CHAPTER TEN

BERKELIUM

David E. Hobart and Joseph R. Peterson

10.1   HISTORICAL

As was the case for the previously discovered transuranium elements, element 97 was first produced via a nuclear bombardment reaction. In December 1949 ion-exchange separation of the products formed by the bombardment of ^{241}Am with accelerated alpha particles provided a new electron-capture activity eluting just ahead of curium (Thompson *et al.*, 1950a,b). This activity was assigned to an isotope (mass number 243) of element 97. The new element was named berkelium after Berkeley, California, USA, the city of its discovery, in a manner parallel to the naming of its lanthanide analog, terbium, after Ytterby, Sweden. The initial investigations of the chemical properties of berkelium were limited to tracer experiments (ion exchange and coprecipitation), and these were sufficient to establish the stability of Bk(III) and the accessibility of Bk(IV) in aqueous solution and to estimate the electrochemical potential of the Bk(IV)/Bk(III) couple (Thompson *et al.*, 1950b,c). Because a complete study of the chemistry of an element is not possible by tracer methods alone, a program for long-term neutron irradiation of about 8 g of ^{239}Pu was initiated in 1952 in the Materials Testing Reactor (Arco, Idaho, USA) to provide macroquantities of berkelium (Cunningham, 1959). In 1958 about 0.6 μg of ^{249}Bk was separated, purified, and used in experiments to determine the absorption spectrum of Bk(III) in aqueous solution and to measure the magnetic susceptibility of Bk(III) (Cunningham, 1959). No Bk(III) absorption was observed over the wavelength range 450–750 nm, but an upper limit of about 20 was set for the molar absorptivity of any

1444

Bk(III) absorption in this wavelength region. The magnetic susceptibility, measured from 77 to 298 K with the Bk(III) ions sorbed in a single bead of cation-exchange resin, was found to conform to the Curie–Weiss law with an effective moment of 8.7 μ_B, suggesting a $5f^8$ electronic configuration for the Bk(III) ion. The first structure determination of a compound of berkelium, the dioxide, was carried out in 1962 (Cunningham, 1963). Four X-ray diffraction lines were obtained from 4 ng of BkO_2 and indexed on the basis of a face-centered cubic (fcc) structure with $a_0 = (0.533 \pm 0.001)$ nm. In the intervening years since this initial work to characterize element 97, considerable information about the physicochemical properties of berkelium has been obtained in spite of the rather limited availability and the short half-life (330 days) of ^{249}Bk, the only isotope available in bulk quantities.

The authors have focused this review of the chemistry of berkelium on open literature references in English or English translation, except where it was deemed necessary to cite a research institution report or technical memorandum or personal communication. References to theses, dissertations, and patents are minimal. The biologic and metabolic effects of exposure to and/or ingestion of berkelium on humans and animals have not been reviewed here (see Chapter 31). Also excluded are references dealing with the determination and/or use of the nuclear properties of the various isotopes of berkelium, with the notable exception of a few modern references dealing with the use of ^{249}Bk as a target material for the production of transactinide elements. The references cited herein are not necessarily inclusive or always the original ones, yet they should be adequate to permit the interested reader to access easily the broader literature beyond.

Earlier reviews of the physicochemical properties of berkelium are available in Keller (1971), in several new supplement series volumes of the *Gmelin Handbuch der Anorganischen Chemie* (e.g. Peterson, 1976), Peterson and Hobart (1984), and in Hobart and Peterson (1986).

10.2 NUCLEAR PROPERTIES, AVAILABILITY, AND APPLICATIONS

Selected nuclear properties of the 14 known isotopes of berkelium, ranging from mass numbers 238 to 251, are listed in Table 10.1 (Appendix II). Included in this list are two neutron-deficient isotopes that have been identified since the publication of the second edition of this text in 1986. These are ^{238}Bk with an electron-capture decay half-life of 2.4 min (Kreek *et al.*, 1994) and ^{241}Bk with an electron-capture decay half-life of 4.6 min (Asai *et al.*, 2003). Only ^{249}Bk is available in bulk quantities for chemical studies, as a result of prolonged neutron irradiation of Pu, Am, or Cm (Bigelow *et al.*, 1981). About 1 g of this isotope has been isolated from target rods irradiated in the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL) in east Tennessee, USA, over the period 1967–2001 (Knauer, 2002). The relative atomic mass of

Table 10.1 *Nuclear properties of berkelium isotopes.*[a]

Mass number	Half-life	Mode of decay	Main radiations (MeV)	Method of production
238	2.4 min	EC		^{241}Am(α,7n)
240	4.8 min	EC		^{232}Th(^{14}Ne,6n)
241	4.6 min	EC	γ 0.2623	^{239}Pu(^{6}Li,4n)
242	7.0 min	EC		^{232}Th(^{14}N,4n) ^{232}Th(^{15}N,5n)
243	4.5 h	EC 99.85% α 0.15%	α 6.758 (15%) 6.574 (26%) γ 0.755	^{243}Am(α,4n)
244	4.35 h	EC > 99% α 6 × 10^{-3}%	α 6.667 (~50%) 6.625 (~50%) γ 0.218	^{243}Am(α,3n)
245	4.94 d	EC > 99.88% α 0.12%	α 6.349 (15.5%) 6.145 (18.3%) γ 0.253 (31%)	^{243}Am(α,2n)
246	1.80 d	EC	γ 0.799 (61%)	^{243}Am(α,n)
247	1.38 × 10^3 yr	α	α 5.712 (17%) 5.532 (45%) γ 0.084 (40%)	^{247}Cf daughter ^{244}Cm(α,p)
248[b]	23.7 h	β^- 70% EC 30%	β^- 0.86 γ 0.551	^{248}Cm(d,2n)
248[b]	>9 yr	decay not observed		^{246}Cm(α,pn)
249	330 d	β^- > 99% α 1.45 × 10^{-3}%	α 5.417 (74.8%) 5.390 (16%) β^- 0.125 γ 0.327 weak	multiple n capture
250	3.217 h	β^-	β^- 1.781 γ 0.989 (45%)	^{254}Es daughter ^{249}Bk(n,γ)
251	55.6 min	β^-	$\beta^- \sim 1.1$ γ 0.178	^{255}Es daughter

[a] Appendix II.
[b] Not known whether ground state nuclide or isomer.

^{249}Bk was given as 249.075 (Audi and Wapstra, 1995), and the most recent determination of its half-life yielded a value of (330 ± 4) days (Popov and Timofeev, 1999).

Besides the research use of ^{249}Bk for the characterization of the chemical and physical properties of element 97, its relatively rapid decay to ^{249}Cf (ca. 0.22% per day) makes it a valuable source of this important isotope of californium for chemical study. This genetic relationship has been exploited in studies of the chemical consequences of beta (β^-) decay in the bulk-phase solid state (Young *et al.*, 1980; Ensor *et al.*, 1981; Young *et al.*, 1984; Peterson *et al.*, 1986).

As a consequence of recent interest in nuclear power reactors to increase fuel burn-up and in the areas of nuclear waste transmutation, nuclear deterrence, and astrophysics, more accurate data on the nuclear characteristics of heavier actinides, including berkelium, are in demand. A recent compilation of the decay characteristics of actinides, including ^{249}Bk and ^{250}Bk, has been published (Popov and Timofeev, 1999). Fission fragment angular distributions for the compound nucleus ^{246}Bk have been measured (Behera *et al.*, 2001). ^{246}Bk was produced via two nuclear reaction pathways, lying on either side of the Businaro–Gallone critical asymmetry parameter.

By combining measured fission probabilities for reactions such as ^{248}Cm(^{3}He, d)^{249}Bk→fission (Gavron *et al.*, 1977) with calculated total neutron inelastic cross sections, empirical predictions for the neutron-induced fission cross sections for several actinides have been obtained (Britt and Wilhelmy, 1979). These predictions ignore differences in angular momentum distributions between the direct reaction products and the incident neutrons when populating the same energy levels in the compound nucleus. As demonstrated by Britt and Wilhelmy (1979), this assumption is reasonably good for equivalent neutron energies (energy of an incident neutron that would leave the identical residual nucleus at the same energy as is reached by the direct nuclear reaction) of greater than about 0.5 MeV. For Bk the equivalent (n,f) cross sections were extracted for the berkelium isotopes with mass numbers 244 to 248. Odd-mass-number Bk nuclei exhibit a strong reduction in the fission probability for excitation energies above the neutron-binding energy that is presumably caused by the opening of a large number of competing decay channels (Britt and Wilhelmy, 1979). Although no experimentally measured fission cross section for ^{248m}Bk has been determined, estimates of up to 1000 barns have been predicted based on correlations with other actinides having similar characteristics (Ronen, 1998).

