. G. and Horwitz, E. P. (1985) *Solvent Extr. Ion Exch.*, **3**, 235.

Kalvius, G. M., Ruby, S. L., Dunlap, B. D., Shenoy, G. K., Cohen, D., and Brodsky, M. B. (1969) *Phys. Lett. B*, **29**, 489–90.

Kamashida, M. and Fukasawa, T. (1996) *J. Nucl. Sci. Technol.*, **33**, 403–8.

Kamashida, M., Fukasawa, T., and Kawamura, F. (1998) *J. Nucl. Sci. Technol.*, **35**, 185–9.

Kaneko, H., Tsujii, M., Abe, M., Morita, Y., and Kubota, M. (1992) *J. Nucl. Sci. Technol.*, **29**, 988.

Kaneko, H., Tsujii, M., and Tamaura, Y. (1993) *Solvent Extr. Ion Exch.*, **11**, 693.

Kanellakopoulos, B., Fisher, E. O., Dornberger, E., and Baumgärtner, F. (1970) *J. Organomet. Chem.*, **24**, 507–14.

Kanellakopulos, B., Charvillat, J. P., Maino, F., and Müller, W. (1975) in *Transplutonium Elements*, *Proc. 4th Int. Symp.*, Baden-Baden, Sept. 13–17, Ed. by Müller, W. Linder, R., North-Holland/Amer. Elsevier.

Kanellakopulos, B., Aderhold, C., Dornberger, E., Müller, W., and Baybarz, R. D. (1978) *Radiochim. Acta* **25** (2), 89–92.

Kanellakopulos, B. (1979) in *Organometallics of the f-Elements* (eds. T. J. Marks and R. D. Fischer), Reidel, Dordrecht, pp. 1–35.

Karraker, D. G. Potassium Bis(Cyclooctatetraenyl) Americium(III). in *Transplutonium Elements, proc. 4th Int. Symp.,* Baden-Baden, Sept. 13–17, Ed. by Müller, W. Lindner, R., North-Holland/Amer. Elsevier, p. 131–5.

Karraker, D. G. (1977) *J. Inorg. Nucl. Chem.,* **39**(1), 87–9.

Kaszuba, J. P. and Runde, W. (1999) *Environ. Sci. Technol.*, **33**, 4427–33.

Katz, J. J. and Gruen, D. M. (1949) *J. Am. Chem. Soc.*, **71**, 2106–12.

Katz, J. J: Seaborg, G. T. (1957) *The Chemistry of the Actinide Elements*, Methuen, London, UK.

Keenan, T. K. (1959) *J. Chem. Educ.*, **36**, 27–31.

Keenan, T. K. and Kruse, F. H. (1964) *Inorg. Chem.*, **3**, 1231–2.

Keenan, T. K. (1965) *Inorg. Chem.*, **4**, 1500–1.

Keenan, T. K. (1966) *Inorg. Nucl. Chem. Lett.*, **2**, 153–6 and 211–14.

Keenan, T. K. (1967) *Inorg. Nucl Chem. Lett.*, **3**, 391–6 and 463–7.

Keenan, T. K. (1968) *Inorg. Nucl. Chem. Lett.*, **4**, 381–4.

Keller, C. (1963) *Nukleonik*, **5**, 41–8.

Keller, C. (1964) *Über die Festkörperchemie der Actiniden-Oxide*, Kernforschungszentrum Karlsruhe.

Keller, C. and Schmutz, H. (1964) *Z. Naturf. B*, **19**, 1080.

Keller, C. (1965) *J. Inorg. Nucl. Chem.*, **27**, 321–7.

Keller, C. and Walter, K. H. (1965) *J. Inorg. Nucl. Chem.*, **27**, 1247–51 and 1253–60.

Keller, C., Eberle, S. H., and Mosdzelewski, K. (1965a) *Radiochim. Acta*, **4**, 141–5.

Keller, C., Koch, L., and Walter, K. H. (1965b) *J. Inorg. Nucl. Chem.*, **27**, 1205–23 and 1225–32.

Keller, C., Eberle, S. H., and Mosdzelewski, K. (1966) *Radiochim. Acta*, **5**, 185–8.

Keller, C. (1967) in *Lanthanide/Actinide Chemistry* (ed. R. F. Gould), American Chemical Society, Washington, DC, , pp. 228–47.

Keller, C. and Fang, D. (1969) *Radiochim. Acta*, **11**, 123.

Keller, C. and Schreck, H. (1969) *J. Inorg. Nucl. Chem.*, **31**, 1121–32.

Keller, C. (1971) *Chemistry of the Transuranium Elements*, Verlag Chemie, Weinheim.

Keller, C., Berndt, U., Debbabi, M., and Engerer, H. (1972) *J. Nucl. Mater.*, **42**, 23–31.

Keller, C. and Berndt, U. (1975) in *Transplutonium, Proc. 4th Int. Symp.,* Baden-Baden, Sept. 13–17, Ed. by Müller, W. Lindner, R., North-Holland/Amer. Elsevier, p. 85–93.

Khopkar, P. K. and Narayankutty, P. (1971) *J. Inorg. Nucl. Chem.*, **33**, 495–502.

Kim, J. I., Rhee, D. S., Wimmer, H., Buckau, G., and Klenze, R. (1993) *Radiochim. Acta*, **62**, 35.

Kimura, T. and Kato, Y. (1998) *J. Alloys Compd*, **271**, 867–71.

King, L. J., Bigelow, J. E., and Collins, E. D. (1973) *Transuranium Processing Plant Semiannual Report of Production, Status, and Plans for Period Ending June* 30, 1972, Oak Ridge National Laboratory.

Kirin, I. S., Moskalev, P. N., and Mishin, V. Y. (1967) *Zh. Obshch. Khim.*, **37**, 1065–8.

Koch, G. and Schoen, J. (1968) German Report KFK-783, Kernforschungszentrum Karlsruhe, Germany.

Koch, G. (1969) Conf. Report CONF-690426, Liege, Belgium.

Kochen, R. L. (1987) *Actinide Removal from Aqueous Solution with Activated Magnetite*, Rockwell International, Golden, CO.

Kochen, R. L. and Navratil, J. D. (1987) *Lanthanide/Actinide Res.*, **2**, 9.

Koehly, G. and Hoffert, F. (1967) *Semiannual Report of the Chemistry Department, Center for Nuclear Studies at Fontenay-aux-Roses, December* 1966–*May* 1967, Argonne National Laboratory.

Kolarik, Z. J. and Horwitz, E. P. (1988) *Solvent Extr. Ion Exch.*, **6**, 247.

Kolarik, Z., Müllich, U., and Gassner, F. (1999) *Solvent Extr. Ion Exch.*, **17**, 23 and 1155.

Koma, Y., Watanabe, M., Nemoto, S., and Tanaka, Y. (1998) *Solvent Extr. Ion Exch.*, **16**, 1357.

Kornilov, A. S., Frolov, A. A., and Vasil'ev, V. Y. (1986) *Radiokhimiya*, **28**(5), 656–60.

Kosyakov, V. N., Timofeev, G. A., Erin, E. A., Andreev, V. I., Kopytov, V. V., and Simakin, G. A. (1977) *Radiokhimiya*, **19**, 511–7.

Krot, N. N., Shillov, V. P., Nikolaevskii, V. B., Nikaev, A. K., Gel'man, A. D.,and Spitsyn, V. I. (1974a) *Dokl. Acad. Sci. USSR*, **217**(3), 525–7.

Krot, N. N., Shillov, V. P., Nikolaevskii, V. B., Nikaev, A. K., Gel'man, A. D., and Spitsyn, V. I. (1974b). Oak Ridge National Laboratory.

Kruse, F. H. and Asprey, L. B. (1962) *Inorg. Chem.*, **1**(1), 137–9.

Kuznetsov, V. I. and Skobelev, N. K. (1966) ORO-tr-3346-15, Joint Inst. for Nuclear Research, Dubna (USSR), translation of Russian report JINR-p7-2984.

