

CHAPTER TWELVE

EINSTEINIUM

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12.1 INTRODUCTION

The discovery of einsteinium, element 99, came about during the analyses of nuclear products produced in and then recovered from test debris following a thermonuclear explosion (weapon test device, 'Mike', November 1952) at Eniwetok Atoll in the Pacific Ocean. The uranium present in this device was subjected to a very intense neutron flux (integrated fluence of about 10^{24} neutrons) in an extremely short time frame (few nanoseconds), which allowed a large number of multiple neutron captures with a minimal degree of decay of the products formed. Nuclei were formed with usually high neutron/proton ratios (very 'heavy' uranium isotopes), which then rapidly beta-decayed into new, transuranium isotopes through element 100. Scientists from several U.S. Government laboratories separated and analyzed extensively the debris samplings in the following weeks. From these investigations came the discovery and identification of einsteinium and fermium. The first element was named in honor of Albert Einstein, and assigned the symbol, E (later changed to the current symbol, Es). Additional details and discussions about the discovery of this element and the scientists involved are given in several references (Thompson *et al.*, 1954; Ghiorso *et al.*, 1955; Fields *et al.*, 1956; Hyde *et al.*, 1964; Seaborg and Loveland, 1990).

Subsequently, einsteinium has been produced in accelerator targets, and in reactors via successive neutron captures, starting with targets of plutonium or higher actinides. The first macroscopic and weighable quantities of einsteinium

(few hundredths of a microgram of ^{253}Es) were obtained in 1961. Today, up to ~ 2 mg can be present in special high-flux isotope reactor targets at the time of release from a reactor.

The transplutonium elements, where einsteinium is the fifth, have chemistries similar to those of the lanthanide elements, especially in their ionic states and in compounds. In essence, elements in the series sequentially add one f-electron in progressing to higher atomic numbers. Einsteinium is therefore an f-electron element, and its 5f electrons are considered fully localized, as opposed to those in the protactinium through plutonium grouping.

Oxidation states of II, III, and IV have been reported for einsteinium, where the best-established state is III (state normally observed in solution) followed by divalent einsteinium, which can be obtained in solid compounds. The tetravalent state has been postulated from vapor transport studies using tracer levels of einsteinium, but this state has not been established fully. More remote is the potential for a hexavalent state, based on the conception that this state may acquire stability from attaining a half-filled, 5f shell ($5f^{11}$ down to $5f^7$), by losing a total of six electrons (Liebman, 1978).

An exception of this similarity of einsteinium to the regular lanthanide elements occurs with the elemental state of einsteinium, where its properties and bonding compare more closely to those for europium and ytterbium metals, rather than to the other lanthanide elements, or more specifically to its apparent lanthanide homolog, holmium. This difference in behavior for einsteinium is readily seen by examining the atomic volumes of the two f-series that are shown in Fig. 12.1. Einsteinium is therefore unique in that it is the first divalent

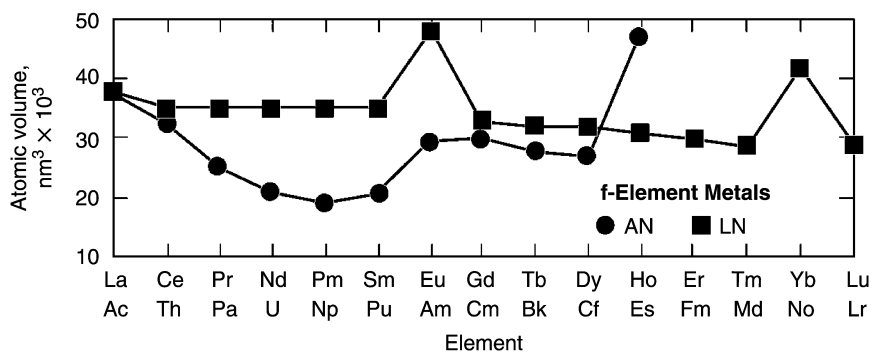


Fig. 12.1 Atomic volumes of the two f-electron series of elements are shown. The behavior of einsteinium shows it is the first divalent actinide metal, with bonding similar to that for europium and ytterbium metals. This behavior for einsteinium metal is very different than that observed with Es(II) and Es(III) in compounds, which is similar to that for the lanthanides in these states. (Haire et al., 2004).

actinide metal. In the lanthanide elements, europium and ytterbium are also divalent metals (two bonding electrons rather than three). The rationale for their metallic divalency is due to stabilization from a half-filled (Eu) or full (Yb) 4f-orbital arrangement. But this is not an appropriate explanation for the divalency of einsteinium metal. As discussed in Section 12.4, this situation for einsteinium is explained by its high 5f-electron promotion energy (energy to change an $f \rightarrow d$).

There are 16 established isotopes of einsteinium (with three isomers), with many having very short half-lives. The longest-lived isotope is ^{252}Es ($t_{1/2} = 471.7$ days), but the ^{253}Es ($t_{1/2} = 20.47$ days) isotope is available in the largest quantity and obtained primarily from nuclear reactors. The quantities of the latter isotope are normally limited to hundreds of micrograms, but frequently only a few micrograms are employed in studies at one time. Up to 2 mg can be discharged from special reactors (i.e. High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory, ORNL) once every 6 months to 2 years, depending on the production schedule used. Even so, studies with it are also severely hindered by its half-life ($\sim 3\%$ daughter 'impurity' ingrowth per day) and intense self-radiation (6.6 MeV alpha, self-heating of 1000 W g^{-1}), which are often detrimental to the studies being performed. A feeling for the magnitude of the energy released by the decaying einsteinium is obtained by looking at Fig. 12.2. The illumination is associated with the radioactive decay from 300 μg of ^{253}Es solid that is in the bottom of a 9 mm diameter quartz cone.

In essence, there are not many practical applications for einsteinium isotopes. Applications are found as target materials for producing elements with even higher atomic numbers, use of the self-irradiation fields of einsteinium for damage studies, and the use of its radiation for medical treatments. The latter application has been limited, but in principle would employ einsteinium chemically bound to biological agents that could deliver the radiation of einsteinium to biological sites for treatment of different disorders. In this regard, studies have been performed where beagles have been injected einsteinium citrate (Lloyd *et al.*, 1975). Other experiments along this line have been tried with the shorter-lived (~ 20 h) ^{255}Fm isotope, a daughter product of ^{255}Es ; the latter is present in einsteinium products from reactors.

Einsteinium can also be useful in certain chemical studies, where its intense self-irradiation can be used for evaluating radiation damage and radiolysis effects both in solution and in the solid phase. One example of the latter would be to prepare a compound of einsteinium and then follow the chemistry of the daughter and granddaughter (i.e. from ^{253}Es one obtains ^{249}Bk , and ^{249}Cf , respectively) products as they grow into the einsteinium material (Young *et al.*, 1981). The main point is that knowing and understanding the science of einsteinium is important for actinide systematics and understanding the changing role of 5f electrons across the series.

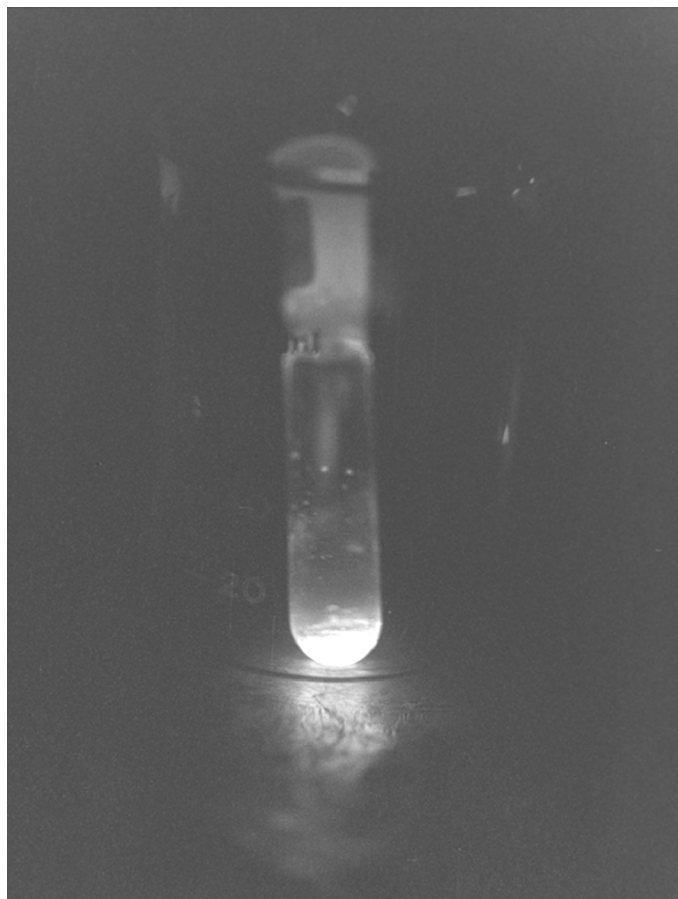


Fig. 12.2 Self-luminescence arising from the intense radiation from $\sim 300 \mu\text{g}$ of ^{253}Es in a quartz cone. The heat and radiation accompanying decay often generate detrimental effects in studies of Es.

12.2 PRODUCTION AND NUCLEAR PROPERTIES

The primary nuclear properties and production schemes for einsteinium are outlined in Table 12.1 and in Appendix II. The reader is also directed in this regard to references discussing these isotopes (Hyde *et al.*, 1964; Seaborg and Loveland, 1990). The nuclear levels of their daughters and the exact atomic mass of each isotope can be established by relating the total decay energies with the masses of the daughter products through studies of the decay processes.

The discovery of einsteinium in nuclear debris involved primarily the ^{253}Es and ^{255}Es isotopes, which have half-lives of 20.47 days and 39.8 h, respectively.

Table 12.1 Nuclear properties of einsteinium isotopes.^a

Mass number	Half-life	Mode of decay	Main radiations (MeV)	Method of production
241	8 s	α	α 8.11	²⁴⁵ Md daughter
242	13.5 s	α	α 7.92	²³³ U(¹⁴ N,5n)
243	21 s	α	α 7.89	²³³ U(¹⁵ N,5n)
244	37 s	EC 96% $\alpha \sim 4\%$	α 7.57	²³³ U(¹⁵ N,4n) ²³⁷ Np(¹² C,5n)
245	1.1 min	EC 60% $\alpha \sim 40\%$	α 7.73	²³⁷ Np(¹² C,4n)
246	7.7 min	EC 90% α 10%	α 7.35	²⁴¹ Am(¹² C, α 3n)
247	4.55 min	EC $\sim 93\%$ $\alpha \sim 7\%$	α 7.32	²⁴¹ Am(¹² C, α 2n) ²³⁸ U(¹⁴ N,5n)
248	27 min	EC 99.7% $\alpha \sim 0.3\%$	α 6.87 γ 0.551	²⁴⁹ Cf(d,3n)
249	1.70 h	EC 99.4% α 0.57%	α 6.770 γ 0.380	²⁴⁹ Cf(d,2n)
250 ^b	8.6 h	EC	γ 0.829	²⁴⁹ Cf(d,n)
250 ^b	2.22 h	EC	γ 0.989	²⁴⁹ Cf(d,n)
251	33 h	EC 99.5% α 0.49%	α 6.492 (81%) 6.463 (9%) γ 0.177	²⁴⁹ Bk(α ,2n)
252	472 d	α 78% EC 22%	α 6.632 (80%) 6.562 (13.6%) γ 0.785	²⁴⁹ Bk(α ,n)
253	20.47 d 6.3×10^5 yr	α SF β stable	α 6.633 (89.8%) 6.592 (7.3%)	multiple neutron capture
254g	275.7 d $>2.5 \times 10^7$ yr	α SF	α 6.429 (93.2%) 6.359 (2.4%) γ 0.062	multiple neutron capture
254m	39.3 h $>1 \times 10^5$ yr	β^- 99.6 SF α 0.33% EC 0.08%	α 6.382 (75%) 6.357 (8%)	²⁵³ Es(n, γ)
255	39.8 d	β^- 92.0% α 8.0% SF $4 \times 10^{-3}\%$	α 6.300 (88%) 6.260 (10%)	multiple neutron capture
256 ^b	25.4 min	β^-		²⁵⁵ Es(n, γ)
256 ^b	~ 7.6 h	β^-		²⁵⁴ Es(t,p)

^a Appendix II.

^b Not known whether ground state nuclide or isomer (Appendix II).

EC = Electron capture

SF = Spontaneous fission

Both elution behavior during ion-exchange purification and the nuclear properties of these isotopes were used to establish the existence of this new element. These two isotopes together with ^{254g}Es ($t_{1/2} = 275.7$ d) are produced by neutron-capture processes. All three isotopes are obtained in high-flux reactors designed to produce synthetic elements, but ^{253}Es and ^{254g}Es are the isotopes normally used for physicochemical studies other than for tracer work given their greater quantities.