The intrinsic single-particle states of ^{249}Bk have been studied by measuring the gamma radiations emitted after the alpha decay of ^{253}Es. The low spin states were studied by measuring gamma rays in the beta decay of ^{249}Cm. Levels in ^{249}Bk were also studied by the reaction ^{248}Cm(α,t)^{249}Bk. A diagram of the intrinsic states for ^{249}Bk, deduced from these decay studies, has been constructed. This well-established nuclear structure information, available only for the heaviest elements for which macro amounts are obtainable, can be used either to determine the parameters of a single-particle potential or to test the nuclear models of super-heavy elements (Ahmad, 2002).

Although currently there are no practical or commercial applications for any known berkelium isotopes, ^{249}Bk has been used extensively as a target material for the production of still heavier actinides such as lawrencium (Brüchle *et al.*, 1988; Scherer *et al.*, 1988) and transactinide elements such as element 104, rutherfordium, and element 107, bohrium (Gregorich *et al.*, 1988; Kratz *et al.*, 1992; Gobrecht *et al.*, 1999; Paulus *et al.*, 1999; Eichler *et al.*, 2000; Wilk *et al.*, 2000).

10.3 PRODUCTION

Methods of production for each of the isotopes of berkelium are listed in Table 10.1 (Appendix II). Only [249]Bk is available in bulk quantities for chemical studies, as a result of prolonged neutron irradiation of Pu, Am, or Cm (Bigelow *et al.*, 1981). About 0.73 g of this isotope was isolated from target rods irradiated with neutrons in the ORNL HFIR over the period 1967–1985 (Ferguson and Bigelow, 1969; King *et al.*, 1981; Bigelow, 1985). Toward the end of 1986, HFIR was shut down for an extended period of time for major maintenance and safety considerations. This action resulted from the nuclear reactor accident at Chernobyl (former USSR) earlier that year. After a 4+ year hiatus, HFIR was restarted with a power limit of 85 MW, down from the previous 100 MW level. Through the HFIR product campaign that started in late 2000, an additional 0.28 g of [249]Bk was recovered during the period 1986–2001. It is not known to the present authors how much [249]Bk has been produced elsewhere in the world, for instance, in the former USSR.

10.4 SEPARATION AND PURIFICATION

Berkelium may be purified by many methods that are also applicable to other actinide elements. Therefore, only those methods that apply specifically to berkelium separation and purification are treated here.

Because berkelium can be readily oxidized to Bk(IV), it can be separated from other, non-oxidizable transplutonium elements by combining oxidation–reduction (redox) methods with other separation techniques. The first application of this approach was performed by oxidizing Bk(III) with BrO_3^- in nitric acid solution (Peppard *et al.*, 1957). The resultant Bk(IV) was then extracted with bis(2-ethylhexyl)phosphoric acid (HDEHP) in heptane followed by back-extraction with nitric acid containing H_2O_2 as a reducing agent. In addition to other reports of the use of BrO_3^- as an oxidizing agent in berkelium purification procedures (Knauer and Weaver, 1968; Weaver, 1968; Fardy and Weaver, 1969; Overman, 1971; Erin *et al.*, 1979b), the use of CrO_4^{2-} (Knauer and Weaver, 1968; Milyukova *et al.*, 1980), $Cr_2O_7^{2-}$ (Moore, 1966; Shafiev *et al.*, 1974; Milyukova *et al.*, 1980), $Ag(I)/S_2O_8^{2-}$ (Milyukova *et al.*, 1978, 1980), PbO_2 (Myasoedov *et al.*, 1971; Myasoedov, 1974; Shafiev *et al.*, 1974), BiO_3^- (Shafiev *et al.*, 1974), O_3 (Myasoedov, 1974), and photochemical oxidation (Myasoedov, 1974) has also been reported.

Separation of the oxidized berkelium has been accomplished by the use of: (1) liquid–liquid extraction with HDEHP (Peppard *et al.*, 1957; Knauer and Weaver, 1968; Kosyakov *et al.*, 1977; Erin *et al.*, 1979b; Yakovlev and Kosyakov, 1983), trioctylphosphine oxide (Kosyakov and Yakovlev, 1983), alkylpyrocatechol (Karalova *et al.*, 1983), 2-thenoyltrifluoroacetone (TTA) (Moore 1966, 1969), primary, tertiary, or quaternary amines (Moore, 1969;

Milyukova and Myasoedov, 1978; Milyukova *et al.*, 1978, 1980; Malikov *et al.*, 1983), or tri(*n*-butyl)phosphate (TBP) (Milyukova *et al.*, 1981; Yakovlev *et al.*, 1982); (2) extraction chromatography with HDEHP (Kooi and Boden, 1964; Kooi *et al.*, 1964; Overman, 1971; Erin *et al.*, 1979a) or zirconium phosphate adsorbant (Myasoedov *et al.*, 1971; Shafiev and Efremov, 1972; Myasoedov, 1974; Shafiev *et al.*, 1974); (3) precipitation of the iodate (Weaver, 1968; Fardy and Weaver, 1969); or (4) ion-exchange methods (Moore, 1967; Overman, 1971; Shafiev and Efremov, 1972; Guseva and Stepushkina, 1987; Guseva *et al.*, 1987, 1991; Firsova *et al.*, 1996, 1998a,b). These techniques can be applied separately or in combination with one another.

The purification procedures outlined above provide separation of berkelium from all trivalent lanthanides and actinides with the notable exception of cerium. Because berkelium and cerium exhibit nearly identical redox behavior, most redox separation procedures include a Bk–Ce separation step (Moore, 1967; Horwitz *et al.*, 1969; Guseva *et al.*, 1971; Chudinov and Pirozhkov, 1972; Shafiev and Efremov, 1972; Shafiev *et al.*, 1974). Separation of Bk(III) from Ce(III) and other trivalent lanthanide and actinide elements can also be accomplished without the use of redox procedures (Moore and Jurriaanse, 1967; Farrar *et al.*, 1968; Horwitz *et al.*, 1969; Aly and Latimer, 1970; Guseva *et al.*, 1971; Chudinov and Pirozhkov, 1972; Harbour, 1972; Shafiev and Efremov, 1972; Horwitz and Bloomquist, 1973; Korpusov *et al.*, 1975; Khopkar and Mathur, 1980; Mathur and Khopkar, 1982; Ensor and Shah, 1984).

During the period 1967–2001, personnel at ORNL isolated and purified a total of about 1 g of ^{249}Bk (King *et al.*, 1981; Bigelow, 1985; Knauer, 2002) using the procedure outlined in Fig. 10.1.

The transcurium elements, partitioned by LiCl-based anion exchange, are precipitated as hydroxides, filtered, and dissolved in nitric acid. Initial isolation is accomplished by high-pressure elution from cation-exchange resins with α-hydroxyisobutyrate solution. The berkelium fraction is oxidized and extracted into HDEHP/dodecane from HNO_3–$NaBrO_3$ solution. The organic fraction containing Bk(IV) is treated with 2,5-di(*t*-butyl)hydroquinone (DBHQ) to reduce the Bk(IV) to Bk(III) before back-extracting (stripping) it into HNO_3–H_2O_2 solution. Then another oxidation/extraction, reduction/back-extraction cycle is carried out. The solution at this point is radiochemically pure except for the fission product cerium. After solvent cleanup and evaporation to dryness, the berkelium is dissolved in 0.1 M HCl for final ion-exchange purification steps including alcoholic HCl elution from cation-exchange resin and cation cleanup columns (Baybarz *et al.*, 1973).