Lam, D. J. and Mitchell, A. W. (1972) *J. Nucl. Mater.*, **44**, 279–84.

Larson, D. T. and Haschke, J. M. (1981) *Inorg. Chem.*, **20**, 1945–50.

Law, J. D., Brewer, K. N., Herbst, R. S., Todd, T. A., and Olsen, L. G. (1998) Report INEL/EXT-98-00004, Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho, USA.

Law, J. D., Brewer, K. N., Herbst, R. S., and Todd, T. A. (1998) Report INEL/EXT-97-00837, Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho, USA.

Lawaldt, D., Marquart, R., Werner, G.-D., and Wigel, F. (1982) *J. Less Common Metals*, **85**, 37–41.

Lebedev, I. A., Pirozhkov, S. V., Razbitnoi, V. M., and Yakovlev, G. N. (1960a) *Radiokhimiya*, **2**, 351–6.

Lebedev, I. A., Pirozhkov, S. V., and Yakovlev, G. N. (1960b) *Radiokhimiya*, **2**, 549–58.

Lebedev, I. A. and Yakovlev, G. N. (1961) *Radiokhimiya*, **3**, 455.

Lebedev, I. A., Pirozhkov, S. V., and Yakovlev, G. N. (1962) *Radiokhimiya*, **4**, 304–8.

Lebedev, I. A., Maksimova, A. M., Stepanov, A. V., and Shalinets, A. B. (1967) *Radiokhimiya*, **9**, 707.

Lebedev, I. A. and Shalinets, A. B. (1968) *Radiokhimiya*, **10**, 233.

Lebedev, I. A., Filimonov, V. T., Shalinets, A. B., and Yakovlev, G. N. (1968) *Radiokhimiya*, **10**, 93.

Lebedev, I. A., Frenkel, V. Y., Kulyako, Y. M., and Myasoedov, B. F. (1979) *Radiokhimiya*, **21**(6), 809–16.

Lederer, C. M. and Shirley, V. S. (1978) in *Table of Radioactive Isotopes*, John Wiley, New York.

Leger, J. M., Yacoubi, N., and Loriers, J. (1981) *J. Solid State Chem.*, **36**, 261–70.

Levakov, B. I. and Shalinets, A. B. (1971) *Radiokhimiya*, **13**, 295.

Le Vert, F. E. and Helminski, E. L. (1973) *Literature Review and Commercial Source Evaluation of Americium-241*, Tuskegee Institute.

Li, J. and Bursten, B. E. (1997) *J. Am. Chem. Soc.,* **119**(38), 9021–32.

Liansheng, W., Casarci, M., and Gasparini, G. M. (1991) *Solvent Extr. Ion Exch.*, **8**, 49.

Liminga, R., Abrahams, S. C., and Bernstein, J. L. (1977) *J. Chem. Phys.*, **67**(3), 1015–23.

Lin, Z., Berne, A., Cummings, B., Filliben, J. J., and Inn, K. G. W. (2002) *Appl. Radiat. Isot.*, **56**, 57–63.

Lindbaum, A., Heathman, S., Litfin, K., Meresse, Y., Haire, R. G., Le Bihan, T., and Libotte, H. (2001) *Phys. Rev. B*, **63**, 214101 (1–10).

Link, P., Braithwaite, D., Wittig, J., Benedict, U., and Haire, R. G. (1994) *J. Alloys Compd.*, **213/214**, 148–52.

Liu, G. K., Beitz, J. V., Huang, J., Abraham, M. M., and Boatner, L. A. (1997) *J. Alloys Compd.*, **250**, 347–51.

Lohr, H. R. and Cunningham, B. B. (1951) *J. Am. Chem. Soc.*, **73**, 2025–8.

Lumetta, G. J. and Swanson, J. L. (1993a) *Sep. Sci. Technol.*, **28**, 43.

Lumetta, G. J. and Swanson, J. L. (1993b) Pacific Northwestern Laboratory.

Lumetta, G. J., Wester, D. W., Morrey, J. R., and Wagner, M. J. (1993) *Solvent Extr. Ion Exch.*, **11**, 663.

Lux, F. (1973) *Proc. Tenth Rare Earth Reasearch Conf.,* Carefree, Arizona, April 30-May 3, Ed. by Kevane, C. J. and Moeller, T., pp. 871–80.

Lychev, A. A., Mashirov, L. G., Smolin, Y. I., Suglobov, D. N., and Shepelev, Y. F. (1980) *Radiokhimiya*, **22**, 43–8.

Lynch, R. W., Dosch, R. G., Kenna, B. T., Johnstone, J. K., and Nowak, E. J. (1975) *The Sandia Solidification Process: A Broad Range Aqueous Waste Solidification Method.*

Madic, C., Guillaumont, B., Morisseau, J. C., and Moulin, J. P. (1979) *J. Inorg. Nucl. Chem.*, **83**, 3373.

Madic, C., Hobart, D. E., and Begun, G. M. (1983) *Inorg. Chem.*, **22**, 1494–503.

Madic, C., Blanc, P., Condamines, N., Baron, P., Berthon, L., Nicol, C., Pozo, C., Lecomte, M., Phillipe, M., Masson, M., Hequet, C., and Hudson, M. J. (1994) French Report CEA-CONF-12297.

Madic, C. and Hudson, M. J. (1998) Report EUR 18038 EN.

Magirius, S., Carnall, W. T., and Kim, J. I. (1985) *Radiochim. Acta*, **38**, 29–32.

Mahajan, G. R., Prabhu, D. R., Manchanda, V. K., and Badheka, L. P. (1998) *Waste Manage.*, **18**, 125.

Maly, J. (1969) *J. Inorg. Nucl. Chem.*, **31**, 1007–17.

Manchanda, V. K. and Mohapatra, P. K. (1995) *Radiochim. Acta*, **69**, 81.

Mapara, P. M., Godbole, A. G., Rajendra, S., and Thakur, N. V. (1998) *Hydrometallurgy*, **49**, 197–201.

Marcu, G. and Samochocka, K. (1965) *Stud. Univ. Babes-Bolyai, Ser. Chem.*, **10**, 71.

Marcu, G. and Samochocka, K. (1966) *Stud. Univ. Babes-Bolyai, Ser. Chem.*, **11**, 15.

Marcus, Y., Givon, M., and Choppin, G. R. (1963) *J. Inorg. Nucl. Chem.*, **25**, 1457–63.

Marcus, Y. and Cohen, D. (1966) *Inorg. Chem.*, **5**, 1740–3.

Marcus, Y. and Shiloh, M. (1969) *Israel J. Chem.*, **7**, 31–43.

Marcus, Y. and Bomse, M. (1970) *Israel J. Chem.*, **8**, 901–11.

Marcus, Y., Yanir, E., and Givon, M. (1972) The standard potential of the americium III/IV couple. An estimate from the formal potential and complex stabilities in phosphoric acid, in *Coordination Chemistry in Solution*, Vol. kungl. Tek. Högsk. Handl. Nr. 265 (ed. E. Högfeldt), Swedish Nat. Sci. Res. Council, pp. 227–38.

Markin, T. L. (1958) *J. Inorg. Nucl. Chem.* **7**, 290–2.

Martella, L. L. and Navratil, J. D. (1979) US Report.

Martensson, N., Johansson, B., and Naegele, J. R. (1987) *Phys. Rev. B*, **35**, 1437–9.

Martinot, L. and Fuger, J. (1985) *The Actinides* in *Standard Potentials in Aqueous Solution*, ed. by Bard, A. J., Parsons, R., Jordan, J., Dekker, New York, USA, p. 631–74.

Mathur, J. N., Murali, M. S., and Natarajan, R. R. (1991) *J. Radioanal. Nucl. Chem.*, **152**, 127.

Mathur, J. N., Murali, M. S., Natarajan, P. R., Bodheka, L. P., and Benerji, R. (1992a) *Talanta*, **39**, 493.

