CHAPTER NINE

CURIUM

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9.1 HISTORICAL

Curium, element 96, is named after Pierre and Marie Curie, by analogy with its lanthanide congener, gadolinium (named after the Finnish chemist, J. Gadolin). Curium is not a naturally occurring terrestrial element.

The first curium isotope, ^{242}Cm, was prepared by Seaborg, James, and Ghiorso in mid-1944 by cyclotron helium ion (He^{2+}) bombardment of ^{239}Pu, and was identified by its characteristic alpha radiation (Seaborg *et al.*, 1949). The discovery of curium preceded that of americium (element 95). G. T. Seaborg described this discovery in a fascinating historical account (Seaborg, 1985). Werner and Perlman (1951) separated the first weighable quantity of curium (40 μg of impure ^{242}Cm oxide), which was prepared by prolonged neutron irradiation of ^{241}Am.

Curium is the element of highest atomic number that is available on the gram scale. However, chemical studies are typically done on the milligram scale using glove boxes, although microchemical techniques were originally used (Seaborg, 1972; Stevenson and Peterson, 1975). Larger scale work usually requires remote handling. Because of the limited availability of long-lived isotopes (especially ^{248}Cm), the high radioactivity of its most common isotopes (^{242}Cm and ^{244}Cm), and its general occurrence in aqueous systems as a 3+ ion, considerably less physical and chemical information about curium is available than for americium. Excellent reviews have been published on various aspects of curium chemistry (Katz and Seaborg, 1957; Brown, 1968; Keller, 1971; Bagnall, 1972; Gmelin, 1972–74; Penneman *et al.*, 1973; Edelstein *et al.*, 1985; Navratil and Schulz, 1993).

This chapter provides an overview of curium chemistry, with emphasis on advances since the publication of the 1986 version of this chapter (Eller and Penneman, 1986). The technical literature indicates that chemical investigations during this period have focused on the following general areas:

- Separations chemistry related to high-level waste management: This topic is addressed in Section 9.5.
- High-temperature superconductivity studies of curium compounds: Soderholm (1992) has provided an excellent review in this area. Additional discussion can be found in Section 9.7 and in Chapter 20.
- Behavior of curium in the environment: This topic is addressed in Chapter 27.
- Use of curium isotopes as targets to prepare superheavy elements: Hoffman (1985) and Lobanov *et al.* (1997) provide examples. This subject is discussed in Chapter 14.
- Use of curium isotopes in analytical space applications: Radchenko *et al.* (1999, 2000), Abramychev *et al.* (1992), and Vesnovskii *et al.* (1996) provide illustrative examples of this type of work applied to alpha spectrometry analysis of extraterrestrial rocks and soils.
- Transmutation in reactors and accelerators: Artisyuk *et al.* (1999), Gerasimov *et al.* (2000), and Raison and Haire (2001) describe this topic.

9.2 NUCLEAR PROPERTIES

Properties of the known curium isotopes, which range in mass from 238 to 251, are summarized in Table 9.1. Additional information is available in the appendix. Electron binding energies, radiation energies, X-ray spectra, and L-shell fluorescence data are available, as well as both alpha and spontaneous fission data (see Chu, 1972; Kerrigan and Banick, 1975; Lederer and Shirley, 1978; Lougheed *et al.*, 1978; Holden, 1989). Three isotopes (^{242}Cm, ^{244}Cm, and ^{248}Cm) are available in quantities sufficient for chemical study. Macroscopic studies with ^{242}Cm and ^{244}Cm are complicated by the high specific alpha activities of these isotopes (half-lives of 163 days and 18.1 years, respectively). The practical limit for chemical operations with ^{248}Cm in glove boxes is 10–20 mg because of the significant neutron exposure hazard from the 8% spontaneous fission yield of this isotope.

Both ^{242}Cm and ^{244}Cm have been used in power sources (thermal and electrical) for space and medical applications (Groh *et al.*, 1965; Abramychev *et al.*, 1992; Vesnovskii *et al.*, 1996). The isotope ^{242}Cm has a specific heat output (122 W g^{-1}) about 43 times higher than that of ^{244}Cm (2.8 W g^{-1}),

Table 9.1 *Nuclear properties of curium isotopes.*

Mass number	*Half-life*	*Mode of decay*	*Main radiations* (MeV)	*Method of production*
237	–	EC, α	α 6.660	^{237}Np(^{6}Li,6n)
238	2.3 h	EC $< 90\%$	α 6.52	^{239}Pu(α,5n)
		$\alpha > 10\%$		
239	2.9 h	EC	γ 0.188	^{239}Pu(α,4n)
240	27 d	α	α 6.291 (71%)	^{239}Pu(α,3n)
	1.9×10^{6} yr	SF	6.248 (29%)	
241	32.8 d	EC 99.0%	α 5.939 (69%)	^{239}Pu(α,2n)
		α 1.0%	5.929 (18%)	
			γ 0.472 (71%)	
242	162.8 d	α	α 6.113 (74.0%)	^{239}Pu(α,n)
	7.0×10^{6} yr	SF	6.070 (26.0%)	^{242}Am daughter
243	29.1 yr	α 99.76%	α 5.785 (73.5%)	^{242}Cm(n,γ)
		EC 0.24%	5.741 (10.6%)	
			γ 0.278 (14.0%)	
244	18.10 yr	α	α 5.805 (76.7%)	multiple n capture
	1.35×10^{7} yr	SF	5.764 (23.3%)	^{244}Am daughter
245	8.5×10^{3} yr	α	α 5.362 (93.2%)	multiple n capture
			5.304 (5.0%)	
			γ 0.175	
246	4.76×10^{3} yr	α	α 5.386 (79%)	multiple n capture
	1.80×10^{7} yr	SF	5.343 (21%)	
		β stable		
247	1.56×10^{7} yr	α	α 5.266 (14%)	multiple n capture
			4.869 (71%)	
			γ 0.402 (72%)	
248	3.48×10^{5} yr	α 91.61%	α 5.078 (82%)	multiple n capture
		SF 8.39%	5.034 (18%)	
249	64.15 min	β^{-}	β^{-} 0.9	^{248}Cm(n,γ)
			γ 0.634 (1.5%)	
250	$\sim 8.3 \times 10^{3}$ yr	SF		multiple n capture
251	16.8 min	β^{-}	β^{-} 1.42	^{250}Cm(n,γ)
			γ 0.543 (12%)	

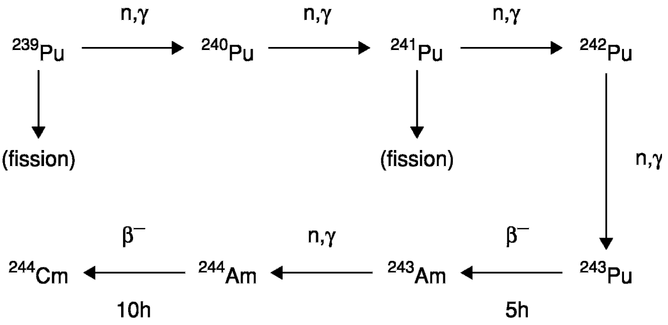
This table is reproduced directly from the compilations in Appendix II of this volume by I. Ahmad.

and a cake of $^{242}Cm_2O_3$ weighing a few grams can be photographed using its own incandescence for illumination. These isotopes provide convenient energy sources for short-period/high-output and long-period/moderate-output applications. However, because of its greater availability and high-energy density, ^{238}Pu has supplanted both ^{242}Cm and ^{244}Cm for many such uses. The isotope ^{248}Cm has been a favored nuclide for accelerator studies attempting to form superheavy elements (Hoffman, 1985; Lobanov *et al.*, 1997).

9.3 PRODUCTION

Intense neutron exposure of ^{242}Pu and ^{243}Am in nuclear reactors forms significant quantities of the isotopes ^{244}Cm, ^{246}Cm, and ^{248}Cm, with lesser amounts of the odd-mass isotopes, ^{245}Cm and ^{247}Cm. Most curium isotopes heavier than ^{244}Cm have longer half-lives, but cannot be prepared isotopically pure by neutron capture. Except for ^{248}Cm, which is available as an essentially pure isotope from the decay of ^{252}Cf, curium isotope enrichment is accomplished in mass separators. The isotope ^{248}Cm is particularly desirable for chemical studies because of its long half-life (3.48×10^5 years). Approximately 100 mg of ^{248}Cm was produced in the 1970s and 1980s in the United States by purification from parent ^{252}Cf.

By far, the greatest quantity of curium exists as the isotope ^{244}Cm, which has been produced on the several kilogram scale at the Savannah River Site (Groh *et al.*, 1965; Baybarz, 1970; Gmelin, 1972–74). This isotope is produced by successive neutron capture starting with ^{239}Pu, ^{242}Pu, or ^{243}Am:



For 20 years following the discovery of curium, only milligram amounts of curium were available from the irradiation of ^{241}Am. It was not until Glenn T. Seaborg became Chairman of the US Atomic Energy Commission that a large-scale national program was instituted. Kilograms of ^{239}Pu were transferred from the weapons program for irradiation at Savannah River Site. This ‘expenditure’ of plutonium required a Presidential Directive. The authors note that, especially in 1960, this transfer from programmatic use was extraordinary and stands in striking contrast to current views regarding the disposition of many tons of excess weapons-grade plutonium. The aim of the irradiation campaign was to produce major amounts of the higher-mass isotopes of plutonium and elements of higher atomic number for research. The demand for large quantities of higher isotopes has diminished, resulting in the disposal of 2–3 kg of Cm from the Savannah River Site in 2002 (Peters *et al.*, 2002).

Initially, 8.5, then 12.0 kg for a total of 20.5 kg of ^{239}Pu, was staged in a Savannah River reactor. This approach was necessary to remove the immense heat produced (3×10^6 Btu h^{-1} ft^{-2}) from ^{239}Pu and ^{241}Pu fission. The yield from 20.5 kg of initial ^{239}Pu was 930 g of ^{242}Pu and 630g of ^{243}Am and ^{244}Cm combined (Penneman and Ferguson, 1971). The mixture was sent for separation to the Oak Ridge National Laboratory (ORNL), where the high-mass plutonium was fabricated into cermet targets for the High Flux Isotope Reactor (HFIR). A neutron flux of 5×10^{15} neutrons cm^{-2} s^{-1} was used for the specific purpose of creating higher-mass/higher-atomic-number isotopes. The plutonium feed composition was initially ^{238}Pu (0.43%), ^{239}Pu (1.12%), ^{240}Pu (1.8%), ^{241}Pu (0.91%), and ^{242}Pu (95.7%) (Bigelow, 2002).

At the height of production, about 1 g of ^{252}Cf was produced per year. Its short alpha decay half-life (2.6 years) yields ^{248}Cm. Production of ^{252}Cf has diminished, but continues because it is desirable for neutron irradiation in health applications. Its decay currently yields 35–50 mg of ^{248}Cm annually (Knauer, 2002).

The relatively stable isotope ^{248}Cm can be obtained in multi-milligram quantities by milking aged, prepurified ^{252}Cf materials that have undergone alpha decay. This method routinely yields milligram amounts of ^{248}Cm with an isotopic purity of 97%. Even so, 99.9% of the alpha activity arises from ^{244}Cm and ^{246}Cm impurities.

$$^{252}\mathrm{Cf} \xrightarrow[2.6\ \mathrm{y}]{\alpha} {}^{248}\mathrm{Cm}$$

Small (microgram) amounts of ^{245}Cm have been separated from alpha decay products of ^{249}Cf, itself a daughter of ^{249}Bk.

To isolate ^{244}Cm, irradiated material is dissolved in nitric acid and tetravalent plutonium is removed by solvent extraction (Groh *et al.*, 1965; Baybarz, 1970). The trivalent species (americium, curium, and the lanthanides) remaining in the aqueous phase are then extracted with 50% tributyl phosphate (TBP) in kerosene, and then back-extracted into dilute acid. For purification from lanthanides, Am/Cm chlorides are extracted with tertiary amines from slightly acidic 11 M LiCl (Tramex process), and then back-extracted into aqueous 7 M HCl. Subsequent precipitation of Am(V) as the potassium double carbonate effectively separates americium, leaving soluble Cm(III) in the K_2CO_3 medium.

The isotope ^{242}Cm is best obtained by neutron irradiation of ^{241}Am at an intermediate flux level. High neutron fluxes diminish the yield of ^{242}Cm because of the increased fission of ^{242}Am:

$$^{241}\mathrm{Am} \xrightarrow{n,\gamma} {}^{242}\mathrm{Am} \xrightarrow[16\,\mathrm{h}]{\beta^-} {}^{242}\mathrm{Cm}$$

Following irradiation of AmO_2/Al cermet targets, hot NaOH is used to dissolve the aluminum. Dissolution in HCl also can be used, in which case Al^{3+} must be removed before further processing. For small-scale separations, the Am/Cm/lanthanide fraction is dissolved in HCl; the solution is then made 11 M in LiCl, and passed through an anion-exchange column. Under these conditions, trivalent actinides (but not rare earth elements) are retained on the column. Alternatively, a tertiary amine extractant can be substituted for the anion-exchange resin to provide a group separation between actinides (extracted) and lanthanides (Baybarz, 1970). A subsequent americium/curium separation step is then required. A combination of anion and cation exchange was used successfully to separate about 1 g of ^{242}Cm from neutron-irradiated ^{241}Am (Thompson, 1972).

