

CHAPTER ELEVEN

CALIFORNIUM

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11.1	Introduction	1499	11.6	The metallic state	1517
11.2	Preparation and nuclear properties	1502	11.7	Solid compounds	1527
11.3	Applications	1505	11.8	Solution chemistry	1545
11.4	Separation and purification	1507	11.9	Gas-phase studies	1559
11.5	Electronic properties and structure	1513	11.10	Concluding remarks	1561
			References	1563	

11.1 INTRODUCTION

The discovery of californium came in the era of the syntheses and identifications of other transplutonium elements, following the end of World War II. The discovery of the element californium, like many of the other actinide elements, hinged on the development of new experimental techniques in conjunction with predictions based on nuclear systematics. Californium was named after the University and State of California where many of the transuranium elements were first identified. This element was discovered by Thompson, Street, Ghiorso, and Seaborg (Hyde *et al.*, 1971; Seaborg and Loveland, 1990) in February, 1950. The discovery of californium came only 2 months after the preparation and identification of the first isotope of berkelium, element 97 (see Chapter 10). An account of the discovery and reminiscences about the early work on californium has been given by Ghiorso (1983).

The first preparative method for californium was to bombard microgram targets of ^{242}Cm with 35 MeV helium ions in a 60 in. cyclotron. This produced ^{244}Cf by a $(\alpha, 2n)$ reaction which decayed primarily by alpha emission ($t_{1/2} = 19.4$ min, with two different alpha energies having a 75% and 25% branching ratios; see Table 11.1). This isotope also has a small decay branch that proceeds via electron capture. Since element 98 ('eka-dysprosium') was expected to have a stable tripositive oxidation state in aqueous solution, its elution behavior in chromatographic separation schemes was predicted and this was used as a guide to estimate which collection fractions should be examined for the new element. In addition to acquire a high degree of decontamination

Table 11.1 Nuclear properties of californium isotopes*.

Mass number	Half-life	Mode of decay	Main radiations (MeV)	Method of production
237**	2.1 s	EC, SF		$^{206}\text{Pb}(^{34}\text{S},3\text{n})$
238**	21 ms	EC, SF		$^{207}\text{Pb}(^{34}\text{S},3\text{n})$
239	39 s	α	α 7.63	^{243}Fm daughter
240	1.06 min	α	α 7.59	$^{233}\text{U}(^{12}\text{C},5\text{n})$
241	3.8 min	α	α 7.335	$^{233}\text{U}(^{12}\text{C},4\text{n})$
242	3.7 min	α	α 7.385 (~ 80%) 7.351 (~ 20%)	$^{233}\text{U}(^{12}\text{C},3\text{n})$ $^{235}\text{U}(^{12}\text{C},5\text{n})$
243	10.7 min	EC ~ 86% α ~ 14%	α 7.06	$^{235}\text{U}(^{12}\text{C},4\text{n})$
244	19.4 min	α	α 7.210 (75%) 7.168 (25%)	$^{244}\text{Cm}(\alpha,4\text{n})$ $^{236}\text{U}(^{12}\text{C},4\text{n})$
245	45.0 min	EC ~ 70% α ~ 30%	α 7.137	$^{244}\text{Cm}(\alpha,3\text{n})$ $^{238}\text{U}(^{12}\text{C},5\text{n})$
246	35.7 h 2.0×10^3 yr	α SF	α 6.758 (78%) 6.719 (22%)	$^{244}\text{Cm}(\alpha,2\text{n})$ $^{246}\text{Cm}(\alpha,4\text{n})$
247	3.11 h	β stable EC 99.96% α 0.035%	α 6.296 (95%) γ 0.294 (1.0%)	$^{246}\text{Cm}(\alpha,3\text{n})$ $^{244}\text{Cm}(\alpha,\text{n})$
248	334 d 3.2×10^4 yr	α SF β stable	α 6.258 (80.0%) 6.217 (19.6%)	$^{246}\text{Cm}(\alpha,2\text{n})$
249	351 yr 6.9×10^{10} yr	α SF	α 6.194 (2.2%) 5.812 (84.4%) γ 0.388 (66%)	^{249}Bk daughter
250	13.08 yr 1.7×10^4 yr	α SF	α 6.031 (83%) 5.989 (17%)	multiple n capture
251	898 yr	α	α 5.851 (27%) 5.677 (35%) γ 0.177 (17%)	multiple n capture
252	2.645 yr	α 96.91% SF 3.09%	α 6.118 (84%) 6.076 (15.8%)	multiple n capture
253	17.81 d	β^- 99.69% α 0.31%	α 5.979 (95%) 5.921 (5%)	multiple n capture
254	60.5 d	SF 99.69% α 0.31%	α 5.834 (83%) 5.792 (17%)	multiple n capture
255	1.4 h	β^-		$^{254}\text{Cf}(\text{n},\gamma)$
256	12.3 min	SF		$^{254}\text{Cf}(\text{t},\text{p})$

SF = spontaneous fission; EC = electron capture

* See Appendix II.

** The existence of these isotopes has been questioned but included for completeness.

from other radionuclides, it was also necessary that the chemical separations be completed rapidly (within about 1 h) due to the short half-life projected for this isotope of californium.

Californium, element 98, is in the second half of the actinide series, where its 5f electrons are further removed from the valence electrons than in the lighter

actinide elements. It is this effect that makes californium more 'lanthanide-like' in many compounds and in solutions. However, in progressing across this half of the actinide series, there is also an increasing tendency for a divalent metallic state and the formation of a divalent state in compounds, and several compounds containing Cf(II) are known. Thus, its comparison to the lanthanide elements has limitations, as seen from topics discussed throughout this chapter. Unlike members of the second half of the lanthanide series, which may exhibit either a divalent or tetravalent oxidation state in addition to their more common trivalent state, californium is known to exhibit a divalent, trivalent, and tetravalent state in compounds. In solution, the trivalent state is dominant, although the II, IV states, and a potential V state have been reported. In its elemental state, californium properties differ from those exhibited by its lanthanide homolog, dysprosium.

When the existence of californium was established, scientific interests and efforts progressed to prepare other isotopes of this element, to determine their nuclear properties, and to investigate the chemistry of the element. These initial studies were performed using only small numbers of atoms, but it is to the credit of the early investigators that considerable amounts of chemical and nuclear data were accumulated in their work. Tracer experiments were sufficient to establish the stability of Cf(III) in solution, as well as some of the element's basic chemistry. Additional information on the chemistry of californium was generated as microgram quantities became available, which also permitted the preparation and study of solid compounds. The first compound of californium of a definitive structure (the oxychloride by Cunningham and Wallmann) was determined a decade after the discovery of the element (Seaborg and Loveland, 1990).

Larger quantities of the transplutonium elements, including californium, subsequently became available by the development of a reactor irradiation program that was initiated in the mid-1960s by the former U.S. Atomic Energy Commission. The U.S. Department of Energy retains the ability to produce these transplutonium elements, including sub-gram amounts of the different californium isotopes yearly in the High-Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory, Oak Ridge, Tennessee. The continued production at HFIR may be limited in the future. Transplutonium elements are also produced in high-flux reactors at Dimitrovgrad in the Russian Federation, and potentially in other reactors. Smaller amounts of californium can be generated by irradiation of special targets in accelerators, but in the best case these smaller quantities only serve for chemical tracer studies or for determining their nuclear properties.

Reactor-produced californium consists of californium isotopes from ^{249}Cf through ^{254}Cf , with the major isotope produced being ^{252}Cf . Californium isotopes produced in accelerators normally have lower atomic masses and obtained in much smaller quantities. Considering these production schemes and the californium daughters formed as daughter products of other decaying isotopes, californium isotopes with masses as small as 237 and as large as 256

have been reported. An example of accelerator-produced californium is the generation of ^{242}Cf reported by Sikkeland and Ghiorso (1967), in the time frame when HFIR was producing californium isotopes through successive neutron capture processes.

This chapter focuses on the chemistry and physical properties of californium that are available in the open literature, and supplementing/evaluating this information when appropriate. An effort was made to minimize the number of references to technical reports, unpublished information, etc., except for cases when such a citation was warranted. The number of publications dealing with technological and medical applications of neutrons from ^{252}Cf is very large. There are numerous references to work done with californium covering biological studies, radiotherapy, neutron radiography, neutron activation analyses, dosimetry, etc. Some 70% of the work published during the last decade concerns efforts in these arenas using the ^{252}Cf isotope. The remaining reports deal with chemical studies and separation work, which normally employ the longer-lived ^{249}Cf isotope.

A significant amount of the basic chemical work on californium has been reported in different publications, but this should not be construed to interpret that additional chemical or physical studies are not needed! Indeed, given some of the recent advances in scientific techniques (i.e. those involving synchrotron sources, such as extended X-ray absorption fine structure (EXAFS), X-ray absorption near edge structure (XANES), photoelectron scattering, etc.), new studies should be pursued with californium and its compounds, and such investigations would be expected to yield even further insights into this element's science. Some of the more recent thrusts in the chemistry and physics of californium have involved its gas-phase chemistry, high-pressure studies of the metal and compounds, and new separation science. These topics are covered in the different sections of this chapter.

11.2 PREPARATION AND NUCLEAR PROPERTIES

It is unlikely that, nor have there been reports or evidence of, primordial californium in nature. Thus, isotopes of californium with mass numbers between 237 and 256 have been prepared as man-made isotopes. A summary of methods for the preparation of and nuclear data for these isotopes is given in Table 11.1, and in Appendix II. The lighter masses (neutron deficient) are produced by accelerator methods, (e.g. the helium bombardment of curium isotopes) which was the initial technique used to generate and discover californium. But californium isotopes can also be prepared by heavy-ion bombardment of elements other than curium. Examples of the latter are bombarding thorium with oxygen ions, and uranium with carbon or nitrogen ions. These preparations involve high-energy accelerators and produce only limited numbers of atoms of the product nucleus, and therefore are not useful for producing

weighable quantities (i.e. even micrograms quantities) of californium needed for the preparation of pure solid compounds. An excellent discussion on the history, preparation, and nuclear properties of californium isotopes is given by Hyde *et al.* (1971) and Seaborg and Loveland (1990).

Californium isotopes with larger neutron contents (higher mass numbers) are usually prepared by irradiation of targets (plutonium through curium) in nuclear reactors that have a high neutron flux ($>10^{15}$ neutrons $\text{cm}^{-2} \text{s}^{-1}$). These and even heavier californium isotopes are also generated in nuclear explosions, where for short periods of time the neutron flux is even higher (fluence $> 10^{29}$ neutrons cm^{-2}). In the latter case, the formation of higher- Z elements and heavier isotopes is favored due to the high density of neutrons and in time spans that are short relative to the various decay half-lives of the materials formed. In principle, the objective would be to favor the significant neutron capture by the uranium to plutonium atoms present in such devices over the decay process of the products formed. This builds very rapidly by capture beyond the particularly short-lived isotopes before they can decay appreciably. Although transplutonium elements have been intentionally produced in underground nuclear explosions, processing of large amounts of 'ore material' (rock debris) in reasonable time periods makes this preparation procedure for these elements impracticable. Thus, weighable quantities of californium are best obtained as direct or indirect products from irradiation of materials in nuclear reactors.

Since the mid-1960s californium has been produced in special nuclear reactors (i.e. the HFIR at Oak Ridge National Laboratory). Most recently the initial targets consist mainly of curium isotopes (^{244}Cm through ^{248}Cm isotopes), which are irradiated in the reactor by neutrons to produce californium isotopes from ^{249}Cf through ^{255}Cf with the major isotope being ^{252}Cf . The HFIR located at Oak Ridge National Laboratory can produce currently up to 0.5 g of ^{252}Cf (together with other californium isotopes) per year. By using larger reactors, this quantity could be conceivably be increased to produce several grams of ^{252}Cf per year, and at one time this was planned in the U.S. but the greater need for this isotope never materialized.

The ^{252}Cf isotope has a 2.6 year alpha decay half-life, and a 85 year spontaneous fission branching half-life, which is the source of the neutrons it emits. Neutrons from its fission offer the main use for this isotope (i.e. neutron activation analysis, medical treatments, neutron radiography, etc.), but it is also useful for chemical tracer work, given its high specific alpha activity and greater availability. However, the neutron field (3×10^6 neutrons $\text{s}^{-1} \mu\text{g}^{-1}$) and the gamma radiation accompanying fission and/or the alpha decay of ^{252}Cf (up to 7 MeV gammas) normally precludes its use for basic chemical/physical studies, as considerable shielding is required to protect personnel and equipment from even microgram amounts of it (gloved box limits are normally only a few micrograms). As a result, the mixture of californium isotopes obtained directly from reactors (which contains ^{252}Cf as the primary isotope) is not

generally considered when multiple micrograms or more of californium are needed for studies without extensive shielding. Instead, the ^{249}Cf isotope is used.

Although in principle, ^{251}Cf has the most desirable radiation characteristics with regard to performing research studies, and it could be isolated from mixed californium isotopes using a mass separator, the cost and low yields (10%) makes this process unattractive. This isotope is only formed at low concentrations, as a result of its high-neutron capture and fission cross sections.

Another isotope, ^{253}Cf , is important as a parent for obtaining isotopically pure ^{253}Es (see Chapter 12). If a chemically pure (i.e. free of einsteinium) fraction of mixed californium isotopes from a reactor is obtained, and the ^{253}Cf present is allowed to decay, then a subsequent chemical separation of this californium fraction allows recovery of its pure ^{253}Es daughter.

For the majority of basic studies, especially those requiring weighable quantities of californium, the ^{249}Cf isotope is desired. Its alpha half-life of 351 years makes it suitable for chemical/physical experiments in gloved boxes, although there is still significant gamma radiation associated with its decay, which may require some shielding for protection. Typically, gloved box studies are rather limited to less than 10 mg because of radiation levels.

Isotopically pure ^{249}Cf is best obtained from the decay of ^{249}Bk (beta emitter, half-life of 330 days; see Appendix II). This latter isotope is the major berkelium isotope obtained from reactor irradiations (^{250}Bk is also formed in reactors but it has a 3.217 h half-life and rapidly decays; see appendix II). Thus, to obtain ^{249}Cf free of other californium isotopes for research studies, it is necessary to generate berkelium in a reactor and then separate it chemically from the other transplutonium elements present. After sufficient decay of the ^{249}Bk to ^{249}Cf , the latter can be subsequently separated chemically from the berkelium fraction. It is possible to obtain multi-milligrams (up to 60 mg at the HFIR at Oak Ridge National Laboratory) per year in this manner. And, as the half-life of ^{249}Cf is 351 years, it is possible to accumulate larger amounts of it over time by recovery operations. The only other known production source of ^{249}Bk in significant quantities, and hence a source of isotopically pure ^{249}Cf by its decay, is in Russia but the quantity available there is often smaller. It is then possible to provide in relatively short time frames multi-milligram amounts of ^{249}Cf .

The half-life of ^{250}Cf (13.08 years), which is produced along with other californium isotopes in reactors, has been determined recently (Popov *et al.*, 1996). The ^{238}Cf nuclide had been reported from bombardment of lead isotopes (^{207}Pb and ^{208}Pb) with ^{34}S and ^{36}S ions (Lazarev *et al.*, 1995). Its mode of decay is suggested to occur by spontaneous fission.

The K series of X-rays generated from californium has been discussed by Dittner and Bemis (1972), and can be used for the identification of californium during its decay processes. The vibration states in californium nuclei have been discussed by Ahmad (1980).

11.3 APPLICATIONS

As mentioned in Section 11.2, californium produced in nuclear reactors is mainly comprised of ^{252}Cf , and only a small quantity of this isotope mixture can be employed for chemical/physical studies outside of heavy shielding or hot cells. Thus, the applications for this ^{252}Cf isotope are for: (1) neutron emissions; (2) a target material for producing transcalifornium elements; (3) a californium tracer, using its higher specific alpha activity; and/or (4) a parent for obtaining ^{248}Cm (^{248}Cm is the alpha-decay product of ^{252}Cf ; see Chapter 9). This long-lived isotope of curium is very useful for basic studies of curium. In practice, a mixture of ^{246}Cm , ^{248}Cm , and small amounts of other curium isotopes are obtained from the decayed californium reactor products ($\sim 97\%$ ^{248}Cm and 3% ^{246}Cm from the alpha decays of ^{252}Cf and ^{250}Cf isotopes present).

Although it is beyond the scope of this work to review such applications of ^{252}Cf fully, or mixtures where this is the main californium isotope, its potential usefulness warrants some coverage here. The reader is also referred to: the ^{252}Cf Information Center at the Savannah River Laboratory (USAEC Rept, 1969), Georgia, U.S.A. or the ^{252}Cf User Facility located at Oak Ridge National Laboratory. More extensive information is also given by Martin *et al.* (1997, 2000) and by Osborne-Lee and Alexander (1995). When ^{252}Cf is used as a neutron source, the data listed in Table 11.2 may be useful. Martin *et al.* (1998; 2004) have discussed applications of ^{252}Cf .

Considering the spontaneous fission half-lives, ^{252}Cf has the shortest one (85 years), a 3.09% fission fraction and yields 3.767 neutrons per fission. One observes a range from 2 to 3.8 neutrons per event for other fissioning actinide isotopes. The calculated neutron emission rate for ^{252}Cf is 2.3×10^{12} neutrons $\text{s}^{-1} \text{g}^{-1}$, although one would rarely expect to have a gram. In contrast, high-flux reactors have fluxes of three orders of magnitude higher. But, this rate for ^{252}Cf is lower than that for ^{254}Cf (1.2×10^{15} neutrons $\text{s}^{-1} \text{g}^{-1}$) due to its 99.7% fission fraction and 3.83 neutrons per fission event. But, this later isotope is not readily available in any significant quantities. For comparison, the neutron emission for ^{248}Cm , which also undergoes spontaneous fission, is only 4.2×10^7 neutrons $\text{s}^{-1} \text{g}^{-1}$. It has a long alpha decay having a half-life of 3×10^5 years, 8.39% fission fraction, and 3.2 neutrons per fission event. Data are summarized in Table 11.2.

Applications of ^{252}Cf can be broadly classified as medical, analyses, and biological studies, where the majority of the work involves in one way or the other the spontaneous-fission neutrons emitted from ^{252}Cf (Karelin *et al.*, 1997). These sources have been useful in such areas as neutron activation analysis, neutron radiography (a technique that complements X-ray radiography), and medical therapy for treatment of cancer. They are most useful where access to nuclear reactors is not possible, or convenient, and/or where a lower neutron flux is adequate for the need at hand. An important application for ^{252}Cf is to

Table 11.2 Data for ^{252}Cf and other selected neutron sources*.

<i>Isotope</i>	<i>Half Life (yrs)</i>	<i>Specific Activity (Ci g⁻¹)</i>	<i>Spontaneous Fission Half-Life (yrs)</i>	<i>Fission Fraction (%)</i>	<i>Neutrons per Fission</i>	<i>Neutron Rate (n s⁻¹g⁻¹)</i>
^{252}Cf	2.645	5.38×10^2	85	3.09	3.767	2.3×10^{12}
^{252}Cf alpha energies:						
			6.118 (84%)			
			6.076 (16%)			
Specific heat from decay of ^{252}Cf						
			38 W g ⁻¹			
Neutrons from (α, n) reaction on Al metal: 1.3×10^7 n s ⁻¹ g ⁻¹						
^{254}Cf	0.17	8.45×10^3	–	99.7	3.83	1.2×10^{15}
^{248}Cm	3.4×10^5	4.25×10^{-3}	41	8.39	3.16	4.2×10^7

*Sources: The Health Physics and Radiological Health Handbook (1998); Osborne-Lee and Alexander (1995).

provide neutrons for the initial start-up of nuclear reactors (Osborne-Lee and Alexander, 1995).

Portable neutron activation analysis systems using ^{252}Cf have been designed for use in deep-sea exploration for minerals, or for space probes (Senftle *et al.*, 1969; Wiggins *et al.*, 1969; Filippov, 1979; Bakiev *et al.*, 1991).

Various sizes and forms of ^{252}Cf sources have been designed for medical applications, both for external irradiation and for internal implantation. How extensive the practical applications of ^{252}Cf can be determined by the success of experiments using this nuclide. The more extensive shielding hinders medical applications needed for the neutrons (greater thickness of paraffin for neutrons versus that of lead for shielding X-rays). Remote operation/delivery of the californium sources to the application site aids in this respect. A large number of such applications have been reported (Castro *et al.*, 1973; Poda and Hall, 1975; Zech *et al.*, 1976a,b; Maruyama *et al.*, 1978, 1980, 1991; Belenkl *et al.*, 1991; Yanch *et al.*, 1993; Patchell *et al.*, 1997; Knapp *et al.*, 1999; Rivard, 1999a,b, 2000a–c; Rivard *et al.*, 1999, 2002, 2004; Wanwilairat *et al.*, 2000; Tacev *et al.*, 2003a,b, 2004a,b).

Studies involving the injection of ^{252}Cf into beagles (Lloyd *et al.*, 1972a,b, 1976; Taylor *et al.*, 1972) and into swine (Mahony *et al.*, 1973; Beamer *et al.*, 1974) have also been reported. Investigations involving mouse mammary-carcinoma and bone were also reported (Fu and Phillips, 1973).