The lighter isotopes of einsteinium are prepared in smaller quantities using accelerators and often other actinides as target materials (see Table 12.1). The synthesis of einsteinium isotopes using bombardment of targets with nitrogen isotopes has been discussed (Mikheev *et al.*, 1967), as has been the alpha decay properties of some lighter einsteinium isotopes (Ahmad and Wagner, 1977). The half-life of ^{252}Es is also addressed specifically in Ahmad *et al.* (1970). McHarris *et al.* (1966) have addressed the decay scheme of ^{254g}Es . Einsteinium isotopes have also been produced by bombardment of ^{209}Bi with ^{40}Ar ions (Ninov *et al.*, 1996). The electron-capture decay fission processes in neutron-deficient einsteinium isotopes have also been discussed (Shaugnessy *et al.*, 2000).

At the present time, einsteinium can be produced in the HFIR at the ORNL, Oak Ridge, Tennessee, and at the Research Institute of Atomic Reactors in Dimitrovgrad, Russia. At the HFIR, the targets for neutron irradiation consist mainly of curium isotopes (^{244}Cm through ^{248}Cm), which are irradiated in the reactor to produce the transcurium elements through fermium. The process involves successive neutron captures and beta decays to reach ^{253}Cf , which then β^- decays to ^{253}Es . The latter einsteinium isotope captures neutrons to reach ^{256}Es (possibility even ^{257}Es) but the einsteinium isotopes removed from the reactor targets consist of essentially ^{253}Es , ^{254g}Es , and ^{255}Es . The HFIR can produce einsteinium once every 12–24 months. The SM-2 loop reactor in Russia has similar power and flux levels, also giving it the potential for producing quantities of these transcurium isotopes.

The direct production in the HFIR in the U.S. is less than 2 mg of ^{253}Es , with the ^{254g}Es and ^{255}Es contents being ~ 0.3 and 0.06% , respectively, at discharge. However, ^{253}Cf is present in the californium isotope fraction that is chemically separated and it β^- decays to ^{253}Es . By subsequent chemical separation of the californium fraction of isotopes, it is possible to obtain chemically the ^{253}Es daughter from the californium fraction at a later time (weeks) and recover isotopically pure ^{253}Es at levels up to 200 μg .

From the mixed einsteinium isotope fraction received from the reactor there are two considerations to be addressed for using this einsteinium fraction. The first concerns the decay of the ^{255}Es present, which is a source of ^{255}Fm at the nanogram level (the longer-lived ^{257}Fm is produced directly in the reactor at only a 1 pg level). Chemical separations of the einsteinium fraction for multiple weeks (i.e. for about a total of four ^{255}Es half-lives) produces a repeated source of a few nanograms of ^{255}Fm . Another aspect is that after decay of—six to ten half-lives of ^{253}Es , the original einsteinium fraction is almost pure ^{254g}Es , and

some 4 μg of it can be obtained essentially free of ^{253}Es . The latter isotope is highly desirable for nuclear syntheses but is of more limited value for physico-chemical work, despite its longer half-life. This is due not only to the smaller amounts of it but also to the highly penetrating radiation field generated from its short-lived ^{250}Bk daughter ($t_{1/2} = 3.217$ h with β^- decay having a 45% branching ratio for a ~ 1 MeV gamma emission) in equilibrium with it. Thus, decisions must be made regarding the needs and the different choices available for the einsteinium products generated.

More detailed discussions on the nuclear properties, preparation of einsteinium isotopes, and their decay schemes are provided in the references. The K-series X-ray energies of einsteinium isotopes are discussed in Dittner and Bemis (1972). The electron-capture delayed fission processes of neutron-deficient isotopes, ^{242}Es and ^{244}Es , have also been reported, and highly asymmetric mass distributions have been noted (Kosyakov *et al.*, 1974). Average pre-neutron total kinetic energies of (183 ± 18) and (186 ± 9) MeV, respectively, were found. The probability of delayed fission was determined to be $(6 \pm 2) \times 10^{-3}$ and $(1.2 \pm 0.4) \times 10^{-4}$, respectively; smaller probabilities were given for the ^{246}Es and ^{248}Es isotopes.

12.3 PURIFICATION AND ISOLATION

The techniques used for the isolation, recovery, and purification of einsteinium isotopes are very dependent on the method of production. Accelerator production often involves thin foils or targets, where the einsteinium products are either recovered simply (washed off) from the target or from 'catcher' foils located behind a thin target. Recovery from 'catcher' foils can be straightforward, and recovery of products may only involve dissolution or washing of the foil followed by a minor purification of the einsteinium product.

In contrast, recovery of einsteinium following a neutron irradiation process can be rather complex. Larger quantities of very radioactive materials are involved in this process and it requires hot cell operations. The actinide targets are placed in some form of 'container' for the reactor irradiation (normally in aluminum rods), which must then be removed mechanically or chemically to reach the irradiated starting and product materials. At that point, one is faced with the starting material (i.e. curium oxide) and various fission products, in addition to the desired transcurium products (i.e. berkelium, californium, einsteinium, and some fermium). The purification and recovery of einsteinium then involves: (1) separation from lanthanide fission products; and (2) separation from curium, berkelium, and the adjacent actinides, californium and fermium. The major obstacle is the great similarity in the chemical properties of their trivalent actinide ions in solution, given their similar ionic radii.

There is only a small contraction in radii with increasing atomic number in the case of transplutonium elements, which provides a small increase in covalency

and complexing ability, but these are sufficient to allow chromatographic methods to be used for separations. An advantage is acquired in the case of berkelium (which is also a daughter product of einsteinium), as this element can be oxidized to a tetravalent state and separated from the curium through fermium trivalent elements. Separation of einsteinium from its berkelium daughter product can be accomplished by solvent extraction. If solvent extraction is used to remove tetravalent berkelium, the extraction can then leave trivalent californium, einsteinium, and fermium ions together. These elements would have to be separated by subsequent ion exchange or chromatography techniques. A schematic for the separation of einsteinium is given in Fig. 12.3, parts A and B.

The details of various chemical separation processes have been published and presented as reviews. Two earlier reviews cover the approaches in the U.S. (Hulet and Bodé, 1972) and in Russia (Myasoedov *et al.*, 1974). A more general overview for separation of the transuranium elements is also available (Hyde *et al.*, 1964), and individual accounts of procedures used worldwide have been published (Müller, 1967; Bigelow, 1974; Ishimori, 1980; King *et al.*, 1981; Collins *et al.*, 1981). The early scheme used for products from the HFIR at ORNL has also been published in separate reports (Baybarz *et al.*, 1973; Benker *et al.*, 1981). Many of these procedures have not changed significantly over the years.

The removal of lanthanides from the actinides can be accomplished in different ways. An early method, suited for laboratory separations of smaller quantities, was through the use of alcoholic hydrochloric acid as an elutant for the

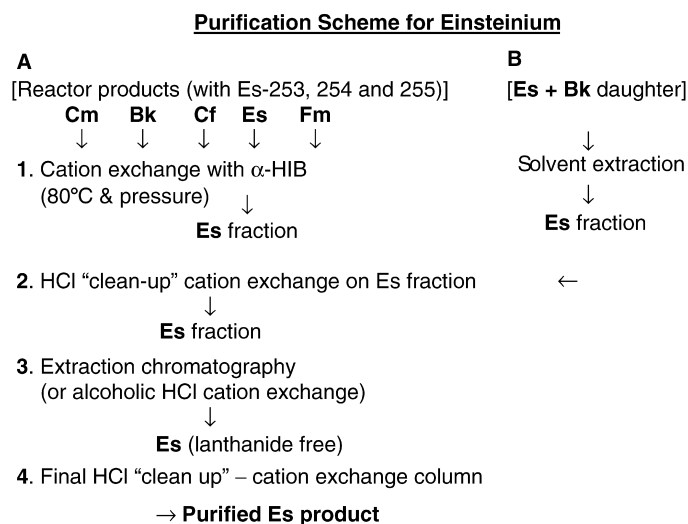


Fig. 12.3 *Einsteinium purification scheme.*

transcurium elements sorbed on cation resin (Street and Seaborg, 1950), where the greater complexing ability of the actinides allowed their desorption as chloride complexes ahead of the lanthanides. A preferred method for larger-scale operations is a lithium chloride anion-exchange process (Shoun and McDowell, 1980), which partitions the actinides from the lanthanides. For small amounts of lanthanides from einsteinium (i.e. the final removal of trace amounts of lanthanides of similar ionic radii) an extraction chromatography column employing ammonium thiocyanate and formic acid can be used (TEVA™ columns; see Horwitz *et al.*, 1994; Porter *et al.*, 1997). These special columns are also available commercially and give excellent separations between the lanthanide and actinide groups.

When the three elements californium, einsteinium, and fermium are considered, the individual elements can be separated by cation-exchange processes. One method that has been used for several decades is to sorb the three ions on a cation resin from dilute acids (i.e. 0.1 M hydrochloric acid) and selectively elute them with ammonium alpha-hydroxyisobutyrate (α -HIB) solutions at a pH in the range 3.8–4.2 (Choppin and Silva, 1956; Baybarz *et al.*, 1973; Bigelow *et al.*, 1980; Myasoedov *et al.*, 1980; Shoun and McDowell, 1980; Campbell, 1981). The elution order is fermium, einsteinium, and then californium; a high-pressure, ion-exchange column operated at 80°C gives the best results. Separation factors are not great but sufficient, ranging from 1 to 2 for different conditions. Details of using high-pressure columns for separation of f-elements have been given by Campbell (1981). However, even when working with only 10–20 μg of ^{253}Es , care must be exercised, as its radiation level is sufficient to char the resin upon standing and makes it difficult to recovery fully the einsteinium from the resin.

Another approach employs extraction chromatography, where either bis(2-ethylhexyl)phosphoric acid (HDEHP) or 2-ethylhexylphenylphosphonic acid (HEMΦP) are placed on an inert (i.e. fine glass particles) support. The actinides are loaded on this column and eluted with a dilute 0.3 M nitric acid solution (Hulet and Bodé, 1972). Separation factors for these actinide elements are again between 1 and 2. Ion-exchange separations of einsteinium from irradiated californium have also been discussed by Elesin *et al.* (1986).

The extraction chromatography behavior of einsteinium with a quaternary ammonium nitrate has been discussed (Horwitz *et al.*, 1966), and extraction of einsteinium with bis(2-ethylhexyl)phosphoric acid was also reported (Horwitz *et al.*, 1969). The extraction of einsteinium by bis(2-ethylhexyl)phosphoric acid and the stability constants for hydroxycarboxylic acids is reported by Aly and Latimer (1970a). The extraction of Es by dibutyl *N,N*-diethyl carbamyl phosphate is also discussed (Aly and Latimer, 1970b). The current separation procedure for einsteinium from neutron-irradiated targets at ORNL dates back many years and has been summarized by Campbell (1970). Other separation methods for einsteinium have been provided by Horwitz *et al.* (1994).

12.4 ELECTRONIC PROPERTIES AND STRUCTURE

Chapter 16 is concerned with spectra and electronic structure of free actinide atoms and ions, and these topics are only touched upon here. As einsteinium belongs to the actinide series of elements it can be considered a 5f electron element, which has localized (non-bonding) 5f electrons, and potentially a 'dsp' or an 's²' type of bonding. In addition, both non-relativistic and relativistic approaches (appropriate because of its high atomic number einsteinium) should be considered with regard to its behavior.

From non-relativistic considerations, the radial probability distributions of the 5f electrons are well within the principal confines of the 6d, 7s, and 7p orbitals, although there is some 'tailing' to the outer regions. This tailing or extension relative to the 7s and 7p orbitals lends itself to a slightly greater degree of covalency than found for the lanthanide's 4f electrons. With the transplutonium elements, the degree of covalency increases slightly when moving to elements with increased atomic number for a given ionic state.

For the relativistic situation, the binding of the electrons becomes greater with higher atomic numbers, which can affect the energies for the different electronic states. Also, potential effects may be found with regard to radii and energies of certain orbitals, spin-orbit splitting, and the expansion of the d- and f-orbitals, all of which can affect chemical behavior. An overview of this electronic picture has been given (Seaborg and Loveland, 1990).

The electronic configurations of einsteinium in neutral and singly ionized gaseous atoms have been analyzed via emission spectra (Gutmacher *et al.*, 1967; Conway, 1979), although full characterization of the ~20000 lines collected is still incomplete. Worden *et al.* (1974) have provided term assignments to a small number of these lines, and Brewer (1971a,b) had estimated energies for the lower spectroscopic terms. Brewer estimated that for a singly ionized atom the f¹⁰s², f¹², and f¹¹d levels should be lower in energy than the f¹¹p level reported by Worden *et al.* (1974).

For the gaseous atom of einsteinium, a 5f¹¹7s² ground state is assumed, and the successively ionized neutral gaseous atom loses first one, then two 7s electrons, while the third and even fourth electron lost are 5f electrons, to give a 5f⁹ configuration for the potential ion. It must be remembered that the gaseous atom configurations are different from those encountered in the metals, which are influenced by other factors including crystal energies.