Numerous other techniques, including high-pressure ion exchange, extraction chromatography, and di(2-ethylhexyl)phosphoric acid (HDEHP) extraction also have been used for Cm separation and purification (Dedov *et al.*, 1965; Baybarz, 1970; Gmelin, 1972–74; Thompson, 1972; Buijs *et al.*, 1973; Haug, 1974; Lebedev *et al.*, 1974; Bigelow *et al.*, 1980; Bond and Leuze, 1980). Pressurized displacement ion-exchange chromatography has been applied to large-scale ^{244}Cm/^{243}Am separation and purification using Dowex® 50 resin in the Zn^{2+} form and diethylenetriaminepentaacetic acid (DTPA) as eluant (Stephanou and Penneman, 1952). Where sufficient quantities of Cm are present to give a substantial band, a pure curium cut can be obtained, since it leads the americium band.

9.4 ATOMIC PROPERTIES

Selected properties of curium-free atoms and ions are summarized in Table 9.2. A set of recommended thermodynamic parameters is available in the recent publication of Konings (2001b). Thermodynamic properties of actinides are addressed in Chapter 19.

The great stability of the $5f^7$ configuration of Cm(III) and its lanthanide congener Gd(III) is shown by the large M(III)–(IV) oxidation potentials (see Section 9.7.1). In contrast, it is noteworthy that the tendency of americium to attain the $5f^7$ configuration by assuming a divalent state is much weaker than that displayed by europium. Isolated Cm(II) compounds are unknown and a value of –2.78 V has been estimated for the Cm(III)/Cm(II) redox potential (Mikheev *et al.*, 1992).

The spectra of the Cm(III) aquo ion and of a metastable Cm(IV) aqueous fluoride solution complex ion are shown in Figs. 9.1 and 9.2, respectively. In contrast to solutions of Gd(III) (Moeller and Moss, 1951), aqueous solutions of

Table 9.2 *Selected properties and references of curium ions and metal.*

Property	*Value*	*Reference*	*Comment*
Cm(0) electronic configuration	$5f^7ds^2$ ($^9D_2$)	Keller (1971, p. 79)	
Cm(III) electronic configuration	$5f^7$	Katz and Seaborg (1957, Chapter 5)	
Metallic radius	1.743 Å	Reichlin *et al.* (1981); Zachariasen (1973)	dhcp form
Cm(III) ionic radius	0.97 Å	Shannon (1976)	six coordination
Cm(IV) ionic radius	0.85 Å	Shannon (1976)	six coordination
first ionization potential	5.99 eV	Deissenberger *et al.* (1995)	
Cm(0)–Cm(III) potential	−2.06 V	Fuger *et al.* (1975)	
Cm(II)–Cm(III) potential	−2.8 V	Mikheev (1983)	
Cm(III)–(IV) potential	−3.1 V	Keller (1971, p. 212)	1 M $HClO_4$
metal cell constants	dhcp, $a = 3.496(3)$ Å, $c = 11.331(5)$ Å; fcc, $a = 5.039$ (2) Å	Reichlin *et al.* (1981); Stevenson and Peterson (1979); Baybarz *et al.* (1976)	
melting point	1345 ± 50°C	Oetting *et al.* (1976); Fuger and Oetting (1976)	
boiling point	3110°C (calcd.)	Ward *et al.* (1975)	
ΔH_{fus}	13.85 kJ mol^{-1}	Ward *et al.* (1975)	
gaseous entropy	47.2 J K^{-1} mol	Edelstein *et al.* (1985, p. 139)	
density	13.5 g cm^{-3}	Reichlin *et al.* (1981)	dhcp form
magnetic moment	8.07 μ_B	Reichlin *et al.* (1981); Kanellakopulos *et al.* (1976)	100–550°K

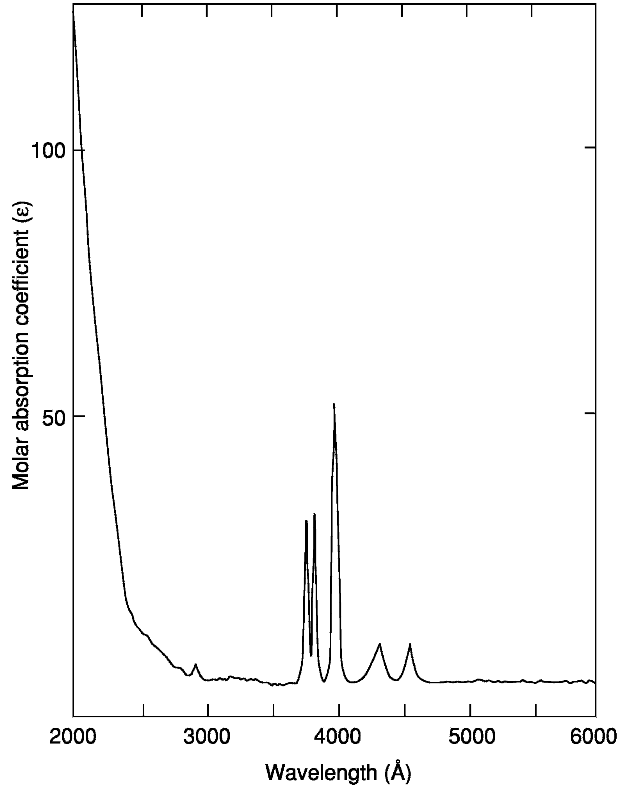


Fig. 9.1 *The absorption spectrum of Cm(III) in* 0.04 N *$HclO_4$ (aq). (Adapted from Carnall* et al., 1958.)

Cm(III) have weak absorption bands in the near-violet region, although intense absorptions are present in the ultraviolet region (Asprey and Keenan, 1958; Keenan, 1961; Barbanel *et al.*, 1977). The absorption spectra of metastable Cm(IV) was measured at Los Alamos by dissolving CmF_4 prepared by fluorination of dry CmF_3, and that of Cm(III) was measured at both Los Alamos and Argonne using curium solutions carefully purified from rare earths and americium. The principal peaks of Cm(IV) strongly resemble those of Am(III), with which it is isoelectronic (Carnall *et al.*, 1958).

Electronic transitions for Cm(III) solutions are shifted 20–30 Å to longer wavelengths compared to the solid state. The addition of complexing ions normally produces a diminution of intensities, and small changes in band positions. The transition energies for CmF_3 are considerably lower than those of GdF_3, due to smaller electrostatic repulsion terms and larger spin–orbit coupling in Cm(III). The spectra in both cases may be interpreted in terms of a $5f^7$ ground-state configuration. The spectrum of $Cs_2NaCmCl_6$, which

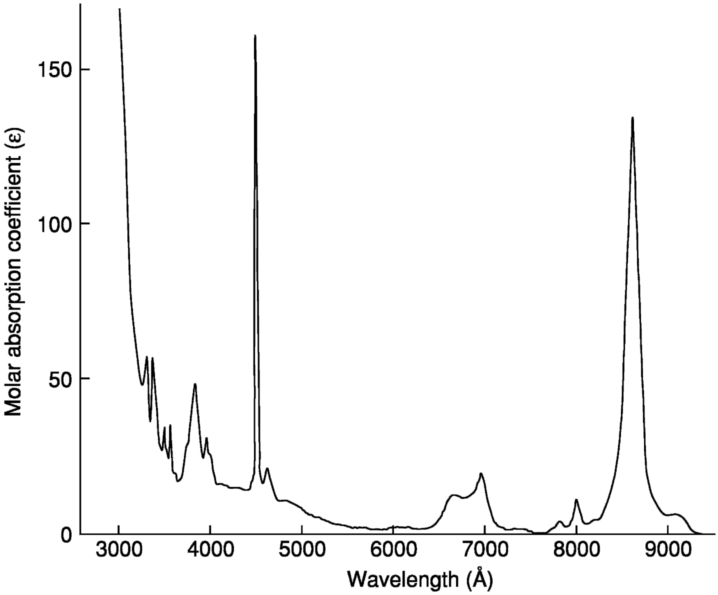


Fig. 9.2 *The absorption spectrum of Cm(IV) in* 15 M *CsF* (*aq*). (*Adapted from Keenan,* 1961.)

contains octahedrally coordinated Cm(III), was reported for both the solid and molten phases (Barbanel *et al.*, 1977). The most notable spectral effect is a sharp diminution in intensity compared to that of aqueous Cm(III) because of the highly symmetric curium coordination, which precludes observation of symmetry-forbidden f–f electronic transitions.

Time-resolved laser-induced fluorescence spectroscopy has been shown to be an especially valuable tool for determining curium concentration and speciation (Elesin *et al.*, 1973; Dem'yanova *et al.*, 1986; Yusov *et al.*, 1986b; Decambox *et al.*, 1989; Kim *et al.*, 1991; Myasoedov and Lebedev, 1991; Myasoedov, 1994; Moulin *et al.*, 1997; Dacheux and Aupais, 1998). Curium solutions have the unique property of strongly fluorescing in the range of 595–613 nm when irradiated with a laser or a mercury-discharge lamp (Myasoedov and Lebedev, 1991; Myasoedov, 1994). The broad unresolved fluorescence emission band is attributed to relaxation from the $^6D_{7/2}$ (*A*) state to the $^8S_{7/2}$ (*Z*) ground state (Kim *et al.*, 1991).

The energy of the emission band is dependent on the ligands attached to the curium ion. Taking advantage of this feature, time-resolved laser-induced fluorescence spectroscopy has been used extensively since the mid-1980s to investigate the fundamental solution chemistry of Cm (see Section 9.8). The method has been used to determine the hydration number for curium in solution (Kimura *et al.*, 1996) and complexation constants for a number of ligands. Furthermore,

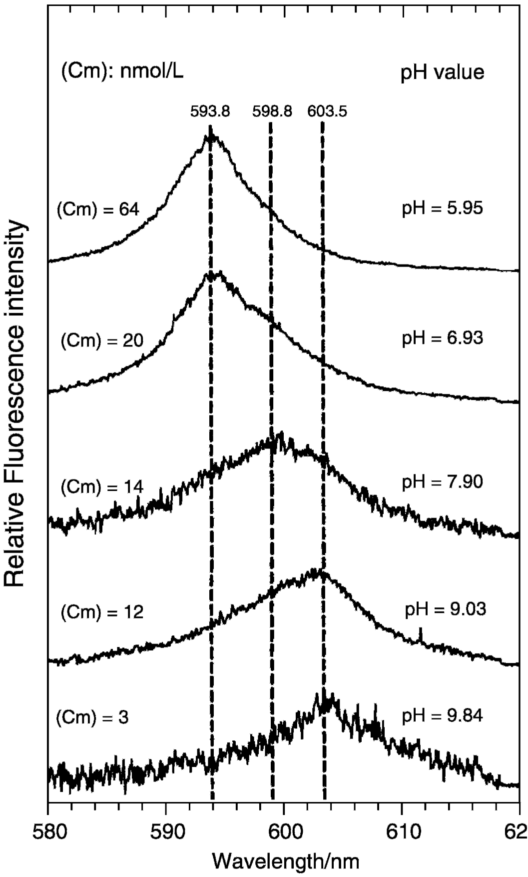


Fig. 9.3 *Curium*(III) *fluorescence emission spectra taken in the course of hydrolysis reaction in the pH range of* 5.05–9.84. *Used with permission from Wimmer* et al. (1992).

time-resolved laser-induced fluorescence spectroscopy has been used to characterize the Cm species present in groundwater taken from sites being considered for disposition of nuclear wastes (Wimmer *et al.*, 1992). Fig. 9.3 displays examples of fluorescence spectra for aqueous Cm species (Wimmer *et al.*, 1992). The examples presented are for Cm(III) as a function of pH and indicate the successive conversion of Cm(III) ion to $[\mathrm{Cm(OH)}]^{2+}$ and $[\mathrm{Cm(OH)_2}]^{+}$ (see Section 9.8 for a more detailed discussion of this topic).

For more thorough discussions of actinide ion absorption and luminescence spectra, see the sections on this subject by Carnall and Crosswhite (Gmelin, 1972–74). Chapter 18 of this work covers additional recent spectroscopic studies, including high-resolution spectra.

9.5 SEPARATION AND PURIFICATION OF PRINCIPAL ISOTOPES

The chemistry of curium in separation and purification is similar to that of other trivalent actinides and lanthanides and involves a series of steps, the number depending on the source of the curium. For example, separation of curium from irradiated uranium or plutonium materials requires more steps than separation of ^{248}Cm from decay of ^{252}Cf. Section 9.3 covers separation of curium from irradiated fuels and targets. This section covers separation and purification from high-level waste and other solutions, which has received more emphasis in recent years. In addition, Section 9.9 contains references to separations done for analysis of curium. Some of the analytical separations are also applicable to separation and purification.