Several biological studies have used ^{252}Cf to examine the effects of neutron radiation. Work on DNA (Tacev *et al.*, 1998; Florjan *et al.*, 1999) has been done, as well as work on its bioefficiency (Cebulska-Wasilewska *et al.*, 1999). The biokinetics of it in marine isopods (Carvalho and Fowler, 1985) and the survival of human cells under irradiation (Todd *et al.*, 1984) have also been published. A solvent extraction/liquid scintillation counting method for determining ^{252}Cf in biological samples has been discussed (Miglio, 1978).

There is an extensive list of reports and publications dealing with the applications. The reader is referred to these for more extensive information. One useful source in this regard is an ORNL Report (Osborne-Lee and Alexander, 1995). Other sources of information involve the use of ^{252}Cf : for cervical carcinoma treatment (a 12 year review by Tacev *et al.*, 2004a,b); a review of other clinical applications (Mignano and Rivard, 2004); and advances in neutron radiographic techniques (Berger, 2004). Dullmann *et al.* (2003) also discuss fission fragment sources using ^{252}Cf .

11.4 SEPARATION AND PURIFICATION

The choice of a separation and purification scheme for californium depends on the nature of its source, the particular isotopes of californium involved, the amount of material, the impurities present, as well as several other factors. In short, the best procedure needs to be customized to the particular situation at

hand. Usually, ion exchange is involved either as the main separation technique, or at least in some secondary capacity. Since californium in aqueous solutions is normally stable only in its tripositive state, oxidation–reduction cycles are not useful for separation. Due to the very similar chemical behavior of the tripositive transplutonium elements, as well as lanthanide ions of comparable ionic radii (i.e. Sm–Tb), the separation chemistry for californium employed must often rely on small differences in chemical behaviors for the different materials to be separated.

The separation procedure most suitable for californium isotopes generated in accelerators may not be the same as that used for californium produced in reactor targets. In some accelerator experiments, the desired californium isotopes generated may be physically separated via recoil mechanisms from the targets, which simplifies the separations and shortens the time required for the shorter-lived isotopes. The need for nuclear or radioactive purity, as opposed to chemical purity, will also affect the particular separation processes to be used. A considerable amount of information on californium chemistry was determined using tracer levels of californium, usually using ^{252}Cf isotope. The major purification schemes for californium at tracer levels have frequently involved ion-exchange techniques to separate californium from other transcurium elements.

For purposes of separation, the transplutonium elements can be placed into two groups: (1) americium and curium and (2) the group of the next several transcurium elements, which includes californium. The separation of californium from its neighbors, especially einsteinium, is therefore more difficult than separating it from americium/curium or from the lighter actinides. Separation of californium from berkelium is simplified by the ability to oxidize berkelium in an aqueous medium, which then permits the solvent extraction of Bk(IV) away from Cf(III).

A number of procedures have been used for the separation/purification of californium. One of the early ion-exchange methods involved the use of cation-exchange resin (Dowex 50) and ammonium citrate or ammonium lactate as eluants. A superior eluant, ammonium α -hydroxyisobutyrate (α -HIBA), was first used over 30 years ago (Choppin *et al.*, 1956), and this reagent is still in use today for the separation of californium from other actinides. Thompson *et al.*, (1954). A very useful group separation between the lanthanides and actinides can be accomplished using concentrated hydrochloric acid as an eluant for the transcurium elements sorbed on cation resin; the separation is improved by using an ethanol–hydrochloric acid mixture as an eluant (Street and Seaborg, 1950). Another method for separation elements from the two groups, especially with smaller quantities has been the use of TEVATM columns (Horwitz *et al.*, 1992, 1993, 1995; Porter *et al.*, 1997). These resin columns are available commercially (Eichrom Industries) and employ thiocyanate and formic acid solutions. The greater complexing ability of the transplutonium elements is evident as they desorb ahead of the lanthanide elements when using these separation approaches. The separation of californium from its actinide neighbors, using

cation- or anion-exchange resins, or elution with either hydrochloric or ethanol-hydrochloric acid mixture, alone is not feasible.

Anion-exchange separation procedures using slightly acidic LiNO_3 or $\text{Al}(\text{NO}_3)_3$ solutions (Surls and Choppin, 1957; Adar *et al.*, 1963; Marcus *et al.*, 1963) or ethylenediaminetetraacetic acid (EDTA; Baybarz, 1966a,b) as eluants have also been reported. Several extraction procedures have been used, such as the extraction of trivalent actinides from concentrated LiCl or LiNO_3 (slightly acidic) solutions and the use of trilaurylamine or other trialkylamines (Baybarz *et al.*, 1963) or quaternary ammonium salts (Moore, 1964, 1966; Horwitz *et al.*, 1966). Extraction chromatography using quaternary ammonium salts or bis(2-ethylhexyl)phosphoric acid (HDEHP) as a stationary phase has also been employed (Gavrilov *et al.*, 1966; Horwitz *et al.*, 1967, 1969a,b). Inorganic ion exchangers such as zirconium phosphate materials have limited applications for californium separations due to their lower selectivity as compared to organic-type extractant materials.

Several summaries of separation procedures have been discussed and can be found in: Miller (1967), Keller (1971), Myasoedov *et al.* (1974), Bigelow (1974), Ishimori (1980), King *et al.* (1981), Collins *et al.* (1981), Benker *et al.* (1981), and Campbell (1981).

Most extraction procedures are useful for separating californium from americium/curium or from lighter actinides, but are limited for separating it from other transcurium elements. For example, HDEHP dissolved in an aromatic diluent has been used to separate Cf and Cm providing a separation factor of about 50, but it is not useful for californium-einsteinium separations. Efforts continue to find new and better extractants with the aim of improving separation factors and selectivity. It is unlikely that a specific extractant for californium alone will be developed but new materials may provide improved separation factors over methods presently used or known. Reviews that discuss californium extraction chemistry are available (Bigelow *et al.*, 1980, 1981; Myasoedov *et al.*, 1980; Shoun and McDowell, 1980).

One application of HDEHP on an inert support material, such as porous glass (i.e. Bioglass), is worth noting. An excellent separation between curium and californium can be achieved using this approach, which is important process for recovering $^{248}\text{Cm}/^{246}\text{Cm}$ from their $^{252}\text{Cf}/^{250}\text{Cf}$ parents. In this procedure, the actinides are loaded onto a column with the agent, and then eluted with 0.1 M HNO_3 . As the californium is retained more strongly due to complexation, the curium is eluted first.

It is also useful to note that berkelium and californium can be readily separated by solvent extraction of Bk(IV) away from Cf(III). This separation is important since isotopically pure ^{249}Cf is obtained from the beta decay of ^{249}Bk . The berkelium can be readily oxidized to Bk(IV) in aqueous solution with a strong oxidant (i.e. bromate ion) in nitric acid solution.

Since the majority of californium is produced in nuclear reactors, or obtained as a by-product from reactor-produced ^{249}Bk , it is appropriate to discuss briefly

a flowsheet for the separation techniques employed in recovering californium for reactor targets. If uranium or plutonium is present as the main target material, then these elements must also be separated from the transplutonium element group (containing the californium) in addition to fission products (lanthanide elements, transition metals, etc.) and other products (aluminum from target assemblies, etc.). If americium and curium, or pure curium, is the main starting material, then only small amounts (if any) of the lighter actinides may be present, which simplifies the situation.

The general separation scheme, Scheme A in Fig. 11.1, is for separating and purifying californium from the HFIR products containing uranium and plutonium at the Oak Ridge National Laboratory. Reports on different aspects of these purification processes are available (Baybarz *et al.*, 1973; King *et al.*, 1981; Bigelow *et al.*, 1981). The procedure begins with alkali dissolution of the aluminum target holders used for the reactor. This leaves the insoluble actinide oxides, which are subsequently dissolved in hydrochloric or nitric acid to generate a solution of the elements to be separated.

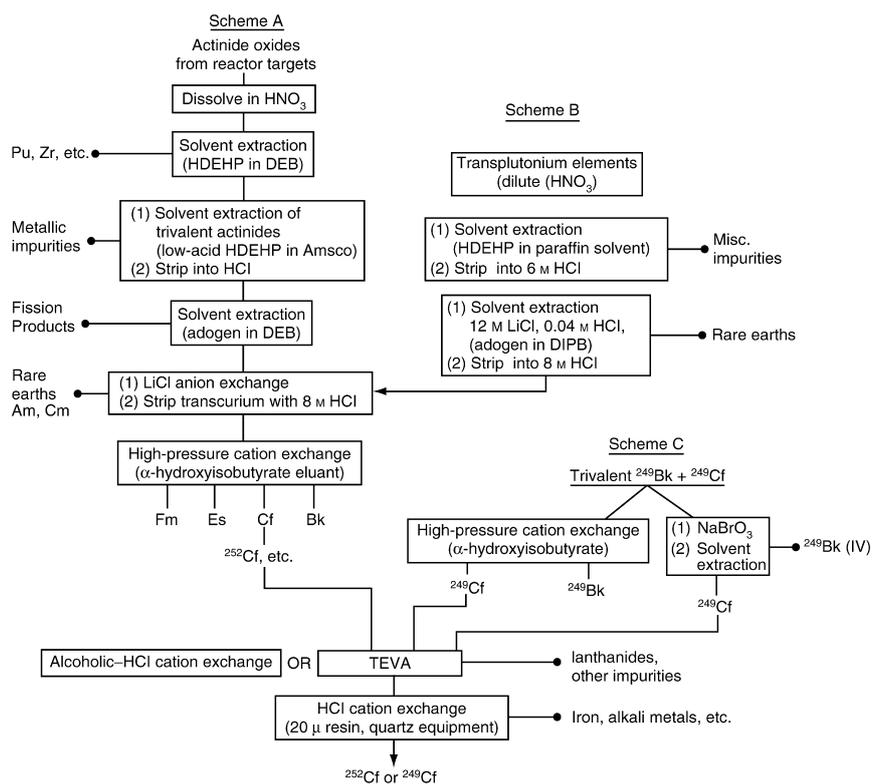


Fig. 11.1 Separation and purification scheme for californium.

Solvent extraction (HDEHP in an aromatic diluent as diethylbenzene) (DEB) removes plutonium and zirconium from the system. Scheme B is given for the situation where only the transplutonium elements are present (i.e. starting with americium and curium targets rather than plutonium).

In both cases, the transplutonium elements are then extracted with HDEHP in an aliphatic solvent, and a subsequent amine extraction (adogen) of these actinides removes them from most of the fission products. At this point, the product contains the transplutonium elements and any lanthanides present (fission products). A LiCl anion-exchange process partitions the transcurium elements from americium, curium, and the lanthanides, leaving the transcurium elements as a separate fraction. Scheme B in the figure considers only mixtures of the transplutonium elements.

The transcurium elements (Bk, Cf, Es, and some Fm) are then separated on high-pressure cation-exchange columns. Using a buffered α -hydroxyisobutyric acid solution as an eluant, californium is obtained as a separate fraction using a high-pressure ion-exchange process (very small resin particles, elevated temperature, at 80°C). The subsequent treatment of the different fractions obtained from this process depends on several factors, which include the final use of the material. The purification requirements for the californium isotopes produced directly in the reactor are based on whether Es or Cm daughters will be recovered, or the medical/industrial uses of the californium isotopes.

The californium fraction is further treated to remove residual lanthanide elements; this is especially important for nuclear studies where traces of radioactive lanthanide isotopes are detrimental, or for target materials, where unwanted reaction products may be generated from any impurities present. An ethanol–hydrochloric column is shown in Fig. 11.1, but it could also be replaced by a TEVA™ column. Horwitz *et al.*, (1992, 1993, 1995); Porter *et al.*, (1997).

Since most basic research studies involving milligram quantities of californium make use of ^{249}Cf obtained from the decay of ^{249}Bk , the purification requirements and processes for the californium produced in this manner is different, and shown in Scheme C in Fig. 11.1. Here, the material normally consists of only ^{249}Bk and ^{249}Cf isotopes plus any non-actinide impurities (i.e. accumulated from berkelium used in research studies). The objective is then to separate californium from its berkelium parent and any other impurities that may be present. To achieve the very high chemical purity desired for basic research work on californium, different things must be considered and the necessary separation processes must be addressed on an individual basis. The easiest situation is when the ^{249}Bk precursor for ^{249}Cf is already available in a highly pure state, and the separation of the californium involves only its separation from a relatively pure parent material. In this case, Scheme C in the figure could apply. For separating berkelium and californium, either a cation-exchange column (with α -hydroxyisobutyrate as the complexing agent) or the solvent extraction of berkelium as Bk(IV) away from trivalent californium (several different extracts schemes can be used). In the latter process, the

berkelium is first oxidized to Bk(IV) in solution with bromate ions, and the californium remains trivalent. An advantage with the ion-exchange process is that it avoids generating higher acid solutions and does not add bromide or bromate ions to the californium fraction.

In general, the purification of ^{249}Cf normally involves multiple pressurized cation-exchange columns with 0.25 M α -hydroxyisobutyric acid as an eluant (using solutions of variable pH from 3.8 to 4.2 at 80°C) to separate californium from other transplutonium elements, which also provides a general purification from other impurities than actinides. Then, a cation-exchange column with an ethanol-hydrochloric acid as an eluant, or a TEVA column, can remove lanthanide elements, alkaline earths, alkali metals, iron, nickel, etc. The columns, especially the final column and product receiver, are often constructed of acid-leached quartz. Special alpha detectors are used to determine the fractions that contain the californium. Using this process, a very pure californium chloride product is obtained, which can then be used for preparing compounds or the metal of californium for research.

Additional separation approaches have been reported in more recent publications. Firsova *et al.* (1998) have used bis(1-phenyl-3-methyl-4-acylpyrazolol-5-one) and its derivatives for solvent extraction, and other chromatographic separation methods (Firsova *et al.*, 1996) for separating berkelium and californium. Extractions using 4-benzoyl-2, 4-dichloro-5-methyl-2-phenyl-3H-pyrazol-3-thione, and tri-*n*-octylphosphine oxide (TOPO) have also been tested (Hannink *et al.*, 1992). Separation exclusion chromatography techniques have also been applied for separating californium from americium, curium, and lanthanides (Firsova *et al.*, 1990). The transplutonium elements have also been extracted from carbonate solutions using oligomers and alkylphenol derivatives (Karalova *et al.*, 1990), and extraction chromatography results with DHDECMP in nitric acid and characterization of DHDECMP/XAD-4 resins have been tested in the purification process (Kimura and Akatsu, 1991).

Extractions approaches for Cf(III) have also been done with aqueous pyrophosphates and lithium polyphosphate solutions with HDEHP (Chakravorty *et al.*, 1989). Extractions have also used HDEHP in nitric acid solutions (Kasimov and Skobelev, 1987). A modified ion-exchange procedure using α -hydroxyl-2-methyl butyrate was reported by Vobecky (1989). The separation of einsteinium from californium irradiation targets by ion exchange has been discussed by Elesin *et al.* (1986). The separation of californium using different salts of HDEHP was published by Dedov *et al.* (1986a,b). The extraction of magnesium and its influence on californium extraction via HDEHP for citric acid-magnesium nitrate systems has also been discussed (Kovantseva *et al.*, 1986). The effect of cations on exchange chromatography of curium and californium has been reported (Erin *et al.*, 1981) and the complexation of Cf(III) in perchlorates was also reported (Lebedev and Mazur, 1981). A simple separation approach for special applications has been suggested by Guseva *et al.* (1973), and a curium-californium extraction chromatography approach

was published by Aly and Abdelras (1972). The use of 8-hydroxyquinoline and 5,7-dichloro-8-hydroxyquinoline for extraction of californium was suggested by Feinauser and Keller (1969).

Three extraction studies involving californium were reported by Horwitz and coworkers. One study involved bis(2-ethyl)orthophosphoric acid (Horwitz *et al.*, 1969a); a second report was made on the same system (Horwitz *et al.*, 1969b); and the third effort was an extraction using high molecular weight quaternary amines in ammonium nitrate solutions (Horwitz *et al.*, 1967). The chelating and extraction of Cf(III) by acetylacetonone and derivatives of it were also reported by Keller and Schreck (1969). Fused salt, molten metal processes have also been examined for separating californium (Knighton and Steunenberg, 1966; Mailen and Ferris, 1971). The analytical chemistry of the actinides has been reviewed by Myasoedov and Lebedev (1991), and several aspects of separation chemistry are also discussed in this work.

In principle, an alternative procedure for the separation of californium in special circumstances may be to reduce a mixture of actinide oxides with thorium metal under vacuum, and distill away the more volatile californium metal and then condense it on a suitable receiver (Haire, 1982). The separation of californium oxide from curium oxide using a vacuum sublimation procedure was also suggested (Aleksandrov *et al.*, 1972).

11.5 ELECTRONIC PROPERTIES AND STRUCTURE

A considerable amount of spectroscopic data has been obtained for californium and a number of theoretical calculations have been made concerning its energy levels. The californium neutral atom's ground state is assigned as $5f^{10}7s^2$ (5I_8) and the Cf^+ ground state as $5f^{10}7s$ ($^6I_{17/2}$) (Worden and Conway, 1970; Martin *et al.*, 1974; Blaise and Wyart, 1992; for further details see Chapter 16). The ionization energy for the neutral californium atom has been calculated from spectroscopic data and were found to be 6.298 eV or 50800 (200) cm^{-1} (Sugar, 1973), respectively, but it now has been determined experimentally and found to be 6.2817(2) eV or 50665(200) cm^{-1} , respectively (Erdmann *et al.*, 1996, 1998) using resonance ionization mass spectrometry. Some of the lowest energy levels and the representative configurations are given in Tables 11.3 and 11.4, and experimental $F^k(ff)$ and Hartree-Fock values are listed in Table 11.5. These values were determined using the ^{249}Cf isotope. Ionova *et al.* (1977) have also discussed the electronic levels of californium.

From limited absorption and self-luminescence spectra for californium, an early partial energy-level scheme was published for the $5f^9$ configuration (Conway *et al.*, 1962a,b). Predictions of the energy-level structure for Cf(III) appeared in 1964 (Fields *et al.*, 1964), and work on the triply ionized form of californium has also been published (Carnall *et al.*, 1973; Varga *et al.*, 1973a,b).

Table 11.3 *Lowest californium electronic levels for configurations listed.*

<i>Species</i>	<i>Configuration</i>	<i>Parity term</i>	<i>Level (cm⁻¹)</i>	<i>G_{obs}</i>	<i>Hfs</i> (10 ⁻³ cm ⁻¹)
²⁴⁹ Cf(II)	5f ¹⁰ 6s	E ⁶ I _{17/2}	0.00	1.28	
²⁴⁹ Cf(II)	5f ¹⁰ 6d	E <i>J</i> = 15/2	19 359.06		
²⁴⁹ Cf(II)	5f ⁹ 6d7s	O <i>J</i> = 19/2	24 213.34	1.27	
²⁴⁹ Cf(II)	5f ¹⁰ 7p	O <i>J</i> = 15/2	26 858.90	1.26	
²⁴⁹ Cf(I)	5f ¹⁰ 7s ²	E ⁵ I ₈	0.000	1.213	0
²⁴⁹ Cf(I)	5f ⁹ 6d7s ²	O <i>J</i> = 8	16 909.355	1.301	-40
²⁴⁹ Cf(I)	5f ¹⁰ 7s7p	O <i>J</i> = 8	17 459.210	1.277	-140
²⁴⁹ Cf(I)	5f ¹⁰ 6d7s	E <i>J</i> = 8	20 043.930		-210
²⁴⁹ Cf(I)	5f ⁹ 7s ² 7p	E <i>J</i> = 7	24 727.600		60
²⁴⁹ Cf(I)	5f ¹⁰ 7s8s	E ⁷ I ₉	32 983.180	1.300	-490
²⁴⁹ Cf(I)	5f ⁹ 6d7s7p	E <i>J</i> = 8	33 952.135		-200
²⁴⁹ Cf(I)	5f ¹⁰ 7s8p	O <i>J</i> = 8	38 225.945		-410
²⁴⁹ Cf(I)	5f107s7d	E <i>J</i> = 8	39 091.175	1.245	
²⁴⁹ Cf(I)	5f ⁹ 7s ² 8s	O <i>J</i> = 8	45 183.155		-150

Source: Chapter 16 and references therein.

Table 11.4 *Lowest electronic levels for neutral californium configurations.*

<i>Configuration</i>	<i>Level (cm⁻¹)</i>
5f ⁹ 6d7s ²	16 909
5f ⁹ 6d ² 7s	31 500
5f ⁹ 6s ² 7p	24 728
5f ⁹ 6d7s7p	33 952
5f ¹⁰ 7s ²	0
5f ¹⁰ 6d7s	20 044
5f ¹⁰ 6d ²	50 000
5f ¹⁰ 7s7p	17 459

Source: Chapter 16 and references therein.

Table 11.5 *Selected experimental values of F^k (ff), Hartree–Fock values and F^k/F^2 ratios for californium.*

<i>Configuration</i>	<i>Element</i>	<i>Parameter</i> (r)	<i>Exp.</i>	<i>Hartree–Fock</i>	F^k/F^2 (exp.)	F^k/F^2 (calc.)	<i>Exp./H.F.</i>	<i>H.F.-exp.</i>
5f ¹⁰ 7s ²	Cf(I)	F^2	57 870	84 799	1.000	1.000	0.682	26 929
5f ¹⁰ 7s ²	Cf(I)	F^4	45 052	55 085	0.779	0.650	0.818	10 033
5f ¹⁰ 7s ²	Cf(I)	F^6	31 873	40 345	0.551	0.476	0.790	8472

Source: Chapter 16 and references therein.