Mathur, J. N., Murali, M. S., and Natarajan, R. R. (1992b) *J. Radioanal. Nucl. Chem.*, **155**, 195.

Mathur, J. N., Murali, M. S., Rizvi, G. H., Iyer, R. H., Michael, K. M., Kapoor, S. C., Dhumwad, R. K., Badheka, L. P., and Bannerji, A., (1994) *Solvent Extr. Ion Exch.*, **12**, 745.

Mathur, J. N., Murali, M. S., Iyer, R. H., Ramanujam, A., Dhami, P. S., Gopalakrishnan, V., Badheka, L. P., and Bannerji, A. (1995) *Nucl. Technol.*, **109**, 216.

Mathur, J. N., Murali, M. S., Ruikar, P. B., Nagar, M. S., Sipahimalani, A. R., Bauri, A. K., and Bannerji, A. (1998) *Sep. Sci. Technol.*, **33**, 2179.

Mathur, J. N., Murali, M. S., and Nash, K. L. (2001) *Solvent Extr. Ion Exch.*, **19**, 357–90.

Matonic, J. H., Scott, B. L., and Neu, M. P. (2001). *Inorg. Chem.*, **40**, 2638.

McIsaac, L. D. and Schulz, W. W. (1976) *Transplutonium 1975*, North-Holland, Amsterdam.

McIsaac, L. D. (1982) *Sep. Sci. Technol.*, **17**, 387.

McIsaac, L. D. and Baker, J. D. (1983) *Solvent Extr. Ion Exch.*, **1**, 72.

McWhan, D. B., Wallmann, J. C., Cunningham, B. B., Asprey, L. B., Ellinger, F. H., and Zachariasen, W. H. (1960) *J. Inorg. Nucl. Chem.*, **15**, 185–7.

Meinrath, G. and Kim, J. I. (1991a) *Radiochim. Acta*, **52/53**, 29.

Meinrath, G. and Kim, J. I. (1991b) *Eur. J. Inorg. Solid State Chem.*, **28**, 383–8.

Melkaya, R. F., Volkov, Y. F., Sokolov, E. I., Kapshukov, I. I., and Rykov, A. G. (1982) *Dokl. Chem.* (*Engl. Transl.*), **262/7**, 42.

Mercing, E. and Duyckaerts, E. (1967) *Anal. Lett.*, **1**, 23.

Michael, K. M., Rizvi, G. H., Mathur, J. N., and Ramanujam, A. (2000) *J. Radioanal. Nucl. Chem.*, **246**, 355.

Mikheev, N. B. and Myasoedov, B. F. (1985) Lower and higher oxidation states of transplutonium elements in solutions and Metals, in *Handbook on the Physics and Chemistry of the Actinides*, ch. 9 (eds. J. A. Freeman and C. Keller), Elsevier Science Publishers, pp. 347–86.

Milligan, W. O. and Beasley, M. L. (1968) *Acta Crystallogr. B*, **24**, 979–81.

Mills, T. R. and Reese, L. W. (1994) *J. Alloys Compd.*, **213/214**, 360–2.

Milyukova, M. S., Litvina, M. N., and Myasoedov, B. F. (1980) *Radiochem. Radioanal. Lett.,* **44**(4), 259–68.

Mishra, S., Chakravortty, V., and Vasudeva Rao, P. R. (1996) *Radiochim. Acta*, **73**, 89.

Mitchell, A. W. and Lam, D. J. (1970a) *J. Nucl. Mater.*, **37**, 349–52.

Mitchell, A. W. and Lam, D. J. (1970b) *J. Nucl. Mater.*, **36**, 110–12.

Moattar, F. (1971) *Compounds of Trivalent Transuranium Compounds Appearing in Mixtures of Complexing Agents.* Report KFK-1416, Kernforschungszentrum Karlsruhe, Germany.

Modolo, G. and Odoj, R. (1998) *J. Radioanl. Nucl. Chem.*, **228**, 83.

Modolo, G. and Odoj, R. (1999) *Solvent Extr. Ion Exch.*, **17**, 33.

Mohapatra, P. K. and Manchanda, V. K. (1991) *Radiochim. Acta*, **55**(4), 193–7.

Mohapatra, P. K. and Manchanda, V. K. (1995) *Polyhedron,* **14**(13–14), 1993–7.

Mohapatra, P. K. and Manchanda, V. K. (1999) *J. Radioanal. Nucl. Chem.*, **240**, 259.

Mohapatra, P. K., Sriram, S., Manchanda, V. K., and Badheka, L. P. (2000) *Sep. Sci. Technol.*, **35**, 39.

Moore, R. H. and Lyon, W. L. (1959) *Distribution of Actinide Elements in Molten System KCl-AlCl$_3$-Al*, General Electric Company, Hanford Atomic Products Operation.

Moore, F. L. (1964) *Anal. Chem.*, **36**, 2158.

Moore, F. L. (1966a) *Anal. Chem.*, **38**, 510.

Moore, F. L. (1966b) US Patent 3 194 494.

Moore, G. E. (1970) *Chemistry Division Annual Progress Report for Period Ending May* 20, 1970, Oak Ridge National Laboratory.

Moore, F. L. (1973) US Patent 3 687 641.

Morita, Y. and Kubota, M. (1988) *Solvent Extr. Ion Exch.*, **6**, 233.

Morita, Y., Yamaguchi, L., Kondo, Y., Shirahashi, K., Yamagishi, I., Fugiwara, T., and Kubota, M. (1993) in Proc. of Technical Committee on *Safety and Environmental Aspects of Partitioning and Transmutation of Actinides and Fission Products*. Report IAEA-TECDOC-783, Vienna, Austria.

Morss, L. R., Siegal, M., Stenger, L., and Edelstein, N. (1970) *Inorg. Chem.*, **9**(7), 1771–5 .

Morss, L. R. and Fuger, J. (1981) *J. Inorg. Nucl. Chem.*, **43**(9), 2059–64.

Morss, L. R. (1982) in *Actinides in Perspective* (ed. N. Edelstein), Pergamon Press, New York, pp. 381–407.

Morss, L. R. (1983) *J. Less Common Metals*, **93**, 301–21.

Morss, L. R. and Williams, C. W. (1994) *Radiochim. Acta*, **66/67**, 99–103.

Moskalev, P. N., Shapkin, G. N., and Darovskikh, A. N. (1979) *Zh. Neorg. khim.*, **24**, 340–6.

Moskvin, A. I., Khalturin, G. V., and Gel'man, A. D. (1959) *Radiokhimiya*, **1**, 141.

Moskvin, A. I., Khalturin, G. V., and Gel'man, A. D. (1962) *Radiokhimiya*, **4**, 162.

Moskvin, A. I. (1967) *Radiokhimiya*, **9**, 718–20.

Moskvin, A. I. (1971) *Radiokhimiya*, **13**, 221–3, 224–30, 575–81, and 668–74.

Moskvin, A. I. (1973) *Radiokhimiya*, **15**, 504–13.

Mosley, W. C. (1970) in *Proc. 4th Internat. Conf. on Plutonium and other Actinides*, Santa Fe, NM, USA, USAEC CONF-701001, Parts II, pp 762–771.

Moulin, V., Robouch, P. B., Vitorge, P., and Allard, B. (1987) *Inorg. Chim. Acta*, **140**, 303.

Müller, W. (1971) *Angew. Chem.*, **83**, 625.

Müller, W., Reul, J., and Spirlet, J. C. (1972) *Atomwirtschaft*, **17**, 415.

Müller, W., Schenkel, R., Schmick, H. E., Spirlet, J. C., McElroy, D. L., Hall, R. O. A., and Mortimer, M. J. (1978) *J. Low Temp. Phys.*, **40**, 361–78.

Mullins, L. J. and Leary, J. A. (1969) US Patent 3420639.

Murali, M. S. and Mathur, J. N. (2001) *Solvent Extr. Ion Exch.*, **19**, 61–77.

Musikas, C. (1973a) *Radiochem. Radioanal. Lett.*, **13**, 255–8.