Procedures for the rapid separation of berkelium from other actinides, lanthanides, and fission products have been developed in order to measure the decay properties of short-lived isotopes. Berkelium and cerium were separated from other elements using solvent extraction with HDEHP followed by cation-exchange high-pressure liquid chromatography (HPLC) using α-hydroxyisobutyrate as the eluant (Liu *et al.*, 1981). The elution curve, showing
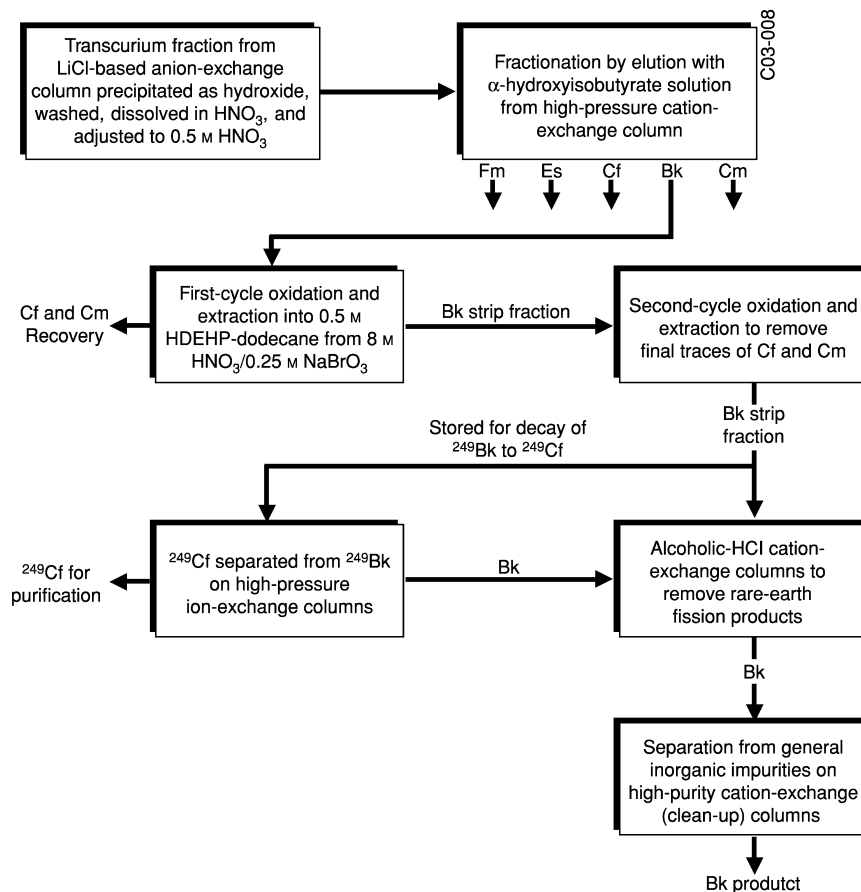
Fig. 10.1 *Schematic diagram of procedures used in the final isolation and purification of berkelium in the transuranium processing plant at the Oak Ridge National Laboratory. (Adapted from Baybarz et al., 1973.)*

a clean separation of Bk from Ce, is shown in Fig. 10.2. The total separation time was reported to be 8 min. (*Note*: A discrepancy exists in the drop number in the abscissa of Fig. 10.2; however, this figure is presented as it appeared in Liu *et al.* (1981).)

The fast separation of berkelium from beryllium foil targets and gold catcher foils has been published (Liu *et al.*, 1983). New, fast separation techniques, involving volatile mineral acid–alcohol solvent systems used to isolate very short-lived isotopes, have been reported (Maruyama *et al.*, 2002).

For additional discussion of berkelium separation procedures, the reader is referred to several reviews and comprehensive texts on the subject (Korkisch, 1966; Ulstrup, 1966; Müller, 1967; Bigelow, 1974; Myasoedov *et al.*, 1974;
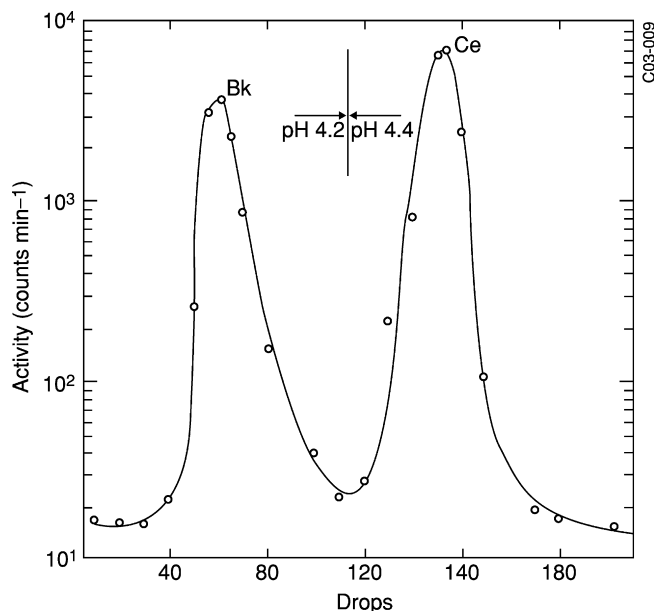
Fig. 10.2 *HPLC elution curve of Bk and Ce using* 0.5 M *ammonium α-hydroxyisobutyrate on a cation-exchange column* (*Liu* et al., 1981).

Campbell, 1981; Collins *et al.*, 1981; Myasoedov, 1987; Myasoedov and Lebedev, 1991).

10.5 PROPERTIES OF FREE ATOMS AND IONS

10.5.1 Thermochromatographic behavior of neutral atoms

The adsorption of ^{250}Bk atoms on niobium foils in a sapphire support tube has been studied (Hübener *et al.*, 2000). A deposition temperature of 1535 K was found in two separate experiments, and the enthalpy of adsorption was calculated to be –332 kJ mol^{-1}. A regular trend in the adsorption enthalpies of Bk–Fm and No is consistent with Bk adsorption on niobium in its trivalent $5f^8 6d^1 7s^2$ state (Taut *et al.*, 1998; Hübener *et al.*, 2000). In another approach by the same research group, the adsorption of elemental ^{248}Bk onto niobium was measured thermochromatographically (Taut *et al.*, 2000). The enthalpy of adsorption was determined to be $-(349 \pm 15)$ kJ mol^{-1}, in agreement with the above value, taking into account the experimental uncertainties.

10.5.2 Electronic energies

The ionization potential of neutral berkelium ($5f^9 7s^2$) was initially derived from spectroscopic data to be (6.229 ± 0.025) eV (Sugar, 1974). The changes in entropy associated with the stepwise ionization of gaseous berkelium atoms have also been calculated (Krestov, 1966). The energy interval between the ground level ($^7H_8$) and the first excited level ($^5H_7$) of singly ionized berkelium was determined from measurements done on plates using a high-resolution emission spectrograph and was found to be 1.48752×10^5 m^{-1} (Worden *et al.*, 1969). Several authors have calculated the energies of, and energy intervals between, the lowest-lying levels of the various electronic configurations of neutral berkelium (Nugent and Vander Sluis, 1971; Brewer, 1971a; Vander Sluis and Nugent, 1972, 1974) and of singly, doubly, and triply ionized berkelium (Brewer, 1971b; Vander Sluis and Nugent, 1974).

More recently, experimental determination of the first ionization potential of neutral berkelium was accomplished by resonance ionization mass spectroscopy (Erdmann *et al.*, 1998; Passler *et al.*, 1998; Waldek *et al.*, 2001). In this elegant approach (Kohler *et al.*, 1997) an atomic beam of Bk atoms was produced from heating a tantalum foil onto which Bk had been electrodeposited and then covered with a thin layer of titanium to reduce the Bk species to the metallic state. The Bk atoms were ionized in the presence of an electric field by multiple resonant laser excitation, and the Bk$^+$ ions were mass-selectively detected in a time-of-flight spectrometer. The first ionization potential was obtained by scanning the wavelength of the laser used for the last excitation step across the ionization threshold (indicated by a sudden increase in the Bk$^+$ count rate) at various electric field strengths. A linear plot of the ionization threshold against the square root of the electric field strength, extrapolated to zero field strength, yielded the first ionization potential of Bk to be (6.1979 ± 0.0002) eV. This value is just below the one derived from an extrapolation of spectral properties (Sugar, 1974). In addition the resonant excitation scheme used provided the energies of three of the excited energy levels of neutral Bk: 17 666.0, 31 541.3, and 32 710.3 cm^{-1} (Kohler *et al.*, 1997; Erdmann *et al.*, 1998; Passler *et al.*, 1998).

From measurements of the energies of a number of internal conversion lines in ^{249}Bk (produced by the alpha decay of ^{253}Es), the atomic electron-binding energies in berkelium were calculated for the K through O shells (Hollander *et al.*, 1965). The K-series X-ray energies and intensities of berkelium were later measured, and the K-shell electron-binding energy was calculated (Dittner and Bemis, 1972). The measured energies and relative transition probabilities agreed well with theoretical predictions (Carlson *et al.*, 1969; Lu *et al.*, 1971). Also available are the results of relativistic relaxed-orbital *ab initio* calculations of L-shell Coster–Kronig transition energies for all possible transitions in berkelium atoms (Chen *et al.*, 1977), relativistic relaxed-orbital Hartree–Fock–Slater calculations of the neutral-atom electron binding energies in berkelium (Huang *et al.*, 1976), and calculations of the K- through O-shell

binding energies and K and L X-ray energies for berkelium (Carlson and Nestor, 1977). Relativistic Hartree–Slater values of the X-ray emission rates for the filling of K- and L-shell vacancies in berkelium have been tabulated (Scofield, 1974). X-ray emission rates for the filling of all possible single inner-shell vacancies in berkelium by electric dipole transitions have been calculated using nonrelativistic Hartree–Slater wave functions (Manson and Kennedy, 1974).