Blaise and Wyart (1992) and Wyart *et al.* (2005) have more recently reported a comprehensive list of electron energy levels for californium, which are recommended values. Additional information is given in Chapter 15.

Absorption spectra of Cf(III) are mainly characteristic of f–f transitions (Laporte forbidden) within the $5f^{10}$ configuration. Spectra of Cf(III) in $\text{DClO}_4\text{--D}_2\text{O}$ have been used to make term assignments and energy levels for californium (Varga *et al.*, 1973a). The electronic spectrum and estimated energies of the electronic configurations of Cf(IV) has also been predicted from spin–orbit coupling (Varga *et al.*, 1973b). Estimated energies of the electronic configurations for californium had appeared earlier (Brewer, 1971a,b), where values were given for singly, doubly, and triply charged californium ions.

A detailed theoretical interpretation of solid-state absorption spectra of CfCl_3 has also been published (Carnall *et al.*, 1973), and energy level assignments made for several californium absorption bands. The observed and calculated free-ion energy levels for Cf(III) have also been compared to the lower energy levels in californium's analog, Dy(III) (Carnall *et al.*, 1973). An attempt to correlate the electronic excitation energies for 4f and 5f elements suggested that the $f^n s^2 \rightarrow f^{n-1} ds^2$ excitation values for californium compare best with the lighter lanthanide elements (Mikheev *et al.*, 1979). A valence-band approach for high-coordination bonding in the californium compounds has also been suggested by Carter (1979); this approach implies d- and f-orbital splitting into bonding hybrids. From quantum chemistry considerations, the monovalent ion of californium should be more stable than monovalent lanthanide or lighter actinide ion, based on its lower calculated excitation energy. Calculations have also shown that, from berkelium to nobelium, the excitation (promotion) energies for the $f^n s^2 \rightarrow f^{n-1} ds^2$ configuration, which is taken as a measure of the stability of the divalent state, increases with the atomic number up to element 103 (Spitsyn, 1977). Thus, Cf(II) should be more stable than Bk(II) but less stable than Es(II). These promotion energies are discussed throughout this chapter and play an important role in the californium chemistry.

Predictions for excitation energies for $7s^2 \rightarrow 7s7p$ and $7s^2 6d$ levels have also been given (Carnall *et al.*, 1977). Experimental data were obtained and crystal field calculations have been made for Cf(III) in different crystal hosts (Carnall *et al.*, 1977). Relativistic Hartree–Fock–Slater calculations have yielded neutral-atom electron binding energies for californium (Haung *et al.*, 1976), and relativistic relaxed-orbital calculations of L-shell Coster–Kronig transition energies have been reported for californium (Chen *et al.*, 1977). An interpolation scheme for cohesive energies provides binding energies for electrons, which can correlate and compare the divalent nature of transplutonium elements; this approach has predicted a divalent metallic state for einsteinium rather than for californium (Johansson and Rosengren, 1975a,b). The divalent metallic state for einsteinium has been verified (see Chapter 12) but this state is less likely for bulk forms of californium (see Section 11.6).

Photoelectron spectrometry of californium has been performed on Cf_2O_3 and Cf_7O_{12} , using an $\text{MgK}\alpha$ excitation source (Krause *et al.*, 1988). Values for the

4f doublet ($4f_{5/2}$ and $4f_{7/2}$) of californium were determined in that work. The spin-orbit splitting for californium was estimated to be 17.5 eV.

The energy spectrum of electrons in ^{252}Cf has been given (Rykov and Yudin, 1998) and the energy levels of ^{249}Cf , both neutral Cf(I) and singly ionized Cf(II), are also available (Blaise and Wyart, 1992; Conway *et al.*, 1995; and Chapter 16). Ionova *et al.* (1989a,b) has reported computational results for the electronic structure of californium. Also see subsequent sections of this chapter regarding discussions of the absorption spectra of Cf(II) in solids and Cf(III) in solution, and californium's electronic behavior in the gas-phase studies (see Section 11.9). The nuclear magnetic moment of ^{249}Cf has been determined and found to be -0.28 nuclear magnetons, and its nuclear spin is accepted as being $9/2$ (see Ahmad, Appendix I).

11.5.1 Emission spectra

The first emission spectrum for californium was reported by Conway *et al.* (1962a,b) and obtained via the copper-spark method. The majority of subsequent work on californium has been carried out using electrodeless lamps, where multi-microgram amounts of material are sealed in quartz envelopes and the californium is excited by external radiation. Emission spectra of californium have been observed from 2400 to $2.5\ \mu\text{m}$, with approximately 25000 lines having been recorded and accurately measured (Conway, 1976; Conway *et al.*, 1977). Fourier transform analyses of data obtained from californium lamps have been carried out with the goal of resolving the hyperfine structure (Blaise and Wyart, 1992; Wyart *et al.*, 2005). The $5f^{10}7s^2$ ground state, the $5f^{10}7s8s$, and $5f^96d7s^2$ configurations have been established from californium spectra (Warden *et al.*, 1970; Conway, 1976; Conway *et al.*, 1977; for further details see Chapter 16).

11.5.2 X-ray emission spectroscopy

The characteristic X-rays resulting from atomic readjustment to inner shell vacancies provide a very useful means for identification of an element (see Dittner and Bemis, 1972). Several X-ray emissions for heavy elements and their bonding energies are known, and such data have been tabulated for californium (Carlson and Nestor, 1977).

Similar calculations using nonrelativistic Hartree-Slater wave functions (Manson and Kennedy, 1974) and relativistic Hartree-Slater theory (Scofield, 1974) have also provided data for californium. The atomic form factors, the incoherent scattering functions (Hubbell *et al.*, 1975), and a total Compton profile have been tabulated for californium (Biggs *et al.*, 1975).

Systematic X-ray photoelectron spectroscopy (XPS) studies have also been carried out on transplutonium oxides through californium, providing experimental binding energies for their electrons, which can be compared to the

calculated energies (Veal *et al.*, 1977). An interpolation scheme has also been reported for determining the binding energies of some lanthanides and actinides, including californium (Johansson and Rosengren, 1975a). The nature of the 5f electrons in the actinide series including californium has also been discussed (Johansson and Rosengren, 1975b).

11.6 THE METALLIC STATE

11.6.1 Preparation

The first attempt to prepare californium metal was made in the late 1960s (Fujita and Cunningham, 1969). Subsequently, several additional attempts have been made to prepare and study this metal. The relatively high volatility of californium metal has made its preparation and study on the microscale more difficult than the first three transplutonium metals. The possibility that the metal may exist in two different metallic valence states has also made it an interesting candidate for study, but it has also complicated the full understanding of californium's metallic state. The potential for californium to exist in two metallic valence states arises due to its $f \rightarrow d$ electron promotion or excitation energy (see subsequent discussion).

Two preparative approaches have been utilized for californium metal. The first approach utilizes the reduction of the trifluoride with lithium metal at elevated temperatures; the excess reductant and lithium fluoride are removed by vacuum distillation. The second preparative method employs thorium or lanthanum metal to reduce one of the californium oxides, permitting the distillation and subsequent condensation of the metal (Haire, 1982) and leaving the thorium or lanthanide metal and their oxides as residues. With thorium metal, the reaction is a solid–solid reaction and thorium has a lower vapor pressure, which should reduce the presence of the reductant in the vaporized product. With lanthanum, one encounters a liquid–solid reaction, as the lanthanum melts at 920°C; it also has a higher vapor pressure than thorium at high temperatures. The latter property must be considered to avoid incorporating lanthanum into the distilled californium product.

With the halide reduction process, where californium is to be retained as a solid residue, the volatility of californium is greater than that of lithium fluoride. This makes it difficult to volatilize the lithium fluoride completely from the californium product without simultaneously volatilizing away significant amounts of californium. In the oxide reduction procedure, the distillation of microgram quantities of metal yields thin films that are difficult to remove from the collection substrate. Also, a very good vacuum (free of residual materials such as hydrogen, oxygen, water or oil vapor, etc.) is required to avoid the formation of undesired compounds during the distillation of the reactive metal. With multi-milligram quantities, the distillation procedure is the best preparative route. The limited availability of the ^{249}Cf isotope and the radiation fields

encountered with this isotope do limit the amount of metal that can be prepared in an unshielded gloved box to 10–20 mg. There is little information about the preparation of ^{252}Cf metal using these procedures, and it is likely little if any has been made by this route.

Some work has been done on preparing californium–palladium alloys via hydrogen reduction of oxide–palladium metal mixtures in conjunction with medical applications of this isotope (Haire and Sato, 1998; Rivard *et al.*, 1999). The latter products are not pure alloys but sufficient for pressing or making extruded sources if the californium content is kept below 20 at%. The malleability of the products is found to decrease with higher californium contents. The reduction in this procedure is driven by the stability of actinide–noble metal alloys. Radchenko *et al.* (1986b) have discussed the formation of CfPt_5 on platinum surfaces.

The preparation of pure ^{249}Cf metal to date has been in the 2–10 mg range, with the largest known amount prepared at one time being about 10 mg (Haire, 1978, 1980, 1982). A picture of a 10 mg ^{249}Cf product is shown in Fig. 11.2, where it is compared to the head of a common safety pin. A more detailed account of the preparation of californium metal is available (Haire, 1982).

The limited quantities of californium metal have placed restrictions on the amount of analytical data that can be obtained for products; normally it is not possible to analyze for hydrogen, nitrogen, and oxygen contents. The quality of the metal has then been ascertained mainly by diffraction analysis, total metal impurities by mass spectrometry, its physical properties and appearance and its behavior (such as the rate and extent of dissolution for enthalpy-of-solution

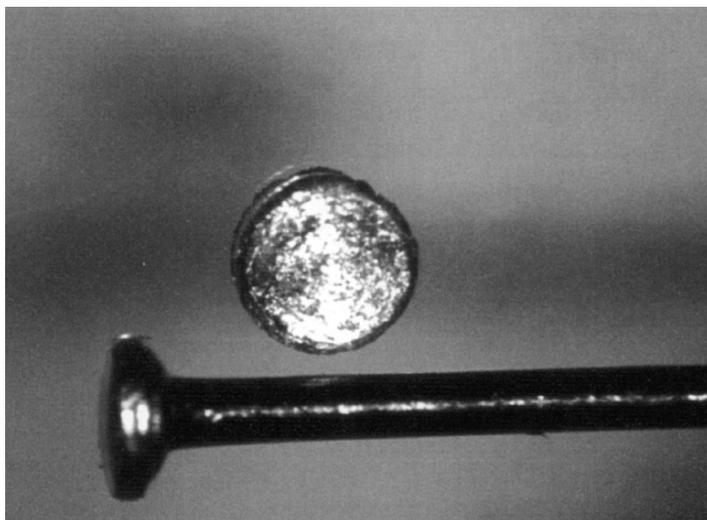


Fig. 11.2 Ten milligram disc of californium compared to a straight pin.

measurements) in experiments performed with the metal. Ideally, a larger quantity of metal would be prepared, characterized, and then used for a number of scientific measurements or experiments. But with californium (and some of the other transcurium metals), the preparation of the metal often becomes an integral part of a subsequent study, and either the major portion or the entire preparation is needed and often consumed in the study at hand (i.e. dissolved in acid in determining the enthalpy-of-solution of the metal) in an experiment.

11.6.2 Physical properties

There have been several different reports regarding the crystal data for californium over the years, and these are summarized in Table 11.6. Based on extrapolations from trivalent americium, curium, and berkelium metals, a double hexagonal close-packed structure with parameters on the order of $a_0 = 3.4 \text{ \AA}$ and $c_0 = 11.0 \text{ \AA}$, and a face-centered cubic (fcc) high-temperature phase with $a_0 \sim 4.8 \text{ \AA}$ would be expected for trivalent californium metal.

In earlier work, a face-centered structure with a parameter of 5.40 \AA was reported, which was from a product obtained by the lithium reduction of its fluoride (Cunningham and Parsons, 1970). This is a difficult technique for preparing californium metal (see Section 11.6.1) and this work also involved very small quantities of californium. A potential explanation for this reported parameter is that it represents a poorly crystallized sesquioxide (body-centered cubic (bcc)), lattice parameter of 10.831 \AA (see Section 11.7.4), which with the absence of weak diffraction lines in a diffraction pattern of marginal quality may be interpreted as arising from a face-centered material of 5.42 \AA ($10.831/2$).

Subsequently, cubic and hexagonal structures were observed by Haire and Baybarz (1973a,b) in very thin films ($<2.5 \text{ \AA}$) of californium distilled onto electron microscopy grids and then analyzed by electron diffraction. These data suggested a metallic radius of slightly greater than 2.0 \AA , suggesting californium may be a divalent metal. An extrapolation by Zachariasen (1975) also suggested that californium metal would be a cubic lattice and a larger radius than the trivalent metal. Subsequently, very small quantities of apparent metal were also analyzed by X-ray diffraction (Noé and Peterson, 1976) that duplicated the 5.747 \AA cubic structure reported by Haire and Baybarz (1973a,b, 1974). Thus, these early data thus suggested californium may be a divalent metal.

With larger quantities of californium, its crystallographic data (Haire and Asprey, 1976; Noé and Peterson, 1976) independently showed that the metal was trivalent with a room temperature double hexagonal close-packed parameters of $a_0 = 3.384 \text{ \AA}$ and $c_0 = 11.040 \text{ \AA}$, which suggests an atomic radius of 1.69 \AA , which is in line with radii reported for americium, curium, and berkelium metals. The crystal forms of californium metal were also determined by Radchenko *et al.* (1986a) and Seleznev *et al.* (1989) for 1.5 mg of californium.

Table 11.6 Crystallographic data reported for californium metal.

Crystal System	Lattice Parameters		Atomic Volume (\AA^3)	Crystal Density (g cm^{-3})	Metallic Radius (\AA)	References
	a_0 (\AA)	c_0 (\AA)				
fcc	5.40	–	39.4	10.5	1.91	Cunningham and Parsons (1970)
fcc	5.743	–	47.4	8.72	2.03	Haire and Baybarz (1970)
hcp	3.988	6.887	47.4	8.72	2.07	Haire and Baybarz (1970)
dhcp	4.002	12.804	44.4	9.31	1.99	Haire and Asprey (1976)
dhcp	3.384	11.040	27.4	15.1	1.69	Haire and Asprey (1976)
fcc	4.94	–	30.1	13.7	1.75	Noé and Peterson (1976)
fcc	5.75	–	47.4	8.72	2.03	Noé and Peterson (1976)
dhcp	3.39	11.01	27.4	15.1	1.69	Noé and Peterson (1976)
fcc	4.78	–	27.4	15.1	1.69	Haire <i>et al.</i> (1986)
dhcp	3.380	11.025	27.3	15.0	1.69	Radchenko <i>et al.</i> (1986); Seleznyov <i>et al.</i> (1989)
fcc	4.994	–	30.1	13.7	1.75	Stevenson (1973)
CfN, fcc	4.94	–	30.1	13.7	–	Haire <i>et al.</i> (1986)

Recommended values for californium are: (a) dhcp 3.384(3) \AA and 11.040(10) \AA and (b) fcc = 4.78(1) \AA . Both yield a metallic radius of 1.69 \AA , a volume of 27.4 \AA^3 and a density of 15.1 g cm^{-3} .

From these efforts double hexagonal lattice parameters of: $a = 3.380(2)$ Å and $c = 11.025(2)$ Å were reported.

A fcc-form (high-temperature form and also a high-pressure form at modest pressures) have been observed for californium. This form of californium was reported to have a fcc structure with a parameter of 4.94 Å (Noé and Peterson, 1976), but this parameter gives an atomic radius for californium that is too large. It agrees better with the parameter for californium nitride ($a_0 = 4.94$ Å; Haire *et al.*, 1986), with an oxynitride (oxygen and nitrogen exchanged in the crystal sites), or could have represented an expanded lattice that was 'quenched in' at elevated temperatures. The proper lattice parameter (4.78 Å) for this cubic form of californium at room temperature and at a pressure 1 atm was observed both with pressure-quenched samples (Haire *et al.*, 1986) and also from larger quantities of californium obtained as foils prepared by distillation (Haire, 1978). The atomic radius derived from this smaller cubic parameter agrees well with that obtained from the ambient temperature, double hexagonal parameters. Pressure-quenched cubic parameters for curium, berkelium, and californium metals have also been found to give identical atomic radii and atomic volumes as obtained from their room temperature, double hexagonal forms, while earlier work with samples quenched from elevated temperatures also resulted in larger (expanded) parameters for curium and berkelium metals (Haire *et al.*, 1986). The preparation and lattice parameters for the californium metal have also been reported by Radchenko *et al.* (1986a) and by Seleznev *et al.* (1989). An alloy of californium and platinum (CfPt₅) was obtained when thin films of californium were vapor deposited on platinum surfaces. The products were analyzed as formed on the surfaces (Radchenko *et al.*, 1986b).

The transition temperature for the hexagonal to cubic phase of californium is not well-established, and only limited efforts have been made to determine it (Noé and Peterson, 1976). It is likely to be in the region of 600–800°C. The dhcp to fcc structural transition occurs under pressure at about 16 GPa (Peterson *et al.*, 1983; Benedict *et al.*, 1984). This cubic phase formed under pressure can be retained at atmospheric pressure and 25°C (Haire *et al.*, 1986), and provides a lattice parameter of 4.78 Å. This transition from a hexagonal to cubic state is a low-energy transition in the transplutonium metals. The different crystal data for californium that have been reported are summarized in Table 11.6.

Californium lies very close to the 'border' between a divalent and trivalent metal due to its f- to d-electron promotion energy (see Fig. 12.4 and discussion in Chapter 12). It is possible that in very thin films californium metal may retain a divalent state (i.e. a metastable state) under the conditions of preparation. A similar situation has been observed previously with very thin films of samarium metal (Allen *et al.*, 1978), where the surface atoms of samarium metal in these films remain divalent, although atoms in bulk metal are normally trivalent. Samarium also exhibits a unique rhombohedral crystal form in bulk form. The next element after samarium in the lanthanide series is europium, and it is a divalent metal. Thus, the situation with the californium structures may be

similar to the samarium case, as the next element after californium, einsteinium, is also a divalent metal (see Chapter 12). However, californium metal is correctly identified as being a trivalent metal in bulk forms, but does display aspects of this 'closeness' to being divalent (see discussion of its enthalpy of sublimation of the metal in section 11.6). The best lattice parameters for both the dhcp and fcc crystal forms of californium metal are those that give an atomic radius of about 1.69 Å.

There has been only one reported value for the melting point of californium metal, which is $(900 \pm 30)^\circ\text{C}$ (Haire and Baybarz, 1973a,b). This value was obtained by observing the 'puddling' of metal particles in an electron microscope with thin films of californium metal. This melting point is lower than those reported for americium, curium, and berkelium metals, but is close to the melting point of einsteinium metal (Haire and Baybarz, 1979). Californium's lower melting point is also in accord with some of its physical properties, and the trend toward divalency (which would yield lower melting points) in going across the actinide series. The properties for californium and the other transplutonium metals are compared in an ASM report by Haire (1990).

Californium metal has been examined under high pressure using X-ray diffraction techniques. Early high-pressure studies showed that its dhcp form transformed to a fcc form at 16 GPa (Peterson *et al.*, 1983). A bulk modulus of (50 ± 5) GPa was derived from those data, which is similar to moduli for many of the trivalent lanthanide metals but much lower than those of the earlier actinides with itinerant 5f electrons (i.e. Pa–Pu). Subsequent work with californium metal under higher pressures up to 48 GPa showed a transition of the fcc structure to a new lower symmetry structure (reported to be orthorhombic, alpha-uranium structure; Benedict *et al.*, 1984). Formation of this structure was interpreted as reflecting the delocalization of californium's 5f electrons and their participation in the metal's bonding. Very recently californium metal has been reexamined under much higher pressures and with the use of synchrotron radiation (Haire *et al.*, 2004). These studies have provided much higher quality data, which have shown the occurrence of three structural transitions, and confirmed that the 5f electrons of californium do indeed delocalize and become involved in bonding at these higher pressures. But the new californium structures observed at higher pressures (after the fcc phase), are very similar to those noted in the behavior of americium metal under pressure (Heathman *et al.*, 2000). Work on the structures of californium observed at pressures above 40 GPa are being finalized and details will be published later. However, in this work on californium, it was very clear that when progressing across the actinide series, it takes higher and higher pressures to force the delocalization of the 5f electrons, as they become further withdrawn from the Fermi surface due to the greater nuclear charges (Haire *et al.*, 2004). Thus, californium requires much higher pressures to force the delocalization of its 5f electrons than do the first three transplutonium metals.

The vapor pressure and enthalpy of sublimation of californium metal have been measured using the Knudsen effusion technique (Ward *et al.*, 1979). The vaporization of californium metal, starting at 298 K with the dhcp crystal form, and over the temperature range of 733–973 K, is described by the following equation:

$$\log p(\text{atm}) = (5.675 \pm 0.0319) - (9895 \pm 34) T^{-1}$$

The $\Delta_{\text{sub}}H_{298.15\text{ K}}^{\circ}$ was calculated to be $(196.23 \pm 1.26) \text{ kJ mol}^{-1}$, and $\Delta_{\text{sub}}S_{298.15\text{ K}}^{\circ}$ was derived to be $120.6 \text{ J K}^{-1} \text{ mol}^{-1}$. The estimated boiling point for the metal is 1745 K. Nugent *et al.* (1973b) had estimated the enthalpy of sublimation of californium to be 163 kJ mol^{-1} and David *et al.* (1976a,b) had predicted a value of 197 kJ mol^{-1} . By comparison, the vapor pressure behavior of californium is intermediate between that of samarium metal (a trivalent metal) and europium metal (a divalent metal), which is discussed by Ward *et al.* (1979).