Musikas, C. C. (1973b) Electrochimie en solution aqueuse, in *Gmelin Handbook of Inorganic Chemistry*, vol. part D1, Verlag Chemie, Weinheim, pp. 5–23.

Musikas, C., Germain, M., and Bathelier, A. (1980a) in *Actinide Separations* (eds. J. D. Navratil and W. W. Schulz) (*ACS Symp. Ser. 117*), American Chemical Society, Washington, DC, pp. 157–73.

Musikas, C., Le Marois, G., Fitoussi, R., and Cuillerdier, C. (1980b). in *Actinide Separations* (eds. J. D. Navratil and W. W. Schulz), (*ACS Symp. Ser. 117*), American Chemical Society, Washington, DC, pp. 131–45.

Musikas, C. and Hubert, H. (1983) *Proc. ISEC '83*, p. 449.

Musikas, C. (1984) *Actinide/Lanthanide Separations, Proc., Int. Symp.*, 19–30.

Musikas, C. (1987) *Inorg. Chim. Acta*, **140**, 197.

Musikas, C., Condamines, C., Cuillerdier, C., and Nigond, L. (1991) *International Symposium on Radiochemistry and Radiation Chemistry*.

Musikas, C. (1995) *Nuclear and Radiochemistry Symposium*.

Myasoedov, B. F., Mikhailov, V. M., Lebedev, I. A., Litvina, M. N., and Frenkel, V. Y. (1973) *Radiochem. Radioanal. Lett.*, **14**, 17–24.

Myasoedov, B. F., Guseva, L. I., Lebedev, I. A., Milyukova, M. S., and Chmutova, M. S. (1974a) *Analytical Chemistry of the Transplutonium Elements,* John Wiley, New York.

Myasoedov, B. F., Lebedev, I. A., Frenkel, V. Y., and Vyatkina, I. I. (1974b) *Sov. Radiochem.*, **16**, 803–7.

Myasoedov, B. F., Milyukova, M. S., Lebedev, I. A., Livina, M. N., and Frenkel, V. Y. (1975) *J. Inorg. Nucl. Chem.*, **37**, 1475–8.

Myasoedov, B. F., Lebedev, I. A., and Milyukova, M. S. (1977) *Rev. Chem. Minér.*, **14**, 160–71.

Myasoedov, B. F., Chmutova, M. K., and Karalova, Z. K. (1980) in *Actinide Separations* (eds. J. D. Navratil and W. W. Schulz), American Chemical Society, Washington, DC, p. 101.

Myasoedov, B. F. and Kremliakova, N. Y. (1985) Studies of americium and curium solution chemistry in the USSR, in *Americium and Curium Chemistry and Technology* (ed. N. M. Edelstein), D. Reidel, Germany, pp. 53–79.

Myasoedov, B. F., Chmutova, M. K., Kochetkova, N. E., Koiro, O. E., Priibylova, G. A., Nesterova, N. P., Medved, T. Y., and Kabachnik, M. I. (1986) *Solvent Extr. Ion Exch.*, **4**, 61.

Myasoedov, B. F. and Lebedev, I. A. (1991) in *Handbook on the Physics and Chemistry of the Actinides* (eds. A. J. Freeman and C. Keller), Elsevier, New York, p. 551.

Myasoedov, B. F. (1994) *J. Alloys Compd.*, **290**, 213–14.

Naegele, J. R., Manes, L., Spirlet, J. C., and Müller, W. (1984) *Phys. Rev. Lett.*, **52**, 1834–7.

Nair, G. M. and Chander, K. (1983) *J. Less Common Metals*, **92**(1), 29–34.

Nash, K. L., Gatrone, R. C., Clark, G. A., Rickert, P. G., and Horwitz, E. P. (1988) *Sep. Sci. Technol.*, **23**, 1355.

Nash, K. L., Gatrone, R. C., Clark, G. A., Rickert, P. G., and Horwitz, E., (1989) *Solvent Extr. Ion Exch.*, **7**, 644.

Nash, K. L. (1994) in *Handbook on the Physics and Chemistry of Rare Earths, Gschneidner* (eds. K. A. Gschneidner, Jr, L. Eyring, G. R. Choppin, and G. H. Lander), New York, Elsevier North-Holland, pp. 197–235.

Natowitz, J. B. (1973) USAEC Report ORO-3924–14.

Nellis, W. and Brodsky, M. B. (1974) in *The Actinides: Electronic Structure and Related Properties*, Academic Press, New York.

Newton, T. W. and Baker, F. (1967) in *Lanthanide/Actinide Chemistry* (ed. R. F. Gould), ACS Adv. Chem. Ser., American Chemical Society, Washing DC, pp. 268–95.

Newton, T. W. (1975) *The Kinetics of the Oxidation–Reduction Reactions of Uranium, Neptunium, Plutonium, and Americium Ions in Aqueous Solutions.*

Nigon, J. P., Penneman, R. A., Staritzki, E., Keenan, T. K., and Asprey, L. B. (1954) *J. Phys. Chem.*, **58**, 403–4.

Nigond, L., Musikas, C., and Cuillerdier, C. (1994) *Solvent Extr. Ion Exch.*, **12**, 261 and 297.

Nikolaev, A. V. and Ionova, G. V. (1991) *Phys. Stat. Sol. (6)* **167**, 613–23.

Nikolaevskii, V. B., Shilov, V. P., and Krot, N. N. (1974) *Radiokhimiya*, **16**, 122–3.

Nikolaevskii, V. B., Shilov, V. P., Krot, N. N., and Peretrukhin, V. F. (1975) *Radiokhimiya*, **17**, 420–2 and 431–3.

NN (2002) *Nucl. News*, **45**(Jan), 58–60.

Nugent, L. J., Baybarz, R. D., Burnett, J. L., and Ryan, J. L. (1971a) *J. Inorg. Nucl. Chem.*, **33**, 2503–30.

Nugent, L. J., Laubereau, P. G., Werner, G. K., and Vander Sluis, K. L. (1971b) *J. Organomet. Chem.*, **27**(3), 365–72.

Nugent, L. J., Baybarz, R. D., Burnett, J. L., and Ryan, J. L. (1973a) *J. Phys. Chem.*, **77**, 1528–39.

Nugent, L. J., Burnett, J. L., and Morss, L. R. (1973b) *J. Chem. Thermodyn.*, **5**, 665–78.

Nunez, L., Buchholz, B. A., Kaminski, M., Aase, S. B., Brown, N. R., and Vandegrift, G. F. (1996) *Sep. Sci. Technol.*, **31**, 1393.

Oetting, F. L., Rand, M. H., and Ackermann, R. J. (1976) in *The Chemical Thermodynamics of Actinide Elements and Compounds, part 1, The Actinide Elements*. IAEA.

Ogawa, T., Shirasu, Y., Minato, K., and Serizawa, H. (1997) *J. Nucl. Mater.*, **247**, 151–7.

Ohyoshi, E. and Ohyoshi, A. (1971) *J. Inorg. Nucl. Chem.*, **33**, 4265.

Okamoto, H. (1998) *J. Phase Euilib.*, **20**, 450–2.

Olson, W. M. and Mulford, R. N. R. (1966) *J. Phys. Chem.*, **70**, 2934–7.

Osipov, S. V., Andreichuk, N. N., Vasil'ev, V. Y., and Rykov, A. G. (1977) *Radiokhimiya*, **19**(4), 522–4.

Ozawa, M., Nemoto, S., Togashi, A., Kawata, T., and Onishi, K. (1992) *Solvent Extr. Ion Exch.*, **10**, 829.

Ozawa, M., Koma, Y., Nomura, K., and Tanaka, Y. (1998) *J. Alloys Compd.*, **538**, 272–3.

Pappalardo, R., Carnall, W. T., and Fields, P. R. (1969a) *J. Chem. Phys.*, **51**(2), 842–3.

Pappalardo, R. G., Carnall, W. T., and Fields, P. R. (1969b) *J. Chem. Phys.*, **51**, 1182–2000.