10.5.3 Emission spectra

Twenty emission lines, produced from 0.2 μg of berkelium in a high-voltage spark, were reported by Gutmacher *et al.* (1965). In 1967 between 3000 and 5000 lines were recorded in the wavelength region 250–900 nm from 38 μg of ^{249}Bk in an electrodeless discharge lamp (Worden *et al.*, 1967). Many of the emission lines exhibited a well-resolved eight-component hyperfine structure, which established the nuclear spin of ^{249}Bk to be 7/2 (Worden *et al.*, 1967). This value is in agreement with that derived from nuclear decay systematics.

The ground state electronic configurations (levels) of neutral and singly ionized berkelium were identified as $5f^9 7s^2$ ($^6H_{15/2}$) and $5f^9 7s^1$ ($^7H_8$), respectively (Worden *et al.*, 1970). A nuclear magnetic dipole moment of 1.5 μ_N (Worden *et al.*, 1969) and a quadrupole moment of 4.7 barns (Conway, 1976) were determined for ^{249}Bk, based on analysis of the hyperfine structure in the berkelium emission spectrum.

The wavenumbers, wavelengths, and relative intensities of 1930 of the stronger emission lines from ^{249}Bk in the 254–980 nm wavelength region are available (Worden and Conway, 1978). The infrared emission spectrum of ^{249}Bk from 830 to 2700 nm has been recorded (Conway *et al.*, 1977). The emission profile of ^{249}Bk(III) in a silicate matrix has been studied as a function of excitation power and temperature (Assefa *et al.*, 1998). With both experimental parameters it was found that the two primary emission bands (believed to originate from f→f transitions) decreased in intensity at different rates with increasing excitation power or temperature, such that the higher-energy band became dominant over the lower-energy one. Thermal quenching and/or energy transfer between neighboring ions are possible factors responsible for this behavior (Assefa *et al.*, 1998).

A preliminary report on the self-luminescence of ^{249}Bk(III) in a LaCl$_3$ host lattice was published by Gutmacher *et al.* (1963), and the self-luminescence spectra of ^{249}Bk-doped BaF$_2$ and SrCl$_2$ were reported by Finch *et al.* (1978). The fluorescence and excitation spectra of Bk^{3+} ions (<0.001 mol fraction) in single-crystal LaCl$_3$ were determined using dye laser techniques (Hessler *et al.*, 1978). Selective laser excitation was used to excite specific Bk^{3+} levels, and then the subsequent fluorescence spectrum was recorded. Determining fluorescence lifetimes of all fluorescing levels and grouping the lines by lifetimes precluded

confusion caused by transference of the excitation energy to a fluorescing level of another ion. The fluorescing manifolds of Bk^{3+} were found to be $J = 6$ at 1.540 μm^{-1} and $J = 4$ at 1.953 μm^{-1} (Hessler *et al.*, 1978). The absence of UV-excited sharp-line sensitized luminescence of ^{249}Bk-doped gadolinium hexafluoroacetyl acetonate has been observed (Nugent *et al.*, 1969, 1970). Such luminescence was absent also in cesium berkelium hexafluoroacetyl acetonate chelate in anhydrous ethanol (Nugent *et al.*, 1969). A study of Bk^{3+} fluorescence in H_2O and D_2O solutions has been reported, and a basis for assessing the use of fluorescence detection for transuranic ions established (Beitz *et al.*, 1981).

The first report of fluorescence from the Bk^{4+} ion included establishment of the total ground state splitting of this ion and probing the higher-lying electronic states of its $5f^7$ configuration (Jursich *et al.*, 1987). The Bk^{4+} ions were stabilized in CeF_4, where it is known that there are two distinct low-symmetry sites to accommodate them. Two Bk^{4+} bands were detected and assigned to transitions to the ground state. From laser excitation spectra taken at 4 K, a $5f^7$ energy-level diagram was proposed, which is consistent with the authors' assumption of a single average D_{4d} site symmetry. Mixing of higher lying states into the ground state caused the total ground state crystal-field splitting of Bk^{4+} in CeF_4 to be 58 cm^{-1} (Jursich *et al.*, 1987). The results of a detailed, systematic spectral analysis of these data, along with those obtained in additional site-selective laser excitation studies of another sample of Bk^{4+} in CeF_4, have been reported (Liu *et al.*, 1994a). A complete set of crystal-field parametric values was given and compared with those derived from the previous five tetravalent actinides. In addition an observed and calculated line list out to about 27 000 cm^{-1} was published (Liu *et al.*, 1994a). Another paper from the same research group focused on the use of fluorescence line narrowing spectra of 0.1 at% Bk^{4+} in CeF_4 to study emissions from the lowest energy component of $^6D_{7/2}$ at 16 375 cm^{-1} to the four components of the $^8S_{7/2}$ ground multiplet (Liu *et al.*, 1994b). A linear relationship was observed between the excitation-laser photon energy and the energies of the Bk^{4+} emission lines. A subsequent study of the influence of the crystal field on the $^8S_{7/2}$ ground state splitting of Bk^{4+} ion in CeF_4, based on the 24 energy levels observed in their earlier work (Liu *et al.*, 1994a), was carried out (Brito and Liu, 2000). The parametric model used a set of nine nonzero parameters (corresponding to C_{2v} point symmetry) and yielded a good correlation between the experimental and calculated energy levels in Bk^{4+} ion. Compared with the isoelectronic Cm^{3+} ion, the large ground state splitting of Bk^{4+} ion in CeF_4 is attributed to the smaller energy gap between the ground state and the low-lying excited states (Brito and Liu, 2000). Subsequently, a model that included relativistic effects in an effective way was used to improve the theoretical reproduction of the splitting of the energy levels for such S-state f-electron ions (Smentek *et al.*, 2001). It was concluded in this work that the fitting procedure applied for the determination of the crystal-field parameters had to be done within the parametrization scheme that included the relativistic weights of the various parameters.

10.5.4 Solid-state absorption spectra

The absorption spectrum of Bk(III) in a lanthanum chloride host matrix at 77 K was first obtained by Gutmacher (1964). A prediction of the energy-level structure of Bk(III) was made by others the same year (Fields *et al.*, 1964). Extensive, low-temperature spectroscopic studies of BkCl$_3$ showed the absence of transitions to excited $J = 0$ and $J = 1$ states (Carnall *et al.*, 1972, 1973). This provided good evidence for a $\mu = 0$ ground level for Bk(III), consistent with that of Tb(III):LaCl$_3$ (Carnall and Fried, 1976). Experimental and theoretical studies of the crystal-field parameters of Bk(III) in a LaCl$_3$ host lattice have also been reported (Carnall *et al.*, 1977).

Microscale spectrophotometric techniques, using 0.5–10 μg berkelium samples, have been applied for identification and characterization of berkelium halides and oxyhalides (Young *et al.*, 1978). The spectra of orthorhombic and hexagonal BkCl$_3$ have been recorded (Peterson *et al.*, 1986) and are shown in Fig. 10.3. Spectra of orthorhombic and monoclinic BkBr$_3$ (Peterson *et al.*, 1977a,b), trigonal and orthorhombic BkF$_3$ (Ensor *et al.*, 1981), and monoclinic BkF$_4$ (Ensor *et al.*, 1981) have been reported. This technique has also been applied to the study of the chemical consequences of radioactive decay in bulk-phase solid-state samples (Young *et al.*, 1980, 1981). It was found that the ^{249}Cf daughter growing into crystalline ^{249}BkBr$_3$ exhibited the same oxidation state and crystal structure as its berkelium parent (Young *et al.*, 1980).

The absorption spectra of Bk(III) and Bk(IV) hydroxides as suspensions in 1 M NaOH have been reported (Cohen, 1976). The solid-state absorption spectrum (Haire *et al.*, 1983) and Raman spectrum (Hobart *et al.*, 1983) of berkelium(III) orthophosphate have been obtained, as well as those for berkelium(III) oxalate decahydrate, Bk$_2$(C$_2$O$_4$)$_3 \cdot$ 10H$_2$O (Morris *et al.*, 2005). Line lists of the absorption bands of two organoberkelium compounds, Bk(C$_5$H$_5$)$_3$ (Laubereau and Burns, 1970) and [Bk(C$_5$H$_5$)$_2$Cl]$_2$ (Laubereau, 1970), have been published.

For additional information (Carnall, 1973) and discussion of the development of the theoretical treatment of berkelium spectra, the reader is referred to other sources (Carnall and Fried, 1976; Conway, 1976; Carnall *et al.*, 1984; Liu *et al.*, 1994a) and to Chapters 16 and 18.