9.5.1 Solvent extraction

Myasoedov and Kremliakova (1985) reviewed Russian literature up to the mid–1980s on americium and curium chemistry, including separations. A subsequent review has updated the work up to 1994 (Myasoedov, 1994). A recent book on separations for nuclear waste management contains reviews of work in the United States, France, and Russia (Choppin, 1999; Jarvinen, 1999; Musikas, 1999).

Extractions with organic phosphates (e.g. TBP, phosphine oxides, dialkylphosphoric acids, high-molecular-weight amines, β-diketones, and combinations of these) have been studied. Extraction by alkylphosphates depends on the structure and nature of the alkyl groups (Myasoedov, 1994; Zhu and Jiao, 1994). For example, mixed alkylphosphates with alkyl chains of six to eight carbons in length are reported to have properties superior to TBP (Zhu and Jiao, 1994). Extraction also depends on the salting agent present in solution. HDEHP has been widely studied for americium and curium extractions from both HNO_3 and LiCl solutions (Myasoedov and Kremliakova, 1985; Choppin, 1999). The latter solution has been used to separate the actinides from the lanthanides. Trioctylamine has been used to separate americium and curium from the lanthanides, with the salting agent and the diluent being important factors for extraction of curium, but not the lanthanides (Myasoedov and Kremliakova, 1985; Choppin, 1999). Russian researchers have studied the β-diketone, 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one, extensively (Myasoedov and Kremliakova, 1985). More recently, studies have been done with 1-phenyl-3-methyl-4-acylpyrazol-5-one in which the length of the carbon chain for the acyl group was varied from 2 to 22 (Takeishi *et al.*, 2001). A flowsheet was demonstrated with an acyl chain length of 8, which resulted in separate uranium, plutonium, and transplutonium fractions. All actinides were extracted from a 1 M HNO_3 solution and sequentially stripped by adjusting the pH with NaOH (Takeishi *et al.*, 2001).

Extensive studies have been done using bifunctional extractants, especially compounds such as octyl(phenyl)-*N*,*N*-diisobutyl carbamoylmethylphosphine oxide (CMPO) to recover transuranium elements, including curium, from high-level waste solutions (Horwitz and Schulz, 1991; Ozawa *et al.*, 1992; Myasoedov, 1994; Felker and Benker, 1995; Choppin, 1999; Musikas, 1999). This class of extractants can extract all the actinides from acid solutions, with separation of uranium, plutonium, and trivalent cations, by using selective stripping solutions. The separation results in a product with both the trivalent lanthanides and the actinides in the same solution, which requires further processing to isolate a pure curium stream.

French researchers have done extensive work on diamides for the extraction of trivalent actinides and lanthanides from plutonium and uranium recovery by extraction (Purex) waste solutions (Musikas, 1999). These bifunctional ligands are stronger extractants than monofunctional ligands and can be destroyed thermally without leaving a solid residue (phosphorus-containing ligands leave a solid residue when incinerated). They have also investigated nitrogen donor ligands for separation of actinides from lanthanides. The neutral tridentate ligand 2,4,6-tris-(2-pyridyl)-1,3,5-triazine has promise, but requires an additive to increase nitrate ion solubility in the organic phase (Musikas, 1999).

The largest separation factors for actinides and lanthanides have been shown with ligands containing sulfur, a 'soft' donor that forms stronger covalent bonds with the actinides than with lanthanides (Jarvinen, 1999; Musikas, 1999). Thio derivatives of acylpyrazolones containing both nitrogen and sulfur donor atoms are good extractants, but give best separation when combined with TBP or a phosphine oxide (Jarvinen, 1999). Dithiophosphoric or phosphinic acids have shown the highest separation factors for actinides and lanthanides (Jarvinen, 1999; Musikas, 1999).

Separation of actinides has also been done with salt mixtures and polyethylene glycol (Myasoedov and Kremliakova, 1985; Myasoedov, 1994). Cm(III) has been extracted from sulfate, carbonate, phosphate, and nitrate solutions. Extraction requires addition of complexants to the salt solutions, with arsenazo-III and xylenol orange being the most effective solution (Molochnikova *et al.*, 1992). Potassium phosphotungstate in salt solution aids in the separation of neptunium from trivalent actinides (Myasoedov, 1994).

Recovery of curium from carbonate and hydroxide solutions has been demonstrated with quaternary ammonium bases, primary amines, alkylpyrocatechols, β-diketones, and *N*-alkyl derivatives of amino-alcohols or phenols (Myasoedov and Kremliakova, 1985; Bukina *et al.*, 1988; Karalova *et al.*, 1988; Novikov *et al.*, 1988; Myasoedov, 1994). This method requires the addition of a complexant to the aqueous phase to maintain the solubility of the actinides in the solutions. The strength of the complexant must differ depending on the mechanism for extraction. Some extractants form ion pairs in the organic phase, while others extract the complexes. In the case of alkylpyrocatechols, the kinetics of extraction of lanthanides and actinides are significantly different, allowing group separation (Novikov *et al.*, 1988).

Am(III) and Cm(III) have also been separated using supported liquid membranes with 1 M HDEHP in hexane (Novikov and Myasoedov, 1987). The separation factor between Am and Cm was increased from 1.1 for simple extraction to 5.0 with the membrane in which potassium phosphotungstate is added to one solution to increase the chemical potential of the membrane and speed the kinetics of the process (Novikov and Myasoedov, 1987).

9.5.2 Ion exchange

Ion exchange in almost all forms has been used for curium separation from americium and the lanthanides. Organic cation and anion resins, chelating resins, chromatographic columns, and inorganic sorbents have been used (Ryan, 1975; Myasoedov and Kremliakova, 1985; Bokelund *et al.*, 1989; Choppin, 1999).

A review in 1975 summarizes the work on ion exchange, with sections on cation, anion, and chelating resins as well as inorganic sorbents (Ryan, 1975). The trivalent actinides and lanthanides are strongly adsorbed from low concentrations of common monovalent acid solutions. Separation of lanthanides from actinides is accomplished by elution with a variety of organic complexants, such as α-hydroxyisobutyric acid, ethylenediaminetetracetic acid (EDTA), or DTPA. Such complexants can also be used to separate trivalent actinides from each other (Lebedev *et al.*, 1974; Ryan, 1975; Myasoedov and Kremliakova, 1985; Bokelund *et al.*, 1989). Extraction chromatography with Zn^{2+} and DTPA was used for separation of kilograms of curium from americium (Haug, 1974). Thiocyanate solutions are also useful in accomplishing similar separations.

Anion-exchange resins have been used with HCl, LiCl, and HNO_3 in both aqueous and aqueous–alcohol mixtures (Ryan, 1975; Myasoedov and Kremliakova, 1985; Bokelund *et al.*, 1989; Choppin, 1999). Solutions of LiCl have been used extensively (Ryan, 1975; Choppin, 1999). A time-resolved laser-induced fluorescence spectroscopic study of a $LiCl/H_2O/CH_3OH$ anion-exchange system suggested the primary Cm species in the solution phase (at 14 M LiCl) is $CmCl_4^-$, but the number of coordinated chloride ions is greater than 4 for the species sorbed to the anion-exchange resin (Arisaka *et al.*, 2002). Thiocyanate solutions have also been used for separation (Myasoedov and Kremliakova, 1985). Solvents that are a mixture of alcohols and acids have been widely used for curium separations (Ryan, 1975).

A variety of zirconium-based inorganic sorbents have been used for separation of Am(III) and Cm(III), either using solutions similar to those employed with organic cation-exchange resins, or by oxidizing Am(III) to Am(V), which does not adsorb (Moore, 1971; Ryan, 1975).

Extraction chromatography with CMPO on an organic support allows ready separation of an americium and curium fraction (Cunningham and Wallmann, 1964; Fuger and Oetting, 1976; Oetting *et al.*, 1976). A commercially available resin based on CMPO has been used in studies (Kaye *et al.*, 1995; Maxwell, 1996).

Different chelate groups have been tried to increase selectivity of resins for curium (Ryan, 1975; Myasoedov and Kremliakova, 1985). A column containing the tertiary amine base, Aliquat-336, was used in combination with a column of HDEHP to obtain 6 g of pure ^{244}Cm (Bokelund *et al.*, 1989). Curium was first loaded onto the Aliquat column from $LiNO_3$, eluted, loaded onto the HDEHP column, and finally eluted with 1 M lactic acid containing DTPA. Other ion-exchange methods are described in Section 9.9.2.

9.5.3 Precipitation

Precipitation has been used for the separation of Cm(III) from americium in its higher valence states of V and VI. Separation at Savannah River was achieved by adjusting the solution to an Am(Cm) concentration of 10 g L^{-1} and 3.5 M K_2CO_3, oxidizing the Am(III) to Am(V) with hypochlorite, peroxydisulfate, or ozone, and precipitating the double carbonate $K_5AmO_2(CO_3)_3$ at 85°C (Groh *et al.*, 1965). Am(III) has also been oxidized to Am(V) electrochemically (Myasoedov and Kremliakova, 1985). A second precipitation is sometimes used to remove residual Am from the Cm solution. This process is based on the original work of Stephanou and Penneman (1952). After precipitation of Am(V) as the complex carbonate, Cm(III) can be precipitated with oxalate, hydroxide, or fluoride. It is noteworthy that the choice of cation is critical; if sodium is used in place of potassium, oxidation of americium proceeds past Am(V) to form the magenta-colored Am(VI) carbonate complex, which is soluble. Based on this observation, and utilizing the insolubility of $Cm(OH)_3$ in $NaHCO_3$, the americium content in the $Cm(OH)_3$ precipitate can be reduced to low levels (Coleman *et al.*, 1963).

9.6 THE METALLIC STATE

9.6.1 Physical properties

Curium is a lustrous, malleable, silvery metal with many properties comparable to those of the lighter actinide elements. The melting point of Cm (dhcp form) is 1345 ± 50°C (Fuger and Oetting, 1976; Oetting *et al.*, 1976), much higher than for the immediately preceding actinide elements, Np–Am (639–1173°C), but very similar to that of gadolinium (1312°C), its lanthanide analog (Cunningham and Wallmann, 1964; Reichlin *et al.*, 1981).

Curium metal exists in two modifications, a double hexagonal close-packed (dhcp) structure (α-lanthanum type) and a high-temperature cubic close-packed (fcc) structure. Using ^{244}Cm, the dhcp form was found to have lattice constants $a = 3.496(3)$ and $c = 11.331(5)$ Å, giving a calculated density of 13.5 g cm^{-3} and a metallic radius of 1.74 Å (Stevenson and Peterson, 1979; Reichlin *et al.*, 1981). Baybarz and Adair (1972) and Baybarz *et al.* (1976) reported the high-temperature fcc phase with $a = 5.039(2)$ Å, prepared by metal volatilization at 1650°C.

Using ^{248}Cm, Stevenson and Peterson (1979) also obtained this phase with $a = 5.065$ Å. Other preparations of Cm metal using ^{248}Cm have been reported. They exhibit the dhcp structure with $a = 3.500 \pm 0.003$ Å and $c = 11.34 \pm 0.01$ Å, and with $a = 3.490 \pm 0.006$ Å and $c = 11.308 \pm 0.018$ Å (Reichlin *et al.*, 1981). Other X-ray diffraction studies of ^{248}Cm metal have yielded evidence for an orthorhombic form as well as delocalization and compressibility data (Benedict *et al.*, 1985; Haire *et al.*, 1985).

The entropy of vaporization for Cm metal is similar to that of gadolinium; its vapor pressure is about double that of gadolinium over the measured range. The vapor pressure of triply distilled ^{244}Cm metal has been measured between 1300 and 2000 K and obeys the following relations (Ward *et al.*, 1975):

$$\log_{10}(p/(\text{atm})) = (6.082 \pm 0.129) - (19\,618 \pm 193)/T(\text{K}) \quad (\text{solid}, 1327\text{–}1639\ \text{K})$$

$$\log_{10}(p/(\text{atm})) = (5.586 \pm 0.157) - (18\,894 \pm 275)/T(\text{K}) \quad (\text{liquid}, 1640-1972\ \text{K})$$

From the latter equation the calculated boiling point of Cm is 3110°C. The derived heat of fusion, entropy of fusion, and average second-law entropy are 13.85 kJ mol^{-1}, 9.16 J K^{-1} mol^{-1}, and 106.7 ± 3.0 J K^{-1} mol^{-1}, respectively. Determination of low-temperature condensed-phase thermodynamic parameters awaits the availability of long-lived isotopes. For excellent discussions of thermodynamic, electronic, and magnetic effects in curium and other actinide and lanthanide metals, the reader is referred to articles by Ward and Hill (1975) and Ward *et al.* (1980). Konings (2001b) has reevaluated the thermodynamic data for curium metal in the solid, liquid, and gaseous states and has reported a set of recommended values that are similar to values by Ward *et al.* (1980).