Pazukhin, E. M., Krivokhatskii, A. S., and Kochergin, S. M. (1987) *Sov. Radiochem.*, **29**(1), 9–13.

Penneman, R. A. and Asprey, L. B. (1950) *The formal potential of the Am(V)-Am(VI) couple*, Los Alamos National Laboratory.

Penneman, R. A. and Asprey, L. B. (1955) *A Review of Americium and Curium Chemistry, Proc. First Int. Conf. on the Peaceful Uses of Atomic Energy*, pp. 355–62.

Penneman, R. A. and Keenan, T. K. (1960) *The Radiochemistry of Americium and Curium*, National Academy of Sciences.

Penneman, R. A., Coleman, J. S., and Keenan, T. K. (1961) *J. Inorg. Nucl. Chem.*, **17**, 138–45.

Penneman, R. A. and Mann, J. B. (1976) *J. Inorg. Nucl. Chem.*, Suppl., 257–63.

Peppard, D. F., Mason, G. W., Driscoll, W. J., and Sironen, R. J. (1958) *J. Inorg. Nucl. Chem.*, **7**, 276–85.

Peppard, D. F., Mason, G. W., Driscoll, W. J., and Sironen, R. J. (1962) *J. Inorg. Nucl. Chem.*, **24**, 881–8.

Pereira, L. C. J., Wastin, F., Winand, J. M., Kanellakopoulos, B., Rebizant, J., Spirlet, J. C., and Almeida, M. (1997) *J. Solid State Chem.*, **134**, 138–47.

Peretrukhin, V. F. and Spitsyn, V. I. (1982) *Izv. Akad. Nauk SSSR, Ser. Khim.*, **31**, 826–31.

Persson, G. E., Svantesson, S., Wingefors, S., and Liljenzin, J. O. (1984) *Solvent Extr. Ion Exch.*, **2**, 89.

Peterson, J. R. (1973) in *Proc. 10th Rare Earth Research Conf.* (eds. C. J. Kevane and T. Moeller), April 30-May 3, Carefree, Arizona.

Petrzilova, H., Binka, J., and Kuca, L. (1979) *J. Radioanal. Nucl. Chem.*, **51**, 107.

Pikaev, A. K., Shilov, V. N., Nikolaevskii, V. B., Krot, N. N., and Spitsyn, V. I. (1977) *Radiokhimiya*, **19**(5), 720–4.

Pilv Vo, R. and Bickel, M. (1998) *J. Alloys Compd.*, **49**, 271.

Pilv Vo, R., La Rosa, J. J., Mouchel, D., Nardel, R., Bichel, M., and Altzizaglau, T. (1999) *J. Environ. Radioact.*, **43**, 343.

Pilv Vo, R. and Bichel, M. (2000) *Appl. Radiat. Isot.*, **53**, 273.

Piskunov, E. M. and Rykov, A. G. (1972) *Radiokhimiya*, **14**, 638.

Potter, R. A. and Tennery, V. J. (1973) US Patent, 3,758, 669.

Proctor, S. G. and Connor, W. V. (1970) *J. Inorg. Nucl. Chem.*, **32**, 3699–701.

Proctor, S. G. (1975) *Cation Exchange Process for Molten Salt Extraction Residues*, Rocky Flats Plant, Dow Chemical Company.

Proctor, S. G. (1976) *J. Less Common Metals*, **44**, 195–9.

Prunier, C., Guérin, L., Faugére, J.-L., Cocuaud, N., and Pidnet, J.-M. (1997) *Nucl. Technol.*, **120**, 110–20.

Radchenko, V. M., Ryabinin, M. A., Selezenev, A. G., Shimbarev, E. V., Sudakov, L. V., Kapashukov, I. I., and Vasil'ev, V. Y. (1982) *Sov. Radiochem.* (*Engl. Trans.*), **24**, 144–6.

Radzewitz, H. (1966) *Festkörperchemische Untersuchungen über die Systeme* $SeO_{1.5}$–ZrO_2 (HfO_2, $AmO_{1.5}$–ZrO_2 (HfO_2, ThO_2)–O_2, und TiO_2–NpO_2 (PuO_2), Kernforschungszentrum Karlsruhe.

Rai, D., Felmy, A. R., and Fulton, R. W. (1992) *Radiochim. Acta*, **56**(1), 7–14.

Rais, J. and Tachimori, S. (1994) *J. Radioanal. Nucl. Chem. Lett.,***188**, 157.

Rao, V. K., Mahajan, G. R., and Natarajan, P. R. (1987) *Inorg. Chim. Acta*, **128**(1), 131–4.

Rao, L. F., Rai, D., Felmy, A. R., Fulton, R. W., and Novak, C. F. (1996) *Radiochim. Acta*, **75**(3), 141–7.

Rapko, B. M. and Lumetta, G. J. (1994) *Solvent Extr. Ion Exch.*, **12**, 967.

Rapko, B. M. (1995) in *Separations of Elements* (eds. K. L. Nash and G. R. Choppin), Plenum Press, New York, p. 99.

Rebizant, J. and Benedikt, U. (1978) *J. Less Common Metals*, **58**, 31–3.

Rizvi, G. H. and Mathur, J. N. (1997), Report BARC/P004, p. 56.

Robel, W. (1970) *Complex Compounds of Hexavalent Actinides with Pyridine Carboxylic Acids*. KFK.

Roddy, J. W. (1973) *J. Inorg. Nucl. Chem.*, **35**, 4141–8.

Roddy, J. W. (1974) *J. Inorg. Nucl. Chem.*, **36**, 2531–3.

Rogozina, E. M., Konkina, L. F., and Popov, D. K. (1974) *Radiokhimiya*, **16**, 383–6.

Roof, R. B., Haire, R. G., Schiferl, D., Schwalbe, L., Kmetko, E. A., and Smith, J. L. (1980) *Science*, **207**, 1353–5.

Roof, R. B. (1982) *Z. Kristallogr.*, **158**, 307–12.

Rosch, F., Reimann, T., Ludwig, R., Dreyer, R., Buklanov, G. V., Khalkhin, V. A., Milanov, M., and Tran Kim, H. (1989) in *Actinides-89 Abstracts*, Tashkent, USSR.

Rose, R. L., Kelly, R. E., and Lesuer, D. R. (1979) *J. Nucl. Mater.*, **79**, 414–16.

Runde, W., Meinrath, G., and Kim, J. I. (1992) *Radiochim. Acta*, **58/59**, 93–100.

Runde, W. and Kim, J. I. (1994) *Chemisches Verhalten von Drei- und Fünfwertigem Americium in Salinen NaCl-Lösungen*, Institut für Radiochemie, Technische Universität München.

Runde, W., Neu, M. P., and Clark, D. L. (1996) *Geochim. Cosmochim. Acta*, **60**(12), 2065–73.

Runde, W., Van Pelt, C., and Allen, P. G. (2000) *J. Alloys Compd.*, **303/304**, 182–90.

Runde, W., Neu, M. P., Conradson, S., and Tait, C. D. (2002) American Chemical Society Meeting ACS 2002, Orlando, Florida, USA.

Runde, W., Bean, A., and Scott, B. (2003) *Chem. Commun.*, 1848–9.

Runnals, O. J. C. and Boucher, R. R. (1955) *Nature*, **176**, 1019–20.

Runnals, O. J. C. and Boucher, R. R. (1956) *Can. J. Phys.*, **34**, 949–58; Great Britain Patent 741441 (1956); and US Patent 2809887 (1975).

Ryan, J. L. (1967) Octahedral complexes of trivalent actinides, in *Lanthanide/Actinide Chemistry* (ed. R. F. Gould), American Chemical Society, Washing DC, pp. 331–4.

Ryan, J. L. (1974) Ion exchange, in *Gmelins Handbuch der Anorganischen Chemie*, vol. 21, *Transurane*, part D2, Verlag Chemie, Weinheim.