10.5.5 Ion–molecule reactions in the gas phase

Organoberkelium ions have been produced by laser ablation of Bk$_2$O$_3$ dispersed in polyimide (Gibson and Haire, 2001a). Characterization of the resulting products via time-of-flight spectrometry identified the primary species as BkCH$_3^+$, BkC$_2^+$, BkC$_2$H$^+$, BkCN$^+$, BkC$_4$H$^+$, Bk(OH)(CN)$^+$, BkOCN$^+$, BkOH$^+$, Bk(OH)$_2^+$, and BkO$^+$, as shown in Fig. 10.4. The product ion compositions and abundance distributions were reasonably explained in the context of the electronic structure and energetics of the Bk$^+$ ion. Several of these organoberkelium species incorporate direct metal ion–carbon bonding via a single
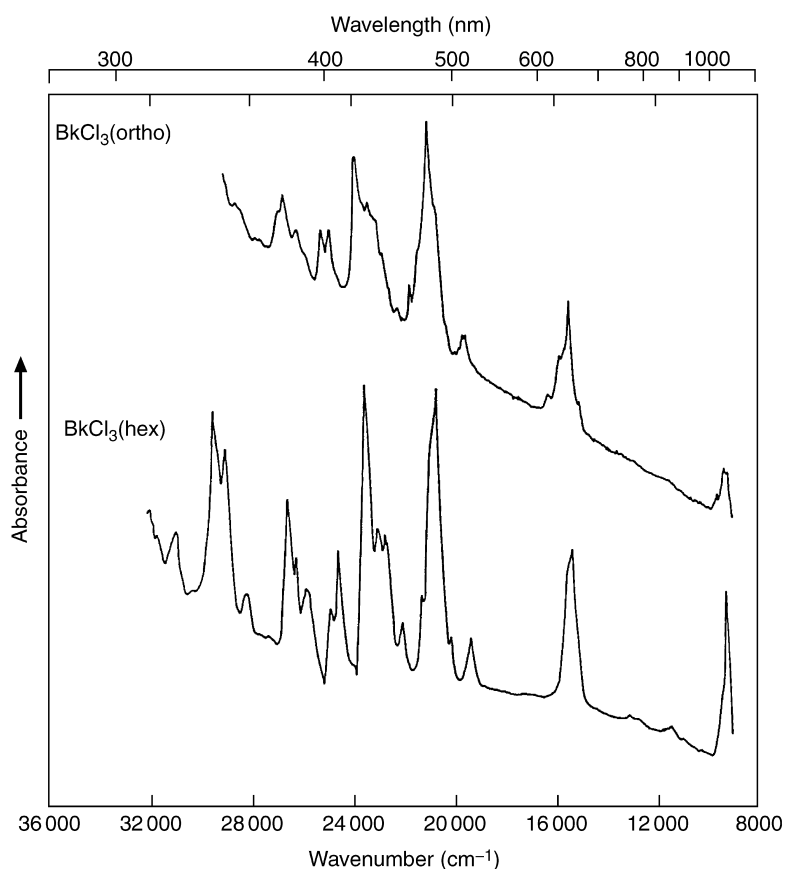
Fig. 10.3 *The solid-state absorption spectra of orthorhombic and hexagonal BkCl₃* (*Peterson* et al., 1986).

σ-type covalent bond. Comparisons of the product ion compositions and abundance distributions of similarly produced organoactinide and lanthanide species provided correlations with the electronic promotion energies required to create a divalent or a monovalent state, capable of forming two or one covalent bonds, respectively (Gibson and Haire, 2001a). In an extension of the above work, gasphase reactions of Bk^+ ion with several alkenes, butylamine, butyronitrile, and other reagents were studied in concert with similar reactions with Pu^+ ion or homologous Tb^+ ion to aid in the interpretation of the results in the context of the electronic structure and energetics of berkelium (Gibson and Haire, 2001b). A key result of this work was the finding that the efficiency of hydrocarbon, nitrile, and amine activation by Bk^+ ion directly reflected the energy required to excite the ion from its ground electronic state, $5f^9 7s^1$, to the lowest lying state with two spin-unpaired non-5f valence electrons, $5f^8 6d^1 7s^1$. Thus it appears that
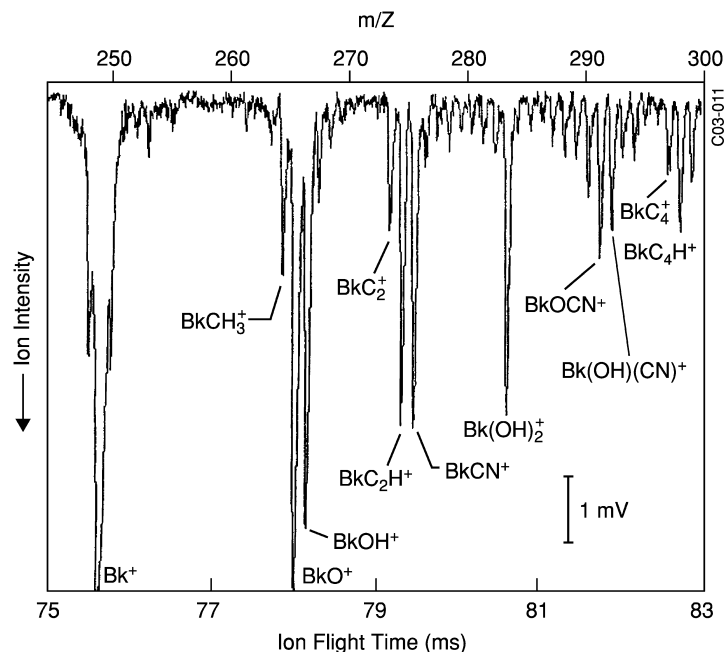
Fig. 10.4 *The mass spectrum of positive ions ablated from a Bk–polyimide target.* (*Reprinted figure with permission from Gibson and Haire* (2001a). *Copyright* 2001 *by Oldenbourg Verlag.*)

the 5f electrons in Bk^+ ions do not participate in organometallic bond activation. A variety of organoberkelium species were identified, as well as a few inorganic ones, e.g. BkF^+. A covalent bonding model was used to estimate the Bk^+–O bonding energy as (610 ± 40) kJ mol^{-1} (Gibson and Haire, 2001b).

10.6 THE METALLIC STATE

10.6.1 Pure metal

(a) Preparation

The first bulk (>1 μg) samples of berkelium metal were prepared in early 1969 by the reduction of BkF_3 with lithium metal vapor at about 1300 K (Peterson *et al.*, 1971). The BkF_3 samples were suspended in a tungsten wire spiral above a charge of Li metal in a tantalum crucible. Berkelium metal samples up to 0.5 mg each have been prepared via the same chemical procedure (Fuger *et al.*, 1975). Elemental berkelium can also be prepared by reduction of BkF_4 with lithium metal and by reduction of BkO_2 with either thorium or lanthanum metal

(Spirlet *et al.*, 1987). The latter reduction process is better suited to the preparation of thin metal foils unless multi-milligram quantities of berkelium are available.

(b)   Physical properties

Berkelium metal exhibits two crystallographic modifications: double hexagonal close-packed (dhcp) and fcc. Thus, it is isostructural with the two preceding actinide elements, both of which also exhibit the fcc structure at high temperature. The room-temperature lattice constants of the dhcp (α) form are $a_0 = (0.3416 \pm 0.0003)$ nm and $c_0 = (1.1069 \pm 0.0007)$ nm, yielding a calculated density of 14.78 g cm^{-3} and a metallic radius (coordination number, CN 12) of 0.170 nm (Peterson *et al.*, 1971). The room-temperature metastable fcc (β) lattice parameter is $a_0 = (0.4997 \pm 0.0004)$ nm, from which the X-ray density and metallic radius (CN 12) are calculated to be 13.25 g cm^{-3} and 0.177 nm, respectively (Peterson *et al.*, 1971). The metallic radius of berkelium, assuming a metallic valence of 3- and 12-fold coordination, has been calculated to be 0.1739 nm (Sarkisov, 1966). On the other hand, the radii (CN 12) of berkelium were predicted to be 0.184 nm for a trivalent metal and 0.1704 nm for a tetravalent metal; so it was proposed that the observed dhcp form corresponds to tetravalent metal, while the fcc form represents a metallic valence of $\sim$3.5 (Zachariasen, 1973).

Although berkelium metal is dimorphic, the transformation temperature is not known with certainty. A change in the appearance of Bk metal samples at (1203 ± 30) K during the course of two melting point determinations might correspond to the dhcp$\rightarrow$fcc phase transformation, which should be accompanied by a 12% change in the volume of the sample (Fahey *et al.*, 1972). By analogy with the behavior of neodymium, a phase-transition temperature of (1250 ± 50) K was assigned by Ward *et al.* (1982), in agreement with the Fahey *et al.* (1972) observation. The melting point of berkelium metal was first determined to be (1259 ± 25) K from measurements on two samples (Fahey *et al.*, 1972). The melting and boiling points of elemental berkelium have been reported to be (1323 ± 50) K and (2900 ± 50) K, respectively (Ward *et al.*, 1982). These two melting-point determinations are in agreement, considering their experimental uncertainties.