Metallic curium obeys a Curie–Weiss magnetic susceptibility relationship between 100 and 550 K with a magnetic moment of 8.07 μ_B (Kanellakopulos *et al.*, 1976; Nave *et al.*, 1981; Reichlin *et al.*, 1981), comparable to earlier values of 7.85–8.15 μ_B (Marei and Cunningham, 1972), although a lower value of 6.0 μ_B was reported recently (Fujita *et al.*, 1976). However, the form of the metal was not identified by X-ray diffraction in the latter case. Schenkel (1977) performed electrical resistance measurements on ^{244}Cm metal, and showed that curium is the first reported magnetically ordered actinide metal, with a Néel temperature of 52.5 K. A neutron diffraction study of the dhcp (α-La) form indicated no structural change down to 5 K and also showed antiferromagnetic ordering below 52 K (Fournier *et al.*, 1977). A careful susceptibility study with ^{248}Cm metal confirmed an antiferromagnetic transition at about 65 K, but the fcc phase reveals a ferrimagnetic transition near 200 K (Eubanks and Thompson, 1969).

9.6.2 Preparation of curium metal

Curium metal can be prepared from CmF_3 by reduction with barium or lithium metal. Dry, oxygen-free CmF_3 is required and the temperatures used (>1600 K) are well above the melting point of the metal. One to ten micrograms of

Cm metal was made using tungsten coils and tantalum crucibles (tantalum is reported to dissolve slightly in Cm) (Cunningham and Wallmann, 1964; Stevenson and Peterson, 1979; Reichlin *et al.*, 1981). Gram quantities of the metal have been prepared in 75–90% yield by reduction with a magnesium–zinc alloy of CmO_2 suspended in a $MgF_2/MgCl_2$ melt (Eubanks and Thompson, 1969). When CmO_2 or Cm_2O_3 and pure hydrogen are heated to temperatures between 1200 and 1500°C in the presence of Pt, Ir, or Rh, alloy phases result with compositions of Pt_5Cm, Pt_2Cm, Ir_2Cm, Pd_3Cm, and Rh_3Cm (Erdmann and Keller, 1971, 1973). Similar alloys with Ni (Radchenko *et al.*, 1995), Al (Radchenko *et al.*, 1996), and Si (Radchenko *et al.*, 1998) have also been reported. Reports on CmPd alloys showed formation of a solid solution of Cm in Pd, with the fcc lattice parameter increasing linearly with at.% Cm (Radchenko *et al.*, 1985, 1989). The Cm–Pu phase diagram has been reported, which indicates that α-Cm (dhcp) predominates at lower wt% Pu and temperature, with β-Cm (fcc) forming as the Pu concentration and temperature increase, ultimately leading to γ-Cm (space group $Im3m$) (Okamoto, 2000). Pure curium metal has been prepared by decomposition of these intermetallic compounds (Müller *et al.*, 1972, 1977). The dhcp form of curium has also been prepared by reducing the dioxide or sesquioxide with thorium metal, followed by volatilization and condensation of the curium metal vapor on a tantalum condenser (Baybarz and Adair, 1972; Damian *et al.*, 1975; Baybarz *et al.*, 1976).

9.6.3 Chemical properties of the metallic state

Metallic curium appears to be even more susceptible to corrosion than the earlier actinide elements, a property due at least in part to radioactive self-heating. The metal dissolves rapidly in dilute acid solutions. The metal surface rapidly oxidizes in air to form a film that may begin as CmO (Cunningham and Wallmann, 1964; Burney, 1980; Reichlin *et al.*, 1981), progresses to Cm_2O_3 at room temperature, and further to CmO_2 at elevated temperatures. The metal is pyrophoric when finely divided.

The direct reactions of curium metal with non-metals such as Bi, P, As, Sb, S, and Se have been reported, and binary compounds with N, P, As, and Sb have been prepared by reactions using curium hydride (see Sections 9.7.5 and 9.7.6) (Charvillat *et al.*, 1975, 1976; Gibson and Haire, 1987; Zhu and Jiao, 1994).

9.7 CLASSES OF COMPOUNDS

9.7.1 General

Because curium is available in macro quantities, a number of Cm compounds have been synthesized and structurally characterized. Table 9.3 lists crystallographic data for Cm metal, alloys, and compounds.

Table 9.3 *Crystallographic data for curium metal, alloys, and compounds.*

				Lattice constants		
	References	*Lattice type*	*Crystal system-space group*	a_0 (Å)	b_0 (Å)	c_0 (Å)
Metal						
α-Cm	Cunningham and Wallmann (1964 Müller *et al.* (1972, 1977)	α-La	hexagonal-$P6_3/mmc$	3.496		11.331
β-Cm	Baybarz and Adair (1972); Baybarz *et al.* (1976)		fcc	5.039		
Alloys						
Pd_3Cm	Erdmann and Keller (1973); Radchenko *et al.* (1985)	Cu_3Au	cubic-$Pm3m$	4.147		
Rh_3Cm	Erdmann and Keller (1973); Radchenko *et al.* (1985)	Cu_3Au	cubic-$Pm3m$	4.106		
Ir_2Cm	Erdmann and Keller (1973); Radchenko *et al.* (1985)	Cu_2Mg	cubic-$Fd3m$	7.561		
Pt_5Cm	Erdmann and Keller (1973); Radchenko *et al.* (1985)	Pt_5Sm	orthorhombic	5.329	9.108	26.38
Pt_2Cm	Erdmann and Keller (1973); Radchenko *et al.* (1985)	Cu_2Mg	cubic-$Fd3m$	7.625		
Ni_5Cm	Radchenko *et al.* (1995)	Cu_5Ca	hexagonal	4.871		4.018
$Ni_{15}Cm_2$	Radchenko *et al.* (1995)	$Ni_{17}Th_2$	hexagonal	8.348		8.071
Al_2Cm	Radchenko *et al.* (1996)	Cu_2Mg	cubic	7.878		
CmSi	Radchenko *et al.* (1998)		orthorhombic	8.288	3.912	5.966
Cm_2Si_3	Radchenko *et al.* (1998)		hexagonal	3.879		4.147
$CmSi_2$	Radchenko *et al.* (1998)		tetragonal	3.977		13.719
$CmSi_{1.88}$	Radchenko *et al.* (1998)		tetragonal	4.029		13.715
Oxides and chalcogenides						
α-Cm_2O_3	Noé *et al.* (1970)	α-La_2O_3	hexagonal- $P\bar{3}m1$	3.7952		5.985
β-Cm_2O_3	Noé *et al.* (1970); Morss *et al.* (1983)	β-La_2O_3	monoclinic	14.282	3.641 $\beta = 100.29$	8.883

Table 9.3 (*Contd.*)

			Crystal system-space	*Lattice constants*		
	References	*Lattice type*	*group*	a_0 (Å)	b_0 (Å)	c_0 (Å)
γ-Cm_2O_3	Noé *et al*. (1970)	γ-Mn_2O_3	cubic-*Ia*3	11.002		
CmO_2	Wallmann (1964); Noé and Fuger (1971); Peterson and Fuger (1971); Mosley (1972)	fluorite	cubic-*Pm*3*m*	5.3584		
CmO	Cunningham and Wallmann (1964)		cubic-*Fm*3*m*	5.09		
CmS	Damien *et al*. (1979a,b)		fcc	5.5754		
CmSe	Damien *et al*. (1979a,b)		fcc	5.791		
CmTe	Damien *et al*. (1979a,b)		fcc	6.150		
Cm_2S_3	Damien *et al*. (1975)	Th_3P_4	bcc	8.452		
$CmS_{1.98}$	Damien *et al*. (1975)	Fe_2As	tetragonal	3.926		8.01
Cm_2Se_3	Damien *et al*. (1975)	Th_3P_4	bcc	8.788		
$CmSe_{1.98}$	Damien *et al*. (1975)	Fe_2As	tetragonal	4.096		8.396
$CmTe_3$	Damien *et al*. (1976)	$NdTe_3$	orthorhombic (pseudotetragonal)	4.34		25.7
$CmTe_2$	Damien *et al*. (1976)	Fe_2As	tetragonal	4.328		8.93
Cm_2Te_3	Damien *et al*. (1976)	η-U_2S_3	orthorhombic	11.94	12.13	4.330
Cm_2O_2S	Haire and Fahey (1977)	Pu_2O_2S	hexagonal	3.889		6.736
Cm_2O_2Te	Damien *et al*. (1976)	La_2O_2Te	tetragonal	3.98		12.58
$Cm_2O_2SO_4$	Haire and Fahey (1977)	$Nd_2O_2SO_4$	orthorhombic	4.209	4.087	13.270
$BaCmO_3$	Haire and Fahey (1977)	perovskite				
$CmAlO_3$	Haire and Fahey (1977)	perovskite				

Pnictides						
CmN	Charvillat *et al*. (1976)	NaCl	fcc	5.041		
CmP	Damien *et al*. (1979a,b)	NaCl	fcc	5.743		
CmAs	Damien *et al*. (1979a,b)	NaCl	fcc	5.887		
CmSb	Damien *et al*. (1979a,b)	NaCl	fcc	6.242		
Cm_2O_2Sb	Charvillat and Zachariasen (1977)	La_2O_2Te	tetragonal–14/*mmm*	3.920		13.41
Cm_2O_2Bi	Charvillat and Zachariasen (1977)	La_2O_2Te	tetragonal–14/*mmm*	3.957		13.359
Halides						
CmF_3	Stevenson (1973); Asprey *et al*. (1965)	LaF_3	trigonal- $P\overline{3}\,Cl$	7.019		7.198
$CmCl_3$	Asprey *et al*. (1965); Peterson and Burns (1973)	UCl_3	hexagonal-$P6_3/m$	7.3743		4.1850
$CmBr_3$	Asprey *et al*. (1965); Burns *et al*. (1975)	$PuBr_3$	orthorhombic-*Cmcm*	4.041	12.709	9.135
CmI_3	Asprey *et al*. (1965)	BiI_3	hexagonal-$R\overline{3}$	7.44		20.4
CmF_4	Asprey and Haire (1973); Haug and Baybarz, (1975)	UF_4	monoclinic-*C*2/*c*	12.500 $\beta = 126.10$	10.488	8.183
$LiCmF_5$	Keenan (1966a)	$LiUF_5$	tetragonal-$I14_1/a$	14.579		6.437
$K_7Cm_6F_{31}$	Keenan (1966b)	$Na_7Zr_6F_{31}$	hexagonal-$R\overline{3}$	14.41		9.661
$Na_7Cm_6F_{31}$	Keenan (1967a)	$Na_7Zr_6F_{31}$	hexagonal-$R\overline{3}$	14.89		10.254
Rb_2CmF_6	Keenan (1967b)	Rb_2UF_6	orthorhombic-*Cmcm*	6.931		7.56
CmOCl	Peterson (1972)	PbClF	hexagonal	3.98		6.75
Hydrides						
CmH_{2+x}	Gibson and Haire (1985)	fluorite	fcc	5.322		
$CmH_{3-\delta}$	Gibson and Haire (1985)	PuH_3	trigonal-$P\overline{3}\,ClCl$	3.769		6.732

The most important chemical characteristic that distinguishes curium from the lighter actinides is the great stability of the 3+ state with respect to oxidation or reduction. The stability of Cm(III) has been attributed to the relative stability of a half-filled ($5f^7$) configuration, and causes a chemical resemblance to lanthanides. All known Cm(IV) compounds are either fluorides or oxides.

In contrast to americium, the oxidation of Cm(III) to Cm(IV) is achieved only with the strongest oxidizing agents, and only two reports claim evidence for an oxidation state greater than IV (Peretrukhin *et al.*, 1978; Fargeas *et al.*, 1986). Transient divalent and tetravalent states have been observed in aqueous perchlorate media using pulse radiolysis techniques (Sullivan *et al.*, 1976). Attempts have been made to induce Cm(III)–Cm(IV) oxidation chemically (using ozone (Pages and Demichelis, 1966) and perxenate (Holcomb, 1967)) or electrochemically (Myasoedov *et al.*, 1973). These attempts have failed, an effect clearly not attributable solely to radiolytic reduction.

However, formation of a red Cm(IV) complex in phosphotungstate solution was achieved by the use of peroxydisulfate as the oxidant (Saprykin *et al.*, 1976). Kosyakov *et al.* (1977) demonstrated that, in such solutions, the Cm(IV) is reduced much more rapidly than can be accounted for by radiolytic effects, while Am(IV) in such solutions is much more stable, being reduced at a rate attributable to radiolytic effects alone. This behavior stands in contrast to the reduction of Cm(IV) in 15 M CsF, which does proceed at the slower radiolytic rate (Keenan, 1961). No value for the E°(Cm(IV)/Cm(III)) is known, but, from existing data, it is substantially more positive than $E^\circ(\mathrm{Am}^{4+}/\mathrm{Am}^{3+})$ and probably about as positive as $E^\circ(\mathrm{Pr}^{4+}/\mathrm{Pr}^{3+})$.

With the more common isotopes ^{242}Cm and ^{244}Cm, intense alpha self-irradiation and heating effects cause aqueous-solution instability (peroxide is always present) and solid-state instability (lattice changes and compound alteration). In some cases, these effects are sufficiently large that certain compounds may be identified in bulk only with the more stable isotopes, e.g. $^{244}\mathrm{CmF}_4$ and $^{248}\mathrm{Cm}(n\text{-}\mathrm{C}_5\mathrm{H}_5)_3$ (Asprey and Keenan, 1958; Laubereau and Burns, 1970b).