Rykov, A. G., Ermakov, V. A., Timofeev, G. A., Chistyakov, V. M., and Yakovlev, G. N. (1970) *Sov. Radiochem.*, **13**, 858–61.

Rykov, A. G., Timofeev, G. A., and Chistyakov, V. M. (1973) *Radiokhimiya*, **15**, 872–4.

Sakama, M., Tsukada, K., Asai, M., Tchikawa, S., Haka, H., Gata, S., Oura, Y., Nishanaka, I., Nagama, Y., Shibata, M., Kojima, Y., Kawada, K., Ebihara, M., and Nikahara, H. (2000) *Eur. Phys. J. A*, **9**, 303–5.

Sakamura, Y., Hijkata, T., Kinoshita, K., Inoue, T., Storvik, T. S., Kreuger, C. L., Grantham, L. F., Fusselman, S. F., Grimmett, D. L., and Roy, J. J. (1998) *J. Nucl. Sci. Technol.*, **35**, 49–59.

Sakanoue, M. and Amano, R. (1975) in *Transplutonium 1975*, *Proc. 4th Int. Symp.*, pp. 123–9.

Sakanque, M. and Nakatani, M. (1972) *Bull. Chem. Soc. Jpn.*, **45**, 3429.

Saprykin, A. S., Spitsyn, V. I., and Krot, N. N. (1976) *Dokl. Akad. Nauk SSSR*, **228**, 649–51.

Sari, C., Müller, W., and Benedict, U. (1972/73) *J. Nucl. Mater.*, **45**, 73–5.

Sasaki, Y. and Tachimori, S. (2002) *Solvent Extr. Ion Exch.*, **20**, 21.

Schleid, T., Morss, L. R., and Meyer, G. (1987) *J. Less Common Metals*, **127**, 183–7.

Schmutz, H. (1966) *Untersuchungen in den Systemem Alkalifluorid-Lanthaniden/Actinidenfluorid* (*Li*, *Na*, *K*, *Rb-La*, *S. E.*, *Y/Np*, *Pu*, *Am*), KFK.

Schoebrechts, J. P., Gens, R., Fuger, J., and Morss, L. R. (1989) *Thermochim. Acta*, **139**, 49–66.

Schulz, W. W. (1974) *Bidentate Organophosphorus Extraction of Americium and Plutonium from Hanford Plutonium Reclamation Facility Waste*, Atlantic Richfield Hanford Company.

Schulz, W. W. (1975) *Trans. Am. Nucl. Soc.*, **21**, 262–3.

Schulz, W. W. (1976) *The Chemistry of Americium*, DOE Technical Information Center.

Schulz, W. W., Koenst, J. W., and Tallant, D. R. (1980) *Actinide Separations,* American Chemical Society, Washington, DC.

Schulz, W. W. and Navratil, J. D. (1982) in *Recent Developments in Separation Science*, vol. 7 (ed. Li, N.), CRC Press, Boca Raton, FL.

Schulz, W. W. and Horwitz, P. (1988) *Sep. Sci. Technol.*, **23**, 1191.

Seaborg, G. T., James, R. A., Ghiorso, A., and Morgan, L. O. (1950) *Phys. Rev.*, **78**, 472.

Seaborg, G. T. (1970) *Nucl. Appl. Technol.*, **9**, 830–50.

Seaborg, G. T. (1972) *Pure Appl. Chem.*, **30**, 539–49.

Sekine, T. (1965) *Acta Chem. Scand.*, **19**, 1476.

Seleznev, A. G., Shushakov, V. D., and Kosulin, N. S. (1979) *Phys. Met. Metall.* (*Engl. Transl.*), **46**, 193–4.

Shafiev, A. I., Efremov, Y. V., Nikolaev, V. M., and Yakovlev, G. N. (1971) *Sov. Radiochem.*, **13**, 123–5.

Shalinets, A. B. and Stepanov, A. V. (1971) *Radiokhimiya*, **13**, 566–70.

Shalinets, A. B. and Stepanov, A. V. (1972) *Radiokhimiya*, **14**, 280–3.

Shalinets, A. B. (1972a) *Radiokhimiya*, **14**, 275.

Shalinets, A. B. (1972b) *Radiokhimiya*, **14**, 33.

Shalinets, A. B. (1972c) *Radiokhimiya*, **14**, 269.

Shannon, R. D. (1976) *Acta Crystallogr. B*, **A32**, 751–67.

Shen, C., Bao, B., Zhu, J., Wang, Y., and Cao, Z. (1996) *J. Radioanal. Nucl. Chem. Art.*, **212**, 187.

Shiloh, M., Givon, M., and Marcus, Y. (1969) *J. Inorg. Nucl. Chem.*, **31**, 1807–14.

Shilov, V. P., Nikolaevskii, V. B., and Krot, N. N. (1974) *Zh. Neorg. Khim.*, **19**, 469.

Shilov, V. P. (1976) *Radiokhimiya*, **18**, 659–60.

Shilov, V. P., Nikalagevsky, V. B., and Krot, N. N. (1976) in *Chemistry of Transuranium Elements* (eds. V. I. Spitsyn and J. J. Katz), Pergamon Press, New York, pp. 225–8.

Shilov, V. P., Garnov, A. Y., Krot, N. N., and Yusov, A. B. (1997) *Radiochemistry* (*Eng. Transl.*), **39**(6), 504–7.

Shilov, V. P. and Yusov, A. B. (1999) *Radiochemiya* (*Moscow*), **41**(5), 445–7.

Shirokova, I. B., Grigor'ev, M. S., Makarenkov, V. I., Den Auwer, C., Fedoseev, A. M., Budantseva, N. A., and Bessonov, A. A. (2001) *Russ. J. Coord. Chem.*, **27**, 729–30.

Shoun, R. R. and McDowell, W. J. (1980) *Actinide Separation*, ch 6.

Shoup, S. and Bamberger, C. (1997) *Radiochim. Acta*, **76**, 63–9.

Siddall, T. H. I. (1963) *J. Inorg. Nucl. Chem.*, **25**, 883–92.

Siddall, T. H. J. (1964) *J. Inorg. Nucl. Chem.*, **26**, 1991.

Silva, R. J. (1982) *Thermodynamic Properties of Chemical Species in Nuclear Waste. Topical Report*: *The Solubilities of Crystalline Neodymium and Americium Trihydroxides*, Lawrence Berkeley National Laboratory, p. 57.

Silva, R. J., Bidoglio, G., Rand, M. H., Robouch, P. B., Wanner, H., and Puigdomenech, I. (1995) *Chemical Thermodynamics of Americium,* Elsevier, New York.

Silvestre, J. P., Freundlich, A., and Pages, M. (1977) *Rev. Chim. Minér.*, **14**, 225–9.

Skobelev, N. K. (1972) *Sov. J. Nucl. Phys.* (*Engl. Transl*), **15**, 249.

Skriver, H. L., Anderson, O. K., and Johannson, B. (1980) *Phys. Rev. Lett.*, **44**, 1230–3.

Smith, J. L. and Haire, R. G. (1978) *Science*, **200**, 535–7.

Smith, G. S., Akella, J., Reichlin, R., Johnson, Q., Schock, R. N., and Schwab, M. (1981) *Actinides – 1981*, Lawrence Berkeley Laboratory.

Smith, B. F., Jarvinen, G. D., Jones, M. M., and Hay, P. J. (1989) *Solvent Extr. Ion Exch.*, **7**, 749.

Smith, L. L., Crain, J. P., Yeager, J. P., Horwitz, E. P., Diamond, H., and Chiarizia, R. (1995) *J. Radioanal. Chem.*, **15**, 194.

Soderholm, L., Skanthakamur, S., Antonio, M. R., and Conradson, S. (1996) *Z. Phys. B*, **101**, 539–45.

Soderland, P., Ahuja, R., Eriksson, O., Johannson, B., and Wills, J. M. (2000) *Phys. Rev. B*, **61**, 8119–24.

Sole, K. C., Hiskey, J. B., and Ferguson, T. L. (1993) *Solvent Extr. Ion Exch.*, **11**, 1993.