Brewer (1971a,b) has calculated that for einsteinium metal the bonding configuration could be 5f¹⁰dsp, where the 6d and 7p orbitals play important roles. In this case, einsteinium would have three bonding electrons in its conduction band. Alternative configurations would be 5f¹¹sp or 5f¹¹s², where only two bonding electrons are present, and in this case, einsteinium would be the first divalent actinide metal. The latter configuration appears to be the correct configuration for einsteinium metal. The reason for the divalency of einsteinium metal can be found in the promotion energy for changing an f-electron to a

d-electron, which would then provide three electrons rather than two electrons for the metallic bonding.

A plot of promotion energies for the actinide is shown in Fig. 12.4 (Haire, 1994), which shows einsteinium's promotion energy as being just above the border between divalent and trivalent metal bonding. This 'borderline' energy relates to the crystal energy recovered when the metal atoms crystallize. Thus, when gaseous atomic einsteinium ($5f^{11}7s^2$) condenses to form a crystal, promotion of a 5f electron must occur to provide three rather than two bonding electrons in the solid if a trivalent metal (i.e. with a ds^2 configuration) is to form. For the earlier transplutonium metals, this promotion energy is provided from the greater crystal energy acquired, but with einsteinium, the promotion

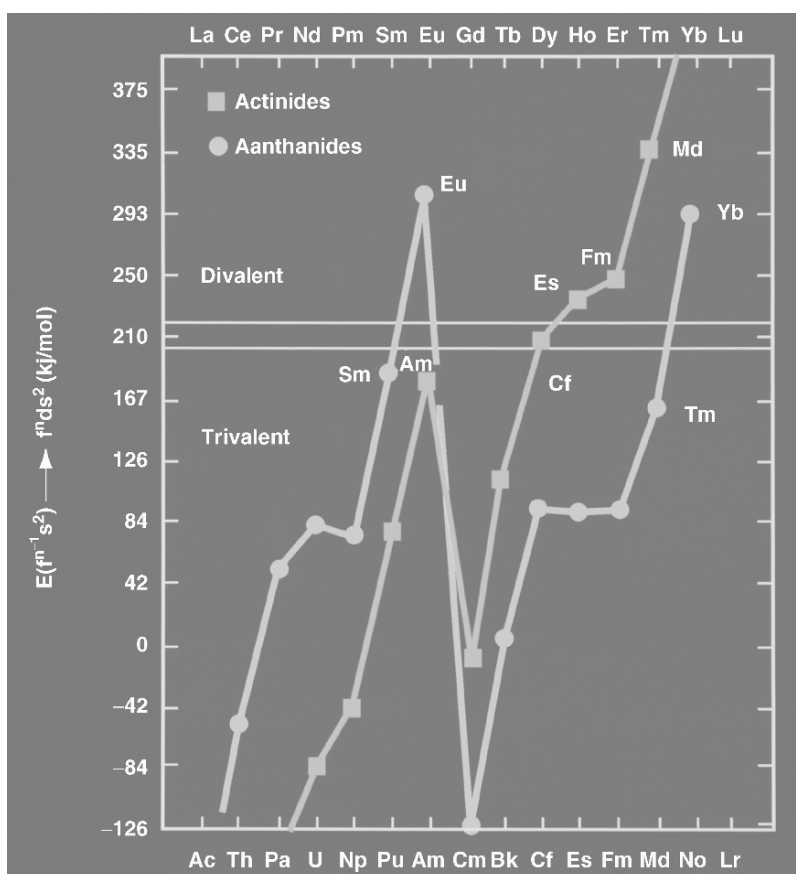


Fig. 12.4 The $f \rightarrow d$ promotion energies for the f -elements (bar across figure is estimate of crystal energy needed to compensate for promotion of an electron from an f to a d level).

energy needed exceeds the crystal energy recovered. Thus, einsteinium remains a divalent metal, as do the next three metals in the series.

Recent gas-phase studies of einsteinium have also provided important new insights into its chemistry. The behavior of einsteinium ions in the gas phase is discussed in Section 12.6.6 and the concept of $f \rightarrow d$ promotion energy again is seen as being important for the different gas species and their reactions.

Blaise and Wyart (1992) have provided tabulated values for einsteinium's energy levels and atomic spectra. Tabulated values for the newer values are given in Table 12.2 for Es(I). The reader is referred to Blaise and Wyart (1992) or Wyart *et al.* (2005) for more extensive data and values for Es(II). Some other atomic values for einsteinium and its ionization potentials are also given in Table 12.3. Estimations of the first ionization potential for einsteinium were earlier given to be 6.42(3) eV (Rajnak and Shore, 1978) but the ionization potential has now been determined accurately by resonance ionization mass spectroscopy using some 10^{12} atoms of ^{254}gEs in an atomic beam (Erdmann *et al.*, 1998; Peterson *et al.*, 1998). The method used is based on measuring photoionization thresholds as a function of an applied electric field, followed by an extrapolation to a zero electric field. The first ionization potential determined experimentally was found to be 6.367(5) eV (see Table 12.3). Goodman *et al.* (1975) also examined the nuclear and quadrupole moments of einsteinium. Table 12.3 provides some basic values for Es, but the reader may find more details in the references.

12.5 THE METALLIC STATE

The scarcity and the high specific radioactivity of einsteinium isotopes have in general impeded the investigation of its chemistry, but particularly so for its metallic state. The self-radiation and accompanying heat are imposing factors, and the former rapidly destroys the metal's crystal lattice. The transplutonium elements are all electropositive metals, and react with water and the oxygen in air, but einsteinium metal is even more reactive. Strong reducing agents are needed to convert einsteinium oxide or its halides to the metal. Einsteinium is the most volatile of all the actinides preceding it, which dictates the preparative methods that can be used. It has been concluded that einsteinium is the first divalent actinide metal, in the sense that there are two bonding electrons in its conduction band compared to three or higher for the preceding actinide metals (see Section 12.4). It is followed by divalent fermium metal, and presumably divalent mendelevium and nobelium metals. The last member of the series, lawrencium, is presumably again a trivalent metal. It is likely to have a filled 5f level and a single d-electron; therefore, the promotion of an f-electron is not necessary for it to become trivalent. Thus, einsteinium is divalent like europium and ytterbium metals, but not trivalent like its homolog holmium, the other lanthanide metals, or the americium through californium metals.

Table 12.2 Atomic properties of einsteinium(I).^a

Configuration	Term	J	Energy (cm ⁻¹)	w (10 ⁻³ cm ⁻¹)	A (10 ⁻³ cm ⁻¹)	B (10 ⁻³ cm ⁻¹)
5f ¹¹ 7s ²	4I ⁰	15/2	0.00	1543	2 725 729	-1 438 749
5f ¹¹ 7s ²	4F ⁰	9/2	7894.54	>792	25 905	159.1
5f ¹¹ 7s ²	2H ⁰	11/2	8759.27	1216	29 109	36
5f ¹¹ 7s ²		13/2	10 244.29	>1391	3113	-1922
5f ¹¹ (4f _{15/2})7s8s	(15/2,1) ⁰	17/2	33 829.35	6252		
5f ¹¹ (4f _{15/2})7s8s	(15/2,1) ⁰	15/2	34 068.94	4153		
5f ¹¹ 7s7p	6I	15/2	17 803.09	3838	68 293	-793
5f ¹¹ 7s7p	6I	17/2	19 209.15	5938	93 954	-2173
5f ¹⁰ 6d7s ²	6I	17/2	19 367.85	-245	-3777	14
5f ¹¹ 7s7p		13/2, 15/2	19 788.32	-2103		
5f ¹⁰ 6d7s ²		13/2	28 118.65	2170	43 477	-289
5f ¹⁰ 6d7s ²		13/2, 15/2, 17/2	28 372.78	52		
5f ¹¹ 7s7p		13/2	28 447.02	4576	92 872	-1714
5f ¹⁰ 6d7s ²		15/2, 17/2	28 578.60	-266		
5f ¹⁰ 6d7s ²		15/2, 17/2	28 689.74	837		
5f ¹¹ 7s7p		15/2, 17/2	29 159.28	952		
5f ¹¹ 7s7p		13/2	29 204.89	3138	63 762	-763
5f ¹⁰ 6d7s ²		13/2	31 829.03	4037	96 233	203
5f ¹⁰ 6d7s ²		13/2	31 886.3	1590		
5f ¹¹ 7s7p		9/2	32 770.06	4437	91 272	573
5f ¹⁰ 6d7s ²		13/2	34 192.6			
5f ¹¹ 7s7p		13/2	35 507.74			
5f ¹⁰ 6d7s ²		11/2	38 634.04			

^a See Blaise and Wyart (1992) or Wyart *et al.* (2005) for complete set of data including Es(0) and Es(II) and references.

Table 12.3 *Properties of ^{253}Es .*

<i>Property</i>	<i>Value</i>	<i>References</i>
first ionization potential	6.42(3) eV (calc.)	Sugar (1974); Rajnak and Shore (1978)
first ionization potential	6.3676(5) eV (exp.)	Peterson <i>et al.</i> (1998); Erdmann <i>et al.</i> (1998)
nuclear spin	$I = 7/2$	Appendix I
electronic ground state	$J = 15/2$	
nuclear dipole moment, μ	4.10(7) μ_{N}	Appendix I
nuclear quadrupole moment, Q_s	6.7(8)	Appendix I
K X-ray energies	$K\alpha_2$ 112.501(10)	Dittner and Bemis (1972)
	$K\alpha_1$ 118.018(10)	Dittner and Bemis (1972)
	$K\beta_3$ 131.848(20)	Dittner and Bemis (1972)
	$K\beta_1$ 133.188(20)	Dittner and Bemis (1972)

Small quantities of transplutonium metals have traditionally been prepared by different methods, two of which are mentioned here (Haire, 1982). The first is reduction of an actinide halide by an active metal (alkali or alkaline earth), and the desired actinide metal is left as a product. This is a suitable technique if the actinide has a lower volatility than the reductant or its halide product (i.e. lithium and lithium fluoride, which are both sufficiently volatile). The second approach is to reduce the actinide oxide with thorium or lanthanum metal and distill away the actinide product. The choice frequently depends on the volatility of the actinide metal. In the case of einsteinium, the latter technique is the most appropriate given its higher volatility. If einsteinium fluoride was reduced with lithium metal, it would be difficult to obtain the metal free of lithium fluoride in the distilled/condensed product.

The first reported attempt to prepare einsteinium metal (Cunningham and Parsons, 1971) used less than 1 μg of einsteinium, and involved distilling lithium metal onto EsF_3 . The temperature was raised to 800°C and the sample then quenched-cooled to give a material contaminated with lithium fluoride. Thin films of pure einsteinium were prepared subsequently by reducing Es_2O_3 with lanthanum metal followed by collecting the einsteinium metal distillate on electron microscopy grids (Haire and Baybarz, 1979). This reduction approach has become the normal preparative route for einsteinium metal, and has provided the first diffraction data from pure einsteinium metal.

Electron diffraction data for the metal prepared by oxide reduction consisted of over 14 diffraction lines and were obtained from 10–200 ng deposits. The very thin films reduced effects from both self-irradiation damage and self-heating in the metal from the ^{253}Es isotope, and they also allowed diffraction powder patterns to be obtained in a few seconds versus the 30–120 min often needed

for X-ray powder analysis. The diffraction data obtained showed a face-centered cubic (fcc) ($Fm\bar{3}m$) symmetry and generated a lattice parameter of 5.75(1) Å, which corresponds to a metallic radius of 2.03 Å. This radius compares with radii of 2.042 and 1.940 Å (Topp, 1965) for divalent europium and ytterbium metals, respectively, compared to much smaller radii (i.e. 1.734–1.877 Å) for the trivalent lanthanide metals and 1.691–1.725 Å for the trivalent americium through californium metals (Haire, 1990). The radii of Ba, Eu, Es, and Yb form a smooth curve, if radii are plotted versus atomic number (see Fig. 12.1 for the volume behavior of the latter three elements). These findings led to the conclusion that einsteinium is indeed the first divalent actinide metal, and this was subsequently supported by studies of the enthalpy of sublimation of einsteinium (see subsequent discussion) and thermochromatography studies with tracer levels of einsteinium. Selected data for einsteinium and selected f-element metals are given in Tables 12.4 and 12.5.

The elements americium through californium are trivalent metals and exhibit a double hexagonal close-packed (dhcp) room-temperature and an

Table 12.4 Structural and physical properties of Es versus other f-electron metals.