The enthalpy of sublimation is an important bulk property of an element, and can be a measure of the metal's cohesive energy. From the magnitude of the enthalpy, the number of bonding electrons can be inferred from it, and this allows systematic comparisons to be made between the two f-electron elements series.

The experimental sublimation data for californium (Ward *et al.*, 1979) are in accord with it being a trivalent metal up to 1026 K, although it is one of the most volatile (has one of the lowest sublimation enthalpies) of the trivalent actinide metals; its high volatility precludes vaporization studies of it above 1073 K. Evidence for CfO was not obtained in this mass spectrometry study, and this finding is in accord with subsequent studies on californium oxides (Haire, 1994; see Section 11.7.3).

Thermochromatographic studies (involving sublimation and adsorption) of californium, einsteinium, and fermium using different metal columns (titanium, tantalum, etc.) were performed to yield enthalpies of adsorption for these actinides. Attempts have been made to relate these adsorption enthalpies to enthalpies of sublimation, but there is a significant difference in the actual numerical values, as they measure different properties. A comparison between the enthalpies of sublimation for the americium through californium trivalent actinide metals and their enthalpies of adsorption is striking, and efforts have been made to compare them (Haire, 1997). Fig. 11.3 shows plots of these values for selected actinides. The enthalpies of sublimation range irregularly for the first four transplutonium elements with the values reflecting in part differences in 5f to 6d promotion energies – smaller promotion energies link with larger, more positive enthalpies of sublimation.

The enthalpy of sublimation for californium is 196 kJ mol^{-1} (Ward *et al.*, 1979, 1986). In contrast, the enthalpy of adsorption for californium ranges from -302 to -310 kJ mol^{-1} (Hübener, 1980; Hübener *et al.*, 1994). The exact value depends on the particular metal substrate used for its adsorption. A comparison between these enthalpies of vaporization and adsorption is shown

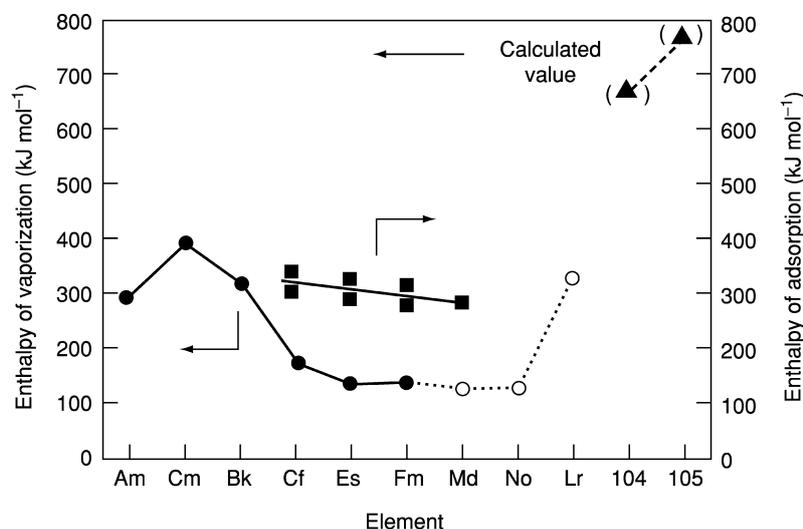


Fig. 11.3 Vaporization and adsorption enthalpies for selected actinides.

in Fig. 11.3 (Haire, 1997) for californium through mendelevium elements, and using some extrapolated values for sublimation of the two transfermium elements. The sublimation values for element 104 (Johnson and Fricke, 1991) and 105 (Pershina *et al.*, 1994) are calculated values, and are included here for comparison purposes. Their larger more positive enthalpies of sublimation reflect that greater bonding (i.e. greater than three electrons) is present in these latter two elements. One advantage of the adsorption technique versus the sublimation method is the former can be used for smaller quantities of materials (tracer levels).

It can be seen from Fig. 11.3 that the sublimation enthalpy for californium and the adsorption enthalpy are close to the comparable enthalpies for divalent einsteinium and fermium; the sublimation enthalpy for californium is considerably smaller (less positive, lower energy required) than values for americium, curium, and berkelium, which are trivalent metals.

Initially, the adsorption behavior (i.e. temperature of adsorption) of californium with different metal columns was taken as an indication of a metallic divalency (Hübener and Zvara, 1982) but more recent interpretations of adsorption enthalpies and the relative behavior of californium through nobelium elements suggests that californium is trivalent but close to the divalent–trivalent border Eichler *et al.* (1997). Using adsorption enthalpies, fermium is considered unquestionably as being divalent (Taut *et al.*, 1997), while californium is trivalent an atomic form source for actinide elements has been discussed (Eichler *et al.* 1997.)

The initial enthalpy of solution of californium metal (dhcp crystal form, trivalent metal) in 1.0 M HCl at 298 K is $-(617 \pm 11)$ kJ mol⁻¹ (Raschella *et al.*, 1982).

This value was corrected in a subsequent determination of this important thermodynamic quantity using larger samples of well-characterized metal to yield an enthalpy of solution value of $-(576.1 \pm 3.1)$ kJ mol⁻¹ for 1 M HCl (Fuger *et al.*, 1984; for further details see Chapter 19). This less-negative enthalpy value shows a trend among the transplutonium metals from americium through californium of less-negative enthalpies with increasing atomic numbers, and is in accord with an increasing trend toward metallic divalency in progressing across the series. This enthalpy of solution of the metal is important for providing the enthalpy of formation of the Cf(III) ion in solution and discussed in a subsequent section (see Section 11.8.3) on thermodynamic properties.

Several efforts have been made to obtain the magnetic susceptibility of californium metal. Magnetic information is valuable in ascertaining the metallic valence of metals and the bonding present. However, in the case of californium, such information is not useful and cannot differentiate between a divalent form (presumably a 5f¹⁰ state) that would have an effective moment of 10.22 μ_B, while the trivalent form (for an 5f⁹ state) would have an effective moment of 10.18 μ_B.

The first magnetic measurements were made by Fujita *et al.* (1976) using two samples believed to represent a fcc form of divalent californium metal from 22 to 298 K. Both samples followed a Curie–Weiss relationship, and the data produced an average moment of 9.75 μ_B. Subsequent magnetic measurements were made on well-characterized samples of the dhcp, trivalent form of californium from 4.2 to 350 K and in applied fields of up to 50 kG (Nave *et al.*, 1983, 1984). These data showed that californium exhibits at least two differing magnetic behaviors as a function of temperature. Below 51 K, the metal was either ferro- or ferrimagnetic; a distinction between the transition type could not be made owing to the inability to obtain a saturated moment of greater than 6.1 μ_B in the highest field of 50 kG. There was also evidence for antiferromagnetic behavior in the temperature range of 48–66 K. Additional magnetic studies of californium compounds (i.e. oxides and nitrides in particular) need to be done to rule out the possibility that their presence as impurities may be responsible for this latter behavior. Above 160 K, californium exhibits paramagnetic behavior. An average effective moment of (10.6 ± 0.2) μ_B was obtained for three different samples, whereas a fourth sample produced a moment of (9.7 ± 0.2) μ_B. Results from Nave *et al.* (1983) indicate that the magnetic behavior of californium is similar in some respects to that of its electronic homolog, dysprosium. Additional comments on magnetic behavior of californium and its compounds are given in Section 11.7.5 and in Table 11.11.

11.6.3 Chemical and mechanical properties

Californium is a fairly reactive metal, comparable to those of the lighter lanthanide metals but is less reactive than europium, which is considered as the most reactive lanthanide metal. This reactivity of europium is related to several factors but in part arises from it being a divalent metal. On standing to air or

when exposed to moisture at room temperature, small bulk pieces or foils of californium quickly form an oxide, but it is not a violent reaction. Moisture and temperature increase the rate of the reaction. One of the difficulties of preparing small quantities of californium metal is that it only takes small amounts of impurities to form reaction products with it. When the temperature is elevated, the reactivity of californium metal increases, and reactions occur readily with hydrogen, nitrogen, the chalcogen elements, etc. The silver colored, relatively soft californium metal quickly adopts a golden or bluish color on its surface when reacting with small amounts of other materials. Pure californium metal is easily cut with a 'razor' blade and is also malleable in its pure state.

When californium is sealed in evacuated quartz containers and when heated to 300°C, especially when it is a film on the quartz surface, the metal quickly deteriorates. Solid pieces of californium metal stored in quartz under vacuum and heated to moderate temperatures (i.e. 300°C) can vaporize sufficiently to form 'mirrors' on the quartz surface. Vaporization and reaction with the quartz worsens at higher temperatures. Products are usually oxides or silicates.

The metal reacts very rapidly with dry gaseous hydrogen halides and aqueous mineral acids to evolve hydrogen. In aqueous media, a Cf(III) solution is obtained, except with the case of hydrogen fluoride, where an insoluble californium trifluoride precipitate is formed.

Californium forms alloys when heated with the lanthanide metals but these products have not been well-characterized. When heated, it 'wets' tantalum, which usually limits the use of tantalum containers for high-temperature work with it. Tungsten containers are preferred, especially those made from single crystals, which prevents the metal from entering the grain boundaries of the containers.

11.6.4 Theoretical treatments

The chemistry of the actinide series can be complex and changes considerably when progressing across the actinide series. The development of a self-consistent model for these elements has had limited success in the past but more recent computational approaches have been more successful. However, even plutonium is still not completely understood, and total agreement on details of its fundamental science is not realized fully even after some 60 years of extensive studies. In comparison, far less effort has been done on californium, although its behavior is more lanthanide-like and has fewer complexities than plutonium, which has delocalized 5f electrons. However, the increased promotion energy for the 5f electrons of californium makes it close to being a divalent metal, and therefore its properties and behavior deviate somewhat from those of the americium through berkelium metals, as well as some of the trivalent lanthanide metals.

Efforts have been made to describe the overall fundamental aspects of these actinide metals, and be able to correlate them with other members of the periodic table (Brewer, 1971a,b; Nugent *et al.*, 1973a,b; Johansson and Rosengren, 1975a,b; Nugent, 1975; David *et al.*, 1976a,b, 1978; Samhoun and David, 1979;

Brooks *et al.*, 1984). These authors provide useful considerations for understanding the series in general and the changes that are observed when moving across it.

With respect to californium, the important questions often have to do with the role of its 5f electrons, their position with respect to the Fermi level, the narrowing of its 5f levels relative to earlier members of the series and the position of the 5f electrons with respect to the other outer electrons. The concept of promotion energy for the 5f electrons ($f \rightarrow d$) is an important factor here. At 1 atm and room temperature, the 5f electrons in californium and its compounds are fully localized, much like the 4f electrons in the lanthanide series.

Several predictions for the properties of californium have been made with regard to its 5f electrons. One of the predictions was addressed by Brooks *et al.* (1984). It was accepted that californium was close to the divalent–trivalent metallic boundary. This pseudo-boundary considered that the crystal energy gained from acquiring three bonding electrons versus two in isolated atoms, had to be greater than the promotion energy needed for promoting a 5f electron to a d-state (to provide three bonding electrons). As with many of the other actinide metals, atomic californium in the vapor state has only two bonding electrons, but upon condensation, a third bonding electron can be acquired by promoting a 5f electron to a ‘6d’ state. True divalency in the metallic state is believed to occur first in the higher members of the series, starting with einsteinium and fermium metals (see Chapters 12 and 13, and Johansson and Rosengren, 1975a,b; Brooks *et al.*, 1984). Additional discussions in this regard on the nature of californium can be found in the literature and in Section 11.9.

Correlation between crystal entropy and metallic radius, atomic weight, magnetic properties, and electronic structure have permitted an accurate calculation of unknown entropies for the actinide elements, including californium (Ward and Hill, 1976). This required a defined electronic structure to predict the entropy values. In addition, thermodynamics for the transplutonium metals have been summarized (Ward *et al.*, 1980; Ward, 1983). A pattern of superconductivity in f-band metals has also received attention over the years. It is unlikely that californium would show superconductivity, due to its large magnetic moment (see Section 11.6.2 on metal properties) and localized 5f electrons. Prospects for superconducting behavior in other actinides have been discussed (Smith, 1979, 1980; Baring and Smith, 2000). Of the first four transplutonium metals, ending with californium, only americium metal (Smith and Haire, 1978) is known to become superconducting at low temperature.

11.7 SOLID COMPOUNDS

11.7.1 General comments

A wide variety of californium compounds have been reported, even though only small amounts of this element (especially the ^{249}Cf isotope) have been available

an overview of Cf solid state chemistry is available (Haire & Gibson, 1989). Most of the expected halides and oxides for californium are established. It is accepted that californium exhibits three oxidation states, II, III, IV, in solids. There are reports that suggest the possibility of a Cf(V) state in solution (see Section 11.8); this state for californium is questionable. The II, III, and IV states are observed in different halides, and the III and IV states are found in oxides. The existence of stable, solid CfO is less probable and a minor product (see Section 11.9 on gas-phase behavior of californium). The trivalent state is the most prevalent state in both compounds and solutions, and the tetravalent state is only observed in the compounds, CfO₂, BaCfO₃, and CfF₄ and special solutions. The divalent state is found in the pure solids CfCl₂, CfBr₂, and CfI₂.

There are other compounds of californium where the oxidation state is less well-defined, such as in compounds with pnictogens, chalcogens, hydrides, etc. For example, in CfN, a formal state of Cf(III) can be assigned but it is not fully clear if this state is correct for a potentially more covalent material, as expected in its nitride. With hydrides, stoichiometries can range between a value of two (dihydride) and three (trihydride), in addition to intermediate hydrogen stoichiometries (i.e. CfH_{2+x} cubic materials and CfH_{3-y} hexagonal products.). This suggests that the bonding in hydrides is other than purely ionic.

Ionic radii for each oxidation state of californium can be established from crystallographic data for these compounds, and some radii are provided in Table 11.7 for comparison. Many similarities in behavior between californium

Table 11.7 Comparison of selected radii of californium and some lanthanides.

<i>Ion</i>	<i>Compound</i>	<i>Radius (Å)</i>	<i>References</i>
Cf ²⁺	CfBr ₂	1.08	Peterson and Baybarz (1972)
Eu ²⁺	EuBr ₂	1.09	Peterson and Baybarz (1972)
Cf ³⁺	CfCl ₃	0.932 ^a	Burns <i>et al.</i> (1973)
Gd ³⁺	GdCl ₃	0.938 ^a	Burns <i>et al.</i> (1973)
Cf ³⁺	Cf ₂ O ₃	0.942 ^b	Baybarz <i>et al.</i> (1972)
Cf ³⁺	Cf ₂ O ₃	0.95	Shannon (1976)
Gd ³⁺	Gd ₂ O ₃	0.938 ^b	Haire and Baybarz (1973a,b)
Eu ³⁺	Eu ₂ O ₃	0.950 ^b	Haire and Baybarz (1973a,b)
Cf ⁴⁺	CfO ₂	0.859 ^c	Baybarz <i>et al.</i> (1972)
Cf ⁴⁺	—	0.821 ^d	Shannon (1976)
Ce ⁴⁺	CeO ₂	0.898 ^c	Haire and Eyring (1994)
Pr ⁴⁺	PrO ₂	0.890 ^c	Haire and Eyring (1994)
Tb ⁴⁺	TbO ₂	0.817 ^c	Haire and Eyring (1994)

^a Derived from apical distances of hexagonal trichloride cells; six-coordinated metal atom.

^b Derived from sesquioxide lattice parameters, using an oxygen radius of 1.46 Å and adding 0.08 Å for covalent M–O bond character; six-coordinate metal ion. (Lattice parameters for are taken from Haire and Eyring, 1994).

^c Derived from dioxide lattice parameters, using an oxygen radius of 1.46 Å, correcting for covalent character of M–O bond (+0.10 Å) and for coordination number of 8 to 6 (–0.08 Å).

^d Radius from plot of r^3 vs volume.

and other actinides and the lanthanides can be made based on ionic radii. It is important when making such comparisons that the radii were calculated in the same manner and perhaps even from the same compounds. In many cases, the transplutonium elements (i.e. californium specifically) with similar radii will likely form the same compounds, have the same structures, display similar phase behaviors, and may even have similar lattice parameters. This affords some predictability for properties of different californium compounds.

It must be recognized that a shift in radii is found between the lanthanide and actinide series, such that Cf(III) has a similar radius to Gd(III) rather than Dy(III), its apparent electronic homolog. Crystallographic data for a number of californium compounds are given in Table 11.8. This ionic radius relationship contrasts with the behaviors of the f-electron metals; metallic radii for the trivalent actinide metals are smaller than their lanthanide counterparts, and the metallic radius for californium is smaller than that of the smallest lanthanide metal, lutetium.

11.7.2 Halides and oxyhalides

Based on the estimated IV and III reduction potentials (Nugent *et al.*, 1971; David *et al.*, 1978) for californium, it would be expected that the only stable, bulk binary Cf(IV) halide would be its tetrafluoride. This compound can be prepared by fluorinating materials such as the oxides or CfF₃ with F₂ or ClF₃ (Asprey, 1970; Asprey and Haire, 1973; Haug and Baybarz, 1975). General preparative routes for the halides are summarized in Table 11.9 and their preparations have been summarized by Haire (1982).

The tetrafluoride has limited thermal stability and decomposes to CfF₃ (Haire and Asprey, 1973a,b) at 300–400°C. This temperature has limited the degree of crystallinity that can be obtained for it. There has been some variation in the lattice parameters reported for CfF₄, which arises mainly from indexing the monoclinic structure using powder diffraction data from samples of moderate crystallinity. A solid-state absorption spectrum has been obtained for the compound, its thermal stability examined and new X-ray data for the compound evaluated using small differences between the reported values (Haire *et al.*, 1980).

Ternary alkali-metal fluoride complexes of the types MCfF₅, M₂CfF₆, M₃CfF₇, and M₇Cf₆F₃₁ (M = Li through Cs) are expected to exist, and these complexes should provide added stability for the Cf(IV) state. These complex salts are well-established for the tetravalent state of lanthanides (Brown, 1968). The existence of CfF₄ in the vapor state has been claimed based on high-temperature (>500°C) chromatographic studies using tracer quantities of californium (Jouniaux, 1979; Bouissières *et al.*, 1980), which appears to conflict with the thermal decomposition of bulk CfF₄ at low temperatures (i.e. 300–400°C).

All of the trihalides and oxyhalides of Cf(III) are known (see Table 11.8), and many of these compounds were among the first prepared and reported for

Table 11.8 Crystallographic data for californium compounds.

Substance	Structure Type	Crystal System	Lattice Parameters			Angle (deg)	References
			a_0 (Å)	b_0 (Å)	c_0 (Å)		
Oxides							
Cf ₂ O _{Green}	Mn ₂ O ₃	bcc	10.839			$\beta = 100.3$	Copeland and Cunningham (1969); Green and Cunningham (1967)
	Sm ₂ O ₃	monoclinic	14.12	3.591	8.809		
Cf ₇ O ₁₂	La ₂ O ₃	hexagonal	3.72		5.96		Baybarz and Haire (1976)
	Tb ₇ O ₁₂	rhombohedral	6.596			$\alpha = 99.40$	Turcotte and Haire (1976)
	CaF ₂	fcc	5.310				Baybarz <i>et al.</i> (1972); Haire (1976) [see also Haire and Eyring (1994) for oxides]
Halides							
CfF ₃	LaF ₃	trigonal	6.945		7.101		Stevenson and Peterson (1973)
CfC ₃	YF ₃	orthorhombic	6.653	7.039	4.393		Stevenson and Peterson (1973)
CfC ₄	UF ₄	monoclinic	12.42	10.47	8.126	$\beta = 126.0$	Haire and Asprey (1973)
	UF ₄	monoclinic	12.33	10.40	8.113	$\beta = 126.44$	Haug and Baybarz (1975)
CfCl ₃	UCl ₃	hexagonal	7.379		4.090		Green and Cunningham (1967)
CfCl ₃	PuBr ₃	orthorhombic	3.859	11.748	8.561		Burns <i>et al.</i> (1973)
CfBr ₂	SrBr ₂	tetragonal	11.50		7.109		Peterson and Baybarz (1972)
CfBr ₃	AlCl ₃	monoclinic	7.215	12.423	6.825	$\beta = 110.7$	Fried <i>et al.</i> (1968)
CfBr ₃	FeCl ₃	rhombohedral	7.58			$\alpha = 56.2$	Burns <i>et al.</i> (1975)
CfI ₂	CdCl ₂	rhombohedral	7.434			$\alpha = 35.83$	Wild <i>et al.</i> (1978)
	CdI ₂	hexagonal	4.557		6.992		Wild <i>et al.</i> (1978)
CfI ₃	BiI ₃	hexagonal	7.587		20.814		Wild <i>et al.</i> (1978)
		rhombohedral	8.205			$\alpha = 55.08$	Wild <i>et al.</i> (1978)

Oxyhalides							
CfOF	CaF ₂	cubic	5.561			Peterson and Burns (1968)	
CfOCl	PbFCl	tetragonal	3.956		6.662	Copeland and Cunningham (1969)	
CfOBr	PbFCl	tetragonal	3.90		8.	Fried <i>et al.</i> (1968)	
CfOI	PbFCl	tetragonal	3.97		9.14		
Cf(IO ₃) ₃	Bi(IO ₃) ₃	monoclinic	8.7994(2)	5.9388(7)	15.157(2)	96.833(2)	Sykora <i>et al.</i> (2006)
pnictides							
CfN	NaCl	fcc	4.98				Haire (1974)
CfAs	NaCl	fcc	5.809				Damien <i>et al.</i> (1980)
CfSb	NaCl	fcc	6.165				Damien <i>et al.</i> (1980)
hydride							
CfH _{2+x}	NaCl	cubic	5.285				Gibson and Haire (1985)
oxysulfide and oxysulfate							
CfO ₂ S	La ₂ O ₂ S	trigonal	3.844		6.656		Barbarz <i>et al.</i> (1974)
Cf ₂ I ₂ SO ₄	La ₂ O ₂ SO ₄	orthorhombic	4.187	4.072	13.008		
cyclopentadienyl							
Cf(C ₅ H ₅) ₃		orthorhombic	1.410	1.750	0.969		Laubereau and Burns (1970)
pyrochlore							
Cf ₂ Zr ₂ O ₇		cubic	10.55				Haire <i>et al.</i> (2002)

Table 11.9 Preparation of californium halides.

tetrafluoride
CfF_3 or Cf oxide + $\text{F}_2 \rightarrow \text{CfF}_4$
trihalides
Cf oxide + $\text{HX} \rightarrow \text{CfX}_3$ (X = F, Cl, Br)
$\text{Cf}^0 + \text{HX} \rightarrow \text{CfX}_3$
$\text{Cf}^0 + \text{X}_2 \rightarrow \text{CfX}_3$
$\text{CfX}_3 + 3\text{HI} \rightarrow \text{CfI}_3 + 3\text{HX}$
oxyhalides
Cf oxide or $\text{CfX}_3 + \text{HX}/\text{H}_2\text{O} \rightarrow \text{CfOX}$
dihalides (X = Cl, Br, I)
$\text{CfX}_3 + \text{Cf}^0 \rightarrow \text{CfX}_2$
$\text{CfX}_3 + \text{H}_2 \rightarrow \text{CfX}_2$

californium. Their crystal structures vary between the different compounds, but are often isostructural with the lanthanide trihalides for lanthanides having comparable ionic radii (i.e. Gd(III)).