9.7.2 Hydrides

The hydrides of Cm are relatively little explored. The first Cm hydride was prepared by Bansal and Damien (1970) by reacting ^{244}Cm metal with hydrogen at 200–250°C. Based on its X-ray diffraction pattern, this hydride was characterized as the face-centered cubic (fcc) CmH_{2+x}, by analogy to NpH_{2+x}, PuH_{2+x}, and AmH_{2+x}. The existence of the dihydride was confirmed by Gibson and Haire (1985), who prepared the dihydride from ^{248}Cm metal. In the latter work, the hexagonal $\mathrm{CmH}_{3-\delta}$ was also prepared. The trihydride was characterized from its x-ray diffraction pattern by analogy to those of known lanthanide and actinide trihydrides.

The dissociation enthalpy for CmH_2 has been reported to be 187 ± 14 kJ mol^{-1}, consistent with the trend in stability of the actinide dihydrides becoming more like that of the lanthanide dihydrides with increasing atomic number (Gibson and Haire, 1990). The order of stability of f-element dihydrides can be summarized as follows:

$$\mathrm{Ln(most\ stable)} > \mathrm{Cm} > \mathrm{Am} > \mathrm{Pu}$$

9.7.3 Halides

The halides represent by far the most extensively characterized class of curium compounds (see Table 9.3). The complete CmX_3 series (X = F, Cl, Br, I), as well as CmF_4 and several complex Cm(IV) fluorides, have been prepared and studied. Several reviews deal specifically with actinide halides; for further information (especially for cross-comparisons of Cm with other actinide halides) the reader is referred to these articles (Katz and Sheft, 1960; Bagnall, 1967; Brown, 1968; Penneman *et al.*, 1973).

Curium trifluoride is a white, sparingly soluble (~10 mg L^{-1}) compound (Cunningham, 1966) with the LaF_3 structure, which precipitates when fluoride ion is added to weakly acidic Cm(III) solutions, or HF to $Cm(OH)_3$. The anhydrous trifluoride is obtained by desiccation over P_2O_5 or by treatment with hot HF(g). The trifluoride melts at 1406 ± 20°C; its standard enthalpy and entropy of formation have been estimated to be 1660 kJ mol^{-1} (Ionova *et al.*, 1997) and 121 J K^{-1} mol^{-1} (Burnett, 1966; Cunningham, 1966) at 298 K, respectively. Curium has an irregular tricapped trigonal prismatic coordination in CmF_3 (Penneman *et al.*, 1973).

Curium trichloride is a white compound that can be obtained by treating curium oxides or CmOCl with anhydrous hydrogen chloride at 400–600°C (Wallmann *et al.*, 1967). The hydrate has been reported to be light green. A single-crystal study showed that $CmCl_3$ has the hexagonal UCl_3-type structure common among the actinide trichlorides. Based on the lattice constants for $CmCl_3$ (Table 9.3), a radius of 0.971 Å has been calculated for Cm(III) (Peterson and Burns, 1973). Curium has nine chloride neighbors in the form of a tricapped trigonal prism, with Cm–Cl lengths of 2.859 and 2.914 Å. A melting point of 695°C (Peterson and Burns, 1973) and an enthalpy of formation (298 K) of −974 ± 4 kJ mol^{-1} (Fuger *et al.*, 1975; Oetting *et al.*, 1976) have been reported. The entropy of formation of $CmCl_3$ at 298 K has been estimated to be 163 ± 6 J K^{-1} mol^{-1} (Konings, 2001a).

Curium tribromide has been prepared by heating the trichloride with NH_4Br at 400–450°C in a hydrogen atmosphere (Asprey *et al.*, 1965) and also by hydrogen bromide treatment of the calcined oxide at 600°C (Burns *et al.*, 1975). The compound melts at 625°C and has the $PuBr_3$ (orthorhombic) structure (Burns *et al.*, 1975). The metal ion is surrounded by eight bromide ions, two at 2.865 Å, four at 2.983 Å, and two at 3.137 Å. An analogous procedure ($CmCl_3+NH_4I$) has been used to prepare CmI_3, a colorless material having the BiI_3 structure (Asprey *et al.*, 1965). Preparation from elemental curium and iodine has also been reported (Seaborg *et al.*, 1949). The standard enthalpies of formation of $CmBr_3$ and CmI_3 are estimated to be 794 and 564kJ mol^{-1}, respectively, at 298 K (Ionova *et al.*, 1997).

The halides of tetravalent curium include the simple fluoride CmF_4 (Keenan and Asprey, 1969; Asprey and Haire, 1973; Haug and Baybarz, 1975), and a series of complex fluorides of the type $M_7Cm_6F_{31}$ (Keenan, 1966b, 1967a), M_2CmF_6 (Keenan, 1967b), and $MCmF_5$ (Keenan, 1966a), where M is an alkali metal. As with terbium, the only reported method for preparing the tetrafluoride is by fluorine oxidation of the trifluoride. CmF_4 is a brownish-tan solid with a monoclinic ZrF_4-type structure, in which curium has an antiprismatic eight coordination (Asprey and Haire, 1973; Penneman *et al.*, 1973; Haug and Baybarz, 1975). Magnetic susceptibility measurements suggest a fluoride-deficient structure, CmF_{4-x} (Haire *et al.*, 1982; Nave *et al.*, 1983).

Evidence for the existence of CmF_6 and $CmOF_3$ (as well as $NpOF_3$, NpF_7, PuO_3F, AmF_5, AmF_6, and EsF_4) has been reported using thermochromatographic techniques (Fargeas *et al.*, 1986). These fluorides were claimed to form in low yield when a deposit of Cm (chemical form not reported) on Ni metal was treated with a mixture of BF_3 and F_2 at 800°C. However, there has been no independent confirmation of these species.

A prominent series of isostructural complex actinide(IV) fluorides, $M_7An_6F_{31}$, with the $Na_7Zr_6F_{31}$ structure have been prepared (Keenan, 1966b, 1967a). With curium, the Na and K salts are known. The compounds were prepared by direct fluorination of evaporated salt mixtures of MX and CmX_3 at about 300°C. This 7:6 type of compound predominates with the larger alkali cations. The basic coordination polyhedron is a square antiprism (Penneman *et al.*, 1973). In tetragonal $LiCmF_5$, the curium coordination is tricapped trigonal prismatic (Penneman *et al.*, 1973). The compound Rb_2CmF_6 is orthorhombic with the Rb_2UF_6 structure, which consists of chains of fluoride dodecahedra (Penneman *et al.*, 1973). The oxychloride CmOCl has been synthesized by treatment of $CmCl_3$ (or Cm_2O_3) at 500–600°C, with the vapor in equilibrium with a 10 M HCl solution (Peterson, 1972):

$$CmCl_3 + H_2O \leftrightarrow CmOCl + 2HCl$$

From the equilibrium and known heats of formation, ΔH°_{f298} for CmOCl was calculated (Weigel *et al.*, 1977, Table 17.4). Marei and Cunningham (1972) found that the magnetic susceptibility of CmOCl follows the Curie–Weiss law over the temperature range 77–298 K, with $\mu_{eff} \sim 7.58\ \mu_B$ and a Curie temperature of approximately 22 K. The structure of CmOCl is of the PbClF-type (hexagonal), with each metal surrounded by four oxides and five chlorides (Peterson, 1972).

9.7.4 Oxides

Konings (2001a,b) has recently reviewed the thermochemical and thermophysical properties of Cm oxides. Crystallographic data for the various oxides are compiled in Table 9.3.

The white to faint tan sesquioxide Cm_2O_3 (m.p. 2270 ± 25°C) (Konings, 2001b) was prepared by thermal decomposition of $^{244}CmO_2$ at 600°C and 10^{-4} torr pressure (Asprey *et al.*, 1955). This material has the Mn_2O_3-type cubic-C lattice, which gradually changes at room temperature to a hexagonal A-form because of self-irradiation effects (Wallmann, 1964; Noé *et al.*, 1970). Haug (1967) prepared monoclinic B-type Cm_2O_3 by reduction of $^{244}CmO_2$ with hydrogen. This study showed that the cubic form described by Asprey *et al.* (1955) predominates at reaction temperatures below 800°C, changing to the monoclinic B-form at higher temperatures (Haug, 1967). These three crystal modifications correspond to the three types observed for lanthanide sesquioxides. Structural data, enthalpy of formation, and magnetic susceptibility were obtained by Morss *et al.* (1983) with B-form $^{248}Cm_2O_3$. The enthalpy of formation at 25°C has been estimated as -1684 ± 14 kJ mol^{-1} for the monoclinic Cm_2O_3 (Konings, 2001b), with the corresponding entropy of formation estimated to be 167 ± 5 J K^{-1} mol^{-1} (Konings, 2001a).

Preparation of the black curium dioxide by ignition in air was first claimed by Asprey *et al.* (1955). The product had a cubic (fcc) structure. The compound is also formed by thermal decomposition of ^{244}Cm(III)-loaded resin (Hale and Mosley, 1973) and by heating $^{244}Cm_2O_3$ to 650°C in 1 atm of oxygen, followed by cooling in oxygen (Noé and Fuger, 1971; Peterson and Fuger, 1971). Others have shown that the dioxide is the stable oxide form in an oxygen atmosphere at temperatures below 400°C (Chikalla and Eyring, 1969). At temperatures between 380 and 420°C, CmO_2 is reduced to $CmO_{1.95}$; above 430°C, rapid decomposition occurs via various intermediate oxides to Cm_2O_3 (Mosley, 1972). The enthalpy of formation at 25°C has been estimated as -912 ± 7 kJ mol^{-1} for CmO_2 (Konings, 2001b).

Curium oxalate, $Cm_2(C_2O_4)_3$, is routinely used for calcination to CmO_2. For example, oxalate precipitation has been used to process kilograms of ^{244}Cm, with subsequent metathesis with 0.5 M hydroxide to $Cm(OH)_3$ (Scherer and Fochler, 1968; Bibler, 1972).

Morss *et al.* (1989) reported a neutron diffraction and magnetic susceptibility study of CmO_2 prepared by calcination of Cm(III) oxalate at 775°C in flowing O_2, followed by annealing for 4 days at 350°C in flowing O_2. Based on the lattice parameter ($a_0 = 5.359 \pm 0.002$ Å), the stoichiometry of this material was reported to be $CmO_{1.99 \pm 0.01}$, indicating that the material essentially contained only Cm(IV). Nevertheless, the effective paramagnetic moment was found to be $(3.36 \pm 0.06)\mu_B$, a value which had previously been attributed to the presence of Cm(III). Based on these data, it has been suggested that the electronic ground states in actinide dioxides may need to be reexamined.

The curium–oxygen phase diagram studies show a great similarity to analogous Pu, Pr, and Tb systems, and indicate the possible existence of two additional Cm_2O_3 phases which have not yet been isolated (Eyring, 1967; Stevenson and Peterson, 1975). Two intermediate oxides, $CmO_{1.72}$ and $CmO_{1.82}$, and two other non-stoichiometric phases close to the composition of CmO_2 and $CmO_{1.5}$, have also been detected (Chikalla and Eyring, 1969). A cubic (fcc) phase, CmO, was reported in an early preparation of the metal (Cunningham and Wallmann, 1964).

The ternary oxides $BaCmO_3$ (Fuger *et al.*, 1993) and Cm_2CuO_4 (Soderholm *et al.*, 1999) have recently been reported. The latter is of interest by its analogy to M_2CuO_4 (M= La, Pr–Eu), which are parent compounds for high-temperature superconductors. When doped with Th^{4+}, the M_2CuO_4 (M = Pr–Eu) materials become superconducting, with T_c of ~32 K. Although Cm_2CuO_4 is isostructural with the M_2CuO_4 (M = Pr–Gd) series, its Th-doped analog is not superconducting. This effect may be due to its high magnetic ordering temperature relative to other M_2CuO_4.

Hale and Mosley (1973) have reported the preparation of curium oxysulfate, $^{244}Cm_2O_2SO_4$, by heating Cm(III)-loaded resin (sulfonate form) in a stream of oxygen at 900°C. The thermogravimetric analysis indicated that heating to 1175°C under otherwise similar conditions yielded Cm_2O_3, which on cooling formed CmO_2. Haire and Fahey (1977) have prepared $Cm_2O_2SO_4$ by calcination of the hydrated sulfate in air at about 750°C. The brown $Cm_2O_2SO_4$ has a body-centered orthorhombic structure, similar to $Nd_2O_2SO_4$ and $Cf_2O_2SO_4$. The computed Cm(III) radius in $Cm_2O_2SO_4$, 0.980 Å, agrees with the value of 0.979 Å derived from Cm_2O_3. The oxysulfide Cm_2O_2S is formed when the sulfate is heated to about 800°C in H_2/Ar (Haire and Fahey, 1977). Cell constants for Cm_2O_2Sb and Cm_2O_2Bi have been reported (Charvillat and Zachariasen, 1977).