Metal	Structure type	Lattice parameters			Atomic radius (Å)	Atomic volume (Å ³)	References
		a ₀ (Å)	b ₀ (Å)	c ₀ (Å)			
Es	fcc ($Fm\bar{3}m$)	5.75(1)			2.03	47.5	Haire and Baybarz (1979)
Eu	bcc	4.578(1)			2.04	48.0	Topp (1965)
Yb	fcc	5.481(1)			1.940	41.2	Topp (1965)
Cf	fcc	4.78(1)			1.69	27.3	Haire (1990)
Cf	dhcp ($P6_3/mmc$)	3.384		11.040	1.691	27.37	Haire (1990)

Table 12.5 Physical properties of Es versus Cf metals.^a

Metal	Structure type	Density (g cm ⁻³)	Melting point (K): boiling point (K)	Enthalpy of sublimation at 298 K (kJ mol ⁻¹)	Entropy (J K ⁻¹ mol ⁻¹)	Bulk modulus (GPa)	References
Es	fcc ($Fm\bar{3}m$)	8.84	1133:1269	134	89.4	15	Haire (1990)
Cf	dhcp ($P6_3/mmc$)	15.10	1173:2018	196	80.3	50	Haire (1990)

^a Note: Am, Cm, and Bk metal values are similar to those for Cf; all four are 'trivalent' metals, while Es is a 'divalent' metal.

elevated-temperature fcc structure. The densities of the four trivalent transplutonium metals range from 13.6 to 15.1 g cm⁻³, while einsteinium has a density of 8.84 g cm⁻³ (Haire, 1990). The cubic structure of einsteinium should be considered as reflecting its electronic bonding configuration rather than being a high-temperature form, as are the room temperature structures of europium (body-centered cubic, bcc) and ytterbium (fcc) in the lanthanide series. Europium remains bcc down to 5 K, even with 'cold working' of the material. In contrast, ytterbium transforms from its fcc structure to a hcp form below 270 K, which can be retained at room temperature. Einsteinium metal has been examined at liquid nitrogen temperature (Haire, 1980), where evidence for a hexagonal structure was obtained. However, it was not resolved in that work whether this was a temperature-induced change (comparable to ytterbium metal) or reflected a change from the effects of radiation damage to the einsteinium lattice.

Alloys of einsteinium with europium and with ytterbium (~1 mol%) have also been prepared by co-distilling the metals (Haire, 1982) from mixed oxides (einsteinium–europium and einsteinium–ytterbium) after reacting the oxide mixtures with lanthanum metal. With 100 µg of ²⁵³Es, the self-heating/radiation in an Es–Yb alloy was sufficient to give rise to partial sublimation of the einsteinium product when it was isolated in vacuum.

A value for the melting point of einsteinium was obtained by observing the heating of deposits in an electron microscope (Haire and Baybarz, 1979). The melting point was taken as the point where "micro-puddles" were formed, in conjunction with calibration studies with other known metals done in a similar fashion. A value of (1133 ± 50) K was reported for the melting point of einsteinium metal. This value can be compared to the melting points of 1099 and 1097 K for europium and ytterbium metals, respectively, while the values for the trivalent lanthanide and americium through californium metals are higher, being (1173–1620) K (Haire, 1990).

At the tracer level, einsteinium–calcium metal mixtures were prepared and studied via thermochromatographic metal columns, where their sorption/condensation behaviors were monitored (Hübener, 1980). Data from this work supported the divalency of einsteinium metal. It was determined that ytterbium, einsteinium, fermium, and mendelevium all condensed at the same column length (~700 K), but deviations were found for europium, samarium, and calcium, where their behaviors were intermediate to the divalent and trivalent metals. One aspect of this thermochromatographic technique has been variation in results when different metals are used for the sorbers or columns.

Volatilities of these metals are correlated with f-electron promotional energies and the number of bonding electrons – the fewer the bonding electrons the higher the volatility. Estimates have been given by Nugent *et al.* (1969a) for the enthalpy of sublimation of these metals via extrapolations. Kleinschmidt *et al.* (1984, 1985) and Haire and Gibson (1989) have also reported experimental data for the enthalpies of sublimation and entropies of einsteinium metal.

The enthalpy for einsteinium also supports that it is a divalent metal. The enthalpy of sublimation of einsteinium is given as 133 kJ mol^{-1} and was found to agree closely with that for fermium (143 kJ mol^{-1}) (Haire and Gibson, 1989), the second divalent actinide metal. In the latter work on fermium, the enthalpy for einsteinium was reevaluated, and a value of 134 kJ mol^{-1} was determined for einsteinium, this value being slightly lower than that for fermium. However, this difference is not significant, given that error bars were estimated at $\pm 12 \text{ kJ mol}^{-1}$. In essence, the two values for einsteinium and that for fermium can be considered the same.

Subsequent studies of heavy elements (including einsteinium) via thermochromatography have been performed (Hübener *et al.*, 1994; Taut *et al.*, 1997, 1998) and results varied significantly with the metal of the columns used – five different metals were used in the work. With iron columns, californium, einsteinium, and fermium behaved the same; with niobium columns, einsteinium was intermediate to positions for californium and fermium, and in titanium columns, einsteinium and fermium behaved similarly (Hübener *et al.*, 1994). It was concluded that einsteinium and fermium were acting as divalent actinide metals while californium was ‘borderline’ between divalent and trivalent. Subsequently, similar studies with californium, einsteinium, and fermium tracers estimated einsteinium’s enthalpy of sublimation to be 167 kJ mol^{-1} (Taut *et al.*, 1997), a significantly higher value than reported earlier by more direct methods (134 kJ mol^{-1}) but still lower than the enthalpy for californium determined by this technique (close to 200 kJ mol^{-1}). It was stated in Taut *et al.*’s work (1997) that the value for einsteinium is still typical for a divalent metal, although it was higher than that for fermium. Additional discussions on einsteinium thermochromatography are given together with the work on nobelium, where the two models are discussed in conjunction with *ab initio* calculations for actinide adsorption enthalpies (Eichler *et al.*, 2002), and in diffusion studies into tantalum (Legoux and Merinis, 1986).

The crystal entropy of einsteinium has been calculated using a correlation (Ward and Hill, 1976; Ward *et al.*, 1980; Ward, 1986) based on ytterbium metal, and a value of $(89.4 \pm 0.8) \text{ J K}^{-1} \text{ mol}^{-1}$ at 298 K was determined. For the 1133 K melting point of einsteinium (Haire and Baybarz, 1979), the enthalpy of melting was calculated to be 9.40 kJ mol^{-1} and the entropy as $8.30 \text{ J K}^{-1} \text{ mol}^{-1}$ by Ward and Hill (1976). The magnetic entropy for a $5f^{11}$ configuration gives a total angular momentum of $J = 15/2$ for the divalent einsteinium. A boiling point of 1269 K was also calculated (Kleinschmidt *et al.*, 1984) for the metal. One additional piece of information has been reported for the metal; its thermal conductivity has been estimated to be $10 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K (Ho *et al.*, 1972). The bulk modulus of einsteinium was estimated to be similar to those for europium and ytterbium metals. See Tables 12.4 and 12.5 for selected properties and values of einsteinium.

More recent work on the preparation of einsteinium metal provided the first isolated piece of pure einsteinium metal ($\sim 100 \mu\text{g}$) and a $60 \mu\text{g}$ deposit ($\sim 200 \mu\text{m}$

in diameter) on platinum. These efforts were in conjunction with attempts to study the high-pressure behavior of the metal (Haire and Heathman, 2000) by energy-dispersive X-ray diffraction using high-intensity tungsten radiation. The pressure behavior of einsteinium metal is very interesting, as it could become a trivalent metal under pressure, where pressure provides the energy necessary to promote an f-electron to a bonding state. In essence, the volume of einsteinium may be reduced under pressure to force additional bonding, similar to that found in the trivalent Am through Cf metals. It was anticipated that applying additional pressure on a potential trivalent einsteinium product could even lead to a further reduction in volume and result in the formation of an einsteinium metal product with itinerant 5f electrons (Haire *et al.*, 2004). This can be understood by examining the volume curves shown in Fig. 12.1, where the volume reduction induces greater bonding. However, the intended study of einsteinium under pressure was not successful, as the intense self-irradiation of einsteinium destroyed both its crystal lattice and the platinum pressure marker present within a few minutes. But the recent preparative effort with einsteinium allowed a new level to be reached in obtaining elemental einsteinium – namely, an einsteinium metal product free of a supporting substrate (i.e. a 100 µg ‘bulk form’ of pure einsteinium metal).

12.6 COMPOUNDS OF EINSTEINIUM

12.6.1 Crystal data

Once the existence of a new element has been established, scientists strive to determine its chemical and physical properties. The extent to which this is possible depends on the availability and nature of the material, and the techniques that are or can be established to study it. With the availability of multiple micrograms of einsteinium it became feasible to prepare and examine ‘bulk forms’ of its compounds, although not without perturbations and limitations caused by its short half-life, high self-radiation field, and the heat associated with the decay (^{253}Es alpha decay corresponds to $15312 \text{ kJ mol}^{-1} \text{ min}^{-1}$). For the preparation of compounds, one normally uses the ^{253}Es isotope (see earlier discussion on isotopes), given its greater availability. Some of the techniques used for microgram-sized samples of einsteinium have been discussed (Haire, 1981, 1982).

Only a few compounds of einsteinium have been prepared and have had their crystal structures identified. In this realm, there are induced changes or destruction of crystal lattices by the isotope’s self-irradiation (alpha emission plus nucleus recoil) and the rapid ingrowth of the berkelium daughter (~3% per day, berkelium ‘impurity’). For diffraction studies, the accompanying penetrating radiation (L, M and N X-rays, the gamma emissions from $^{254\text{g}}\text{Es}$ and its short-lived daughter, ^{250}Bk , also have serious effects on both X-ray

detectors and/or X-ray film in a short time frame (the film is often used for small 1–2 μg sized samples).

Even with rotating anode-type generators with higher X-ray intensities, these difficulties with einsteinium are not overcome. Electron diffraction techniques do afford major advantages, as only small, very thin samples (which can be smaller than the alpha particle's range, where a minimum amount of its energy is transferred) are needed. This technique requires very short exposure times (seconds) and that the detection mode is located approximately 1 m from the sample, which avoids film or detector problems from the einsteinium radiations.

Although synchrotron radiation can supply more intense radiation for diffraction studies with einsteinium samples, two difficulties are encountered: (1) the destruction of the crystal lattice during the time of 'transportation' to the synchrotron beamline; (2) the difficulty of obtaining approvals to use the activity levels from the einsteinium at the synchrotron, or for setting up an apparatus for *in situ* preparation of the compounds on the beamline. Yet, the latter remains an option for dealing with some of the experimental problems with einsteinium's rapid radioactive decay.

As with many of the transuranium compounds, halides and oxides were among the first compounds of einsteinium to be prepared and studied, which is in accord with the fact that these have frequently been among the first to be prepared for new elements. These are also used often as a starting platform for synthesizing other materials. To overcome the experimental difficulties encountered with diffraction analysis of ^{253}Es or ^{254}Es compounds, three approaches have been successful. One has been constant resynthesis of the compound during X-ray analysis, while another has been the use of very thin films, especially in conjunction with electron diffraction. The third has been to use very short exposures as can be accomplished by electron diffraction. Crystal data have been collected for the following materials: EsCl_3 , EsOCl , Es_2O_3 , EsBr_3 , and EsI_3 (See Table 12.6). A discussion of X-ray diffraction techniques for einsteinium compounds is also available (Haire and Peterson, 1979).

The first crystal data for einsteinium compounds were obtained for the trichloride and the oxychloride via the constant synthesis technique (Fujita *et al.*, 1969a,b). The approach was to resynthesize these materials *in situ* at $\sim 430^\circ\text{C}$. The trichloride was found to be hexagonal, isostructural with the actinium through californium trichlorides and the lanthanum through gadolinium trichlorides (UCl_3 -type, space group $C_{6h}^2-C6_3/m$). The oxychloride was found to crystallize in the tetragonal PbFCl structure (space group D_{4h}^7-P4/nmm) and is isostructural with the trivalent lanthanum through erbium oxychlorides and the known actinium through californium oxychlorides. The lattice parameters, corrected to 298 K, are given in Table 12.6.

Einsteinium sesquioxide was the next compound for which diffraction data were acquired, and this involved the use of the electron diffraction technique. The samples were prepared by calcining an einsteinium nitrate salt *in situ* on

Table 12.6 Compounds of di- and trivalent einsteinium characterized by structural and/or spectroscopic analysis.