The oxyhalides can be prepared by incomplete halide formation starting from oxides, careful hydrolysis of the anhydrous halides or thermal decomposition of hydrated halides. They are also prepared by hydrohalogenation of Cf_2O_3 or via treatment of a californium oxide with moist interhalogens at an elevated temperature. The anhydrous trihalides can be prepared by treating californium oxides with dry hydrogen halides or the metals with hydrogen halides or elemental halogens. However, the reaction of the oxide with hydrogen iodide does not give satisfactory results; the triiodide can be prepared by treating CfBr_3 or CfCl_3 with hydrogen iodide, or the metal with iodine. The trihalides have relatively low-melting temperatures and can be melted in inert atmospheres and/or in vacuum. Careful melting and cooling of such anhydrous halide melts have been used to create single crystals.

The trifluoride is dimorphic (orthorhombic, YF_3 -type; high-temperature form, trigonal, LaF_3 -type) with the transition temperature above 600°C (Cunningham and Ehrlich, 1970; Stevenson and Peterson, 1973). Treatment of CfF_3 with water vapor above 700°C or non-purified/moist HF produces CfOF (Peterson and Burns, 1968). The enthalpy of formation of CfF_3 at 298.15 K is accepted as being $-1553(35)$ kJ mol^{-1} (see Chapter 19).

Californium trichloride is also dimorphic, exhibiting the UCl_3 -type hexagonal structure (low-temperature form) and the PuBr_3 -type orthorhombic structure (Green and Cunningham, 1967; Burns *et al.*, 1973). The melting point of CfCl_3 is 545°C (Burns *et al.*, 1973).

Treatment of Cf_2O_3 with moist hydrogen chloride, or CfCl_3 with water vapor, at elevated temperatures produces tetragonal CfOCl (Copeland and Cunningham, 1969). The preparation and measurement of the enthalpy of solution for CfOCl was also reported (Burns *et al.*, 1998). From the solution data, the enthalpy of formation ($\Delta_f H^\circ(\text{CfOCl}_{\text{cr}})$) at 298 K was calculated to be $-970(7)$ kJ mol^{-1} . This value is also discussed in Chapter 19.

Californium tribromide is trimorphic, but only two of these forms have been prepared by a direct synthetic route. The high-temperature form ($>500^{\circ}\text{C}$) is an AlCl_3 -type, monoclinic structure (Fried *et al.*, 1968; Burns *et al.*, 1975; Young *et al.*, 1976). A less well-characterized form, a FeCl_3 -type rhombohedral structure, has also been reported (Burns *et al.*, 1975). A third form, a PuBr_3 -type orthorhombic structure was acquired indirectly, aged (after a few half-lives of decay) from an orthorhombic form of its BkBr_3 parent (Young *et al.*, 1980). Interestingly, when mixed tribromides of californium–berkelium were synthesized, the orthorhombic structure did not form if the californium content exceeded 45 at%. And, when heating the orthorhombic CfBr_3 above 330°C , it immediately transforms into the monoclinic structure, which illustrates that the orthorhombic form is limited to the region of the ionic radius of californium (Young *et al.*, 1980). In contrast, applying pressure on monoclinic CfBr_3 (>3 GPa) transforms it to the orthorhombic structure (Peterson *et al.*, 1985). The oxybromide of californium, CfOBr (Fried *et al.*, 1968), is isostructural with CfOCl (Copeland and Cunningham, 1969), and both are prepared by the same methods (see Table 11.9). The molar enthalpy of formation of CfBr_3 has been reported to be -752.5 (3.2) kJ mol^{-1} at 298.15 K (Fuger *et al.*, 1990; see Chapter 19).

Californium triiodide is monophasic, and exhibits the BiI_3 -type hexagonal structure (Fried *et al.*, 1968; Wild *et al.*, 1978). It is prepared by treating ‘californium hydroxide’ with hydrogen iodide at 800°C (Fried *et al.*, 1968), but a preferred synthetic route is to heat CfBr_3 or CfCl_3 with hydrogen iodide (Wild *et al.*, 1978). The CfOI is isostructural with CfOCl and CfOBr , and is prepared by the same procedure used for the latter two compounds (see Table 11.9).

The dichloride, dibromide, and diiodide of californium have all been prepared but the difluoride has not been reported. It would be expected that the Gibbs energy change between the di- and trivalent compounds would be the least for the iodides and hence the diiodide would be the most stable. The first compound of Cf(II) was CfBr_2 prepared by hydrogen reduction of CfBr_3 at elevated temperature (Peterson and Baybarz, 1972; Fried *et al.*, 1973). Subsequently, it was observed, and shown by absorption spectra, that lime-green CfBr_3 could also be reduced by thermal treatment alone (760°C) to produce an amber-colored CfBr_2 (Young *et al.*, 1975). The structure of CfBr_2 is tetragonal (SrBr_2 -type; Peterson and Baybarz, 1972). Table 11.8 gives some crystallographic data for these compounds.

The first preparation of CfI_2 produced the high-temperature CdI_2 -type hexagonal form (Young *et al.*, 1975); subsequently, a second structural form (CdCl_2 -type rhombohedral structure) was reported (Wild *et al.*, 1978). The diiodide can be obtained via hydrogen or thermal reduction of the triiodide.

Of the three californium dihalides, CfCl_2 proved to be the most difficult to prepare, and many early attempts to prepare it were unsuccessful (Fujita and Cunningham, 1969; Young *et al.*, 1980). It was eventually prepared by hydrogen reduction of the trichloride at 700°C (Peterson *et al.*, 1977). The X-ray structure

of CfCl_2 still has not been resolved; the existence of this compound is based on its solid-state spectra. It is expected that CfCl_2 would exhibit either the PbCl_2 -type orthorhombic or the SrBr_2 -type tetragonal structure (Young *et al.*, 1975; Peterson *et al.*, 1977).

There is some evidence that californium halides may form so-called mixed-valence compounds (M_5X_{11} , $\text{M}_{11}\text{X}_{24}$ or M_6X_{13} , where M = metal ion and X = halide ion) like those reported for some of the lanthanide elements (Bärnighausen, 1976; Haschke, 1976; Luke and Eick, 1976). To avoid the necessity of carefully controlling reduction of californium to the proper stoichiometry, mixtures of gadolinium and californium (both have comparable III radii; see subsequent section) were used such that total reduction of the californium to Cf(II) would produce the desired cation II/III stoichiometry for formation of the structures, $\text{Cf}_4\text{GdCl}_{11}$ and $\text{Cf}_4\text{GdBr}_{11}$ (Haire *et al.*, 1978).

It has been reported that Cf(II) can be obtained in crystalline strontium tetraborate matrices (Peterson and Xu, 1996). It appears that this tetraborate matrix provides stability for the divalent state of the lanthanides and actinides. It was concluded from spectral data that Cf(II) existed in the material.

Except for the trifluoride, anhydrous californium trihalides are hygroscopic and must be protected from moisture. The dihalides are very sensitive to both moisture and oxygen. Normally, their syntheses are carried out in glass (except for the fluorides) so that products can be flame-sealed *in situ*, avoiding subsequent transfers of the products. Some preparative and experimental techniques for studying californium halides have been reviewed (Young *et al.*, 1978; Haire, 1982). In general, californium forms the same halide compounds and structures as lanthanide elements having a similar ionic radius.

11.7.3 Oxides

Oxides of californium have received a great deal of study, in part because they are primary compounds of interest and use, and were among the first compounds of this element that were investigated given their ease of formation. Oxides often serve as starting materials for preparing other compounds and can be obtained by calcining in air different materials (e.g. nitrates, oxalates, etc.) obtained from solutions. The stoichiometries (O/M ratios), crystal structures, and oxidation states of the californium oxide obtained, all depend on the experimental conditions employed. Haire *et al.* (1972) have discussed the californium-oxygen system.

Oxides of both Cf(III) and Cf(IV) (the sesquioxide and dioxide) are well known, as well as oxides with intermediate oxide compositions (i.e. between O/M of 1.5 and 2.00). The compound, Cf_7O_{12} , which is isostructural with Tb_7O_{12} , has also been established and its crystal structure and stability are known. It exists as a rhombohedral structure over a very narrow stoichiometry range (Turcotte and Haire, 1976). Although the monoxide has been observed in the vapor state, a true CfO solid has not been identified. This is in accord with the difficulty of preparing a true monoxide of ytterbium, although EuO is

known. It is likely that an oxynitride (i.e. Cf(O,N)) or oxycarbonitride (i.e. Cf(O, N,C)) may exist as a solid phase; if so, a variation of lattice parameter (likely fcc-type structure) would be expected for these compounds depending on the actual O/N/C ratios. The formation of californium monoxide may be possible by reacting stoichiometric quantities of the metal and sesquioxide under high pressure and at elevated temperatures. If formed, it would be expected to exhibit a fcc structure with a parameter of 4.8–5.0 Å. This high-pressure preparation of monoxides has been used with selected lanthanides to prepare their monoxides (Leger *et al.*, 1980), but often small residues of metal or oxides remain in the products.

Crystallographic data for the sesquioxides are listed in Table 11.8. Three structures are known for californium sesquioxide: a bcc, a monoclinic, and a hexagonal form. A phase diagram for the transneptunium sesquioxides is shown in Fig. 11.4, where it can be seen that the hexagonal form of californium sesquioxide exists only over a very narrow temperature range up to its melting point of about 1750°C (Haire and Eyring, 1994). There is a trend of decreasing melting point of the actinide sesquioxides with atomic number, which contrasts with the trend observed with the lanthanide compounds. The cubic sesquioxide exists below 1400°C but the monoclinic to cubic transition is very difficult to achieve and appears irreversible, whereas the reverse transition occurs readily. Fig. 11.5 shows the relationship in the molecular volumes for the sesquioxides of the f-elements, where it can be seen that the density for the three californium

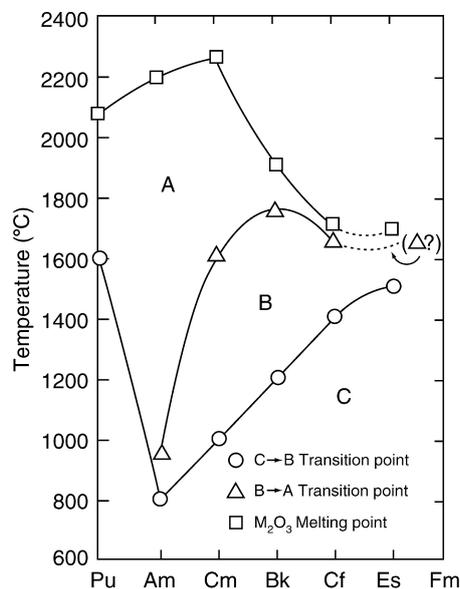


Fig. 11.4 Phase diagram for the Pu through Es sesquioxides.

forms increases in going from the cubic to the monoclinic to the hexagonal structures (Baybarz and Haire, 1976; Haire and Eyring, 1994). This trend for the californium compounds is in accord with those seen for the other f-element sesquioxides.

The monoclinic form of Cf_2O_3 (Sm_2O_3 -structure type) was established early (Green and Cunningham, 1967) and the bcc ($\alpha\text{-Mn}_2\text{O}_3$ -type) was observed subsequently (Copeland and Cunningham, 1969). It was noted that slight oxidation of the bcc form may occur when it was heated in air. The hexagonal form of Cf_2O_3 was established later and was difficult to retain on cooling – it could be retained in samples quenched rapidly with helium from the melt (Baybarz, 1973; Baybarz and Haire, 1976; Haire and Eyring, 1994). One aspect of this monoclinic sesquioxide is its oxygen to metal ratio is ‘fixed’ at 1.5, whereas the cubic sesquioxide readily adds oxygen to its lattice up to a oxygen to metal ratio of 1.67.

As stated above, the hexagonal form of the californium sesquioxide exists over a narrow temperature region (Fig. 11.4). This structural form of berkelium sesquioxide is known and the hexagonal form of californium sesquioxide has also been observed in old samples of hexagonal Bk_2O_3 after berkelium has decayed to californium.

The transition temperature for the bcc to monoclinic form of californium sesquioxide was reported to be both 1100°C (Green and Cunningham, 1967) and 1400°C (Baybarz, 1973; Baybarz and Haire, 1976). The transition from the monoclinic to the hexagonal form was set at 1700°C, just 50°C below the oxide’s melting point. While the monoclinic to cubic transition appears irreversible, the hexagonal to monoclinic form is readily reversible.

The fcc dioxide has been prepared by heating lower oxides of californium with atomic oxygen or under high-pressure molecular oxygen (Baybarz *et al.*, 1972; Haire, 1976). It usually appears as a black or dark-brown material, whereas the sesquioxide is very light green to light-tan color. With time, the dioxide’s lattice parameter increases slightly, due to swelling and/or small losses of oxygen, both processes probably being due to self-irradiation. When heated in air above 200°C, the dioxide begins to lose oxygen and eventually forms Cf_7O_{12} or lower oxides at temperatures above 400°C (Haire, 1976).

A capacitance manometer system, capable of analyzing oxygen overpressures for samples as small as 1.4 mg of californium, together with X-ray diffraction analyses have established the californium–oxygen system between $1.50 < \text{O/Cf} < 1.72$ (Turcotte and Haire, 1976). In that work it was shown that Cf_7O_{12} (a rhombohedral structure) was the stable oxide in air or oxygen up to 750°C. At higher temperatures this compound loses oxygen to eventually form the sesquioxide. A stoichiometric bcc sesquioxide is obtained when these higher oxides of californium are heated in vacuum to 800–1000°C, or when an air-calcined oxide is subsequently treated in hydrogen or carbon monoxide at 850–1000°C.

Thus, the californium sesquioxide system is trimorphic, and there are also the established Cf_7O_{12} and CfO_2 compounds. The bcc sesquioxide lattice can also

accept additional oxygen, and this structure exists for an O/M ratio of 1.5 to 1.67. It is expected that californium oxides with O/M compositions between 1.8 and 2.0 would have fcc structures but this has not been well established. Both the bcc lattice parameters for the sesquioxides up to an O/M of 1.67, and the fcc lattice parameters for the oxides having an O/M of 1.8–2.0, decrease in magnitude with the addition of oxygen to the lattices. In many respects (e.g., stability, formation of specific oxides, structures with specific O/M ratios, etc.), the californium–oxygen system is similar to that of the terbium–oxygen system (Haire and Eyring, 1994).

One other aspect regarding californium oxides is the behavior of (Bk,Cf) oxides as a function of the californium content (Turcotte, 1980). It appears that with californium contents up to 25 at%, the actinides can be oxidized up to an O/M of 2.0 (behaving like pure berkelium oxide). When the californium content is 64 at% or greater, the californium now controls the behavior of berkelium and limits the stoichiometry of the products to M_7O_{12} .

Although the preparation of CfO_2 normally requires strong oxidizing conditions and moderate temperatures, under certain conditions lower oxides of californium stored in air or oxygen can ‘self-oxidize,’ presumably due to an active oxygen species (atomic oxygen?) generated by the alpha radiation field (Haire, 1976); in contrast, small (few micrograms) samples of CfO_2 may lose oxygen under these conditions. The exact composition of aged californium oxides is difficult to ascertain by X-ray analyses alone, as the lattice parameters measured reflect both radiation damage to the lattice (swelling, larger parameter) and/or oxidation that affects the O/M ratios (decrease in parameter with greater oxygen content). Both effects may be operational in these systems. There are reviews on the effects of radiation damage on actinide oxides (Fuger, 1975; Fuger and Matzke, 1991).

The high-temperature vaporization of californium oxides has been explored by Knudsen effusion studies (Haire, 1994). With californium, oxides with O/M ratios > 1.5 lose oxygen, especially in vacuum, when heated (see above discussion) so that vaporization studies at higher temperatures basically deal with the sesquioxide. From the phase behavior in Fig. 11.4, vaporization from solid Cf_2O_3 should involve its monoclinic or hexagonal phases. Vaporization products observed for Cf_2O_3 were atomic Cf and CfO, in a ratio of $\sim 1:10$ at 1800 K. This low concentration of CfO (i.e. CfO is not a dominant species, even though CfO may be expected) is due to the relatively low dissociation energy of CfO (about 498 kJ mol^{-1}) as compared to CmO (about 728 kJ mol^{-1} ; Cm/CmO < 0.1) (Haire, 1994). A value for the enthalpy of formation of the Cf_2O_3 from the vaporization studies was reported as between -1650 and $-1700 \text{ kJ mol}^{-1}$ (Haire, 1994), which compares to $-1653(10) \text{ kJ mol}^{-1}$ obtained from solution calorimetry experiments (see Chapter 19).

A systematic treatment of data for the lanthanide and actinide oxides has generated estimated thermochemical values for the oxides of californium (Morss, 1983). A comparison of the lanthanide and actinide oxygen systems

in detail, which includes discussions of the californium oxides, is also available (Haire and Eyring, 1994). In Section 11.9, discussions on the gas-phase behavior of californium are presented and include other chemical aspects of californium oxides. Both experimental and computational thermochemical data for californium oxides are given in Chapter 19.

There are a number of more complex oxide materials (i.e. ternary systems for one) that are outside the scope of the present chapter. However, one system, the zirconium–californium oxide pyrochlores, is discussed given its potential applications and systematic comparisons with other comparable actinide pyrochlores. The zirconium–californium–oxygen compound has the stoichiometry of $\text{Cf}_2\text{Zr}_2\text{O}_7$. These f-element materials are called pyrochlores given their similarity of their structures to that of the mineral, ‘pyrochlore.’ A related system to these pyrochlores involves solid solutions of zirconium and californium dioxides, which can be prepared from the pyrochlores by adding oxygen to their lattice.

Applications for the americium and curium pyrochlore counterparts include transmutation and nuclear waste matrices, although these uses are not considered for the californium products. The californium–zirconium oxide pyrochlore is cubic with a lattice parameter of 10.57 Å, and it is isostructural with comparable compounds formed with the trivalent actinides plutonium through presumably einsteinium and zirconium or hafnium (Haire *et al.*, 2002). The fit of the lattice parameter of the californium compound with the plutonium through californium and lanthanide zirconium pyrochlores is shown in Fig. 11.6, which can be used to generate a linear equation for the parameters of mixed f-elements or ascertain the oxygen content of a particular pure pyrochlore. This relationship is useful to analyze mixed actinide or lanthanide–actinide pyrochlores when encountered.

11.7.4 Other compounds of californium

In addition to the oxides and halides, several other compounds of californium have been prepared and their crystallographic data reported (see Table 11.8). Some of these data represent preliminary values or even results from a single experiment. In some cases (pnictides, chalcogenides, etc.), the limited supply of californium metal has precluded the preparation of specific compounds via the reaction of the metal, especially where close control of the stoichiometries is required (for example, the preparation of the potential compound, CfS). The general preparative techniques for the different pnictides and chalcogenides of the transuranium elements have been reviewed (Damien *et al.*, 1979).