The first studies of berkelium metal under pressure were performed with a diamond anvil pressure cell using energy-dispersive X-ray powder diffraction analysis (Haire *et al.*, 1984). Three different metallic phases were observed as the pressure was increased to 57 GPa. The normal-pressure dhcp form changed to an fcc form at about 8 GPa. Above 22 GPa (reported to be at about 32 GPa in later reports; Itié *et al.*, 1985; Peterson *et al.*, 1987), the fcc form was transformed to the alpha-uranium-type orthorhombic structure (Haire *et al.*, 1984). A 12% shrinkage in volume accompanied the latter transition. This collapse was associated with delocalization of the 5f electrons (Benedict *et al.*, 1984).

Below 22 GPa, a bulk modulus (compressibility) of (30 ± 10) GPa was estimated for berkelium metal (Haire *et al.*, 1984). This bulk modulus only for the normal-pressure dhcp phase of Bk metal was reported later to be 52 GPa (Itié *et al.*, 1985). Berkelium metal under pressure behaves similarly to americium, curium, and some light lanthanide metals and does not appear to undergo an isostructural phase transition corresponding to a change in metallic valence before delocalization of the 5f electrons (Johansson *et al.*, 1981).

Retention of the fcc phase in Bk metal after release of pressure (pressure quenched) allows comparison of the atomic volume of this cubic phase at room temperature and pressure (RTP) with the atomic volume of the same phase produced via thermal treatment and quenching to RTP (temperature quenched) (Haire *et al.*, 1986). The values obtained were 2.80×10^{-2} nm^3 for the pressure-quenched fcc phase and 3.12×10^{-2} nm^3 (Peterson *et al.*, 1971) for the temperature-quenched fcc phase. Similar results were found in the cases of Cm and Cf metals. In fact, for the three metals, the atomic volumes of their temperature-quenched fcc phases are all larger than those of their RTP dhcp phases. In contrast, the atomic volumes of their pressure-quenched fcc phases at RTP are in good agreement with those of their RTP dhcp phases (Haire *et al.*, 1986). The argument is made that the lattice parameter of the pressure-quenched fcc phase of these metals is preferred to that of the temperature-quenched fcc phase, in that it provides consistency with the atomic volumes of their RTP dhcp phases and the known trend in lattice parameters of their corresponding mononitrides (Haire *et al.*, 1986).

In the first experiments to measure the vapor pressure of metallic berkelium using Knudsen effusion target-collection techniques, the preliminary data were fitted with a least-squares line to give a provisional vaporization equation for the temperature range 1326–1582 K and $\Delta_v H^0_{298} = (382 \pm 18)$ kJ mol^{-1} (Ward *et al.*, 1980). Later measurements of the vapor pressure of Bk metal over the temperature range 1100–1500 K, using combined Knudsen effusion mass-spectrometric and target-collection techniques (Ward *et al.*, 1982), led to the vaporization equations:

$$\log p(\text{atm}) = (5.78 \pm 0.21) - (15718 \pm 253)/T(\text{K})$$

for solid Bk between 1107 and 1319 K, and

$$\log p(\text{atm}) = (5.14 \pm 0.17) - (14902 \pm 244)/T(\text{K})$$

for liquid Bk between 1345 and 1528 K. The enthalpy of fusion was calculated to be 7.92 kJ mol^{-1}, and the enthalpy associated with the dhcp→fcc transition was calculated to be 3.66 kJ mol^{-1} (Ward *et al.*, 1982). The crystal entropy, S^0_{298}, of berkelium was estimated to be (76.2 ± 1.3) J K^{-1} mol^{-1} (Ward and Hill, 1976) and then later to be (78.2 ± 1.3) J K^{-1} mol^{-1}, and the average of data according to the second and third law data analysis yielded (310 ± 6) kJ mol^{-1} for its enthalpy of vaporization, $\Delta_v H^0_{298}$ (Ward *et al.*, 1982). Earlier correlation systematics had suggested that the standard enthalpy of sublimation of berkelium

metal, $\Delta_f H^0$(Bk(g)), is 280 kJ mol^{-1}, and that the standard enthalpy of formation of aqueous Bk(III), $\Delta_f H^0$ (Bk^{3+}(aq)), is -615 kJ mol^{-1} (Nugent *et al.*, 1973a; Johansson and Rosengren, 1975). A later modification of the systematics (Nugent *et al.*, 1973a) led to values of (320 ± 8) kJ mol^{-1} and $-(590 \pm 21)$ kJ mol^{-1} for $\Delta_f H^0$ (Bk(g)) and $\Delta_f H^0$ (Bk^{3+}(aq)), respectively (David *et al.*, 1976). There is very good agreement between the value of (320 ± 8) kJ mol^{-1} for $\Delta_f H^0$ (Bk(g)) derived from systematics and the value of (310 ± 6) kJ mol^{-1} for $\Delta_v H^0_{298}$, which is the same thermodynamic quantity, derived from experiment.

The enthalpy of solution of Bk metal (dhcp) to Bk^{3+}(aq) in 1 M HCl at 298 K was determined from five measurements to be $-(576 \pm 25)$ kJ mol^{-1} (Fuger *et al.*, 1975). The error limits reported did not reflect the precision of the calorimetric measurements but rather the uncertainties in the purity of the berkelium metal. A new determination of the enthalpy of solution of Bk metal (dhcp) in 1 M HCl at (298.15 ± 0.05) K has yielded a value of $-(600.2 \pm 5.1)$ kJ mol^{-1} (Fuger *et al.*, 1981). From this value $\Delta_f H^0$ (Bk^{3+}(aq)) was derived to be $-(601 \pm 5)$ kJ mol^{-1}, in good agreement with the value from systematics (David *et al.*, 1976), and, using reasonable entropy estimates, the standard potential of the Bk(III)/Bk(0) couple was calculated to be $-(2.01 \pm 0.03)$ V (Fuger *et al.*, 1981).

Studies of the magnetic susceptibility of berkelium metal have been hampered by the difficulty in obtaining well-characterized, single-phase bulk samples containing minimal amounts of daughter californium. Recent results obtained from a 21 μg sample of dhcp Bk metal (~12 at% Cf) indicated a transition to antiferromagnetic behavior at about 34 K and paramagnetic behavior between 70 and 250 K (Nave *et al.*, 1980). Applying the Curie–Weiss susceptibility relationship to the berkelium data obtained at fields greater than 0.08 T (where the field dependency was saturated) yielded $\mu_{eff} = 9.69$ μ_B and $\theta = 101.6$ K. The agreement of this value with the theoretical free-ion effective moment (9.72 μ_B) calculated for trivalent berkelium with LS coupling suggests that dhcp Bk metal exhibits high-temperature magnetic behavior like its lanthanide homolog, terbium. The results of earlier magnetic measurements on smaller samples of berkelium metal exhibiting mixed phases were reported by others (Fujita, 1969; Peterson *et al.*, 1970).

(c) Chemical properties

During the handling of microgram-sized samples of berkelium metal, it was observed that the rate of oxidation in air at room temperature is not extremely rapid, possibly due to the formation of a 'protective' oxide film on the metal surface (Peterson *et al.*, 1970). Berkelium is a chemically reactive metal, and berkelium hydride (Fahey *et al.*, 1972), some chalcogenides (Fahey *et al.*, 1972; Damien *et al.*, 1979, 1981), and pnictides (Stevenson and Peterson, 1979; Damien *et al.*, 1980) have been prepared directly from the reaction of Bk metal with the appropriate nonmetallic element. Berkelium metal dissolves

rapidly in aqueous mineral acids, liberating hydrogen gas and forming Bk(III) in solution.

(d) Theoretical treatment

A hybridized nondegenerate 6d and 5f virtual-bound-states model has been used to describe the properties of the actinide metals, including berkelium (Jullien *et al.*, 1972). It accounted for the occurrence of localized magnetism in Bk metal. A review of the understanding of the electronic properties of berkelium metal as derived from electronic band theory was published shortly thereafter (Freeman and Koelling, 1974). Included was the relativistic energy band structure of fcc Bk metal ($5f^8 6d^1 7s^2$), and the conclusion was that berkelium is a rare earth-like metal with localized (ionic) 5f electrons resulting from less hybridization with the 6d and 7s itinerant bands than occurs in the lighter actinides.