Compound	Structure type	Lattice parameters				β (degree)	Major absorption bands (cm^{-1})	References
		a_0 (Å)	b_0 (Å)	c_0 (Å)				
Es ₂ O ₃	Mn ₂ O ₃ -bcc	10.766(6)				–	Haire and Baybarz (1973)	
Es ₂ O ₃	monoclinic	14.1	3.59	8.80	100	–	Haire and Eyring (1994)	
Es ₂ O ₃	La ₂ O ₃ -hexagonal	3.7		6.0		–	Haire and Eyring (1994)	
EsCl ₃	UCl ₃ -hexagonal	7.40(2)		4.07(2)		12 800, 20 000, 23 000	Fujita <i>et al.</i> (1969a, b)	
EsCl ₂	–					11 100, 18 500, 24 500	Peterson <i>et al.</i> (1979); Fellows <i>et al.</i> (1977)	
EsOCl	PbFCl-tetragonal	3.948(4)		6.702(19)		12 800, 16 300	Young <i>et al.</i> (1981)	
EsBr ₃	AlCl ₃ -monoclinic	7.27(2)	12.59(3)	6.81(2)	110.8(2)	12 600, 19 800	Fellows <i>et al.</i> (1975)	
EsBr ₂	–					11 100, 18 300	Young <i>et al.</i> (1976)	
EsOBr	–					12 700	Peterson <i>et al.</i> (1979)	
EsI ₃	BiI ₃ -hexagonal	7.53(4)		20.84(5)		12 300	Haire (1978); Peterson (1979)	
EsI ₂	–					11 100	Young <i>et al.</i> (1981)	
EsOI	–					12 700, 16 100	Young <i>et al.</i> (1981)	
EsF ₃	–					13 200, 20 300, 27 000	Ensor <i>et al.</i> (1981)	

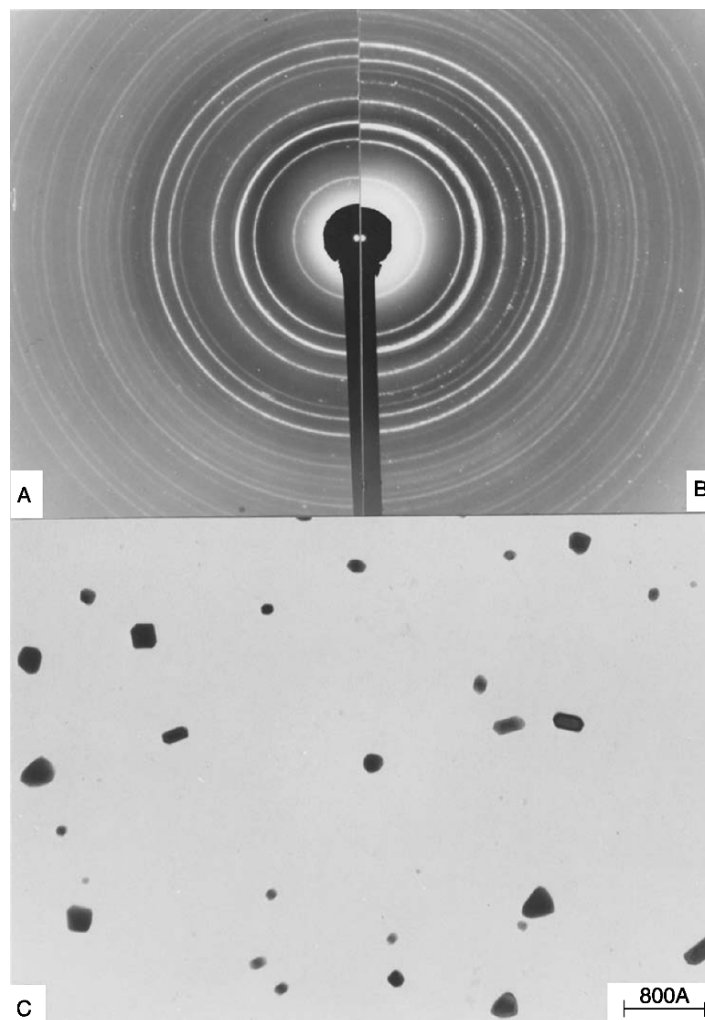


Fig. 12.5 Electron diffraction patterns of (a) Es_2O_3 and (b) Gd_2O_3 ; particles of (c) Es_2O_3 (Haire and Baybarz, 1973).

electron microscope grids in different atmospheres up to 1000°C , and then analyzing the products by electron diffraction (Haire and Baybarz, 1973).

Fig. 12.5 shows an electron diffraction pattern of cubic Es_2O_3 together with isostructural Gd_2O_3 and the small particles from which the einsteinium pattern was obtained. A bcc ($\alpha\text{-Mn}_2\text{O}_3$ -type, space group $Ia3$) Es_2O_3 was formed, which had a lattice parameter of $10.766(6)$ Å. Evidence for a higher oxide of einsteinium was not obtained. The parameter and ionic metal radius (calculated to be

Table 12.7 Ionic radii of einsteinium and selected f-elements.^a

<i>Ion</i>	M^{2+} (CN 6)	M^{3+} (CN 6)	M^{3+} (CN 8)	M^{4+} (CN 6)	M^{4+} (CN 8)	<i>References</i>
<i>Selected values from calculations</i>						
Cf	1.125	0.945	1.066	0.827	0.925	David (1986)
Es	1.102	0.934	1.053	[0.818]	[0.914]	David (1986)
Fm	1.083	0.922	1.040	[0.811]	[0.906]	David (1986)
Eu	1.166	0.946	1.065	[0.807]	[0.903]	David (1986)
Gd	[1.140]	0.937	1.055	[0.799]	[0.894]	David (1986)
Tb	[1.119]	0.923	1.040	0.792	0.886	David (1986)
<i>Calculated from consistent set of experimental oxide data</i>						
Cf	–	0.949	–	0.859	–	Haire and Eyring (1994)
Es	–	0.928	–	–	–	Haire and Eyring (1994)
Eu	–	0.950	–	–	–	Haire and Eyring (1994)
Gd	–	0.938	–	–	–	Haire and Eyring (1994)
Tb	–	0.920	–	0.817	–	Haire and Eyring (1994)

^a Radii are given in Å; [–] indicates interpolations.

0.928 Å) for this oxide were intermediate to those for Gd₂O₃ and Tb₂O₃, and just smaller than those for Cf₂O₃ (see Table 12.7).

Lattice parameters and ionic radii for the cubic sesquioxides of the f-elements are shown in Fig. 12.6, where a smooth relationship can be seen. These behaviors differ from the volume behaviors of the metals (see Fig. 12.1). The properties of einsteinium oxide and a comparison of its properties are also discussed in reviews (Baybarz and Haire, 1976; Haire and Eyring, 1994). As opposed to the metal, compounds of einsteinium (i.e. the oxide here) display lattice parameters and ionic radii similar to the comparable transplutonium and lanthanide compounds. All of the first five transplutonium sesquioxides form this cubic crystal form, but some may also exist in a monoclinic structure (Sm₂O₃-type, space group *C2/m*) or a hexagonal form (La₂O₃-type, space group *P3m1*), depending on the thermal history and the particular element in question (see Haire and Eyring, 1994).

Self-irradiation may also convert one structural form of the sesquioxide to another; this radiation effect has been discussed in an earlier review (Fuger, 1975). For einsteinium sesquioxide, both a monoclinic and a hexagonal form have been recorded (Haire *et al.*, 1985; Haire and Eyring, 1994). The monoclinic form was observed during oxidation of metal films below 1273 K, and this effect has also been observed with gadolinium metal films. The hexagonal oxide was observed in ‘aged’ cubic einsteinium sesquioxide. It could not be ascertained whether the monoclinic and/or hexagonal forms of Es₂O₃ resulted from being heated, from self-heating, or from self-irradiation damage. It is probable that the hexagonal form resulted from one of both of the latter two consequences; the hexagonal form of Es₂O₃ would be expected from systematics to be formed

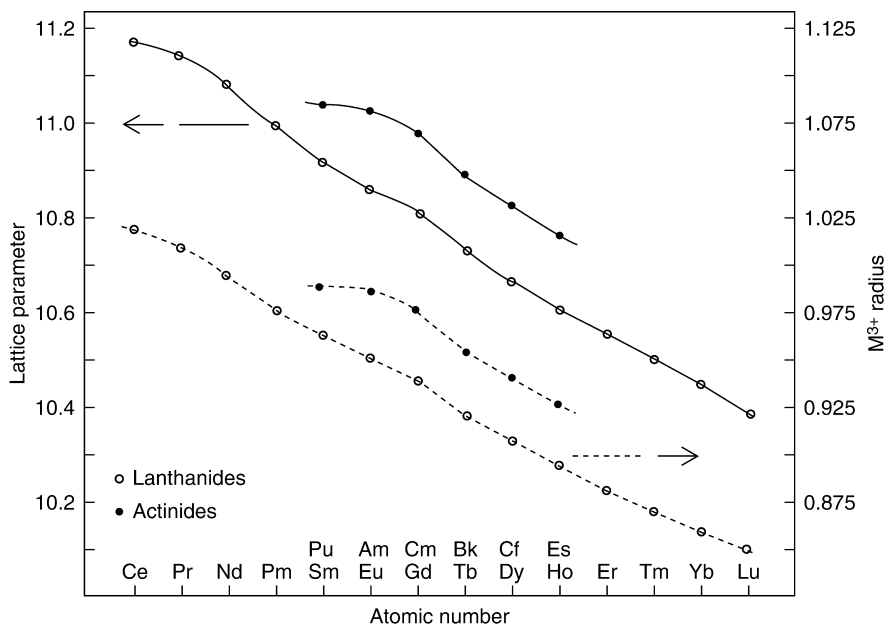


Fig. 12.6 Lattice parameters and calculated radii for the cubic sesquioxides. A regular trend is observed with $Es(III)$, as opposed to the different behavior observed with Es metal (Haire and Eyring, 1994). Parameters and radii are given in Å.

only near its melting point (Baybarz and Haire, 1976; Haire and Eyring, 1994). Lattice parameters for the monoclinic and/or hexagonal structural forms of einsteinium sesquioxide must also be considered in this context. The monoclinic form of einsteinium sesquioxide was obtained after heating at temperatures lower than would be expected to bring about the thermal transformation from its cubic form. The values for the lattice parameters of the monoclinic and hexagonal forms of Es_2O_3 are however reasonable, based on ionic systematics for the lanthanide and first four transplutonium sesquioxides (Haire and Eyring, 1994), and allowing for some lattice expansion due to self-irradiation.

X-ray data were also obtained for $EsBr_3$ (Fellows *et al.*, 1975, 1977) and EsI_3 (Peterson, 1979; Haire, 1980). The $EsBr_3$ data were acquired from very small ($\sim 1 \mu\text{g}$) pieces immediately after annealing at 400°C . Fifteen diffraction lines were obtained and indexed as a monoclinic $AlCl_3$ -type structure, which is isostructural with $BkBr_3$ and $CfBr_3$ (Burns *et al.*, 1975). The information for EsI_3 was obtained from freshly sublimed films formed in a quartz capillary. The diffraction lines were indexed as belonging to a hexagonal BiI_3 -type structure, which is also formed by the transneodymium triiodides and the five transplutonium triiodides. The first four lanthanide triiodides form a $PuBr_3$ -type structure (Brown, 1968). Important factors in obtaining these diffraction data were the very small samples or thin films and some luck.

12.6.2 Spectrometry – solids

Another important technique for characterizing einsteinium compounds was the use of absorption spectrometry of solids (as well as for actinides in solution, see Section 12.6.3). Divalent compounds of einsteinium were characterized entirely by this technique, given the difficulties in obtaining diffraction data. A great aid in this technique was incorporation of a ‘fingerprint’ approach, where correlations between spectra and short-range local environment (‘crystal environment’; X-ray diffraction requires ‘longer-range order’) allowed important conclusions to be drawn for the einsteinium compounds. This technique depends partly on the changes in metal ion coordination in the structures. One advantage of this technique is it allows samples to be prepared, annealed, and/or chemically converted in quartz capillaries, while permitting spectral analyses of intermediate products to follow the completeness of the changes being sought (i.e. reduction of a trihalide with hydrogen) in the same system. This approach was particularly suited to halides, as they had modest melting points, and with care, the melts can be solidified to transparent solids or even single crystals. The technique employed a microscope–spectrometer system, which has been described (Young *et al.*, 1976, 1978, 1981). The einsteinium solid-state absorption spectra are characterized normally by sharp electronic $f-f$ transitions. In addition, luminescence spectra have been obtained but the self-radiation of einsteinium also excites trace amounts of impurities and the quartz envelopes containing it, producing an additional source of luminescence that must be considered. Some of the solid-state absorption spectra for einsteinium compounds are shown in Fig. 12.7.

As discussed in Section 12.6.5, potentials ranging from -1.6 to -1.2 V are reported for the $\text{Es}^{3+}-\text{Es}^{2+}$ couple in aqueous solutions; a value of -1.3 V is adopted in Chapter 19. This potential offers an explanation for the ability to reduce einsteinium trihalides with hydrogen at elevated temperatures. This potential for einsteinium contrasts with the more negative $\text{Am}^{3+}-\text{Am}^{2+}$ through $\text{Bk}^{3+}-\text{Bk}^{2+}$ potentials, whose trihalides cannot be reduced by hydrogen. This smaller potential is in accord with the greater tendency for obtaining divalency with einsteinium (also see Section 12.6.5).