Stoichiometries other than 1:1 ratio are not expected for the californium pnictides. These materials can be prepared by direct reaction of the elements, and exhibit a NaCl-type, cubic structure. From preparations of CfN, a fcc lattice constant of 4.94 Å has been derived (Haire, 1988). This parameter is only slightly different or the same as reported for samples of fcc californium metal (4.994 Å, Stevenson, 1973; or 4.94 Å, Noé and Peterson, 1976; see Section 11.6)

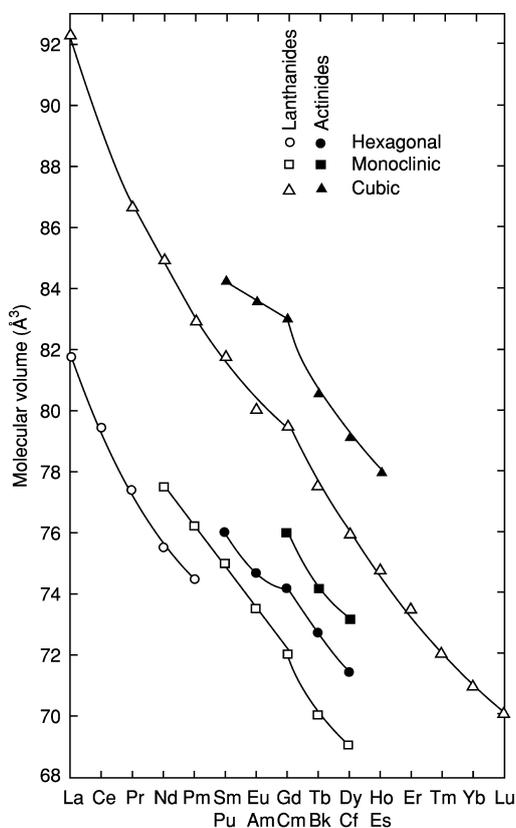


Fig. 11.5 Molecular volumes of f-element sesquioxides.

but much larger than the 4.78 \AA parameter reported for the metal by Haire (1978) and Haire *et al.* (1986). It should be noted that carbon, nitrogen, and oxygen can replace one another in f-element, cubic NaCl-type compounds as the mononitride. The substitution going from carbon to nitrogen to oxygen increases the compound's parameter. For the remaining pnictogens, the monophosphide of californium has not been reported, but the monoarsenide and monoantimonide have been prepared (Damien *et al.*, 1980; see Table 11.8).

In contrast to the pnictides, californium chalcogenides of different stoichiometries can be prepared (Damien *et al.*, 1980). Preparation of the monochalcogenides requires close control of the reactant stoichiometries to avoid the formation of higher chalcogenides, and attempts to prepare californium monochalcogenides as single-phase products have not been successful to date. Another difficulty is that the monosulfide can convert to higher sulfides by volatilizing californium metal and driving the stoichiometry to a higher sulfide. The tritelluride, ditelluride, diselenide, disulfide, sesquiselenide, and sesquisulfide of

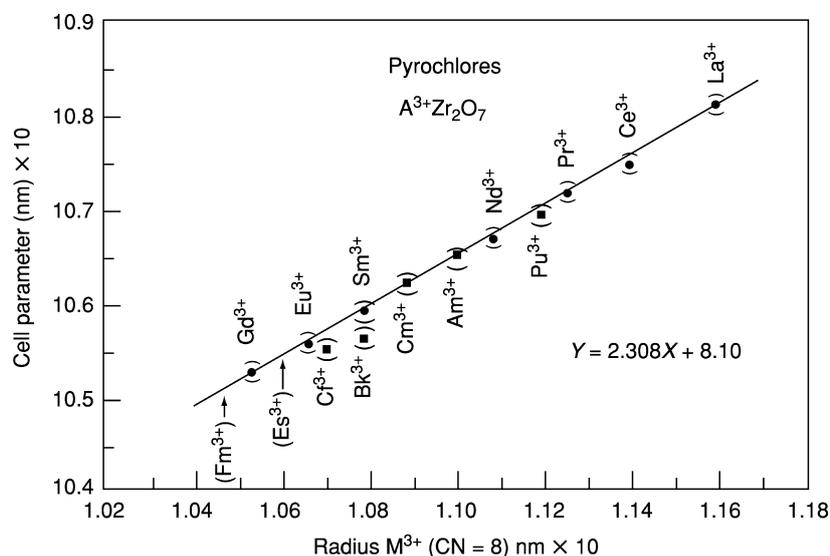


Fig. 11.6 Relationship of lattice parameters and radii for *f*-element pyrochlore oxides. (units shown are equivalent to Ångströms)

californium have all been prepared (Damien *et al.*, 1980). These higher chalcogenides are normally prepared by direct combination of the elements, and lower stoichiometries can be obtained by thermal decomposition of compounds having higher compositions. Lattice parameters for many of these californium compounds have not been reported. It is believed the tritelluride of californium has an orthorhombic structure isomorphous with the NdFe structure. All the dichalcogenide compounds crystallize in the anti-FeAs-type of tetragonal structure (as do the corresponding plutonium, americium, curium, and berkelium compounds). Four transuranium sesquichalcogenide structure types are known; but the sesquisulfide and sesquiselenide of californium have been obtained as the alpha form (bcc; anti-Th₃P₄ type of structure; Damien *et al.*, 1980).

There have been different reports on the preparation of californium hydrides (Gibson and Haire, 1985). The hydrides are generally prepared by reaction of californium metal with hydrogen at elevated temperatures. It was believed that the stoichiometries of the products were close to that for the dihydride (CfH_{2+x}). The products exhibited fcc structures with an average lattice parameter of $a = 5.285$ Å, which is slightly larger than expected for the compound based on extrapolations of parameters for preceding actinide dihydrides. This larger parameter and the inability to prepare a trihydride of californium in the initial efforts were believed to reflect a tendency for californium to be divalent. In the lanthanide-hydrogen system, the hydrides of divalent europium and

ytterbium metals also deviate from the behavior of the other lanthanide hydrides (Topp, 1965). Reports of californium hydrides up to trihydride were subsequently published, which also included stoichiometries intermediate to the dihydride and trihydride (Gibson and Haire, 1987).

The oxysulfate (orthorhombic) and the oxysulfide (trigonal) of californium have also been reported (see Table 11.8); Baybarz *et al.*, 1974). These compounds can be prepared by thermally decomposing either Dowex ion-exchange resin beads containing Cf(III) or hydrated $\text{Cf}_2(\text{SO}_4)_3$ salt. The oxysulfide is obtained by heating these materials in a vacuum or a reducing (hydrogen-containing) atmosphere. The oxysulfate does not decompose to the sesquioxide when heated in air until the temperature exceeds 860°C.

A solid organocalifornium compound, $\text{Cf}(\text{C}_5\text{H}_5)_3$, has been prepared and characterized crystallographically (Laubereau and Burns, 1970a,b; see Table 11.8). Both powder and single-crystal X-ray data were obtained for this orthorhombic, cyclopentadienyl compound, which was prepared by reacting anhydrous CfCl_3 and molten $\text{Be}(\text{C}_2\text{H}_5)_2$, and the crystalline product was isolated by vacuum sublimation (135–200°C). A solid-state absorption spectrum of Cf(C_5H_5)₃ was obtained from these crystals, which showed a broad absorption from 600 nm to lower wavelengths. This was accredited to the presence of an electron-transfer process in the system.

Some work has also been reported on a californium dipivaloylmethanato complex, where the volatility of the complex was compared to complexes of other lanthanides and actinides (Sakanoue and Amano, 1976). These tracer studies suggested that the californium complex deposited at lower temperatures than the americium or plutonium complexes. Other studies have been done on formation of californium β -diketonates, and their thermochromatography behavior has been described (Aizenberg *et al.*, 1988).

11.7.5 Magnetic properties of compounds

A limited amount of magnetic work has been reported for californium and its compounds. Magnetic data for the metallic state of californium have been described in Section 11.6. The transplutonium metals with localized 5f electrons behave as though they consist of ions embedded in a sea of conduction electrons. It is these 5f electrons that are then mainly responsible for the susceptibility. With this simple model, the effective moment for californium metal should be the same as that for a californium ion, where the same number of nonbonding 5f electrons is present.

In Table 11.10 magnetic data for some f-element metal ions are listed, including californium, and their calculated magnetic moments based on LS coupling and Hund's rule. On this basis, the moments of Cf(IV), Tb(III), or Bk(III) would be the same, the moments of Cf(III), Dy(III), or Es(IV) would be identical, and the moments of Cf(II), Es(III), or Ho(III) would be equal. It is unfortunate that the measured moments cannot differentiate between Cf(II) and Cf(III),

Table 11.10 Electronic states (3+) and effective magnetic moments given by *LS* coupling and Hund's rule: expected moments of californium.^a

Lanthanide	Actinide	3+ Ion configur- ation	Basic level	<i>L</i>	<i>S</i>	<i>J</i>	<i>g_J</i>	$\frac{g_J}{[J(J+1)]^{1/2}}$	μ_{eff}^*
Gd	Cm	f ⁷	⁸ S _{7/2}	0	7/2	7/2	2	7.94	7.66
Tb	Bk	f ⁸	⁹ F ₆	3	3	6	3/2	9.7	9.40
Dy	Cf	f ⁹	⁶ H _{15/2}	5	5/2	15/2	4/3	10.63	10.22
Ho	Es	f ¹⁰	⁵ I ₈	6	2	8	5/4	10.60	10.18

Based on these assumptions: Cf(II) = 10.60 μ_B; Cf(III) = 10.63 μ_B; and Cf(IV) = 9.72 μ_B.

^a Edelstein and Karraker (1976) and Huray and Nave (1987). Based on intermediate coupling as opposed to pure *LS* coupling.

and that the calculated difference between Cf(III) and Cf(IV) is only 0.9 Bohr magnetons (see Table 11.10). However, the magnetic behavior of these materials as a function of temperature and/or magnetic field can still provide very useful information, and by itself may be sufficient to differentiate between these states.

The first magnetic data reported for californium compounds were obtained from 56 ng of californium; this small quantity required a microscope to measure the deflections of a Faraday apparatus (Cunningham, 1959). The objective of this experiment was to confirm that californium, deposited on an ion-exchange resin bead, had a radon core plus 5f⁹ electrons. The results showed that the sample followed the Curie–Weiss law and produced a moment of 9.2 μ_B. A subsequent experiment with larger samples (0.3–1.2 μg) of californium on resin beads gave effective moments of 9.1–9.2 μ_B. Magnetic studies on oxides, Cf₂O₃, Cf₇O₁₂, CfO₂, and BaCfO₃, have been reported (Moore *et al.*, 1986). The magnetic moments obtained in these studies were in agreement with the charge states assigned to californium based on the stoichiometries in the materials. Magnetic studies have also been carried out on three mononpnictides, CfN, CfAs, and CfSb (Nave *et al.*, 1985) and on the two structure types of CfCl₃ (Nave *et al.*, 1986).

In other studies, the moment of californium in a Cs₂NaYCl₆ host has been measured (Karraker and Dunlap, 1976). An electron paramagnetic resonance study on Cf(III) in a cubic NaLuCl₄ host (<1% Cf by weight) produced a 10-line spectrum to confirm the nuclear spin to be 9/2 (Edelstein and Karraker, 1976). The crystal field ground state was also identified in this work and the nuclear dipole moment of ²⁴⁹Cf was determined to be –0.28 μ_n. The magnetic properties of californium compounds and metal are summarized and compared in Table 11.11.

11.7.6 Solid-state absorption spectra

The anhydrous transplutonium halides have been extensively studied by absorption spectrophotometry. The f–f and f–d transitions in californium spectra

Table 11.11 Effective magnetic moments of californium metal and compounds.

Material	<i>T</i> range (K)	θ (K)	μ_{eff} (μ_{B})	T_{N} (K)	References
CfO ₂	80–320	–70	9.1(2)	7(2)	Nave <i>et al.</i> (1981)
Cf ₇ O ₁₂	80–320	95	9.5(2)	8(2)	Moore <i>et al.</i> (1986)
CfF ₄	150–340	–51	9.4(1)		Chang <i>et al.</i> (1990)
CfF ₄ (aged)	150–340	–33	9.1(1)	9–12	Chang <i>et al.</i> (1990)
Cf ³⁺ (on a resin bead)	77–298	–5.6	9.14(6)		Fujita and Cunningham (1969)
BaCfO ₃	80–320	–210	9.2(2)	7(2)	Moore <i>et al.</i> (1986)
Cf ₂ O ₃ (monoclinic)	80–320	–80	10.1(2)	8(2)	Moore <i>et al.</i> (1986)
Cf ₂ O ₃ (bcc)	80–320	–115	9.8(2)	19(2)	Moore <i>et al.</i> (1986)
Cf ₂ O ₃ (bcc)	90–300	–80	9.7	–	Morss <i>et al.</i> (1987)
CfF ₃	150–340	–20	10.2(1)	6–7	Chang <i>et al.</i> (1990)
CfCl ₃	60–340	13	10.1(2)	7	Moore <i>et al.</i> (1988)
Cs ₂ NaCfCl ₆	2–14	–2.8	7.36(20)	–	Karraker and Dunlap (1976)
Cs ₂ NaCfCl ₆	20–100	–13.5	10.0(1)	–	Karraker and Dunlap (1976)
Cf metal	28–298	3.24	9.84		Fujita <i>et al.</i> (1976)
	22–298	–3.00	9.67		
Cf metal	100–340	40	9.7(2)		Nave <i>et al.</i> (1985)
CfN	4–340	41	10.3(2)	25	Nave <i>et al.</i> (1986)
CfAs	4–340	29	10.3(2)	25	Nave <i>et al.</i> (1986)
CfSb	4–340	18	10.3(2)	25	Nave <i>et al.</i> (1986)

can be utilized to ascertain the oxidation state and coordination number of californium in the compounds. A valuable technique in these spectroscopy studies was the use of a ‘fingerprint’ approach, where spectra of materials with known structures were used to compare with other compounds. Some of these experimental techniques employed for studying microgram quantities of californium halides have been reported (Green, 1965; Green and Cunningham, 1966; Fujita and Cunningham, 1969; Young *et al.*, 1978). One of the first absorption spectra for californium was obtained from a single crystal of anhydrous CfCl₃. Subsequently, other spectra have also been obtained for this compound (Carnall *et al.*, 1972; Peterson *et al.*, 1977) and for CfCl₂ (Peterson *et al.*, 1977). Absorption spectra have also been obtained for anhydrous CfBr₃ (Young *et al.*, 1975, 1980); CfBr₂ (Young *et al.*, 1980), CfI₃ and CfI₂ (Wild *et al.*, 1978), plus CfF₄ and CfF₃ (Haire *et al.*, 1980).

In Fig. 11.7 solid-state absorption spectrum for CfCl₂ is shown, which is compared with a spectrum for CfCl₃. There is a distinct difference between the absorption spectrum for Cf(III) and Cf(II) states. For a given oxidation state, differences in absorption spectra as well as emission spectra can be noted when the crystal structures are different. This arises from symmetry conditions and how they affect the splitting of electronic levels in the californium compounds. These spectra, once assigned to specific structures, may be used to identify the

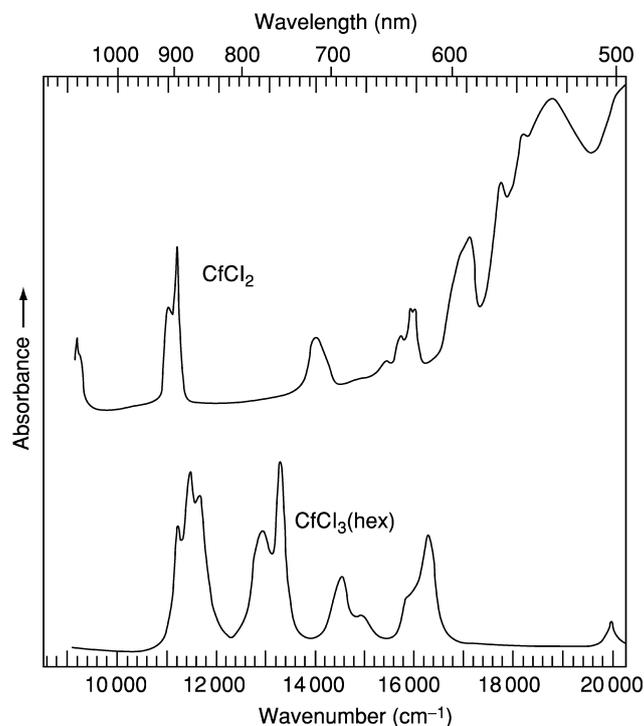


Fig. 11.7 Solid-state spectra for CfCl_2 and CfCl_3 .

structure type by a 'fingerprint' technique. Thus, one finds the spectral envelopes of the absorption spectrum for the hexagonal form of CfCl_3 differs from that of the orthorhombic form of this compound. A review of solid-state spectral studies on californium halides is available (Wilmarth and Peterson, 1991a,b). In this review the authors also give a discussion of Raman spectra obtained for californium.

Laser-induced fluorescence of Cf^{3+} in a LaCl_3 host has also been reported (Caird *et al.*, 1976; Hessler *et al.*, 1978). A limited amount of spectral information has been reported for the dicyclopentadienyl californium compound, where Cf exists as Cf(III) (Laubereau and Burns, 1970a,b). The spectra of Cf(IV) in CeF_4 matrices has also been discussed (Liu *et al.*, 1993) and information obtained was interpreted in terms of line broadening.

Infrared spectra for californium materials have also been obtained (Conway *et al.*, 1977). Crystal field calculations and parameters for the trivalent actinides in crystal hosts have been made and published (Carnall and Fried, 1976; Conway *et al.*, 1977; Crosswhite, 1977). The spectroscopic properties of californium compounds pertinent to potential laser applications have also been discussed, and the transition from the $J = 11/2$ state at 6500 cm^{-1} to the ${}^6\text{H}_{15/2}$ ground

state appears to be a likely candidate in this regard (Weber, 1980). Free-ion energy levels and the optical properties for californium have also been published (Hessler and Carnall, 1980).

In addition, absorption spectra of californium halides have been obtained and examined as a function of time, looking at the daughter or granddaughter products in studies that examined the chemical and structural consequences of the radioactive decay processes (Young *et al.*, 1980, 1981, 1984). Following the chemistry and structural forms through radioactive decay processes by examining the californium granddaughter products produced from the decay of Es-253 halides (i.e. Es-253 \rightarrow Bk-249 \rightarrow Cf-249 \rightarrow ...) is an example. It is worthwhile to note that in the latter decay sequence, Cf(III) halide product was produced from an initial Es(III) halide product and a Cf(II) halide product when starting with a Es(II) halide. Essentially, the oxidation state was retained through two decay events, first an alpha and then a beta decay). This implies that a Bk(II) product was formed in the transition although Bk(II) has not been synthesized directly.

11.8 SOLUTION CHEMISTRY

11.8.1 General comments

Although californium exhibits oxidation states of II, III, and IV in the solid state, its solution chemistry is basically that of a trivalent ion. There has been only a couple of unsubstantiated reports of an oxidation state above Cf(IV) in solution even though formation of Cf(V) presumably would acquire some stabilizing influence by attaining a half-filled, 5f-orbital state (5f⁷).

To retain the tetravalent state in solution is also more difficult than generating it in the solid state, and for solutions it requires a high degree of complexation to afford sufficient stabilization to maintain this state. It has been reported (Kosyakov *et al.*, 1977) that Cf(IV) was stabilized in phosphotungstate solutions, where M(IV)/M(III) couples can be shifted by as much as 1.0 V (Barnanov *et al.*, 1981). Another report for stabilizing Cf(IV) in solution involved the use of triphenylarsine oxide in acetonitrile (Payne and Peterson, 1987).

It is expected to be easier to stabilize Cf(II) than Cf(IV) in solutions. Nonaqueous solvents also offer some promise for obtaining both the II and IV oxidations states of californium. But in all cases, the effects of self-irradiation and the potential for generating oxidizing and/or reducing conditions must be considered and factored into the picture.

Although californium is the electronic homolog of dysprosium, its divalent-trivalent behavior in solution should be considered to be more similar to that of samarium, and its trivalent-tetravalent behavior may be comparable to that of terbium. Thus, samarium and terbium can be used as template elements for testing the oxidation behavior of californium.

Trivalent californium's behavior in solution is very similar to the behaviors of the trivalent lanthanide ions in solution, except californium has a greater tendency to form complexes (is more covalent). This arises from the somewhat extended 5f orbitals of actinides compared to the 4f orbitals, which provides a slightly greater degree of complexing ability to afford californium's greater covalent nature. The higher degree of complexation found with the transplutonium (III) ions in ethanol-HCl solution, as compared to the lanthanide (III) ions (see Section 11.4), has used this condition as one method for a group separation.

As with the lanthanides, both fluoride and oxalate ions will precipitate trivalent californium from dilute acid solutions. Addition of hydroxide to a Cf(III) solution produces a gelatinous, light green-tinted precipitate, which is presumably its trihydroxide. In non-complexing solutions (i.e. dilute acid solutions, 0.1 M perchloric or hydrochloric acids), Cf(III) exists as a hydrated cation; at higher acid concentrations (i.e. 6 M HCl), complexation is sufficient so that californium will not be held on cation-exchange resins but will elute as an anion complex. This difference in complexation forms the basis for a number of group separations between trivalent lanthanides and actinide ions. The greater complexing nature of the actinides allows them to be removed from cation-exchange resins with different reagents while the lanthanides are retained on the columns.