Spjuth, L., Liljenzin, J. O., Hudson, M. I., Drew, M. G. B., Iveson, P. B., and Madic, C. (2000) *Solvent Extr. Ion Exch.*, **18**, 1.

Stadler, S. and Kim, J. I. (1988) *Radiochim. Acta*, **44/45**, 39–44.

Standifer, E. M. and Nitsche, H. (1988) *Lanthanide and Actinide Res.*, **2**, 383.

Staritzky, E. and Truitt, A. L. (1954) Optical properties of some compounds of Uranium, Plutonium, and related elements, in *The Actinide Elements* (eds. G. T. Seaborg and J. J. Katz), Natl. Nucl. En. Ser., Div. IV, Vol. 14A, McGraw-Hill, New York, chapter 9.

Stary, J. (1965) *Talanta*, **13**, 421.

Stary, I. (1966) *Radiokhimiya*, **8**, 504.

Stepanov, A. V. and Makarova, T. P. (1965) *Radiokhimiya*, **7**, 670.

Stepanov, A. V., Makarova, T. P., Maksimova, A. M., and Shalinets, A. B. (1967) *Radiokhimiya*, **9**, 710.

Stepanov, A. V. (1971) *Zh. Neorg. Khim.*, **16**, 2981.

Stephanou, S. E. and Penneman, R. A. (1952) *J. Am. Chem. Soc.*, **74**, 3701–2.

Stephanou, S. E., Nigon, J. P., and Penneman, R. A. (1953) *J. Chem. Phys.*, **21**, 42–5.

Stephens, D. R., Stromberg, H. D., and Lilley, E. M. (1968) *J. Phys. Chem. Solids*, **29**, 815–21.

Stronski, I. and Rekas, M. (1973) *Radiochem. Radioanal. Lett.*, **14**, 297.

Sullivan, J. C., Hindman, J. C., and Zielen, A. J. (1961) *J. Am. Chem. Soc.*, **83**, 3373.

Sullivan, J. C., Gordon, S., Mulac, W. A., Schmidt, K. M., Cohen, D., and Sjoblom, R. (1976) *Inorg. Nucl. Chem. Lett.*, **12**, 599–601.

Sullivan, J. C., Gordon, S., Mulac, W. A., Schmidt, K. M., Cohen, D., and Sjoblom, R. (1978) *Inorg. Chem.*, **17**, 294–6.

Surls, J. P. J. and Choppin, G. R. (1957) *J. Inorg. Nucl. Chem.*, **4**, 62–73.

Swanson, J. L. (1991) Reports PNL-7716, 7734, and 7780, Pacific Northwestern Laboratory, Richland, Washington, USA.

Tabuteau, A., Pages, M., and Freundlich, W. (1972) *Radiochem. Radioanal. Lett.*, **12**, 139–44.

Tabuteau, A. and Pages, M. (1978) *J. Solid State Chem.*, **26**(2), 153–8.

Tagawa, H. (1971) *Nippon Genshiryoku Gakkaishi*, **5**, 267.

Tan, X.-F., Wang, U.-S., Tan, T.-Z., Zhou, G.-F., and Bao, B.-R. (1999) *J. Radioanal. Nucl. Chem. Art.*, **242**, 123.

Tananaev, I. G. (1990a) *Radiokhimiya*, **32**(5), 53–7.

Tananaev, I. G. (1990b) *Radiokhimiya*, **32**(4), 4–6.

Tananev, I. G. (1991) *Sov. Radiochem.*, **33**, 224–30.

Tanner, S. P. and Choppin, G. R. (1968) *Inorg. Chem.*, **7**, 2046.

Templeton, D. H. and Dauben, C. H. (1953) *J. Am. Chem. Soc.*, **75**, 4560–2.

Thouvenot, P., Hubert, S., Moulin, C., Decambox, P., and Mauchien, P. (1993) *Radiochim. Acta*, **61**, 15–21.

Tian, G. X., Zhu, Y. J., Xu, J. M., Hu, T. D., and Xie, Y. N. (2002) *J. Alloys Compd.*, **334**, 86–91.

Tikhonov, M. F., Nepomnyaskeru, V. Z., Kalinina, S. V., Khokhlov, A. D., Bulkin, V. I., and Filin, B. M. (1988) *Radiokhimiya*, **28**, 804–9.

Tomkins, F. S. and Fred, M. (1949) *J. Opt. Soc. Am.*, **39**, 357–63.

Torres, R. A. and Choppin, G. R. (1984) *Radiochim. Acta*, **35**, 143.

Trautmann, N. (1994) *J. Alloys Compd.*, **213/214**, 28–32.

Tsukada, K., Ichikawa, Y., Hatsukawa, Y., Nishinaka, I., Hata, K., Nagame, Y., Oura, Y., Ohyama, T., Sueki, K., Nakahara, H., Asai, M., Kojima, Y., Hirose, T., Yamamoto, H., and Kawade, K. (1998) *Phys. Rev. C*, **57**, 2057–60.

Uchiyama, G., Mineo, H., Hataku, S., Asakura, T., Kansi, K., Watanabe, M., Nakano, Y., Kimura, S., and Fujine, S. (2000) *Prog. Nucl. Energy*, **35**, 151–6.

UCRL (1959) Chemistry Division Semiannual Report for December 1958 Through May 1959 and Chemistry Division Semiannual Report for June Through December 1959.

Ueno, K. and Hoshi, M. (1971) *J. Inorg. Nucl. Chem.*, **33**, 1765 and 2631–3.

Valenzuela, R. W. and Brundage, R. T. (1990) *J. Chem. Phys.*, **93**, 8469–73.

Varga, L. P., Mann, J. B., Asprey, L. B., and Reisfeld, M. J. (1971) *J. Chem. Phys.*, **55**(9), 4230..

Varga, L. P., Baybarz, R. D., Reisfeld, M. J., and Asprey, L. B. (1973) *J. Inorg. Nucl. Chem.*, **35**, 2775–85.

Vladimirova, M. V., Ryabova, A. A., ulikov, I. A., and Milovanova, A. S. (1977) *Radiokhimiya*, **19**(5), 725–31.

Vladimirova, M. V. (1986) *Radiokhimiya*, **28**(5), 649–56.

Vogt, O., Mattenberger, K., Löhle, J., and Rebizant, J. (1998) *J. Alloys Compd.*, **271–273**, 508–12.

Volkov, Y. F., Kapshukov, I. I., Visyasheva, G. I., and Yokovlev, G. N. (1974) *Radiokhimiya*, **16**, 859–63, 863–7, and 868–73.

Volkov, Y. F., Visyasheva, G. I., Tomilin, S. V., Kapshukov, I. I., and Rykov, A. G. (1981) *Sov. Radiochem.*, **23**, 195.

Vorob'eva, V. V., Elesin, A. A., and Zaitsev, A. A. (1973a) *Complexing of Trivalent Americium, Curium, Californium, Promethium, and Yttrium Ions with Dioxymethylphosphinic Acid.*

Vorob'eva, V. V., Elesin, A. A., and Zaitsev, A. A. (1973b) *Complexing Trivalent Americium, Curium, Californium, and Yttrium Ions with Bis*(*hydroxymethyl*)*phosphinic Acid.*

Wall, N., Borkowski, M., Chen, J., and Choppin, G. (2002) *Radiochim. Acta*, **90**(9–11), 563–8.

Wapstra, A. H. and Gove, N. B. (1971) *Nucl. Data Tables*, **9**, 265–468.

Ward, J. W., Müller, W., and Kramer, G. F. (1975), in *Transplutonium Elements, Proc. 4th Int. Symp.*, Baden-Baden, Sept. 13–17, (eds. W. Müller and R. Lindner), Elsevier, North-Holland/Amer. Elsevier, p. 161–71.

Ward, J. W. and Hill, H. H. (1976) *Heavy Elements Properties,* North-Holland, Amsterdam.