Several halide materials have been prepared and their solid-state absorption spectra obtained: EsCl_2 (Fellows *et al.*, 1975, 1977; Peterson *et al.*, 1977, 1979; Peterson, 1979; Young *et al.*, 1981); EsBr_2 and EsI_2 (Young *et al.*, 1976, 1978; Peterson *et al.*, 1979); for EsF_3 (Ensor *et al.*, 1981); and EsBr_3 and EsCl_3 (Fellows *et al.*, 1975, 1977; Peterson *et al.*, 1979; Young *et al.*, 1981). Efforts to prepare EsF_2 have not been successful and attempts to prepare EsI_3 have encountered difficulties involving the thermal reduction to EsI_2 . The spectra obtained for the three divalent halides of einsteinium and that for EsBr_3 are shown in Fig. 12.7 (Peterson *et al.*, 1979). The distinct differences between the spectra of EsBr_2 and EsBr_3 are obvious, while the similarities in the spectra for the three dihalides are also evident. The cutoff in the near UV for the diiodide reflects charge transfer occurring in this sample. The absorption spectrum of

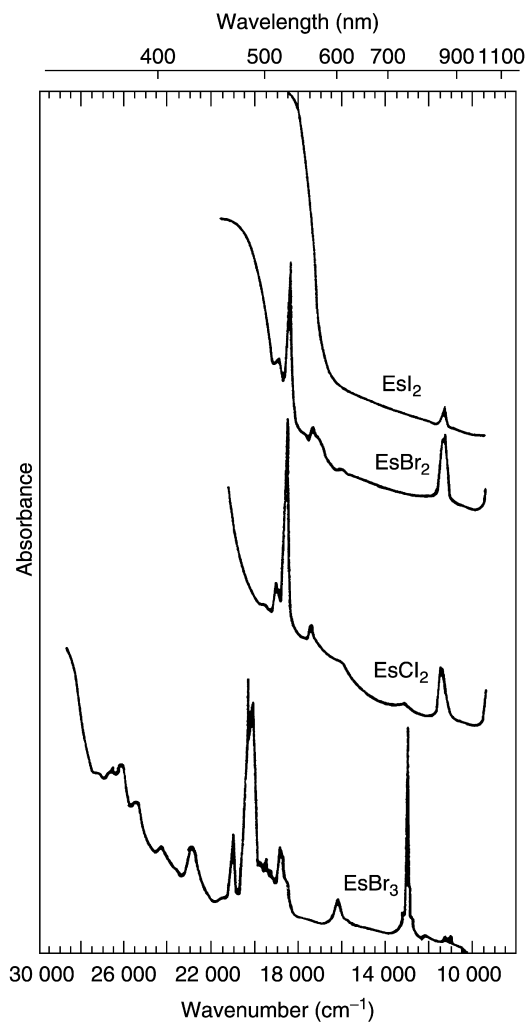


Fig. 12.7 Solid-state absorption spectra for *Es* halides (Peterson *et al.*, 1979).

EsOBr is similar to that of EsBr₃, but it is sufficiently different to differentiate between the spectra of the two compounds and identify them.

Absorption spectrometry has also been used to study EsF₃ (Ensor *et al.*, 1981) and to then follow the decay products (²⁴⁹Bk and ²⁴⁹Cf, daughter and granddaughter) as they formed in the solid-state sample. From the spectrometric data, it was concluded that EsF₃ initially formed as a LaF₃-type trigonal phase.

Silicate matrices containing ²⁵³Es have also been prepared. Results of recent spectroscopic investigations of their properties have been reported (Assefa *et al.*, 1999; Assefa and Haire, 2000, 2001). These studies concentrated on

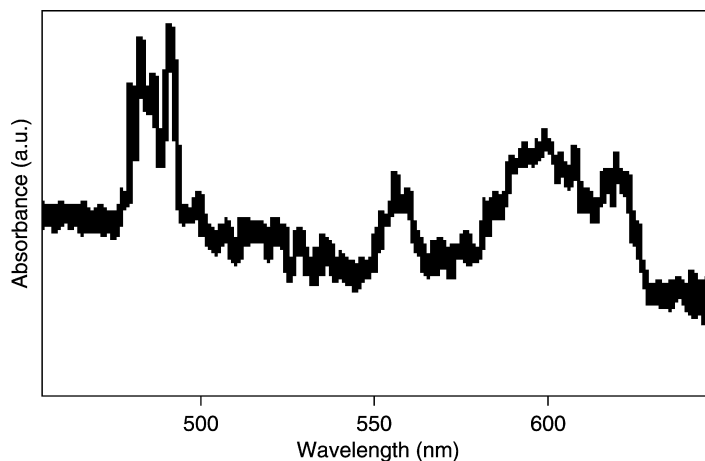


Fig. 12.8 Absorption spectrum of *Es* in a borosilicate glass: absorption bands correspond to *Es(III)* (Assefa and Haire, 2001).

self-luminescence from the materials, and examined the effects of the excitation source used, power of excitation, sample age, and nature of the sample matrix. Also obtained in that work were the absorption spectra of the einsteinium in this host matrix. The self-luminescence arising from einsteinium in these matrices was attributed to defect centers within the Si–O–Si network, nonbonding oxygen holes and Si cluster sites. It was determined that *Es(III)* was present; evidence for *Es(II)* was not found. The different spectra obtained for einsteinium in silicate matrices are shown in Figs. 12.8 and 12.9.

12.6.3 Other results – solids

Electron paramagnetic resonance spectra have been obtained for einsteinium placed in single-crystal hosts of CaF_2 (Edelstein *et al.*, 1970; Edelstein, 1971), in BaF_2 and SrF_2 (Bouissières *et al.*, 1980), and in BaF_2 and SrCl_2 (Boatner *et al.*, 1976). The spectra of Es^{2+} were similar in CaF_2 and BaF_2 . The immediate reduction of *Es(III)* to *Es(II)* in the matrix from electron displacement via the alpha radiation field was suggested as the cause of the einsteinium reduction observed in these efforts. A $5f^{11}$ configuration with a ground state close to the $^4I_{15/2}$ (with a small admixture of a $^2K_{15/2}$ state) state was assigned to einsteinium. This indicated that only a minor perturbation of the inner 5f orbitals occurred from the crystal fields in the solids. A value of $\mu_n = 3.62(50)$ nm was reported for einsteinium.

Some information has also been acquired for the magnetism of einsteinium compounds. Preliminary magnetic measurements on einsteinium metal did not show a low temperature transition (Huray *et al.*, 1983). Studies on Es_2O_3 and EsF_3 indicated moments of 10.2(1) and 10.5(1) Bohr magnetons, respectively. When corrected for the berkelium ingrowth present in the oxide sample, a value

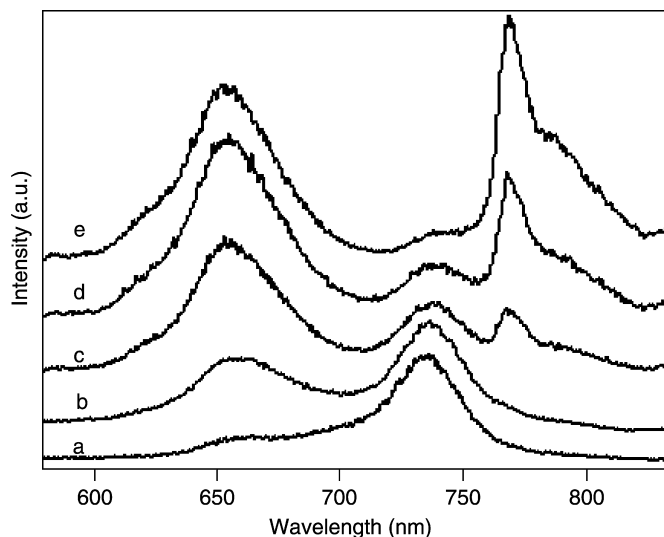


Fig. 12.9 Photoluminescence spectra from a borosilicate glass doped with Es: excitation was with 488 nm. Spectra were recorded at laser powers of (a) 100; (b) 310; (c) 600; (d) 800; and (e) 1000 mW (Assefa and Haire, 2001).

of 10.6(1) is obtained, which is in excellent agreement with a calculated $5f^{10}$ free-ion value (Huray *et al.*, 1983; Huray and Nave, 1987).

Preliminary information for the vaporization behavior of Es_2O_3 has been reported (Haire, 1994). The primary mode of vaporization for this oxide is the generation of atomic metal vapor, rather than via a monoxide (Es/EsO in the vapor was greater than 10:1). This situation arises as a result of the lower dissociation energy of EsO, which was estimated to be 460 kJ mol^{-1} . More recent calculations and work (Gibson, 2003; Gibson and Haire, 2003) discuss the electronic states, dissociation energies, and gaseous behavior of einsteinium. A brief discussion on these topics is given in Section 12.6.6.

The thermal behavior of einsteinium sesquioxide and the reduced formation of EsO(g) compares closely to the behaviors of europium and ytterbium oxides. The sesquioxides of europium and ytterbium also decompose mainly to atomic europium and ytterbium rather than form monoxides. A calculated estimate for the standard Gibbs energy of formation of Es_2O_3 at 298 K has been given as $-1605 \text{ kJ mol}^{-1}$, and that for EsO_2 as -701 kJ mol^{-1} (Chapter 19). A tentative value for the Gibbs energy of formation for Es_2O_3 based on experimental behavior was given to be between -1650 and $-1700 \text{ kJ mol}^{-1}$ (Haire, 1994). Attempts to form EsO_2 or other compounds containing Es(IV) (i.e. BaEsO_3 or other materials that might help stabilize Es(IV)) have produced negative results (Haire and Bourges, 1980). Several estimated values for thermodynamics of formation of Es_2O_3 , EsO_2 , EsF_3 , EsF_4 , EsCl_2 , and EsCl_3 are also given in Chapter 19.

12.6.4 Spectrometry – solutions

Spectrometry of einsteinium in solution has also been pursued, but only its trivalent state has been observed. The solution properties of the trivalent state are similar to those of the previous four transplutonium elements, and coordination number is an important variable. Given that the trivalent ion is present, bonding with ligands is often due to electrostatic effects. But as covalence for a given oxidation state increases across the series, second-order contributions from covalent interactions are possible. The ionic radius of einsteinium in solution should be only slightly smaller than that of californium(III). The free-ion energy levels for trivalent actinides have been given by Blaise and Wyart (1992) and Wyart *et al.* (2005). The ground state of einsteinium (Es(III)) is given as 5I_8 , with the first excited state appearing at $\sim 10 \times 10^3 \text{ cm}^{-1}$ higher in energy (see Table 12.2).

The first observation of a solution spectrum was for EsCl_3 in hydrochloric acid by Cunningham *et al.* (1967), which was obtained by a special technique, where the micro-sized volume of the solution was kept constant by ‘pumping’ in liquid to overcome evaporation/radiolysis effects. Superior results were obtained subsequently with larger amounts of einsteinium, and 18 peaks between 370 and 1060 nm were obtained in a later work (Fujita *et al.*, 1969b). Electronic energy level and intensity correlations have also been made for Es(III) aquo ion, using data from dilute perchloric acid solutions (Carnall *et al.*, 1973). The absorption spectrum of Es(III) in solution, as demonstrated by Carnall *et al.*, is shown in Fig. 12.10. The band structure and intensities of einsteinium have also been discussed (Nugent *et al.*, 1969b, 1970; Varga *et al.*, 1973a,b).

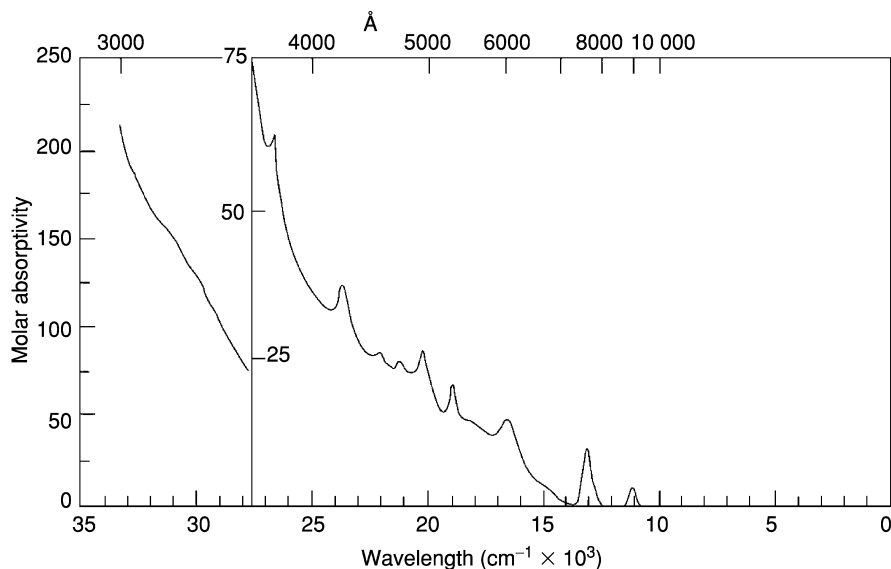


Fig. 12.10 Solution spectrum of Es(III) in dilute perchloric acid (Carnall *et al.*, 1973).

The spectra fit the behavior expected for an Es(III) free ion, where the f–f transitions were believed to arise from mixed eigenstates, due to coupling that was intermediate between LS and jj.

Photoelectron spectrometry of einsteinium oxide provided spectra of the 4f lines obtained with MgK α excitation (Krause *et al.*, 1988). Binding energies for 4f_{5/2} (569.3(4) eV) and 4f_{7/2} (550.8(3) eV) of einsteinium were reported and compared to values for other actinides. These values compared well (within –1.0 and –0.1 eV, respectively) with theoretical binding energies. The spin–orbit splitting for the 4f level was also measured and compared to the values obtained from theory. Beitz *et al.* (1992, 1998) have reported on the spectrometry and dynamics of the 5f electron states in Es(III) placed in a LaF₃ matrix.