11.8.2 Oxidation-reduction reactions

Several reduction potentials for californium have been derived from both experimental data and from systematic calculations, and some of these values are given in Table 11.12. The calculated Cf(IV)/(III) couple of 3.2 V (Nugent *et al.*, 1971) is in accord with the inability to obtain Cf(IV) in most aqueous media. This value for californium can be compared to the Tb(IV)/Tb(III) couple of 3.1–3.3 V, the Am(IV)/Am(III) couple of 2.2–2.5 V, and the Cm(IV)/Cm(III) couple of 3.1–3.5 V (Nugent *et al.*, 1973a,b). It is difficult to maintain Am(IV) and essentially not feasible to produce Cm(IV) in most aqueous solutions. Preparation of these higher oxidation states for the actinides in general should be more favorable in alkaline than acidic media, but complexation can also offer stabilization. Thus, in principle, the ease of forming Cf(IV) should be comparable to forming Tb(IV) or Cm(IV) in solution, which are more difficult than forming Am(IV) in solution. This relative behavior of californium in solution may be likened to that in the solid state: the formation of californium dioxide is comparable to preparing terbium dioxide, with both being more difficult to prepare than americium or curium dioxide (see Section 11.7.3).

The ability to oxidize Cf(III) to Cf(IV) in a phosphotungstate solution has been summarized in a paper on the solution behavior of the transplutonium elements (Myasoedov, 1982). Both Tb(IV) and Am(IV) can be stabilized in strong carbonate; thus, it would appear possible to prepare Cf(IV) in a strong carbonate medium, utilizing the expected shift of 1.7 V in the Cf(IV)/Cf(III) couple arising from carbonate complexation of the Cf(IV). Two conflicting reports exist on the

Table 11.12 Reduction potentials for californium.

<i>Couple</i>	<i>Potential</i> (V vs NHE)	<i>Method</i>	<i>References</i>
Cf(IV)/Cf(III)	3.3; 3.2	calculated	Nugent <i>et al.</i> (1971, 1973a,b)
Cf(IV)/Cf(III)	3.2		Chapter 19
Cf(III)/Cf(II)	-2.0; -1.9	calculated; spectra	Nugent <i>et al.</i> (1969)
	-1.6		Chapter 19
	-1.4	calculated	David (1970a,b,c)
	-1.6	calculated; spectra	Friedman <i>et al.</i> (1972)
	-1.47	polarographic/voltammetric	Musikas <i>et al.</i> (1981)
	-1.6	polarographic (acetonitrile)	Friedman <i>et al.</i> (1972)
Cf(III)/Cf(0)	-2.32	calculated	David (1980)
	-2.01	radiopolarography	David <i>et al.</i> (1978)
			and Samhoun and David (1976)
	-2.06	calculated	Raschella <i>et al.</i> (1982)
	-1.93		Chapter 19
Cf(III)/Cf(Hg)	-1.61	Calculated	Musikas <i>et al.</i> (1981)
Cf(III)/Cf(Hg)	-1.503	radiopolarography	Samhoun and David (1976)
Cf(II)/Cf(Hg)	-1.68	polarographic/voltammetric	Samhoun and David (1976)
Cf(II)/Cf(0)	-2.1		Chapter 19

oxidation of Cf(III) in carbonate. One group (Hobart *et al.*, 1981, 1983) was unable to find evidence for Cf(IV) after chemical or electrical treatments, while a second team (Myasoedov *et al.*, 1986) reported that 20% of the Cf(III) present in a K₂CO₃ solution could be oxidized electrochemically.

The behavior of californium and the next two actinide elements in molten salts where strong reducing agents were present has been reported (Kulyukhin *et al.*, 1997). The ease of preparing the divalent state increases in going across the series to einsteinium.

A number of studies have supported the potential for the existence of Cf(II) in solution. In one study, the tendency for californium to form amalgams rapidly is compared to the behavior of the lanthanides known to acquire a divalent state (Maly, 1967; Maly and Cunningham, 1967; Nugent, 1975). In early work, the inability to reduce Cf(III) in 0.1 M NH₄Cl suggested a potential limit of -1.4 V for the Cf(III)/Cf(II) couple (Cunningham *et al.*, 1970). David (1970a-c) also proposed a value of -1.4 V from radiopolarographic and amalgamation behaviors using tracers.

Studies on the coprecipitation behavior of californium (Cohen *et al.*, 1968; Fried and Cohen, 1968; Mikheev *et al.*, 1972a,b) have also supported the existence for Cf(II) in solution. The difference in formal potentials between the Sm(III)/Sm(II) and Cf(III)/Cf(II) couples has been estimated to be 0.045 V (californium being more negative) by studies on coprecipitation of chloride salts in

aqueous ethanol solutions (Mikheev *et al.*, 1972a,b). Another comparison between the reduction behavior of californium and samarium was made in anhydrous acetonitrile (Friedman *et al.*, 1972), where the Cf(III)/Cf(II) and Sm(III)/Sm(II) couples were found to be nearly identical; a value of -1.58 V was proposed for the Cf(III)/Cf(II) couple. Essentially the same value (-1.60 V) for this couple was reported from co-crystallization studies (Mikheev *et al.*, 1972a,b). Nugent *et al.* (1969, 1973a) have suggested the potential for the Cf(III)/Cf(II) couple is -1.6 V, based on systematic analyses of electron-transfer bands. Radiopolarographic experiments on californium have resulted in two reports regarding its behavior. The first report (David, 1970a) suggested two couples: -2.32 V for Cf(III)/Cf(0) and -1.4 V for Cf(III)/Cf(II). Subsequent work (Samhoun and David, 1976) concluded that the first radiopolarographic results were incorrect, and that Cf(III) is reduced directly to Cf(Hg) in one step ($E_{1/2} = 1.503$ V): correcting for the amalgamation process yields a Cf(III)/Cf(0) couple of -2.01 V. Guminski (1996) has discussed the Hg-Cf system.

Subsequently, a polarographic and voltammetric study (Musikas *et al.*, 1981) on larger amounts of californium concluded that californium is reduced via a two-step process as is found with samarium: (1) Cf(III) \rightarrow Cf(II) and (2) Cf(II) \rightarrow Cf(Hg). Potentials for these processes were given as -1.47 and -1.68 V, respectively. These data yield a calculated value of -1.61 V for Cf(III)/Cf(0). An evaluation of earlier amalgamation experiments has also led to a proposed value of -2.2 V for the Cf(II)/Cf(0) couple (Nugent, 1975).

These reported differences for californium have not been resolved and additional work needs to be done to resolve the system. Since Cf(II) can be prepared and maintained in the solid state, there still remains a good possibility that Cf(II) can be stabilized in aqueous and/or nonaqueous solvents. David *et al.* (1990a,b) and David and Bouissières (1968) discuss the electrochemical reduction in aqueous solution for separations, and for the formation of intermetallic compounds and amalgams. Other work on the radiopolarography of californium has also been published (Skiokawa and Suzuki, 1984).

Evidence for Cf(II) in molten-salt systems has also been reported (Ferris and Mailen, 1971). The distribution coefficient of californium between molten lithium chloride and lithium-bismuth metals at 640°C indicated that divalent californium was present in the salt phase. However, evidence for the existence of Cf(II) was not found in lithium fluoride-beryllium fluoride melts (Ferris and Mailen, 1970).

It is generally accepted that the stability of the divalent state increases for the second half of the actinide series of elements, and it has been accepted that californium metal is close to being a metal having only two bonding electrons (see earlier section). Starting with californium, the M(III)/M(II) couples increase regularly in the order: No $>$ Md $>$ Fm $>$ Es $>$ Cf, with values ranging from -1.45 V for nobelium to -1.60 V for californium (Myasoedov, 1982).

In discussing the oxidation states of californium in solution, the possibility of attaining Cf(V) could be enhanced by the attainment of a $5f^7$ electronic state.

Some early coulometric data obtained with a few micrograms of californium suggested that Cf(v) may have been attained in a 1 M H₂SO₄ solution (Propst and Hyder, 1969), but these results have not been confirmed and are likely to be incorrect. More recently, a claim for the generation of Cf(v) in a carbonate media was made based on results of coprecipitation experiments (Kosyakov *et al.*, 1982a,b). In this work, small amounts (<10%) of californium, generated from the decay of Bk(IV) in the solution, were found in Na₄UO₂(CO₃)₃ 'wet' solids precipitated from the solutions. The presence of 'co-precipitated' californium in these precipitates was interpreted as reflecting the presence of an oxidized form of californium (Cf(IV) or Cf(V) i.e. as the CfO²⁺ or CfO₂⁺ ion) within the uranium precipitate. These results must be accepted with some caution, as other explanations for the behavior can be given. It is likely that Cf(IV) would accompany Bk(IV) in such situations. Thermodynamic (David *et al.*, 1978) and quantum-chemical calculations (Ionova *et al.*, 1980) have been made that indicate it may be possible to obtain Cf(V) state in the solid state, which could be considered for the solid phases mentioned above. However, it would seem most plausible that Cf(IV) or Cf(V) would be stabilized in alkaline conditions/materials, oxygenated complexes, complex polyanion materials (i.e. polytungstates), etc.

11.8.3 Complexation chemistry

A considerable portion of the published data dealing with californium concerns the complexation and solvent extraction chemistry of Cf(III). This is in part a consequence of the fact that a large amount of this information could be obtained using tracer quantities of the more abundant ²⁵²Cf isotope, which also has a higher specific activity. In addition, there was an impetus to perform this type of study using the small quantities available during the investigation/development of californium's separation chemistry for processing. A compilation of stability constants for californium complexes and chelates is given in Table 11.13.

Some of the first data on californium complexes involved materials such as halides, citrates, lactates, α -hydroxyisobutyrate complex, etc., as these materials played a role in early separation/purification schemes (Katz and Seaborg, 1957; Keller, 1971) for californium (see Section 11.4). In general, it is expected that only small differences in stability would exist between Cf(III) and its two trivalent near neighbors, Bk(III) and Es(III), with potentially larger differences existing between Cf(III) and Am(III). A general discussion of actinide complexes (including californium) in aqueous solution is available (Jones and Choppin, 1969). Horwitz *et al.* (1997) discuss complexer in solution.

From the initial studies on Cf(III) and sulfate ions (De Carvalho and Choppin, 1967) it was concluded that 1:1 and 1:2 complexes Cf(SO₄)⁺ and Cf(SO₄)₂⁻ were formed, but subsequent work in the sulfate system suggested that mono-, di-, and trisulfate species were formed (McDowell and Coleman, 1972).

Table 11.13 Stability constants of $Cf(III)$ complexes and chelates.

Ligand	Experimental method	Log of stability constants ^a at 25°C	References
fluoride ion	solv. extract.	$\beta_1 = 3.03$ $\mu = 1.0$	Choppin and Unrein (1976)
hydroxide ion	solv. extract	$\beta_1 = 5.62$ $\beta_1 = 5.05$ $\mu = 2.00$	Desiré <i>et al.</i> (1969)
sulfate ion	solv. extract.	$\beta_1 = 1.36$ $\beta_2 = 2.07$ $\mu = 2.0$ $K_{01} = -3.73$ $K_{02} = -5.58$ $K_{03} = -5.09$ $\mu = 0$	De Carvalho and Choppin (1967)
thiocyanate ion	solv. extract. solv. extract.	$\beta_1 = 3.06$ $\beta_1 = 3.71$ $\beta_2 = 0.28$ $\beta_3 = 2.65$ $\beta_1 = 2.11$ $\mu = 1.0$ $\beta_3 = 12.5$ $\mu = 0.1$	Choppin and Ketels (1965) Coleman (1972)
acetate ion	solv. extract.	$\beta_1 = 2.11$ $\mu = 1.0$ $\beta_3 = 12.5$ $\mu = 0.1$	Choppin and Schneider (1970) Stary (1966)
oxalate ion	— electromigr.	$\beta_1 = 5.50$ $\beta_2 = 3.87$ $\mu = 0.1$ $\beta_3 = 6.08$ $\mu = 0.15$ $\beta_3 = 6.09$ $\mu = 0.5$ $\beta_3 = 6.08$ $\mu = 0.5$	Stepanov (1971) Stary (1966)
lactic acid	— solv. extract. ion exchange		Ermakov and Stary (1967) Ermakov and Stary (1967)

α -hydroxyiso- butyric acid	ion exchange	$\beta_3 = 6.9$ $\mu = 0.5$	Desiré <i>et al.</i> (1969)
tartaric acid	—	$\beta_2 = 6.8$ $\mu = 0.1$	Desiré <i>et al.</i> (1969)
ethylenediaminetetraacetic acid	solv. extract. ion exchange	$\beta_2 = 5.86$ $\beta_1 = 19.09$	Aly and Latimer (1970) Fuger (1958)
1,2-diaminocyclohexane- tetraacetic acid	ion exchange	$\beta_1 = 19.42$	Baybarz (1966a,b)
diethylenetriaminopentaacetic acid	—	$\beta_1 = 22.6$ $\beta_1 = 22.57$	Stary (1966) Baybarz (1965)
glycolate ion	ion exchange solv. extract.	$\beta_1 = 25.19$ $\beta_1 = 2.63$	Brandau (1971) Choppin and Degischer (1972)
2-methylactic acid	solv. extract.	$\beta_2 = 1.97$ $\mu = 2.0$ (33°C) $\beta_1 = 4.10$	Aly and Latimer (1970)
malic acid	solv. extract.	$\mu = 0.1$ $\beta_1 = 7.02$	Aly and Latimer (1970)
citric acid	solv. extract.	$\mu = 0.1$ $\beta_1 = 11.61$	Aly and Latimer (1970)
	electromigr.	$\mu = 0.1$ $\beta_1 = 7.93$ $\beta_2 = 3.3$	Stepanov (1971)
	solv. extract.	$\mu = 0.1$ $\beta(C\frac{2}{2}) = 10.90$ $\mu = 0.1$ $\beta(C\frac{3}{2}) = 12.26$	Hubert <i>et al.</i> (1974)
	solv. extract.	$\beta(M(HCit)^-)_2 = 5.8;$ $\mu = 0.1$ $\beta(M(HCit)(Cit^{2-})) = 9.9;$ $\mu = 0.1$	Guillaumont and Bourderie (1971)

Table 11.13 (Contd.)

<i>Ligand</i>	<i>Experimental method</i>	<i>Log of stability constants^a at 25°C</i>	<i>References</i>
thenoyltrifluoroacetone	solv. extract.	$\beta_3 = 14.94$ $\mu = 0.1$	Keller and Schreck (1969)
benzoyltrifluoroacetone	solv. extract.	$\beta = 16.06$ $\mu = 0.1$	Keller and Schreck (1969)
naphthoyltrifluoroacetone	solv. extract.	$\beta = 18.83$ $\mu = 0.1$	Keller and Schreck (1969)
nitriodiace-to-	ion exchange	$\beta_1 = 10.94$	Eberle and Ali (1968)
monopropionic acid	ion exchange	$\beta_2 = 18.45$	Eberle and Ali (1968)
nitriotriacetic acid	ion exchange	$\beta_1 = 11.92$ $\beta_1 = 11.3$ $\beta_2 = 21.0$ $\mu = 0.1$	Sary (1966)
<i>N</i> -2-hydroxyethyl-ethylenediaminetriacetic acid	ion exchange	$\beta_1 = 16.27$ $\beta_2 = 28.5$ $\mu = 0.1$	Eberle and Ali (1968) Eberle and Bayat (1967)
2-hydroxy-1,3-diamino-propane tetraacetic acid		$\beta_1 = 13.18$	Baybarz (1967)
5,7-dichloro-8-hydroxyquinoline	solv. extract.	$\mu = 0.1$ $\beta_3 = 22.59$	Feinauser and Keller (1969)
4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one	solv. extract	$\beta_3 = 17.78$ $\mu = 0.1$	Keller (1971)

4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one	solv. extract	$\beta_3 = 13.48$ $\mu = 0.1$	Keller (1971)
2-hydroxyethyl-iminodiacetic acid	solv. extract.	$\beta_1 = 9.61$ $\mu = 0.1$	Ermakov <i>et al.</i> (1971b)
o-hydroxyphenyl-iminodiacetic acid		$\beta_1 = 7.38$ $\beta_2 = 12.28$ $\mu = 0.1$	Ermakov <i>et al.</i> (1971)
2-ethylhexylphenyl-phosphoric acid		$\beta_1 = 6.03$ $\beta_2 = 2.00$ $\mu = 0.1$	Barketov <i>et al.</i> (1975)
thenoyltrifluoroacetone		$\beta_1 = 6.90$ $\mu = 0.1$	Khopkar and Mathur (1977)

^a Overall formation constants:

$$\beta_1 = \frac{[\text{CfA}^{(3-n)+}]}{[\text{Cf}^{3+}][\text{A}^{n-}]}, \quad \beta_2 = \frac{[\text{CfA}_2^{(3-2n)+}]}{[\text{Cf}^{3+}][\text{A}^{n-}]^2} \quad \text{etc.}$$

stepwise constants:

$$K_2 = \frac{[\text{CfA}^{(3-2n)+}]}{[\text{CfA}^{(3-n)+}][\text{A}^{n-}]} \quad \text{etc.}$$

A similar situation exists for the thiocyanate complexes reported for Cf(III). Initially a 1:1 complex, $\text{Cf}(\text{SCN})^{2+}$, was reported (Choppin and Ketels, 1965), but subsequent work indicated that three different complexes could form: $\text{Cf}(\text{SCN})^{2+}$, $\text{Cf}(\text{SCN})_2^+$, and $\text{Cf}(\text{SCN})_3$, where the 1:3 complex was of the inner-sphere type (Coleman, 1972).

The hydrolysis behavior of Cf(III) is expected to be similar to that of trivalent lanthanides, and more specifically to that of Eu(III) or Gd(III), which have nearly the same ionic radii. The first hydrolysis reaction (i.e. $\text{Cf}^{3+} + \text{H}_2\text{O} \rightarrow \text{CfOH}^{2+} + \text{H}^+$; i.e. the K_1 value) has also been determined for Cf(III); $\log K_1$ values for it were given as -5.62 (Desiré *et al.*, 1969) and -5.05 (Hussonnois *et al.*, 1973).

Several quite stable complexes can be formed with Cf(III) (see Table 11.13). Complexes of diketones and aminopolycarboxylic acids have been found to be considerably more stable than those of tartrate, lactate, oxalate, etc. In some cases, adduct chelates can also form with Cf(III), such as with the californium thenoyltrifluoroacetone (TTA) chelate and methyl isobutyl ketone (MIBK) (i.e. $\text{Cf}(\text{TTA})^{3+}$ and $\text{Cf}(\text{TTA}) \rightarrow \text{MIBK}$ or $\text{Cf}(\text{TTA})_3 - 2 \text{MIBK}$; Desiré *et al.*, 1969).

With the monodentate ligands, such as tributyl phosphate (TBP), the extractable californium adduct from nitric acid solutions has been assigned as being a 1:3 species $\text{Cf}(\text{NO}_3)_3 \cdot 3 \text{TBP}$ (Healy and McKay, 1956). Quaternary ammonium bases and alkylpyrocatechols (i.e. 4-dioctylethyl pyrocatechol) can form californium complexes in alkaline solutions (Derevyanko *et al.*, 1976), which affords a different medium for complexation. One recent extraction study has examined the influence of the extractant's structure on the extraction behavior of californium (Derevyanko *et al.*, 1976). A large number of materials have been investigated for forming extractable complexes of californium, and the reader is referred to reviews on the subject (Ishimori, 1980; Myasoedov *et al.*, 1980; Shoun and McDowell, 1980). Takeiski *et al.* (2001) have discussed the solvent extraction of californium by derivatives of bis(1-phenyl-3-methyl-4-acylpyrazol-5-one).

Exchange kinetics of Cf(III) with europium ethylenediaminetetraacetate (Eu EDTA) in aqueous solution ($\mu = 0.1$) has also been reported (Williams and Choppin, 1974). The exchange was found to be a first-order reaction having both acid-dependent and acid-independent terms.

From a study of the relationship between distribution coefficients for californium with sodium nitrate in extractions using organic ammonium nitrates, the apparent mean molar activity coefficient of Cf(III) was calculated in terms of a polynomial ($\log k = a + bm + cm^2 + dm^3$, where $a = 0.00397$, $b = -0.154$, $c = 0.0252$, and $d = 0.00119$) (Chudinov and Pirozhkov, 1973).

Some initial studies of californium complexes involving 6-methyl 2-(2-pyridyl)-benzimidazole and derivatives of it have been carried out. The initial studies involved photoluminescence and Raman spectroscopy investigations, where it was concluded that 1:1, 1:2, 1:3, and 1:4 complexes were formed (Assefa *et al.*, 2005).

A general discussion of the hydrolysis of actinide ions is given in a review by Ahrlund (1991). Although little is mentioned about californium, several general concepts discussed there are useful for the trivalent actinides. In another review, Bhattacharyya and Natarajan (1991) discuss the radiation chemistry of actinide solutions. A rate constant for the oxidation of Cf^{2+} by water ($K = 7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$) and a rate constant for the reduction of Cf^{3+} ($K = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) at a pH of 5.3 are quoted.

11.8.4 Thermodynamic data

The thermodynamic behavior of californium has been addressed in Chapter 19. Given there are the recommended values for californium that have been arrived at after considering various reports.