Weaver, B. and Kappelmann, F. A. (1964) *Talspeak: A New Method of Separating Americium and Curium from the Lanthanides by Extraction from and Aqueous Solution of an Aminopolyacetic Acid Complex with a Monoacidic Organophosphate or Phosphonate*, Oak Ridge National Laboratory.

Weaver, B. and Shoun, R. R. (1971) in *Proc. 9th Rare Earth Research Conf.*, p. 322.

Weaver, B. (1974) in *Ion Exchange and Solvent Extraction,* (eds. J. A. Marinsky and Y. Marcus), A Series of Advances, vol. 6 , Marcel Dekker, New York.

Wei, Y. Z., Kumagai, M., Takashima, Y., Modolo, G., and Odoj, R. (2000a) *Nucl. Tech.*, **132**, 413–23.

Wei, Y. Z., Sabharwal, K. N., Kumagi, M., Asakara, T., Uchiyama, G., and Fujine, S. (2000b) *J. Nucl. Sci. Technol.*, **37**, 1108–10.

Weifan, Y., Junsheng, G., Wantong, M., Keming, F., Zaiguo, G., Hongye, L., Lijun, S., Shuifa, S., Shuanggui, Y., Shuhong, W., Denming, K., and Jimin, Q. (1999) *J. Radioanal. Nucl. Chem.*, **240**, 379–81.

Weigel, F., Ollendorff, W., Scherer, V., and Hagenbruch, R. (1966) *Z. Anorg. Allg. Chem.*, **345**, 119–28.

Weigel, F. and Meer, ter N. (1967) *Inorg. Nucl. Chem. Lett.*, **3**, 403–8.

Weigel, F. and Meer, ter N. (1971) *Z. Naturf. B*, **26**, 504–12.

Weigel, F., Wishnevsky, V., and Hauske, H. (1975), in *Transplutonium Elements, Proc. 4th Int. Symp.*, Baden-Baden, Sept. 13–17, (eds. W. Müller and R. Lindner), Elsevier, North-Holland/Amer., p. 217–26.

Weigel, F., Wittmann, F. D., and Marquart, R. (1977) *J. Less Common Metals*, **56**, 47–53.

Weigel, F., Wishnevsky, V., and Wolf, M. (1979) *J. Less Common Metals*, **63**, 81–6.

Weigel, F., Wittmann, F. D., Schuster, W., and Marquart, R. (1984) *J. Less Common Metals*, **102**(2), 227–38.

Werner, L. B. and Perlman, I. (1950) *J. Am. Chem. Soc.*, **73**, 495–6.

Wheelwright, E. J., Roberts, F. P., and Bray, L. A. (1968) *Simultaneous Recovery and Purification of Pm, Am, and Cm by the Use of Alternating DTPA and NTA Cation-Exchange Flowsheets*, Pacific Northwest Laboratories.

Williams, C. W., Antonio, M. R., and Soderholm, L. (2000) *J. Alloys Compd.*, **303/304**, 509–13.

Wittmann, F. D. (1980) University of Munich.

Woods, M., Cain, A., and Sullivan, J. C. (1974) *J. Inorg. Nucl. Chem.*, **36**, 2605–7.

Woods, M. and Sullivan, J. C. (1974) *Inorg. Chem.*, **13**, 2774–5.

Woods, M., Montag, T. A., and Sullivan, J. C. (1976) *J. Inorg. Nucl. Chem.*, **38**, 2059–61.

Wruck, D. A., Palmer, C. E. A., and Silva, R. J. (1999) *Radiochim. Acta*, **85**, 21–4.

Yaita, T., Tachimori, S., Edelstein, N. M., Bucher, J. J., Rao, L., Shuh, D. K., and Allen, P. G. (2001) *J. Synchrotron Radiation*, **8**, 663–5.

Yakovlev, G. N. and Gorbenko- Germanov, D. S. (1955) in *Proc. Int. Conf. on the Peaceful Uses of Atomic Energy*, pp. 306–8.

Yakovlev, G. N., Gorbenko- Germanov, D. S., Zenkova, R. A., Razbitnoi, V. L., and Kazanski, K. S. (1958) *J. Gen. Chem. USSR*, **28**(2653).

Yakovlev, G. N. and Kosyakov, V. N. (1958a) *An Investigation of the Chemistry of Americium*, *Proc. 2nd Int. Conf. on the Peaceful Uses of Atomic Energy*, pp. 373–84.

Yakovlev, G. N. and Kosyakov, V. N. (1958b) *Spectrophotometric Studies of the Behaviour of Americium Ions in Solutions*, *Proc. 2nd Int. Conf. on the Peaceful Uses of Atomic Energy*, pp. 363–8.

Yamagishi, I., Morita, Y., and Kubota, M. (1996) *Radiochim. Acta*, **75**, 27–32.

Yamamoto, M. and Sakanoue, M. (1982) *J. Radiat. Res.*, **23**, 261.

Yamana, H. and Moriyama, H. (1996) *J. Nucl. Sci. Technol.*, **33**, 288–97.

Yanir, E., Givon, M., and Marcus, Y. (1959) *Inorg. Nucl. Chem. Lett.*, **6**, 415–9.

Yanir, E., Givon, M., and Marcus, Y. (1969) *Inorg. Nucl. Chem. Lett.*, **5**, 369–72.

Yusov, A. B. (1989) Photoluminescence of americium(III) in aqueous and organic solutions, in *Actinides '89*, p. 240 and pp. 241–2.

Yusov, A. B. (1993) *Radiochem. Radioanal. Lett.*, **35**, 1–14.

Zachariasen, W. H. (1948a) *Phys. Rev. B*, **73**, 1104–5.

Zachariasen, W. H. (1948b) *Acta Crystallogr.*, **1**, 265–9.

Zachariasen, W. H. (1949a) *Acta Crystallogr.*, **2**, 288–91.

Zachariasen, W. H. (1949b) *Acta Crystallogr.*, **2**, 388–90.

Zachariasen, W. H. (1949c) *Phys. Rev.*, **73**, 1104.

Zachariasen, W. H. (1949d) *Acta Crystallogr.*, **2**, 57–60.

Zachariasen, W. H. (1954) in *The Actinide Elements* (eds. G. T. Seaborg, L. R. Morss and J. J. Katz), McGraw-Hill, New York, pp. 769–95.

Zachariasen, W. H. (1978) *J. Less Common Metals*, **62**, 1–7.

Zaitsev, A. A., Kosyakov, V. N., Rykov, A. G., Sobolev, Y. B., and Yakovlev, G. N. (1960a) *Radiokhimiya*, **2**(3), 348–50.

Zaitsev, A. A., kosyakov, V. N., Rykov, A. G., Sobolov, Y. P., and Yakovlev, G. N. (1960b) *Sov. At. Energy*, **7**, 562–9.

Zemlyanukhin, V. I., Savoskina, G. P., and Pushlenkov, M. F. (1962) *Sov. Radiochem.*, **4**, 501–5.

Zhu, Y. (1995) *Radiochim. Acta*, **68**, 1995.

Zhu, Y., Chen, J., and Choppin, G. R. (1996a) *Solvent Extr. Ion Exch.*, **14**, 543.

Zhu, Y., Chen, J., and Jiao, R. (1996b) *Solvent Extr. Ion Exch.*, **14**, 61.

Zhu, Y. and Jiao, R. (1994) *Nucl. Technol.*, **108**, 361–9.

Zhu, Y., Xu, J., Chen, J., and Chen, Y. (1998) *J. Alloys Compd.*, **742**, 271–3.

Zubarev, V. G. and Krot, N. N. (1982) *Sov. Radiochem.* (*Engl. Transl.*), **24**, 264–7.

Zubarev, V. G. and Krot, N. N. (1983a) *Sov. Radiochem.*, **25**, 601.

Zubarev, V. G. and Krot, N. N. (1983b) *Sov. Radiochem.*, **25**, 594.

Zur Nedden, P. (1969) *Z. Anal. Chem.*, **247**, 236.