The consequences of self-irradiation from einsteinium on selected clay minerals for waste isolation have also been probed employing ²⁵³Es in solution. The einsteinium was sorbed from aqueous solution using two different clay minerals (kaolin and attapugite) and the morphology of the clay was followed with time using electron microscopy (Haire and Beall, 1979). The conclusion reached was that although the clay structure became damaged, einsteinium was still retained by the clay debris and not released to the solution.

12.6.5 Related studies in solution

The complex-ion chemistry of einsteinium has often been studied in conjunction with an examination of the stabilities of other trivalent actinide ions in solution, and often at the tracer level. Although einsteinium exhibits oxidation states of II, III with a potential for IV in the solid state, its solution chemistry is essentially that of a trivalent ion, and is often comparable to the actinide and lanthanide ions having similar radii. A list of the reported stability constants for einsteinium is given in Table 12.8. It has been concluded that chloride and possibly some thiocyanate complexes are the only outer-sphere complexes (water of hydration found between the ligand and the metal ion). The majority of the complexes are instead the inner-sphere type, which has been inferred from an increased stability constant as a function of increased atomic number, and from the enthalpy and entropy values for the formation of the complexes. Several different complexes have been studied, and these are shown in Table 12.8.

The radii and hydration numbers for actinide(III) ions have been derived from the Stokes' law approach using migration rates in electric fields or diffusion coefficients of tracers in electrolytes (Lundqvist *et al.*, 1981; Latrous *et al.*, 1982; Fourest *et al.*, 1983). David (1986) have also discussed the radii of actinides. In line with an expected greater covalent nature when progressing across the series, the Es(III) and Fm(III) hydrated ions are larger than those for earlier members of the series. A value of 0.492 nm (with up to ~16 molecules of water in the hydration sphere) has been estimated for the radius of einsteinium(III).

Several thermodynamic values have also been reported for einsteinium: (1) the molar activity coefficient in sodium nitrate solutions (Chudinov and Pirozhkov,

Table 12.8 Cumulative stability constants of einsteinium complexes.

Complex*	Log stability constants			References
	β_1	β_2	β_3	
EsCl ²⁺	-0.18			Harmon and Peterson (1972a)
EsOH ²⁺	8.86			Hussonnois <i>et al.</i> (1973)
Es(SO ₄) _n ³⁻²ⁿ	-2.19	-4.3	-4.93	McDowell and Coleman (1972)
Es(SCN) _n ³⁻ⁿ	0.559	-1.4	0.468	Harmon and Peterson (1972b)
EsHCit ²⁻	10.6			Hubert <i>et al.</i> (1974)
Es(Cit) ₂ ³⁻	12.1			Hubert <i>et al.</i> (1974)
Es(α HIB) ²⁺	4.29			Aly and Latimer (1970a)
Es(tartrate) ⁺	5.86			Aly and Latimer (1970a)
Es(malate) ⁺	7.06			Aly and Latimer (1970a)
EsDTPA ²⁻	22.62			Myasoedov <i>et al.</i> (1974)
EsDCTA ⁻	19.43			Myasoedov <i>et al.</i> (1974)
EsEDTA ⁻	19.11			Myasoedov <i>et al.</i> (1974)
Es(II) PB (water)	6.2	106.4		Mikheev <i>et al.</i> (1988a)
Es(II) PB (acetonitrile)	6.6			Mikheev <i>et al.</i> (1988a)
Es(II) 18-6	log <i>K</i> = 2.64 water log <i>K</i> = 4.70 ethanol-water			Mikheev <i>et al.</i> (1986, 1988a,b, 1993a,b); Veleshko <i>et al.</i> (1993)

* Cit = citrate ion; α HIB = alphahydroxyisobutyrate; DTPA = diethylenetriaminepentaacetate; DCTA = trans-1,2 diamino cyclohexanetetraacetate ion; EDTA = ethylenediaminetetraacetate ion; PB = tetraphenyl borate; 18-6 = 18-crown-6.

1973); and (2) the Gibbs energy, enthalpy, and entropy of formation (Nugent, 1975; David *et al.*, 1978, 1986; Lebedev, 1978). The following values given were: enthalpy of formation, $\Delta_f H^0 = -603 \text{ kJ mol}^{-1}$; the entropy of formation, $\Delta_f S^0 = -100 \text{ J K}^{-1} \text{ mol}^{-1}$; and the Gibbs energy, $\Delta_f G^0 = -573 \text{ kJ mol}^{-1}$.

Morss (1986) has provided estimates for several thermodynamic properties of einsteinium, ranging from the formation of aqueous ions, the activity products for the trihydroxide and dioxide, hydration enthalpies and ionization energies, and the enthalpies of formation and solution for the sesquioxide and dioxide. Also given are the calculated enthalpies of formation and solution for the dichlorides and trihalides (fluoride, chloride, bromide, and iodide) and the enthalpy of formation of the four tetrahalides.

Electrode potentials and diffusion coefficients for einsteinium were measured by radiopolarography using solutions and a dropping mercury cathode (Samhoun and David, 1979). A single half-wave for the III to 0 standard potential for reduction/amalgamation was reported as $-1.460(5) \text{ V}$ and a diffusion coefficient of $6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. Nugent (1975) suggested a corrected, more negative value ($-1.98(7) \text{ V}$; after correcting for the amalgamation energy) as given in

Chapter 19. David (1986) discussed other values and gave selected ionic radii for several actinides, including einsteinium.

The amalgamation behavior of einsteinium and other actinide elements had been investigated earlier, where it was noted that amalgams of californium, einsteinium, and fermium displayed an anomalous behavior (Maly, 1969). This work suggested that these three elements may display a divalent state, given their preference to form amalgams in comparison to other actinides. Radiopolarography frequently employs mercury as one phase but phase diagrams for mercury alloys or dilute amalgams are not available for many of the transplutonium elements. One report (Guminski, 1996) has tabulated information from pre-1970 publications that contained incorrect data, which makes this publication of limited value.

Although einsteinium is the first element in the series to be divalent, the divalent ionic states of americium and californium have also been reported (see Chapters 8 and 11). The III \rightarrow II reduction potential for einsteinium was initially estimated to be -1.6V , based on the lowest state for electron transfer (Nugent *et al.*, 1969b; Nugent, 1975), but was later suggested to be -1.21 V (from work with chloroaluminate salts (Duyckaerts and Gilbert, 1977)) and -1.18 V from radiopolarographic experiments (David *et al.*, 1978). Using a method of cocrystallization of einsteinium tracer with SmCl_2 , Mikheev *et al.* (1972a,b) and Mikheev and Rumer (1972) had suggested einsteinium's reduction potential should be close to that for samarium ($-1.55(6)\text{ V}$). A value of -1.3 V is adopted in Chapter 19 for the standard potential of the $\text{Es}^{3+} - \text{Es}^{2+}$ couple.

A series of papers over several years have dealt with Es^{2+} in selected solutions. These have been tracer-level studies involving different facets of the co-crystallization technique and of complexation studies. One of these papers (Mikheev *et al.*, 1986) investigated the cocrystallization of divalent ions of californium, einsteinium, fermium, samarium, europium, and ytterbium with SrI_2 (18-crown-6) using tetrahydrofuran as a solvent. The Tm^{2+} ion controlled the oxidation potential of the solution. Cocrystallization coefficients relative to strontium were given as close to 1, where the coefficients of the three actinides fell between values of 1.10 for samarium and 0.83 for ytterbium.

The behavior of einsteinium (together with other Am, Cf, and Fm) in $\text{LiCl-NdCl}_2\text{-NdCl}_3$ and in LiI-PrI_2 systems was examined (Kulyukhin *et al.*, 1997a,b). In the first molten salt, Nd(II) reduced Cf and Fm to a divalent state. In the second salt system, it was not clear if these actinides were reduced to their divalent or monovalent states. Ratios of the actinide distribution coefficients to those of samarium were reported for both salt systems. Mikheev *et al.* (2004) have reviewed the lower oxidation states of actinides with regard to cocrystallization coefficients in melts, and provided a distribution coefficient for einsteinium versus strontium ($D_{\text{Es}/\text{Sm}} = 0.94$).

Complexation and cocrystallization of einsteinium with 18-crown-6 in water and water-ethanol mixtures were reported by Mikheev *et al.* (1993a,b). Log K values measured for water and the water-ethanol mixtures were 2.64

and 4.70, respectively. The solvent effects on cocrystallization of Es^{2+} with SrCl_2 were reported by Mikheev *et al.* in the 1993b reference. Mikheev *et al.* (1986) had also looked at cocrystallization of Es^{2+} with SrI_2 -18-crown-6 complexes, and the effects of water on the cocrystallization and solubility of einsteinium in $\text{Sr}(\text{Sm})\text{SO}_4$ systems (Mikheev *et al.*, 1987). In the latter work, hydration values could be estimated for Es^{2+} from radii considerations of the different ions. Solubility products for einsteinium complexes with 18-crown-6, boron tetrafluoride, and boron tetraphenyl in tetrahydrofuran were discussed by Kulyukin and Mikheev (1997a,b). The distribution of einsteinium in molten salts containing reductants was described by Kulyukin *et al.* (1997). Veleshko *et al.* (1993) discussed the complexation of Es^{2+} with tetraphenylborate in acetonitrile, and Mikheev *et al.* (1988b) reported the data for the latter with water-ethanol mixtures.

Another study examined the effects of water on the cocrystallization of divalent europium, ytterbium, and einsteinium ions in the $\text{Sr}(\text{Sm})\text{SO}_4$ -ethanol system (Mikheev *et al.*, 1988a,b). Water affected the Es^{2+} coefficients up to 10 M water. The Gibbs energies of hydration were given for Eu^{2+} , Yb^{2+} , and Sr^{2+} ions and were assumed to extend to Es^{2+} . Values ranged from 1361 to 1461 kJ mol⁻¹. The coordination of these three ions was also examined with sodium tetraphenylborate in water-ethanol solutions (Mikheev *et al.*, 1988b). The coordination constants, β_1 and β_2 , were determined and the observed trend suggested that the hydrated Es^{2+} ion was smaller than the two divalent lanthanide ions. The β_1 and β_2 values were given as log values: 6.2 and 106.4 for Es^{2+} ; 1.7 and 52.7 for Eu^{2+} ; and 6.5 and 25.7 for Yb^{2+} .

The effect of the solvent on the cocrystallization of Es^{2+} complexed with tetraphenylborate in acetonitrile and tetrahydrofuran was reported (Mikheev *et al.*, 1993a,b), where the einsteinium was complexed in the acetonitrile but not in the other solvent. The stability constants of the Es^{2+} complexes in acetonitrile were given as $\log \beta_1 = 6.6$ and $\log \beta_2 = 16.0$. Additional work on the complexation of Eu^{2+} , Yb^{2+} , and Es^{2+} with this reagent in different solvents suggested that outer sphere complexes are formed due to electron tunneling from the cation into the unsaturated π -bonds of the anion to form a single-electron bond (Mikheev *et al.*, 1993). The β_1 and β_2 values were given for the three divalent ions in water-ethanol mixtures, acetonitrile, and tetrahydrofuran. From the complexation of Es^{2+} in ethanol-water, acetonitrile, and tetrahydrofuran with the tetraphenylborate ion, it was concluded that complexes are not formed in tetrahydrofuran, as the solvent molecule is too large (Veleshko *et al.*, 1993). In the other two solvents, the smaller solvent molecule is inner sphere and complexes are formed.

The complexation of Es^{2+} with 18-crown-6 in aqueous ethanol and in water was studied, and the stability constants of the complex were determined (Mikheev *et al.*, 1993a,b). The $\log K$ values for einsteinium were given as 2.70 in water and 4.70 in ethanol-water (10 M). In both solvents, the $\log k$ varied in the order: $\text{Eu}^{2+} > \text{Es}^{2+} > \text{Yb}^{2+}$. The effect of perchlorate, tetrafluoroborate,

and tetraphenylborate ions on the crystallization behavior of Es^{2+} with Sr-10-crown-6)I in tetrahydrofuran was reported (Kulyukhin and Mikheev, 1997a,b). The first two ions affected the cocrystallization constants but the tetraphenylborate ion did not, as it did not form complexes with the metal ion in this solvent. The stability constants were found to increase in going from the tetrafluoroborate to the perchlorate ions.

12.6.6 Compounds in the vapor state

The chemistry of elemental einsteinium in the vapor state was covered in Section 12.5. Elemental einsteinium vapor was generated by direct vaporization of it while ions as Es^+ or EsO^+ were produced by laser ablation of solid matrices or by heating oxides.