A phenomenological model based on crystal structure, metallic radius, melting point, and enthalpy of sublimation has been used to arrive at the electronic configuration of berkelium metal (Fournier, 1976). An energy difference of 0.92 eV was calculated between the $5f^9 7s^2$ ground state and the $5f^8 6d^1 7s^2$ first excited state. The enthalpy of vaporization of trivalent Bk metal was calculated to be 2.99 eV (288 kJ mol^{-1}), reflecting the fact that berkelium metal is more volatile than curium metal. It was also concluded that the metallic valence of the fcc form of berkelium metal is less than that of its dhcp modification (Fournier, 1976).

A relativistic Hartree–Fock–Wigner–Seitz band calculation has been performed for Bk metal in order to estimate the Coulomb term U (the energy required for a 5f electron to hop from one atomic site to an adjacent one) and the 5f electron excitation energies (Herbst *et al.*, 1976). The results for berkelium, in comparison to those for the lighter actinides, show increasing localization of the 5f states, i.e. the magnitude of the Coulomb term U increases through the first half of the actinide series with a concomitant decrease in the width of the 5f level.

10.6.2 Intermetallics

There have been no reports of berkelium intermetallics. Bk–Cf alloys formed from the natural decay of ^{249}Bk metal samples have been studied and are discussed in Section 10.6.3.

10.6.3 Alloys

^{249}Bk ($t_{1/2}$ = 330 days) decays by β$^-$ emission to ^{249}Cf, and because this transition occurs on an atomic scale at randomly distributed lattice sites, truly homogeneous solid solutions (alloys) result. Two such alloys, one Bk-rich (65%)

and the other Cf-rich (60%), have been studied under pressure via energy-dispersive X-ray powder diffraction (Itié *et al.*, 1985; Peterson *et al.*, 1987). The Bk-rich alloy exhibited the same phases with increasing pressure as did pure Bk metal, and the Cf-rich alloy exhibited the same phases with increasing pressure as did pure Cf metal (Peterson *et al.*, 1987). Continuity was observed between the values for pure Bk and Cf metals in the phase-transition pressures, the relative volume and volume decrease upon delocalization (point at which the α-uranium structure is first exhibited), and the bulk modulus. Thus one can consider these alloys as actinide metals with nonintegral atomic numbers (Itié *et al.*, 1985).

Two ^{248}Cm–Bk alloys have been prepared by reduction of their mixed anhydrous trifluorides (precipitated from aqueous solution and treated with fluorine) with lithium metal (Heathman and Haire, 1998). One alloy contained 30% Bk and the other contained 54% Bk. The stated goal of this work was to understand the phase and relative volume behavior of both alloys in terms of chemical bonding, each element's electronic configuration, and the alloys' pressure behavior relative to that reported for the pure Am–Cf metals (Heathman and Haire, 1998). The structural behavior of these two alloys was monitored by energy-dispersive X-ray powder diffraction. Both exhibited the expected RTP dhcp phase that transformed to the fcc phase at 12 GPa (30% Bk) or 8 GPa (54% Bk). The fcc phase changed to a third, unidentified phase at 35 GPa (30% Bk) or at 24 GPa (54% Bk), which was retained up to the maximum pressure studied (53 GPa) (Heathman and Haire, 1998). These results are consistent with the phase-transition pressures in pure Cm and Bk metals, i.e. the greater the concentration of Bk in the alloy, the lower the corresponding phase transition pressure.

10.7 COMPOUNDS

10.7.1 General summary

The trivalent oxidation state of berkelium prevails in the known berkelium compounds, although the tetravalent state is exhibited in BkO_2, BkF_4, Cs_2BkCl_6, and $[N(CH_3)_4]_2BkCl_6$. Selected crystallographic data for a number of berkelium compounds are collected in Table 10.2. In cases where there have been multiple reports of lattice parameters for a particular compound, the ones considered more reliable by the present authors are given in Table 10.2. The interested reader is encouraged to refer to the citations given in the table and text for complete details. An inherent difficulty, not addressed here, in the determination of lattice constants of 'pure' ^{249}Bk compounds concerns the ingrowth of daughter ^{249}Cf at the rate of about 0.22% per day. Two experimental methods to address this problem are: (1) the determination of the lattice parameters of berkelium compounds as a function of californium content and

then extrapolation to zero californium content; and (2) the utilization of Vegard's law to correct measured berkelium lattice parameters for the presence of a known amount of californium (assuming, of course, that the lattice parameters of the isostructural 'pure' californium compound are known).

A summary and discussion of the structural aspects of solid-state actinide chemistry are presented in Chapter 22, so no attempt is made to do so here for the compounds of berkelium. Estimated thermochemical values for many compounds of berkelium can be found in Chapter 19. Only those values determined by direct experiment are discussed here.

An empirical set of 'effective' ionic radii in oxides and fluorides, taking into account the electronic spin state and coordination of both the cation and the anion, have been calculated (Shannon and Prewitt, 1969). For six-coordinate Bk(III), the radii values are 0.096 nm, based on a six-coordinate oxide ion radius of 0.140 nm, and 0.110 nm, based on a six-coordinate fluoride ion radius of 0.119 nm. For eight-coordinate Bk(IV), the corresponding values are 0.093 and 0.107 nm, respectively, based on the same anion radii (Shannon and Prewitt, 1969). Other self-consistent sets of trivalent and tetravalent lanthanide and actinide ionic radii, based on isomorphous series of oxides (Peterson and Cunningham, 1967a; Shannon, 1976) and fluorides (Peterson and Cunningham, 1968b; Shannon, 1976), have been published. Based on a crystal radius for Cf(III), the ionic radius of isoelectronic Bk(II) was calculated to be 0.114 nm (Ionova *et al.*, 1977). It is important to note, however, that meaningful comparisons of ionic radii can only be made if the values compared are calculated in like fashion from the same type of compound, with respect to both composition and crystal structure (Shannon, 1976).

The thermal decomposition of $Bk(NO_3)_3 \cdot 4H_2O$, $BkCl_3 \cdot 6H_2O$, $Bk_2(SO_4)_3 \cdot 12H_2O$, and $Bk_2(C_2O_4)_3 \cdot 4H_2O$ has been studied in air, argon, and H_2–Ar atmospheres and compared to that of the corresponding hydrates of cerium, gadolinium, and terbium (Haire, 1973). In air or Ar the final berkelium product was BkO_2; in H_2–Ar it was Bk_2O_3.

10.7.2 Hydrides

The preparation of berkelium hydride has been accomplished by treatment of berkelium metal at 500 K with H_2 gas derived from thermal decomposition of UH_3 (Fahey *et al.*, 1972). The product exhibited an fcc structure with lattice parameter $a_0 = (0.523 \pm 0.001)$ nm determined from nine observed X-ray diffraction lines. By analogy with the behavior of the lanthanide hydrides (Holley *et al.*, 1955), the stoichiometry BkH_{2+x} ($0 < x < 1$) was assigned. Later studies of the berkelium–hydrogen system resulted in products with either fcc symmetry, identified as the dihydride, or hexagonal symmetry, which was taken to be berkelium trihydride, BkH_{3-x} ($0 < x < 1$) (Gibson and Haire, 1985). Additional work is required to characterize fully the berkelium–hydrogen system.

Table 10.2 *Selected crystallographic data for berkelium compounds.*

Substance	Structure type	Crystal system	Lattice parameters[a]				Other[b]	References
			a_0 (nm)	b_0 (nm)	c_0 (nm)	β (degree)		
Hydrides								
BkH_{2+x}	CaF_2	cubic (fcc)	0.523					Fahey *et al.* (1972)
BkH_{2+x}	CaF_2	cubic (fcc)	0.5248					Gibson and Haire (1985)
BkH_{3-x}	LaF_3	trigonal	0.6454		0.6663			Gibson and Haire (1985)
Oxides								
BkO_2	CaF_2	cubic (fcc)	0.53315					Fahey *et al.* (1974)
Bk_2O_3	$(Fe,Mn)_2O_3$	cubic (bcc)	1.0887					Peterson and Cunningham (1967a)
Bk_2O_3	Sm_2O_3	monoclinic	1.4197	0.3606	0.8846	100.23		Baybarz (1973)
Bk_2O_3	La_2O_3	hexagonal	0.3754		0.5958		V72.7	Baybarz (1973)
Halides								
BkF_4	UF_4	monoclinic	1.2396	1.0466	0.8118	126.33	V70.7	Haug and Baybarz (1975)
BkF_3	LaF_3	trigonal	0.697		0.714		ρ10.15	Peterson and Cunningham (1968b)
BkF_3	YF_3	orthorhombic	0.670	0.709	0.441		ρ9.70	Peterson and Cunningham (1968b)
$BkCl_3$	UCl_3	hexagonal	0.7382		0.4127			Peterson and Cunningham (1968a)
Cs_2BkCl_6	Rb_2MnF_6	hexagonal	0.7451		1.2097		ρ4.155	Morss and Fuger (1969)
$Cs_2NaBkCl_6$	$(NH_4)_3AlF_6$	cubic (fcc)	1.0805				ρ3.952	Morss and Fuger (1969)
$BkCl_3 \cdot 6H_2O$	$GdCl_3 \cdot 6H_2O$	monoclinic	0.966	0.654	0.797	93.77	ρ3.06	Burns and Peterson (1971)
$BkBr_3$	$PuBr_3$	orthorhombic	0.403	1.271	0.912		V116.8	Burns *et al.* (1975)