9.7.5 Chalcogenides

Damien *et al.* (1975) prepared $^{244}CmS_2$ and $^{244}CmSe_2$ by slow reaction of excess sulfur or selenium vapor with curium hydride in vacuum. The resulting solids gave powder patterns indicating the tetragonal Fe_2As-type cell (isostructural with AmS_2 and $AmSe_2$) with lattice parameters (Table 9.3) showing the materials to be non-stoichiometric.

The sesquisulfide Cm_2S_3 forms a defect body-centered cubic (bcc) phase of the Th_3P_4-type (Damien *et al.*, 1975). The sesquiselenide was obtained by thermal dissociation of $CmSe_2$ at 620°C, again yielding a Th_3P_4-type phase (Damien *et al.*, 1975). Unlike gadolinium or plutonium, no other sesquiselenide forms were observed, even after thermal treatment at various temperatures.

The monochalcogenides were prepared by heating stoichiometric mixtures of chalcogen and curium metal at 700–750°C for 15 h, followed by heating at 1250–1500°C under high vacuum (Damien *et al.*, 1979a). The monochalcogenides have fcc structures. In these preparations, accessory phases, possibly γ-Cm_2S_3, Cm_2O_2S, γ-Cm_2Se_3, and Cm_2O_2Te, were detected.

The oxysulfide Cm_2O_2S was prepared by partial oxidation of CmS_2 at 700°C (Damien *et al.*, 1975; Haire and Fahey, 1977). This compound has a hexagonal structure and is isostructural with the Np, Pu, and Cf analogs (Haire and Fahey, 1977).

Damien *et al.* (1976) have reported the preparation of $CmTe_3$ by the reaction of the hydride with tellurium at 400°C. At temperatures above 400°C, the tritelluride decomposes to form the successive lower tellurides $CmTe_2$ and Cm_2Te_3. At 1100°C in a quartz tube, the oxytelluride Cm_2O_2Te is formed.

9.7.6 Pnictides

The syntheses of the pnictide compounds CmX, where X = N, P, As, and Sb, have been reported (Charvillat *et al.*, 1975, 1976; Kanellakopulos *et al.*, 1976; Damien *et al.*, 1979a,b; Stevenson and Peterson, 1979; Nave *et al.*, 1981). The compounds were obtained by heating curium hydride or metal with the respective pnictide element in a sealed tube to temperatures of 350–950°C. The N, P, As, and Sb compounds all have the NaCl structure (Charvillat *et al.*, 1975, 1976; Kanellakopulos *et al.*, 1976; Damien *et al.*, 1979a,b; Nave *et al.*, 1981). Damien *et al.* (1979a,b) prepared the monopnictides (N, P, As, Sb) by directly heating stoichiometric mixtures of the elements. CmN and CmAs are ferromagnetic, with T_c of 109 and 88 K, respectively (Kanellakopulos *et al.*, 1976; Nave *et al.*, 1981). The calculated effective magnetic moments are 7.02 and 6.58 μ_B, lower than expected for a pure $5f^7$ configuration, probably because of strong spin–orbit coupling and crystal field effects (Kanellakopulos *et al.*, 1976; Nave *et al.*, 1981).

The possibility of using mixed nitride fuels for transmutation of minor actinides has gained recent attention because it is anticipated that the actinide nitrides are mutually miscible. The miscibility of CmN and PuN has been confirmed by the carbothermic synthesis of (Cm,Pu)N (Takano *et al.*, 2001). This was achieved by heating graphite and $(Cm_{0.4}Pu_{0.6})O_{2-x}$ at 1773 K in N_2. The lattice parameter of the resulting mixed nitride was close to that expected from the known lattice parameters for CmN and PuN.

9.7.7 Miscellaneous compounds

The trihydroxide, $Cm(OH)_3$, has been prepared from aqueous solution and crystallized by aging in water (Haire *et al.*, 1977). The compound has the lanthanide trihydroxide (hexagonal) structure. Although there have been no reports of Cm carbide, the silicides CmSi, $CmSi_2$, Cm_2Si_3, and Cm_5Si_3 have been reported (Weigel and Marquardt, 1983; Radchenko *et al.*, 2000).

The oxalate $Cm_2(C_2O_4)_3 \cdot 10H_2O$ forms when aqueous Cm(III) and oxalic acid are mixed. The compound dehydrates in a stepwise fashion when heated *in vacuo*, yielding the anhydrous oxalate at 280°C, which then converts to a carbonate above 360°C (Scherer and Fochler, 1968). A differential thermal analysis (DTA) investigation of the hydrated Cm oxalate under helium revealed endothermic events centered at 145 and 400°C, corresponding to the release of water and the formation of $Cm_2O_2CO_3$, respectively. Above 500°C, the $Cm_2O_2CO_3$ converts to Cm_2O_3 (Vasil'ev *et al.*, 1989). The hydrated oxalate dissolves readily in aqueous alkali-metal carbonate solutions (Bibler, 1972; Burney and Porter, 1967). The compound has a solubility (~0.8 mg Cm per liter at 23°C) lower than that of the americium analog in 0.1 M $H_2C_2O_4$/0.2 M HNO_3. The solubility increases rapidly with temperature.

Curium nitrate can be isolated by evaporation of solutions formed by dissolving curium oxide in nitric acid. DTA analysis of the freshly prepared $^{244}Cm(NO_3)_3$ indicated the decomposition pathway is the same under an oxygen atmosphere as it is under helium (Vasil'ev *et al.*, 1990). The thermal decomposition is characterized by endothermic events centered at 90, 180, 400, and 450°C. By analogy to the thermal decomposition of lanthanide nitrates, the first two endotherms have been assigned to melting of the crystalline hydrated nitrate and its dehydration, respectively. The last two endotherms (which overlap) are associated with the decomposition of the anhydrous Cm nitrate. The final product of the thermal decomposition is CmO_2, indicating the Cm is oxidized to Cm(IV) during the decomposition process. The enthalpy of formation of the anhydrous crystalline $Cm(NO_3)_3$ was estimated to be -700 kJ mol^{-1} from the DTA data.

Complex sulfates of the type $MAn(SO_4)_2 \cdot xH_2O$, where M = alkali metal, have been precipitated from solutions of M_2SO_4 and the appropriate trivalent actinide ion in dilute HCl or H_2SO_4 (Dedov *et al.*, 1965). Structural characterization is lacking for these compounds.

A series of actinide phosphates having the formulation $AnPO_4 \cdot 0.5H_2O$ has been prepared (An = Pu, Am, Cm) (Weigel and Haug, 1965; Kazantsev *et al.*, 1982). These compounds form when aqueous Cm(III) solutions are mixed with Na_2HPO_4 or $(NH_4)_2HPO_4$. The structures of the $AnPO_4 \cdot 0.5H_2O$ compound are unknown. The hydrated phosphate of Cm(III) dehydrates at 300°C to $CmPO_4$, which has the monazite structure (Weigel and Haug, 1965; Kazantsev *et al.*, 1982).

The compound $Cm[Fe(CN)_6]$ forms as a dark red precipitate when $K_3[Fe(CN)_6]$ is added to a solution of Cm nitrate in 0.2 M HNO_3 (Kulyako *et al.*, 1993). This contrasts to the lanthanides (Eu, Ce, Pr) that do not form precipitates under identical conditions, but is similar to the behavior of Am.

The compounds $CmNbO_4$ and $CmTaO_4$ are isotypic with the corresponding lanthanide compounds and are obtained by heating the precipitated, mixed hydroxide/hydrous oxides at 1200°C (Keller and Walter, 1965).

Heating mixtures of curium oxide and alumina affords $CmAlO_3$, which gives either a rhombohedral or a cubic product depending upon the quenching conditions (Mosley, 1971). The rhombohedral phase transforms to the cubic phase at room temperature. $BaCmO_3$ has also been reported (Haire, 1980; Nave *et al.*, 1983). The addition of K_2CO_3 to Cm(III) solution precipitates $Cm_2(CO_3)_3$ (Dedov *et al.*, 1965). The compound is soluble in 40% K_2CO_3.

The salt $CsCm(HFAA)_4 \cdot H_2O$, where HFAA = hexafluoroacetylacetone, has been studied in detail (Nugent *et al.*, 1969). This compound, as well as the Eu, Gd, Tb, Nd, Am, Bk, Cf, and Es analogs, forms readily when HFAA is added to ethanol solutions of Cm(III) in the presence of cesium ion. Of the actinides studied for possible laser properties, only Cm displayed UV-excited, sharp-line sensitized luminescence (Nugent *et al.*, 1969). Cm(III) was found to be a highly efficient emitter (resembling Eu(III)) in the crystalline state, in ethanol solution, and doped into a $CsGd(HFAA)_4$ crystal matrix; hence laser emission should be demonstrable. Strong luminescence has been observed from ^{244}Cm (III) on an anion-exchange resin and in solution (Gutmacher *et al.*, 1964; Beitz and Hessler, 1980).

A number of adducts of the type $CmL_3 \cdot nQ$ have been prepared, where L is a fluorinated β-diketonate and Q is TBP or trioctylphosphine oxide (Davydov, 1978). The volatility, thermal, and radiation stabilities were studied with consideration of such compounds for gas chromatographic separation of Am and Cm.

9.7.8 Organometallics

Despite substantial recent advances in the organometallic chemistry of other actinide elements, progress with curium has been slow. This lack of progress apparently results from the radiolytic properties of the element rather than an inherent chemical instability of the organometallic compounds. For more detailed discussion of actinide organometallic compounds, the reader is directed to Chapters 25 and 26.

The synthesis and spectroscopic characterization of milligram quantities of white, crystalline tris(η^5-cyclopentadienyl)curium, $Cm(C_5H_5)_3$, has been reported from the reaction of $^{248}CmCl_3$ with $Be(C_5H_5)_2$ (Baumgärtner *et al.*, 1970; Laubereau and Burns, 1970b). The compound can be sublimed in vacuum at 180°C and is isostructural with the Pr, Pm, Sm, Gd, Tb, Bk, and Cf analogs (Laubereau and Burns, 1970a,b). Mass spectrometric evidence for volatile $Cm(C_5H_5)_3$ using microgram amounts of ^{244}Cm was obtained (Baumgärtner *et al.*, 1970).

In terms of structural properties, volatility, thermal stability, and solubility, $Cm(C_5H_5)_3$ closely resembles other actinide and lanthanide tris(cyclopentadienide) compounds and hence the bonding must be similar. Nugent *et al.* (1971) studied the optical spectrum of $^{248}Cm(C_5H_5)_3$ and found weak bands, typical for Cm(III). These workers derived a value for the nephelauxetic parameter $d\beta$ of 0.050 ± 0.004, corresponding to very weak covalency in the organometallic bond. Thus, like the lanthanide analogs, the bonding in $Cm(C_5H_5)_3$ appears to have rather little covalent character. The ^{248}Cm compound fluoresces bright red under 360 nm irradiation (Nugent *et al.*, 1971).

Gas-phase reactions of Cm^+ and CmO^+ ions with small organic compounds have been investigated (Gibson and Haire, 1998, 1999). The gas-phase Cm ions used in these studies were generated by laser ablation of Cm_7O_{12} and the reaction products were characterized by mass spectroscopy. Using this methodology, a number of Cm organometallic fragments have been identified, including Cm_2^+, CmC_2H^+, $CmCN^+$, and a series of $CmC_xH_y^+$ species. The relative ability of Cm^+ to activate C–H bonds is less than that for U^+ or Tb^+ ions.

9.8 AQUEOUS CHEMISTRY

9.8.1 Inorganic

The aqueous solution chemistry of curium is almost exclusively that of Cm(III). Relatively little non-aqueous solution chemistry has been reported with curium other than that related to separations and environmental applications. Dilute Cm(III) solutions are normally colorless, but Cm(III) in concentrated HCl appears greenish. Curium-242 solutions with concentrations of about 1 g l^{-1} will boil unless cooled. The hydration number for the Cm(III) ion is estimated to be 9, based on fluorescence lifetimes (Kimura and Choppin, 1994; Kimura *et al.*, 1996). In HCl solution, the hydration number for the Cm(III) ion remains 9 up until 5 M HCl, then decreases with increasing HCl concentration (Kimura *et al.*, 1998). At 11 M HCl, the hydration number is 7. In contrast, the hydration number for Cm(III) drops steadily with increasing HNO_3 concentration from 0 to 13 M, with the hydration number being 5 at 13 M HNO_3. The differences between the HCl and HNO_3 systems are presumably simply due to the stronger binding affinity of the nitrate ion compared to chloride.

For dissolution of dhcp Cm metal in 1 M HCl, the value of ΔH is -615 ± 4 kJ mol^{-1} at 298.2 K, which, with an estimated $S° = -194$ J mol^{-1} h^{-1} for the Cm^{3+} (aquo) ion, yields an estimated -2.06 ± 0.03 V for the Cm(III)/Cm(0) couple (Fuger *et al.*, 1975) (see Chapter 17). Raschella *et al.* (1981) found $\Delta H = -606.5 \pm 11.7$ kJ mol^{-1} for dissolution using ^{248}Cm metal. From electron-transfer spectra, the Cm(III)/Cm(II) couple was estimated at -4.4 V (Nugent *et al.*, 1973), but the results of the pulse radiolysis study and the potential of the hydrated electron place a lower value on this couple (Sullivan *et al.*, 1976). From studies in a melt, Mikheev (1983) obtained -2.8 V for $E°$(Cm(III)/Cm(II)). Fuger and Martinot (1985) report $E°$(Cm(III)/Cm(IV)) to be -3.1 V.