Recent gas-phase studies of einsteinium have provided important new insights into its chemistry. The concept of $f \rightarrow d$ promotion energy is also very important for different gas species and their reactions. The promotion energies for einsteinium's 5f electrons in the elemental state and in different ions are given in Figs. 12.11–12.13, which are taken from Gibson and Haire (2003). One plot is for the promotion energies for An^+ and Ln^+ ions from their ground state electronic configuration to the lowest-lying configurations that have two unpaired non-f valence electrons (i.e. $5f^{n-2}6d7s$), where the value for einsteinium requires some 150 kJ mol^{-1} more energy than its homolog, holmium. The second plot in Fig. 12.12 compares promotion energies for an An^+ ion from the ground state to a configuration having two non-5f valence electrons, a $5f^{n-2}6d7s$ versus a $5f^{n-2}7s^2$ state. The promotion energy for an einsteinium ion having two unpaired 7s electrons is lower. The third comparison in

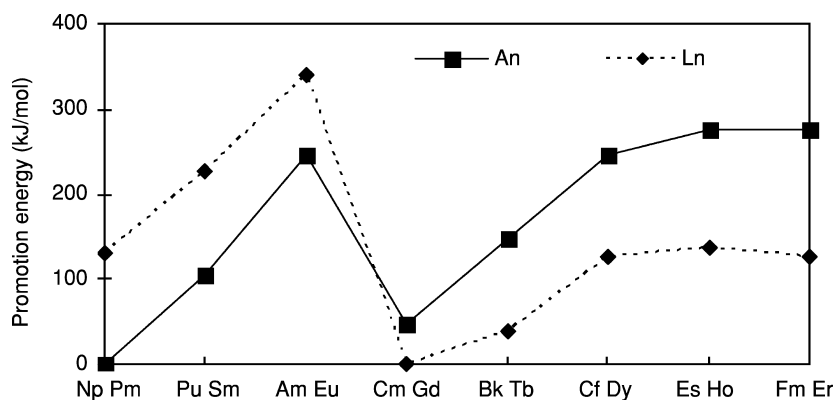


Fig. 12.11 Promotion energies for An^+ and Ln^+ from ground states to the reactive lowest lying onfiguration having two unpaired, non-f electrons. (Gibson and Haire, 2003). Note the different trend with the higher members of each series.

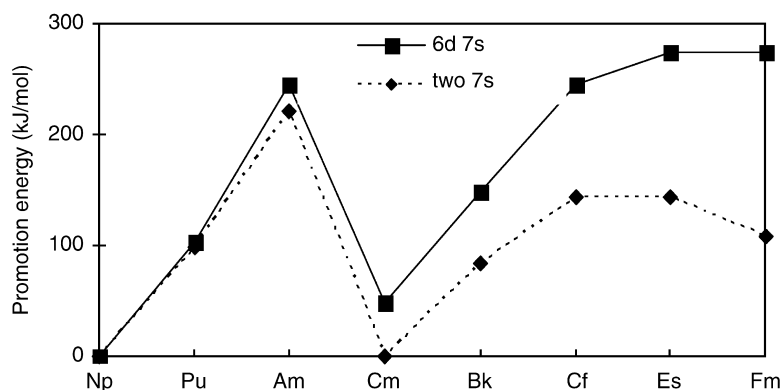


Fig. 12.12 Promotion energies for An^+ ground state to produce a reactive state with two unpaired f electrons and a $6d7s$ state (solid line) versus a paired $7s^2$ state (dashed line). Additional energy is needed to acquire the $6d7s$ reactive state. (Gibson and Haire, 2003).

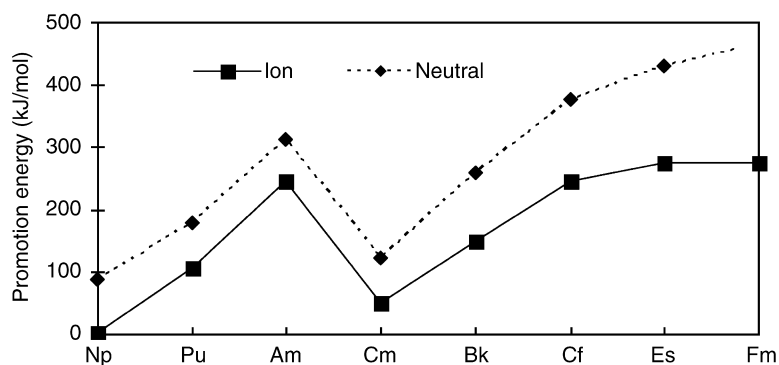


Fig. 12.13 Promotion energies for An^+ for atomic ions and for An neutral atoms. The energies are for excitation from the ground states to $6d7s$ "divalent" configurations for An^+ and for $6d7s$ "trivalent" configurations for the atoms. (Gibson and Haire, 2003).

Fig. 12.13 is made for the promotion energies from the ground state to the neutral atom ('trivalent' configuration, $5f^{n-3} 6d^2 7s$) and the Es^+ ion ('divalent' configuration, $5f^{n-2} 6d 7s$), where the neutral atom has a promotion energy twice that for forming the An^+ ion.

Important information has been acquired from gas-phase studies of einsteinium, where laser ablations were used in conjunction with mass spectrometry (Gibson and Haire, 2003). The small yields of EsO^+ obtained relative to Es^+ ions indicated that the Es^+-O bond is significantly weaker than that for the earlier actinides.

Fluorination of Es^+ by extraction of fluorine atoms from hexafluoropropene demonstrated the stability of the divalent state of einsteinium. Using this technique, the first organometallic complex of einsteinium was observed (EsC_4H_8^+) in the gas phase. From this work the bond dissociation energy for EsO^+ was established and it was found to be smaller than those for EuO^+ and YbO^+ , being more similar to that for TmO^+ .

Systematic trends of einsteinium's chemistry terms of electronic structure and the energetics of the actinides and lanthanides were developed in this work (Gibson and Haire, 2003). The bond dissociation energy for Es^+-O was estimated to be $(470 \pm 60) \text{ kJ mol}^{-1}$, higher than the values for Eu^+-O (389 kJ mol^{-1}) and Yb^+-O (372 kJ mol^{-1}), but similar to that for Tm^+-O (478 kJ mol^{-1}) (Gibson and Haire, 2003). The dissociation energy for EsO was earlier reported to be 443 kJ mol^{-1} (Haire, 1994), smaller than dissociation energies for the americium through californium monoxides but similar to those for europium and ytterbium. Thus, einsteinium sesquioxide at high temperatures produces mainly elemental einsteinium rather than a monoxide, where the latter is found when heating curium sesquioxide to very high temperatures.

An important finding was that for einsteinium to become a reactive species, it was necessary to promote the Es^+ ion's ground state electronic configuration to the lowest-lying configuration having two unpaired non-5f valence electrons (i.e. $6d7s$ rather than $7s^2$). The Es^+ ion was found to be the least efficient of the Th^+ through Cf^+ ions at the dehydrogenation of organic materials, although it was only slightly less efficient than Am^+ and Cf^+ ions (Gibson and Haire, 2003).

In conjunction with the proposal that a hexavalent state of einsteinium could exist based on the added stability acquired from formation of a half-filled 5f orbital (i.e. $[\text{Rn}]5f^{11}7s^2 \rightarrow [\text{Rn}]5f^7$ for $\text{Es}(\text{VI})$); Liebman, 1978), a potential compound could be the hypothetical EsF_6 . As a molecular material, it would be expected to be volatile like UF_6 and PuF_6 . From limited attempts to make this material, there is no experimental evidence to support its existence. Attempts to prepare AmF_6 have also proven it to be an elusive material, and far less stable than UF_6 or PuF_6 . Therefore, it is unlikely that EsF_6 would be stable.

Studies have also been performed on the formation of volatile molecules using the concepts of thermochromatography (see Section 12.5), and the idea that a molecule in an unusual oxidation state may have a greater potential to form or to exist in the vapor state. From tracer experiments with ^{254}Es , evidence was claimed to support the existence of EsF_4 (Bouissières *et al.*, 1980). The technique consisted of treating EsF_3 with flowing fluorine and determining the temperature where the einsteinium's activity was deposited. This temperature was correlated with deposition temperatures for five other (Pu–Cf) actinide materials, also assumed to be transported as tetrafluorides. The volatility of fluorides should increase with higher oxidation states, so that the order of volatility would be expected to be hexafluoride > tetrafluoride > trifluoride. A point of concern with einsteinium may be the ability to form a tetrafluoride from its trifluoride at temperatures above the expected

decomposition temperature of the tetrafluoride, as estimated from the behaviors of other actinide tetrafluorides.

Thermochromatography of ^{254g}Es in chlorinating carrier gas was used to estimate the adsorption of EsCl_3 , and was found to be in agreement with a Monte Carlo model for its behavior (Eichler *et al.*, 2002). Volatile einsteinium hexafluoroacetylacetonate (HHFA) complexes have also been reported (Fedoseev *et al.*, 1987a,b). At the tracer level, these materials can form by passing vapors of the HHFA over einsteinium chloride solids at 200°C . A thermochromatographic study was then used to follow the reaction products. Mixed ligand complexes and lanthanide complexes were also studied. Solvated complexes of HHFA (as well as other organic materials) and the oxychlorides were found to be less volatile in the system. It was concluded that the complexes contained Es(III) rather than Es(II) , the latter having a lower volatility.

The gas-phase chemistry of Es^+ and EsO^+ ions has been studied by a laser ablation technique (Gibson and Haire, 2003). The behavior of the Es^+ ion was found to be comparable to that of other actinide ions. The yield of EsO^+ ions suggests that the Es^+-O bond energy is significantly lesser than that of other such actinide ions (i.e. Bk^+-O). By performing chemical reactions in the gas phase between these einsteinium ions and other materials (halogenated organics, alkenes, etc.), it was possible to ascertain important aspects of the chemical behavior of einsteinium in the gas phase, and the ability to form organometallic compounds of einsteinium.

12.7 ATOMIC AND IONIC RADII, AND PROMOTION ENERGIES – THEIR IMPORTANCE IN EINSTEINIUM’S OVERALL SCIENCE

The radii of ions, molecules, and atoms are important in the chemistry and physics of materials as well as for estimation/interpolation of their behaviors. For einsteinium there is a considerable difference in its atomic radius compared to the four previous transplutonium elements, and this is reflected in its properties and science. For divalent and trivalent einsteinium ions, much of their solid and solution behaviors reflect their radii, and in these states einsteinium often behaves similarly to the comparable oxidation states of the other transplutonium and lanthanide ions. In the gas state, bonding energies and potentials (oxidation and promotion) are also of major chemical importance.

The atomic and ionic radii for a given number of bonding electrons or for an oxidation state of the f-elements, in principle, should decrease in a uniform manner across each series (well-established f-element contraction phenomena). This contraction with atomic number has been found to be in good agreement with multidimensional Dirac–Fock calculations (Desclaux and Freeman, 1984). Ionova *et al.* (1978) have also calculated einsteinium’s radius via Hartree–Fock approximations. Thus, these radii are often useful for extrapolations of behavior and properties.

In the case of atomic radii, one observes that einsteinium's radius compares well with radii of europium and ytterbium; as a result of it being a divalent rather than a trivalent metal (see Section 12.5 and Fig. 12.1). The divalent atomic radii of these elements are considerably larger than the trivalent atomic radii of these f-elements, as expected from one less bonding electron. This comes about in part due to the larger promotion energy for changing an f-electron in einsteinium to a 'd' state to enable additional bonding. As a result, einsteinium is the first divalent actinide metal.

With ionic compounds, many are found to form similar, isostructural phases, which is well established in oxide systems (Haire and Eyring, 1994). The ion-exchange behavior of the trivalent ions in solution also shows this correlation (Seaborg and Loveland, 1990). The ionic radius of Es(III), which varies with the coordination number, has been determined from different compounds. From sesquioxide lattice parameters for the actinides and lanthanides (Haire and Eyring, 1994), the ionic radius of Es³⁺ (0.928 Å) is slightly smaller than that of Cf³⁺, and midway between the radii for Tb³⁺ (0.920 Å) and Gd³⁺ (0.938 Å). Another set of ionic radii has been given by David (1986), which shows a similar relationship. Thus, similar oxide-phase behavior is expected for these ions. The relative behaviors of the sesquioxide lattice parameters and the ionic radii are shown in Fig. 12.6 and Table 12.7, including calculated radii for Es(II) ions. Values are also given for potential Es(IV) ions; these ions would have different coordination numbers and show somewhat different behaviors than the Es(II) and Es(III) ions.

Einsteinium's sesquioxide and trivalent halide-phase behaviors in several solid compounds are found to be comparable to the lanthanides discussed above. In the case of cation-exchange behavior, the elution behavior from ion-exchange columns for a given oxidation state is generally in the order of the radii of the hydrated ions, with the largest or more readily complexed ions eluting first (einsteinium before californium). With elution from a cation column using α -HIB, einsteinium is found at a position between dysprosium and holmium (einsteinium's lanthanide homolog; Seaborg and Loveland, 1990).

Thus, einsteinium's atomic and ionic radii are important factors in the science of einsteinium. They often serve as useful information to understand, predict, and/or extrapolate the behavior of einsteinium. And the f→d electron promotion energy is also very important to understanding elemental einsteinium, as well as several facets of einsteinium's gas-phase chemistry.

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