Selected thermodynamic data for the formation of Cf(III) in solution (according to the following reaction):



are given in Table 11.14 (also see Section 11.6.2 on californium metal for comments on its enthalpy of solution), which has been used for calculating the enthalpy of formation of aqueous ions. The enthalpy of formation, $\Delta H_{298,f}^{\circ}(\text{Cf}^{3+}, \text{aq})$ was derived from the enthalpy of solution (Fuger *et al.*, 1984) as being $-577(5) \text{ kJ mol}^{-1}$. The entropy, $S^{\circ}(\text{Cf}^{3+}, \text{aq})$, has been accepted as $-197(17) \text{ J K}^{-1} \text{ mol}^{-1}$ (see Chapter 19). Using these values and $S^{\circ}(\text{Cf, cr, } \alpha \text{ phase, } 298.15 \text{ K}) = 81(5)$ (Ward, 1983; see Chapter 19) one obtains $\Delta_f G(\text{Cf}^{3+}, \text{aq}) = -533(7) \text{ kJ mol}^{-1}$. A standard potential for the $\text{Cf(III)}/\text{Cf(0)}$ couple was calculated to be $-(1.92 \pm 0.03) \text{ V}$ in that work. Earlier estimates for this potential ranged from -1.95 to -2.03 V (Nugent, 1975; David *et al.*, 1976a,b; David *et al.*, 1978; Samhoun and David, 1979).

Other estimates for $\Delta H_f(\text{Cf}^{3+}, \text{aq})$ have appeared in the literature. Nugent *et al.* (1973a,b) proposed a value of -623 kJ mol^{-1} ; David *et al.* (1986) suggested $-(586 \pm 21) \text{ kJ mol}^{-1}$; and Nugent (1975) subsequently arrived at a value of $-(602 \pm 21) \text{ kJ mol}^{-1}$. A value of -603 kJ mol^{-1} was estimated for californium in a comparison given for thermochemical properties for the lanthanide and actinide elements (Morss, 1983). This latter work also presents other thermochemical values for californium.

Predictions of the standard free energy (ΔG_f) and the enthalpy of hydration (ΔH_{hyd}) for the trivalent californium ion have been made based on an electrostatic hydration model (Goldman and Morss, 1975). Assuming a crystallographic radius of 0.94 \AA and a gas-phase radius of 1.516 \AA for Cf(III) , and using a primary hydration number of 6.1, ΔG_{298}° and ΔH_{298}° were calculated to be -3385 and $-3582 \text{ kJ mol}^{-1}$, respectively.

Thermodynamic data for the 1:1 complex, $\text{Cf}(\text{SO}_4)^+$, have been calculated from the temperature dependence of the stability constant (De Carvalho and

Table 11.14 *Thermodynamic data for californium.*

A. Metal, crystal at 298.15 K and 10 ⁵ Pa							
S° (J K ⁻¹ mol ⁻¹)				$\Delta_{\text{sub}}H^\circ$ (kJ mol ⁻¹)			
81(5)				196 (10)			
B. Metal, gas at 298.15 K and 10 ⁵ Pa							
S° (J K ⁻¹ mol ⁻¹)				C_p (J K ⁻¹ mol ⁻¹)			
201.3(30)				20.786(20)			
C. High temperature heat capacity of the metal [$C_p/\text{J K}^{-1} \text{ mol}^{-1} = a(T/\text{K})^{-2} + b + c(T/\text{K}) + d(T/\text{K})^2 + e(T/\text{K})^3$]							
<i>form</i>	$A \times 10^{-6}$	b	$C \times 10^3$	$D \times 10^6$	e	T/K	$\Delta_{\text{trs}}H$ (kJ mol ⁻¹)
dhcp		23.651	9.7865	9.0983		863	2.64
fcc	0.0580	37.6				1173	7.51
D. Aqueous ions at 298.15 K							
Cf^{3+}		Cf^{3+}		Cf^{4+}		Cf^{4+}	
S° (J K ⁻¹ mol ⁻¹)		$\Delta_f H^\circ$ (kJ mol ⁻¹)		S° (J K ⁻¹ mol ⁻¹)		$\Delta_f H^\circ$ (kJ mol ⁻¹)	
-197(17)		-577(5)		-405(17)		-483(5)	
E. Solid CfO ₂ at 298.15 K							
S_{exs} (J K ⁻¹ mol ⁻¹)			S° (J K ⁻¹ mol ⁻¹)			$\Delta_f H^\circ$ (kJ mol ⁻¹)	
21.3			87(5)			-858	
F. Standard entropy and enthalpy of formation of Cf ₂ O ₃ at 298.15 K							
S° (J K ⁻¹ mol ⁻¹)				$\Delta_f H^\circ$ (kJ mol ⁻¹)			
176.0(50)				-1653(10)			
G. Properties of californium halides at 298.15 K.							
Halide		S° (J K ⁻¹ mol ⁻¹)			$\Delta_f H^\circ$ (kJ mol ⁻¹)		
CfF ₄					-1623		
CfF ₃					-1553(35)		
CfCl ₃		167.2(6)			-965(20)		
CfBr ₃		202(5)			-752.5		
CfI ₂		154			-669		

Source: Chapter 19.

Choppin, 1967). Values for this complex are: $\Delta G_{298} = -7.9 \text{ kJ mol}^{-1}$, $\Delta H_{298} = 19 \text{ kJ mol}^{-1}$, and $\Delta S_{298} = 88 \text{ kJ mol}^{-1}$. Similarly, data for the 1:1 CfF^{2+} complex have been calculated (Nugent *et al.*, 1973a,b), and have been given as: $\Delta G_{298} = 17.3 \text{ kJ mol}^{-1}$, $\Delta H_{298} = 27.2 \text{ kJ mol}^{-1}$, and $\Delta S_{298} = 14 \text{ kJ mol}^{-1}$.

Other thermodynamic data have also been reported for californium (David *et al.*, 1978). The reader is also referred to Chapter 19 for a more complete summary of thermodynamic data for californium.

11.8.5 Solution absorption spectra

The first absorption spectrum for Cf(III) was obtained from the solid state (Green, 1965; see Section 11.7.6). The first solution absorption spectrum was obtained shortly thereafter, using 592 μg of mainly ^{252}Cf isotope, which introduced experimental problems regarding both shielding and radiolytic gassing. Nineteen absorption bands were recorded between 280 and 1600 nm from a 1 M DClO_4 solution (see Table 11.15; Fig. 11.6). The absorption spectrum from this work was confirmed using milligram quantities of ^{249}Cf (Carnall and Fried, 1976).

Table 11.15 Absorption data for Cf(III) in 1 M DClO_4 ,^a

Wavelength (nm)	Wavelength (cm^{-1})	Absorption coefficient, μ ($\text{L mol}^{-1} \text{cm}^{-1}$)
1560.0	6 410	5.3
1211.0	8 260	1.6
840.3	11 900	2.5
769.8	12 990	6.3
745.2	13 420	6.4
673.8	14 840	2.5
640.2	15 620	1.7
602.0	16 610	4.9
490.0	20 410	1.9
469.9	21 280	8.9
442.1	22 620	10.3
434.8	23 000	9.8
401.9	24 880	0.9
353.4	28 300	1.0
334.0	29 940	1.5
325.0	30 770	3.8
304.9	32 800	1.1
295.0	33 900	2.4
284.0	35 210	1.9

^a Conway *et al.* (1966).

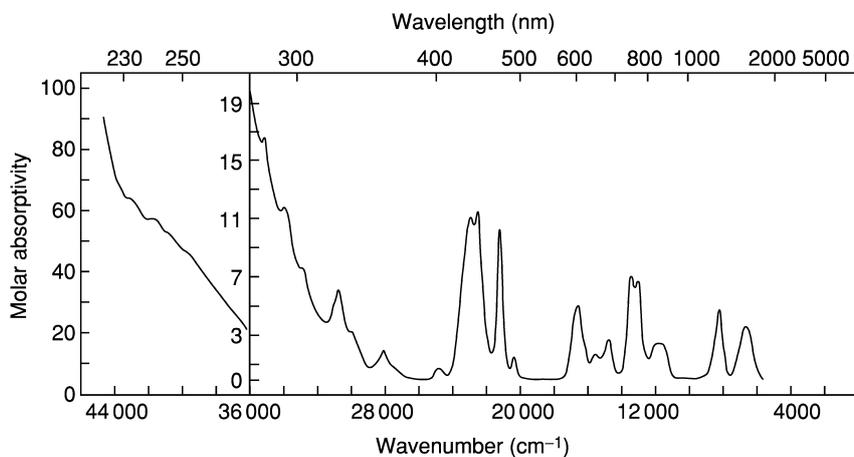


Fig. 11.8 Solution absorption spectrum of Cf(III) in 0.1 M $\text{HClO}_4\text{-DClO}_4$.

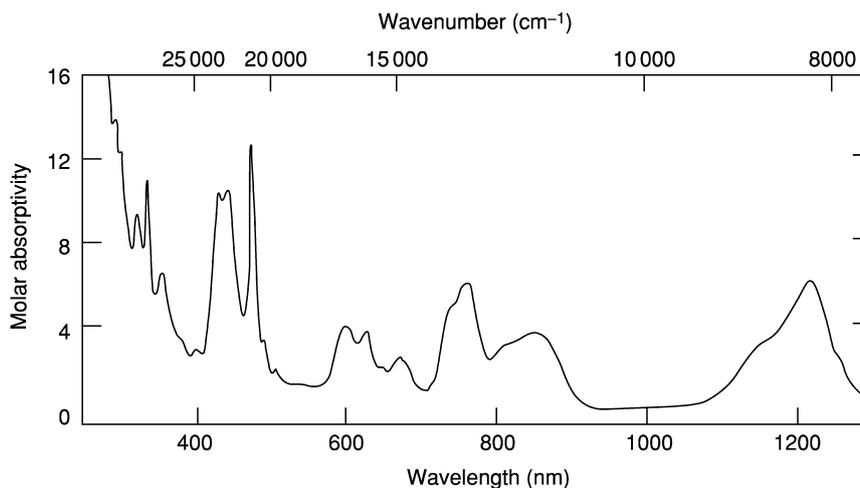


Fig. 11.9 Solution absorption spectra of Cf(III) in 0.12 M Na_2CO_3 at pH 12.

Fig. 11.8 shows the Cf(III) absorption spectrum obtained from a 0.1 M $\text{HClO}_4\text{-DClO}_4$ solution. The absorption spectrum of Cf(III) in 2 M Na_2CO_3 (Hobart *et al.*, 1982) is shown in Fig. 11.9, and the intensities of the absorptions in the carbonate solution is given in Table 11.16. The spectrum of Cf(III) in the Na_2CO_3 solution is similar to that observed in 1 M DClO_4 , but shifts in wavelength and enhancement of intensity occur for some peaks. See Chapter 16 for a comprehensive overview of actinide spectroscopy.

Table 11.16 Absorption data for Cf(III) in 2 m Na₂CO₃.^a

Wavelength (nm)	Wavelength (cm ⁻¹)	Absorption coefficient, μ (L mol ⁻¹ cm ⁻¹)
293	34 100	14
303	33 000	12
322	31 000	9.3
336	29 800	11
355	28 200	6.5
402	24 900	2.9
430	23 200	10
443	22 600	11
474	21 100	13
491	20 400	3.3
506	19 800	2.0
600	16 700	4.0
625	16 000	3.8
674	14 800	2.4
740	13 500	4.9
757	13 200	6.0
850	11 800	3.7
1140	770	2.8
1214	8 240	6.1

^a Hobart *et al.* (1983).

The absorption spectrum of Cf(IV) and Cf(III) in a potassium phosphotungstate medium has been reported (Kosyakov *et al.*, 1977; Myasoedov, 1982). The phosphotungstate ion stabilizes the Cf(IV) oxidation state sufficiently to permit spectra to be obtained (half-life approximately 70 min at room temperature). This Cf(IV) oxidation state was achieved by using potassium persulfate at elevated temperatures; attempts to oxidize Cf(III) electrochemically in this medium were not successful. The absorption spectrum of Cf(IV) in this medium is characterized by a broad absorption band beginning at 1030 nm and increasing in intensity down to 390 nm. The maximum absorption appears at about 450 nm, which is similar to the absorption maximum obtained for Cm(IV) and Tb(IV) in this medium (Myasoedov, 1982). The absorption of a comparable Cf(III) phosphotungstate solution did not show a significant absorbance over this spectral region.

11.9 GAS-PHASE STUDIES

In addition to studies in the solid phase and in solution, investigations of reactions in the gas phase provide important insights into the chemistry and electronic make-up of californium. These studies in the gaseous state examine the reactions of Cf ions with other molecules, as opposed to addressing the vaporization of the metal (see Section 11.6), or other solids such as oxides

(see Section 11.7.3), which can provide important thermodynamic parameters for these materials (i.e. their enthalpies of vaporization and formation).

The gas-phase chemistry of californium has been studied by mass spectrometry time-of-flight, and Fourier transform ion resonance mass spectrometry (FTIRMS), and the latter offers an especially powerful technique in this regard. In this technique, metal ions can be isolated and then reacted with other specific materials, which can lead to bond dissociation energies, reaction kinetics, and ionization potentials for the metal ions being studied. Important information about californium's electronic configuration, which can be used for systematic comparisons with other actinides, is also obtained from these gas-phase reactions.

One area of this californium gas-phase chemistry has involved the dehydrogenation of alkenes, thiols, ethers, and perfluorohydrocarbons by Cf^+ (Gibson and Haire, 2000). The emphasis in that work was on the efficiency of dehydrogenation of alkenes by Cf^+ ions, and direct comparisons with the comparable reactivities of Cm^+ , Pr^+ , and Tm^+ for similar reactions. It was determined that Cf^+ is inefficient at C–H bond activation, due to its particular electronic structure and energy levels, and evidence was not found for the direct participation of its 5f electrons in the reactions studied.

In related studies, organometallic ions of californium were produced in the gas phase by laser ablation of Cf_2O_3 dispersed in polyimide matrices. This process was followed by mass spectrometric analyses (Gibson and Haire, 2001). Primary products formed were: CfC_2H^+ , CfCN^+ , CfC_4H^+ , $\text{Cf}(\text{OH})(\text{CN})^+$, CfOCN^+ , CfOH^+ , $\text{Cf}(\text{OH})_2^+$, and CfO^+ . Some of these products represent the first organometallic materials for californium where it is directly bonded to carbon. It was concluded that the composition and abundance of the products are dependent on the ability of californium to have two non-5f valence electrons at the Cf^+ center for participation in the bonding, which involves a single sigma-type bond with the organic material. Thus californium exhibits 'monovalent character' (one direct actinide-carbon bond; as do americium and berkelium) versus 'divalent character' of thorium, uranium, neptunium, plutonium, and curium (two direct actinide-carbon bonds).

This behavior is electronically orientated and associated with the $f \rightarrow d$ promotion energies of the actinides to give a chemically active 6d orbital. As the promotion energy for californium is higher (i.e. $\sim 200 \text{ kJ mol}^{-1}$, see Fig. 11.10) than earlier actinides, this diminishes the generation of reaction products for it. More recent work with Cf^+ and Es^+ (see Chapter 12) has shown that a greater reactivity is observed with pentamethylcyclopentadiene than with most other alkenes. It was found that Cf^+ reacts with this reagent to produce $[\text{MCp}^*]^+$ and other products. This behavior of Cf^+ allows estimates for low-lying electronic levels (Gibson and Haire, 2005).

In studies of californium with several alkenes (Gibson and Haire, 2004), it was determined that the relative C–H activation of Cf^+ was $< 1\%$ of that for Cm^+ . Thus, instead of C–H activation from insertion of the metal center into a

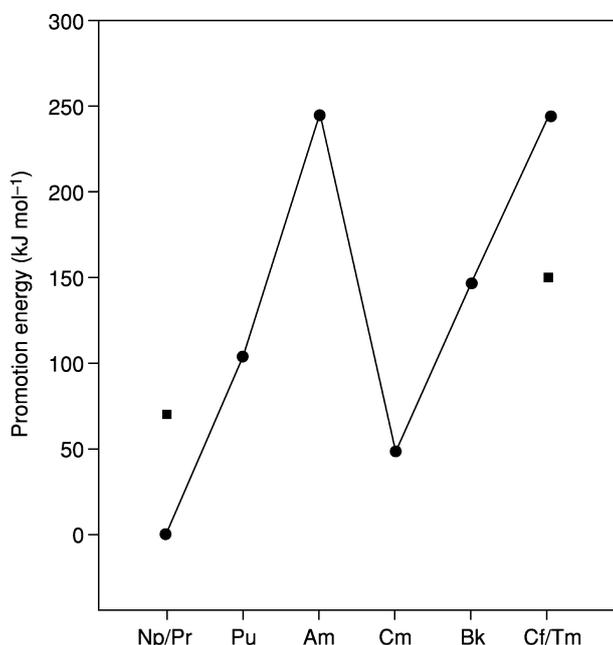


Fig. 11.10 The *f-d* promotion energies for selected actinides. Values for Pr and Tm (solid blocks) are given for comparison. (Gibson, 2003).

C–H bond (i.e. C–Cf⁺–H), reactions of Cf⁺ with butyronitrile produces an adduct, M⁺-butryonitrile. Californium also resisted the formation of CfO⁺ ions, consistent with its preference to be ‘divalent’ rather than ‘trivalent’ – attempts to oxidize Cf⁺ with N₂O to yield CfO⁺ in the gas phase were not successful.

In reactions of Cf⁺ with perfluorophenanthrene (Gibson and Haire, 2005) only minor yields of CfF₂⁺ were observed, again in accord with its propensity to remain divalent. This is also in accord with results noted in the vaporization of Cf₂O₃ at high-temperatures (Haire, 1994). Very little CfO is found in the vapor state as compared to atomic Cf vapor (see Section 11.7.3). This latter behavior is similar to that observed with Eu₂O₃ and Yb₂O₃ and results from the lower dissociation energy of CfO compared to CmO (Haire, 1994). The dissociation energies of the monoxides are also linked to the *f-d* promotion energies for *f*-electrons and the formation and availability of active 6*d* orbital–7*s* electron orbitals (Haire, 1994; Gibson, 2003).

11.10 CONCLUDING REMARKS

A considerable quantity of chemical and physical data have been acquired for californium over the years. In many instances this information was obtained

using tracer levels or microgram quantities of the element, often using the ^{252}Cf isotope. With the availability of multi-milligram amounts of ^{249}Cf isotope, it became possible to expand studies of californium and prepare pure samples of the metal. This allowed important information to be obtained for californium; acquiring the enthalpy of solution (Fuger *et al.*, 1984) and the sublimation of californium metals (Ward *et al.*, 1980) are two such examples. These data then allowed thermodynamic cycles to be established for the element and many of its compounds.

Given the limited supplies of ^{249}Cf (i.e. perhaps a total of some 50–100 mg exist) as well as other experimental limitations (given its radioactive decay process, the accompanying heat, personnel radiation exposures, etc.) it may not be possible to perform all the desired experiments or to be able to carry them out to the degree of perfection that may be desired. However, californium is the element with the highest atomic number in the periodic table expected to be available in weighable amounts (milligrams) and that has a reasonably long half-life. This allows many studies with it that cannot be done with higher members of the actinide series or periodic table. The next element, einsteinium (see Chapter 12) is available in only multi-microgram amounts, but its very high specific radioactivity and the short half-lives of its isotopes severely limit the experiments can be performed with it. Therefore, data on californium can provide insights/extrapolations into the chemical/physical properties of the higher members of the actinide series, in addition to the importance of its own data in providing a better understanding of the architecture of the periodic table.

Oxidation states of 0, II, III, and IV have been established for Cf, with the III state being the most prevalent and the only state presently known to have a reasonable stability in aqueous solutions. The existence of Cf(V) has been suggested but needs confirmation. It may be more probable to generate this oxidation state in solids or nonaqueous solutions and/or molten salts than in aqueous solutions. Future investigations of californium may place emphasis on stabilizing oxidation states other than Cf(III).

Studies of californium in the gaseous state offer important new thrusts in californium chemistry. Using ion cyclotron resonance mass spectrometry, californium ions can be selected, held, and then reacted with a variety of materials to establish important parameters, thermodynamic properties, bond dissociation energies, reaction kinetics, etc.

Although a considerable amount of information has been acquired for californium metal, there are still unanswered questions about it, for example, concerning a potential divalent form of the metal under certain conditions. Recent high-pressure diffraction studies on the metals have provided important new aspects about the behavior of their 5f electrons under pressure and reduced interatomic distances. Indeed, under these very high pressures (i.e. 100 GPa or higher), the electronic nature of californium metal changes, and it adopts

lower-symmetry structures normally displayed by the lighter actinide metals (Pa–Pu), which have itinerant 5f electrons at atmospheric pressure. These high pressures on californium metal forces the involvement of its 5f electrons into its bonding and changes its physical properties. Thus, pressure can bring about a form of modern alchemy in californium metal with regard to its structure and properties.

There is also a considerable amount of work that can be done on californium compounds, such as the mononitrides and chalcogenides – the mononitride and monosulfide both offer interesting compounds to study in detail. Investigations of its compounds under high pressure should also provide new findings about californium's chemistry. Applying modern tools (synchrotron-based, EXAFS, XANES, photon scattering, etc.) offers the potential to learn new facets about californium materials.

In short, there is a considerable amount of scientific work that needs to be done on californium, perhaps the highest atomic numbered element available for performing the usual actinide studies. The scope of such studies will be limited only by the imagination and skill of the investigators.

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