Solution reactions of Cm(III) resemble those of the trivalent lanthanides and other trivalent actinides. The fluoride, oxalate, phosphate, iodate, and hydroxide are essentially water-insoluble, and the chloride, iodide, perchlorate, nitrate, and sulfate are water-soluble. The first hydrolysis constant for Cm(III), i.e. for the reaction

$$\mathrm{Cm(III)} + H_2O \rightarrow CmOH^{2+} + H^+$$

is 1.2×10^{-6} ($\mu = 0.1$; 23°C), which is within experimental error of the value for Am^{3+} but ten times greater than that for Pu^{3+} (Désiré *et al.*, 1969; Korotkin, 1974). The formation constants for $[Cm(OH)]^{2+}$ and $[Cm(OH)_2]^{+}$ have been determined by time-resolved laser-induced fluorescence spectroscopy (Fanghänel *et al.*, 1994). The measurements were made under high ionic strength (up to 6 M NaCl). Extrapolation to zero ionic strength yielded values of $\log \beta_{11} = 6.44$ and $\log \beta_{12} = 12.3$. Ionic strength significantly affects the distribution of hydrolyzed species with the Cm(iii) ion becoming more easily hydrolyzed as the ionic strength increases (Fig. 9.4).

Stability constants for Cm(iii) complexes have been determined for a number of inorganic and organic liquids in aqueous solution (Table 9.4). Most recent stability constant measurements for Cm(iii) have been performed using time-resolved laser-induced fluorescence spectroscopy; these studies provide the most self-consistent set of stability constant data for Cm(iii). Cm(iii) is a 'class A' or 'hard' metal ion, and thus complexes far more strongly to oxygen and fluoride donors than to more polarizable donors such as chloride or sulfur. This is reflected in the fact that β_1 for F^- is three orders-of-magnitude greater than that for Cl^-. The stability constants for oxygen donors (e.g. OH^- and CO_3^{2-}) are even higher than that for F^-.

Cm(iii) forms complexes with a number of polytungstate and heteropolytungstate anions and the luminescence properties of these complexes have been extensively studied. Included in this class of compounds are $CmW_{10}O_{36}^{9-}$, $Cm(SiW_{11}O_{39})_2^{13-}$, $CmSiW_{11}O_{39}^{5-}$, $Cm(PW_{11}O_{39})_2^{11-}$, $CmPW_{11}O_{39}^{4-}$, $Cm(P_2W_{17}O_{61})_2^{17-}$, and $CmP_2W_{17}O_{61}^{7-}$ (Yusov and Fedoseev, 1989b, 1990). The polytungstate ligands quench the luminescence of Cm(iii), evidently due to charge transfer between the excited Cm*(iii) and W(vi). This effect is magnified when the solutions of these complexes are frozen, resulting in a sharp decrease in

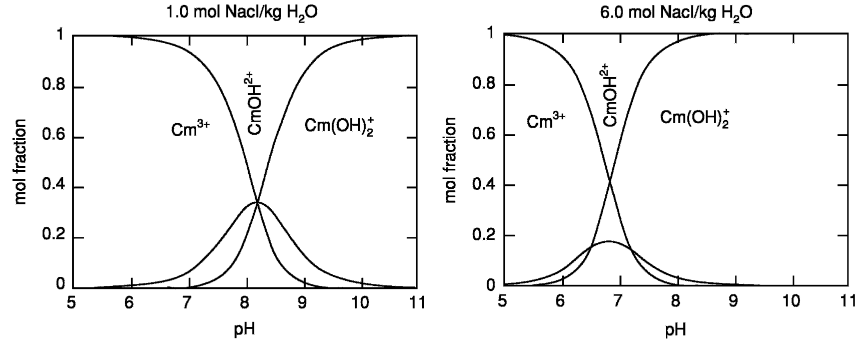


Fig. 9.4 *Comparison of Cm(iii) species distribution as function of pH at two NaCl molalities. The speciation determination is based on Cm(iii) fluorescence spectra. Used with permission from Fanghänel* et al. (1994).

Table 9.4 *Stability constants for selected Cm(III) complexes.*

Ligand	*Conditions*	*Stability constants*	*References*
OH^-	time-resolved laser fluorescence spectroscopy extrapolated to $\mu = 0$	$\beta_1 = 2.75 \times 10^6$; $\beta_2 = 2.00 \times 10^{12}$	Fanghänel *et al.* (1994)
F^-	time-resolved laser fluorescence spectroscopy, $\mu = 0$	$\beta_1 = 1.45 \times 10^3$	Aas *et al.* (1999)
F^-	extraction with di(2-ethylhexyl) phosphoric acid, pH = 3.6, $\mu = 0.50$	$\beta_1 = 2.21 \times 10^3$: $\beta_2 = 1.50 \times 10^6$: $\beta_3 = 1.2 \times 10^9$	Aziz and Lyle (1969)
F^-	extraction, $\mu = 1.0$	$\beta_1 = 4 \times 10^2$	Choppin and Unrein (1976)
Cl^-	extraction with dinonylnaphthalene sulfonic acid, $\mu = 1.0$	$\beta_1 = 1.6$; $\beta_2 = 0.9$	Khopkar and Mathur (1980a)
Cl^-	time-resolved laser fluorescence spectroscopy, $\mu = 6.8$ m, $T = 25°C$	$\beta_1 = 0.02$; $\beta_2 = 0.0007$	Fänghanel *et al.* (1995)
Cl^-	time-resolved laser fluorescence spectroscopy and Pitzer parameterization, $\mu = 0$ m, $T = 25°C$	$\beta_1 = 1.7$; $\beta_2 = 0.2$	Könnecke *et al.* (1997)
N_3^-	extraction with dinonylnaphthalene sulfonic acid pH = 5.9, $\mu = 0.5$, $T = 25°C$	$\beta_1 = 4.36$	Choppin and Barber (1989)
SCN^-	extraction with dinonylnaphthalene sulfonic acid pH = 2.8, $\mu = 1.0$	$\beta_1 = 1.53$; $\beta_2 = 4.08$	Khopkar and Mathur (1974, 1980b)

NO_2^-	extraction with dinonylnaphthalene sulfonic acid	$\beta_1 = 6.6$	Vasudeva Rao *et al.* (1978)
NO_3^-	extraction with dinonylnaphthalene sulfonic acid, $\mu = 1$, $T = 30°C$	$\beta_1 = 2.2$; $\beta_2 = 1.3$	Khopkar and Mathur (1980a)
CO_3^{2-}	time-resolved laser fluorescence spectroscopy and Pitzer parameterization, $\mu = 0$ m, $T = 25°C$	$\beta_1 = 1.3 \times 10^7$; $\beta_2 = 1.0 \times 10^{13}$; $\beta_3 = 1.6 \times 10^{15}$; $\beta_4 = 1.0 \times 10^{13}$	Fänghanel *et al.* (1999)
SO_4^{2-}	extraction, pH = 3.0, $\mu = 2.0$, $T = 25°C$	$\beta_1 = 22$; $\beta_2 = 73$	de Carvalho and Choppin (1967)
SO_4^{2-}	ion exchange	$\beta_1 = 32$; $\beta_2 = 241$	Khopkar and Mathur (1980a)
SO_4^{2-}	time-resolved laser fluorescence spectroscopy, $\mu = 3$ m	$\beta_1 = 8.5$; $\beta_2 = 4.1$	Paviet *et al.* (1996)
$P_3O_9^{3-}$	ion exchange	$\beta_1 = 4.4 \times 10^3$	Elesin *et al.* (1967)
$PW_{11}O_{39}^{7-}$	luminescence spectroscopy 0.1 M HNO_3	$\beta_1 = 5.0 \times 10^6$	Ioussov and Krupa (1997)
$SiW_{11}O_{39}^{8-}$	luminescence spectroscopy 0.1 M HNO_3	$\beta_1 = 3.2 \times 10^6$	Ioussov and Krupa (1997)
acetate	ion exchange, $\mu = 0.5$, $T = 20°C$	$\beta_1 = 114$; $\beta_2 = 1240$	Grenthe (1963)
glycolate	ion exchange, $\mu = 0.5$, $T = 20°C$	$\beta_1 = 700$; $\beta_2 = 5.6 \times 10^4$	Grenthe (1963)
glycinate	extraction, $\mu = 2.0$, $T = 25°C$	$\beta_1 = 6.4$	Tanner and Choppin (1968)
lactate	extraction, $\mu = 0.5$	$\beta_1 = 5.5 \times 10^2$; $\beta_2 = 3.0 \times 10^2$; $\beta_3 = 1.3 \times 10^6$	Nikolaev and Lebedev (1975)
2-hydroxyisobutyrate	cation exchange, $\mu = 0.5$	$\beta_1 = 2.7 \times 10^3$; $\beta_2 = 5.1 \times 10^4$; $\beta_3 = 1.7 \times 10^5$	Dedov *et al.* (1961)

Table 9.4 (*Contd.*)

Ligand	*Conditions*	*Stability constants*	*References*
5-sulfosalicylate	time-resolved laser fluorescence spectroscopy, $\mu = 0.05$	$\beta_1 = 2.8 \times 10^6$; $\beta_2 = 9.8 \times 10^8$	Klenze *et al.* (1998)
$C_4O_4^{2-}$	solubility ion exchange, $\mu = 0.2$	$\beta_1 = 9.1 \times 10^5$; $\beta_2 = 1.40 \times 10^{10}$	Lebedev *et al.* (1960, 1962)
citrate	extraction, $\mu = 0.1$	$\beta_1 = 4.9 \times 10^{10}$; $\beta_2 = 8.5 \times 10^{11}$	Hubert *et al.* (1974)
ethylenediaminetetraacetate	cation exchange, $\mu = 0.1$	$\beta_1 = 2.5 \times 10^{17}$	Elesin and Zaitsev (1971)
nitrilotriacetate	ion exchange, $\mu = 0.1$, $T = 25°C$	$\beta_1 = 6.3 \times 10^{11}$; $\beta_2 = 4.0 \times 10^{20}$	Eberle and Ali (1968)
ethylenediamine-bis(methyl) phosphonic acid	ion exchange, $\mu = 0.5$, $T = 25°C$	$\beta_1 = 2.5 \times 10^6$	Elesin *et al.* (1973)
thenoyltrifluoroacetone	extraction ($CHCl_3$), $\mu = 0.1$, $T = 25°C$	$\beta_3 = 2.5 \times 10^{13}$	Keller and Schreck (1969)

the luminescence lifetimes. However, upon further cooling, the luminescence quenching decreases and sharp luminescence bands are observed for these complexes at 77 K. The luminescence quenching is severe in Cm(III) complexes with $P_2W_{17}O_{61}^{10-}$ as these complexes do not luminesce in solution at 293 K. In contrast, $CmW_{10}O_{36}^{9-}$, $CmPW_{11}O_{39}^{4-}$, $CmSiW_{11}O_{39}^{5-}$, $Cm(SiW_{11}O_{39})_2^{13-}$, and $Cm(PW_{11}O_{39})_2^{11-}$ all display luminescence in D_2O at 293 K. At 77 K, the luminescence spectra of the $P_2W_{17}O_{61}^{10-}$ complexes are very similar to the other Cm(III) polytungstate complexes. Addition of molybdate to solutions of the Cm(III) polytungstate or heteropolytungstate complexes results in rapid quenching of the Cm(III) luminescence (Yusov and Fedoseev, 1992a,b). This behavior is the opposite of what is observed for the analogous Eu, Nd, and Yb systems.

The trends for the complexation of carboxylate ligands to Cm(III) are somewhat difficult to interpret. The β_1 values at $\mu = 0.5$ can be compared for acetate, glycolate, lactate, and 2-hydroxyisobutyrate (Table 9.4). The β_1 value increases from 114 to 700 in going from acetate to glycolate, which could be due to interaction of the hydroxyl group in glycolate with the Cm(III) center. One would expect that the inductive effect of an added methyl group would lead to a further increase in β_1 for complexation of lactate ion, but the β_1 value drops to 550 for lactate. On the other hand, addition of yet another methyl group does result in a significant increase in β_1 for 2-hydroxyisobutyrate ($\beta_1 = 2700$). The anomaly for lactate may simply reflect the differing experimental conditions under which the measurements were made. As would be expected, the chelating carboxylate ligands display substantially stronger binding to Cm(III) than the monocarboxylate ligands.

There are a limited number of reports concerning Cm(IV) in aqueous media. A fluoride complex of Cm(IV) was obtained when CmF_4 was dissolved in concentrated (15 M) MF solution (M = alkali–metal ion) (Asprey and Keenan, 1958; Keenan, 1961) (see Fig. 9.2). Even under these conditions, and using ^{244}Cm, the self-reduction rate because of alpha decay is about 1% per minute. When CmF_4 is added to aqueous NH_4F, an immediate oxidation–reduction reaction occurs, with deposition of CmF_3. This is in sharp contrast to the stability of Am(IV) in NH_4F solution (Asprey and Penneman, 1962).

Other than the CmF_4/MF system, the only claims for chemically generated Cm(IV) in solution are the reports that red solutions result when aqueous Cm(III) solutions are mixed with potassium peroxydisulfate and heteropolyanions such as $[P_2W_{17}O_{61}]^{10-}$ (Saprykin *et al.*, 1976; Kosyakov *et al.*, 1977). Cm(IV), produced by persulfate oxidation of Cm(III) in phosphotungstate solution, converts back to Cm(III) at a rate that suggests that the reduction involves both radiolytic mechanisms and direct reduction by water (Kosyakov *et al.*, 1977). In contrast, reduction of Am(IV) to Am(III) under similar conditions is dominated by radiolytic processes. Electrochemical generation of Cm(IV) in phosphate solutions was unsuccessful, owing to the large Cm(IV)/Cm(III) potential, estimated to be greater than 2 V in these systems (Myasoedov *et al.*, 1973, 1974). Other attempts to prepare Cm(IV) by oxidation of Cm(III) in solution have failed. These attempts include electrochemical methods (Myasoedov *et al.*, 1973, 1974; Ionova and Spitsyn, 1978) and the use of sodium perxenate (Holcomb, 1967) and ozone (Pages and Demichelis, 1966), agents which readily oxidize Am(III) to Am(V) or Am(VI). $Cm(OH)_3$ in $NaHCO_3$ is not oxidized by ozone or $Na_2S_2O_8$, conditions which produce Am(VI) as a carbonate complex (Coleman *et al.*, 1963).

The polytungstate Cm(IV) complexes – $CmW_{10}O_{36}^{8-}$, $Cm(SiW_{11}O_{39})^{12-}$, and $Cm(PW_{11}O_{39})_2^{10-}$ – display chemiluminescence upon reduction to Cm(III) (Yusov *et al.*, 1986a,b). The brightest chemiluminescence was observed when the initial complexes were treated with 1–3 M alkali, in which case water in the system most probably served as reductant. Chemiluminescence has also been observed during dissolution of the Cm(IV) double oxide Li_xCmO_y in mineral acids (Yusov and Fedoseev, 1989a, 1991).

Despite the numerous unsuccessful attempts to oxidize Cm(III) and Cm(IV) compounds to higher oxidation states, some theoretical work suggests the possibility that Cm(VI) may be even more stable than Am(VI), and the lack of success in preparing Cm(VI) may result from the low stability of Cm(V) and the high Cm(IV)/Cm(III) potential (Ionova and Spitsyn, 1978; Spitsyn and Ionova, 1978). One report claims the synthesis of Cm(VI) by beta decay of $^{242}AmO_2^+$ (Peretrukhin *et al.*, 1978).

$$^{242}AmO_2^+ \xrightarrow[16h]{\beta^-} CmO_2^{2+}$$

The $K_3AmO_2(CO_3)_2$ starting material was aged 18–40 h and then dissolved in 0.1 M $NaHCO_3$ in the presence of ozone, followed by addition of $Na_4UO_2(CO_3)_3/K_2CO_3$ solution to precipitate MO_2^{2+} species as $K_4MO_2(CO_3)_3$. From the enhancement of Cm in the precipitate over that expected for Cm(III), it was concluded that a 30–60% conversion to Cm(VI) had occurred.

Cm(II) is unknown other than as a transient aqueous species and a species coprecipitated from melts, and possibly in CmO. Pulse radiolysis, producing OH radicals as oxidant and the aquo electron as reductant, produced changes in aqueous americium and curium perchlorate solutions. The new absorbances were attributed to transient formation of Cm(II), A_{max} 240 nm, and Cm(IV), A_{max} 260 nm (Sullivan *et al.*, 1976).

9.8.2 Organic

Studies of Cm chemistry in pure organic solvents are rare. The solvation of Cm(III) in non-aqueous and binary mixed solvents has been investigated by luminescence spectroscopy (Kimura *et al.*, 2001). This study revealed that the relative preference for solvation of Cm(III) ion is dimethylsulfoxide > dimethylformamide > H_2O > methanol.

Very few curium compounds containing organic ligands have actually been isolated (see Section 9.7.8), although it seems likely that efforts to isolate such compounds would prove fruitful. Because of the interest in extraction schemes for treating radioactive wastes, a substantial number of studies have determined stability constants and distribution coefficients for solutions containing curium and various organic ligating agents. However, these experiments have often involved tracer amounts of curium and have employed a variety of experimental conditions (ionic strength, temperature, concentrations, etc.); therefore, quantitative comparisons of the determined values are difficult. As with the inorganic anions, values, and in some cases even trends, can vary markedly under seemingly similar conditions. Most studies do not involve isolation or definitive formulation of the actual species in solution, and it is possible that complicated structures occur, e.g. $CmF_3 \cdot (HDEHP)_x$ (Aziz and Lyle, 1969).

Furthermore, crystal structure determinations for a number of pertinent lanthanide and actinide extractant complexes illustrate that surprises may be expected when more definitive structural information becomes available (Burns, 1982; Bowen *et al.*, 1984). Because of these complications, we have not tried to analyze the voluminous Cm extraction data that are available, but included in Table 9.4 the data for only a few of the more important extractants. The reader is referred to a more extensive compilation for additional data of this type (Jones and Choppin, 1969).

Keller and Schreck (1969) have shown that Cm(III), as well as Ac(III), Am(III), and Cf(III), are extracted with β-diketone ligands as 1:3 chelates only, with stability constants ($\log \beta_3$) decreasing in the series Cf > Cm ~ Am > Ac. Keller *et al.* (1966) have also shown that Am(III) and Cm(III) are extracted from aqueous solutions into chloroform solutions of 8-hydroxyquinoline ligands as AnL_2Y, where L is the 8-hydroxyquinolate anion and Y is probably OH^-, in contrast to the lanthanides, which are extracted as LnL_3 chelates.

Distribution ratios (chloroform–water) have been reported for curium complexes with 8-hydroxyquinoline, cupferron, and *N*-benzoylphenylhydroxylamine (Akatsu *et al.*, 1968). Only 1:3 complexes with Cm(III) and Am(III) were reported, and extraction into the organic phase appears to be very high at pH values above 5. Solution interaction of Cm(III) with bis(salicylidene)ethylenediimine and derivatives has also been studied (Stroński and Rekas, 1973). With the reagent arsenazo-III, both Cm(III) and Am(III) form 1:1 and 1:2 complexes (Myasoedov *et al.*, 1970).

During the last 20 years, the use of neutral bifunctional compounds as extractants for trivalent actinides has been extensively investigated. These compounds include carbamoylmethylphosphonates, CMPOs, and diamides. The mechanism by which these extractants operate is still open to debate. Slope analysis studies often give varied results. For example, Mincher (1992) has reported the extraction of trivalent actinides (including Cm) by CMPO to be due to formation of $M(NO_3)_3(CMPO)_4$ complexes, whereas most other studies indicate a stoichiometry of the type $M(NO_3)_3L_3$ (Horwitz *et al.*, 1981). Similar confusion can be cited for the diamide extractants, although mechanistic studies have not been performed specifically with Cm for this class of ligands.

9.9 ANALYTICAL CHEMISTRY

The analysis for curium has been done by the typical methods for metal ions and alpha-emitting actinides, such as alpha, gamma, and neutron spectroscopy, nuclear track detection, photon/electron-rejecting alpha liquid scintillation, mass spectrometry, spectrophotometry of highly colored complexes such as arsenazo, and time-resolved laser-induced fluorescence or luminescence spectroscopy (Buijs, 1973). In most cases, at least some separations are required before analysis of curium.

9.9.1 Analysis of curium

The curium isotopes, 242, 243, and 244, emit high-energy alpha particles (see Table 9.1) that are easily quantified in the presence of lower-energy α emitters without extensive separations. Curium isotopes 245–248 emit lower-energy alpha particles and generally require more extensive separations before alpha analysis. Alpha spectrometry is typically used for curium determination, although photon/electron-rejecting alpha liquid scintillation has been shown to have lower detection limits when combined with extractive scintillators (Metzger *et al.*, 1995; Dacheux and Aupais, 1998). One extractive scintillator was a combination of HDEHP and CMPO, allowing the separation and analysis to occur in one step (Metzger *et al.*, 1995). The key to alpha spectrometry is the preparation of counting plates with minimal solids to degrade the energy of the alpha particles. Various deposition techniques have been used, including electrodeposition, evaporation, and precipitation of insoluble compounds (Trautmann and Folger, 1989; Kaye *et al.*, 1995; Gascon *et al.*, 1996; Rameback and Skalberg, 1998; Diakov *et al.*, 2001). Precipitation can involve addition of a lanthanide ion to act as a carrier for curium (Kaye *et al.*, 1995). Nuclear track analysis has been shown to be useful for very low concentrations of curium, such as environmental samples and waste streams at nuclear power plants (Lancsarics *et al.*, 1988; Espinosa *et al.*, 1995). The alpha energies were determined by the size of the track after calibration with sources of known energy.

Spontaneous fission occurs for the even isotopes of curium, allowing neutron counting to be used for their determination, especially for ^{244}Cm and ^{248}Cm, but this method requires pure isotopes for quantification (Trautmann and Folger, 1989). Curium analyses have been done by inductively coupled mass spectrometry and isotope dilution thermal ionization mass spectrometry after separation to obtain a pure curium solution (Kinard *et al.*, 1995; Niese and Gleisberg, 1995; Chartier and Aubert, 1999).

As has been mentioned previously, time-resolved laser-induced fluorescence spectroscopy has been shown to be an especially valuable tool for investigating Cm solution chemistry, but it has also proved useful for quantitative determination of Cm (Elesin *et al.*, 1973; Dem'yanova *et al.*, 1986; Yusov *et al.*, 1986a,b; Decambox *et al.*, 1989; Kim *et al.*, 1991; Myasoedov and Lebedev, 1991; Myasoedov, 1994; Moulin *et al.*, 1997; Dacheux and Aupais, 1998). The Cm fluorescence emission signal is strong enough that no separations from other transuranium or lanthanide elements are required to use this technique to quantify Cm ion in solution. Sensitivity for curium detection is about 5×10^{-11} M in carbonate solution without separation from matrix elements (Radchenko *et al.*, 1999). An even lower detection limit of 5×10^{-13} M has been observed at 612 nm (Moulin *et al.*, 1997).

9.9.2 Separations for analysis

Separations are a primary component of most analytical procedures. Initial separation is from non-radioactive elements and the large quantity of uranium that may be present in the sample. Plutonium is often separated to allow determination without interference from the higher actinides. Separation of curium from americium and the lanthanides is possible, but may not be necessary, depending on the method of final analysis. A variety of separation methods have been reported, including ion exchange, extraction chromatography, and solvent extraction, or combinations of several of these methods. Early work was summarized in Gmelin (Buijs, 1973). A more recent review summarizes many of the methods for analytical separations (Myasoedov, 1994).

Anion-exchange resins have been used with HCl and HNO_3 in both aqueous and aqueous–alcohol mixtures (Trautmann and Folger, 1989; Gascon *et al.*, 1996; Diakov *et al.*, 2001). Anion exchange alone usually results in a product containing all trivalent actinides and lanthanides. Cation exchange from HCl solutions has been used to separate lanthanides from actinides, or with α-hydroxyisobutyric acid to separate both lanthanides and actinides (Myasoedov, 1994). Anion exchange from HCl has also been used to remove uranium and plutonium, followed by a rapid separation of curium from americium by high-pressure liquid chromatography (HPLC) using 2-hydroxy-2-methylbutyric acid as the eluent (Trautmann and Folger, 1989). Americium–curium separation was rapid, with no overlap between curium and americium peaks. Anion exchange has been combined with HDEHP to separate an americium–curium product (Gascon *et al.*, 1996).

Another method involves a combination of extraction of plutonium with trioctylphosphine oxide in cyclohexane from HNO_3, then absorbing the metal ions onto Dowex® 50 resin from an HCl solution containing oxalic acid.

Washing the column with 2 M HCl removed impurities, followed by americium–curium elution in 6 M HNO_3 (Niese and Gleisberg, 1995).

Extraction chromatography with CMPO on an organic support allows ready separation of an americium and a curium fraction. A commercially available resin based on CMPO has been used (Kaye *et al.*, 1995; Maxwell, 1996).

Separations by solvent extraction include extraction of all the actinides into HDEHP, with selective back-extraction of americium and curium into 5 M HNO_3 (Rameback and Skalberg, 1998). Another method used extraction of plutonium from HCl solution with triisooctylamine in xylene. Americium and curium were then extracted with dibutyl-*N*,*N*-diethylcarbamoyl phosphonate and stripped into dilute acid (Kimura *et al.*, 1996). CMPO has been used extensively for solvent extraction separations of americium and curium (Myasoedov and Lebedev, 1991). Other separation methods are given in the review by Myasoedov (1994).

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