Compound	Structure type	System	a	b	c	angle	V/ρ[b]	Reference
BkBr$_3$	AlCl$_3$	monoclinic	0.723	1.253	0.683	110.6	V144.8	Burns et al. (1975)
BkI$_3$	BiI$_3$	hexagonal	0.7584		2.087			Fellows et al. (1977)
Chalcogenides								
BkS$_{2-x}$	anti-Fe$_2$As	tetragonal	0.3902		0.792			Damien et al. (1981)
Bk$_2$S$_3$	deficit Th$_3$P$_4$	cubic (bcc)	0.8358					Damien et al. (1981)
BkSe$_{2-x}$	anti-Fe$_2$As	tetragonal	0.404		0.828			Damien et al. (1981)
Bk$_2$Se$_3$	deficit Th$_3$P$_4$	cubic (bcc)	0.8712					Damien et al. (1981)
BkTe$_3$	NdTe$_3$	orthorhombic	0.4318	0.4319	2.5467			Damien et al. (1979, 1981)
BkTe$_{2-x}$	anti-Fe$_2$As	tetragonal	0.4314		0.8945			Damien et al. (1979)
Bk$_2$Te$_3$	Sc$_2$S$_3$	orthorhombic	1.226	0.8685	2.605			Damien et al. (1979)
Pnictides								
BkN	NaCl	cubic (fcc)	0.4951					Damien et al. (1980)
BkP	NaCl	cubic (fcc)	0.5669					Damien et al. (1980)
BkAs	NaCl	cubic (fcc)	0.5829					Damien et al. (1980)
BkSb	NaCl	cubic (fcc)	0.6191					Damien et al. (1980)
Other inorganic compounds								
BkOCl	PbFCl	tetragonal	0.3966		0.6710		ρ9.45	Peterson and Cunningham (1967b)
BkOBr	PbFCl	tetragonal	0.395		0.81			Cohen et al. (1968)
BkOI	PbFCl	tetragonal	0.3986		0.9149			Fellows et al. (1977)
Bk$_2$O$_2$SO$_4$	La$_2$O$_2$SO$_4$	orthorhombic	0.4195	0.4083	1.3110			Haire and Fahey (1977)
Bk$_2$O$_2$S	Pu$_2$O$_2$S	trigonal	0.3861		0.6686			Haire and Fahey (1977)
Bk$_2$(C$_2$O$_4$)$_3$·10H$_2$O	La$_2$(C$_2$O$_4$)$_3$·10H$_2$O	monoclinic	1.112	0.9746	0.987	114.1		Morris et al. (2005)
Coordination compounds								
[Bk(C$_5$H$_5$)$_2$Cl]$_2$	[Sm(C$_5$H$_5$)$_2$Cl]$_2$							Laubereau (1970)
[N(CH$_3$)$_4$]$_2$BkCl$_6$	K$_2$PtCl$_6$	cubic (fcc)	1.308					Morss et al. (1991)
Organometallic compounds								
Bk(C$_5$H$_5$)$_3$	Pr(C$_5$H$_5$)$_3$	orthorhombic	1.411	1.755	0.963		ρ2.47	Laubereau and Burns (1970)

[a] See original source for precision claimed on these room-temperature values and for information regarding sample purity.
[b] ρ = density in 10^3 kg m^{-3} (g cm^{-3}); V = formula volume in 10^6 pm^3(Å^3).

10.7.3 Oxides

The first compound of berkelium identified on the basis of its characteristic X-ray powder diffraction pattern was BkO_2 (Cunningham, 1963). Other researchers have since confirmed its CaF_2-type fcc structure with $a_0 = 0.533$ nm (Peterson and Cunningham, 1967a; Baybarz, 1968, 1973; Fahey *et al.*, 1974; Sudakov *et al.*, 1977). The thermal expansion of BkO_2 in 1 atm of oxygen was determined and shown to be reversible with temperature (Fahey *et al.*, 1974). The data were fitted by the expression

$$a_0(t) = 5.3304 + (4.32 \times 10^{-5})t + (15.00 \times 10^{-9})t^2,$$

where $a_0(t)$ is the unit cell edge (in Å) at temperature t (in °C). In addition, the instantaneous expansion coefficients at 25 and 900°C were calculated to be 8.25×10^{-6} °C^{-1} and 13.2×10^{-6} °C^{-1}, respectively (Fahey *et al.*, 1974).

The results of a preliminary study of a sample of berkelium oxide (BkO_2, Bk_2O_3, or a mixture of the two) via X-ray photoelectron spectroscopy (XPS) included measured core- and valence-electron-binding energies (Veal *et al.*, 1977). The valence-band XPS spectrum, which was limited in resolution by phonon broadening, was dominated by 5f electron emission. The photoelectron spectrum of the 4f lines of Bk in BkO_2 was recorded, and the binding energies of the $4f_{5/2}$ electrons determined to be 515.6(4) eV, and those of the $4f_{7/2}$ electrons, 499.6(4) eV (Krause *et al.*, 1988). These values were reported to be slightly lower than theoretical estimates, but the spin–orbit splitting of the 4f levels, 16.0 (3) eV, was in good agreement with the results of relativistic Hartree–Slater calculations (Krause *et al.*, 1988).

A capacitance manometer system was used to measure the equilibrium oxygen decomposition pressures over non-stoichiometric BkO_x (1.5 x < 2.0) (Turcotte *et al.*, 1971). Three broad non-stoichiometric phases were defined: $BkO_{1.5-1.77}$; $BkO_{1.81-1.91}$; and BkO_{2-x} ($x \leq 0.07$). Later, an X-ray diffraction investigation of this BkO_x system under equilibrium conditions was undertaken to correlate the above data with structural behavior (Turcotte *et al.*, 1980). A phase diagram was suggested, showing above 673 K two widely non-stoichiometric phases: body-centered cubic (bcc) for 1.5 < O/Bk ≤ 1.70 and fcc for 1.78 ≤ O/Bk < 2.00. Interestingly, no evidence was found for the formation of Bk_7O_{12}, expected to exhibit a rhombohedral structure based on its common presence in other MO_x (1.5 < x < 2.0) systems. Using the data from the work of others (Peterson and Cunningham, 1967a; Baybarz, 1968, 1973; Turcotte *et al.*, 1980), a berkelium–oxygen phase diagram was constructed over the range from 59 to 67 at% oxygen and from 200 to 900°C (Okamoto, 1999). Also provided is a summary of Bk–O crystal structure data.

The stable room-temperature form of berkelium sesquioxide exhibits the bixbyite-type bcc structure with $a_0 = 1.0887$ nm (Peterson and Cunningham, 1967a). This has been corroborated by an independent study (Baybarz, 1968, 1973). The cubic sesquioxide has also been analyzed by electron diffraction

(Haire and Baybarz, 1973). The high-temperature behavior of Bk_2O_3 has been studied, with the finding that the cubic-to-monoclinic transition at (1473 ± 50) K is irreversible, while the monoclinic-to-hexagonal transition at about 2025 K is reversible (Baybarz, 1973). In addition, the melting point of Bk_2O_3 was determined to be (2193 ± 25) K. Thus berkelium continues the trend of actinide sesquioxides exhibiting trimorphism; with increasing temperature, the structure of Bk_2O_3 changes from bcc (C-form) to monoclinic (B-form) to hexagonal (A-form).

The possibility of the existence of BkO has been considered (Fahey *et al.*, 1972). The true identity of the brittle, gray material exhibiting an fcc structure with $a_0 = 0.4964$ nm is still in doubt. This phase might represent a nitride or an oxide nitride.

A preliminary report of the synthesis and structural characterization of polycrystalline $Bk_2M_2O_7$ and solid solutions of $(Bk,M)O_2$, where M = Zr or Hf, has been given, but no specifics were provided (Haire and Raison, 2000). In a later report the lattice parameter for $Bk_2Zr_2O_7$ was presented to be 1.058 nm in a graph (Haire *et al.*, 2002).

As part of an investigation of the fundamental chemistry and materials science of the 4f and several 5f elements in glass matrices, berkelium was put into two high-temperature (850 and 1450°C), silicate-based glasses and into one sol–gel glass (formed by the hydrolysis of a silicate ester) (Haire *et al.*, 1998). Berkelium (along with cerium and americium) provided an exception to the general observation that the oxidation state of the f element in the high-temperature glasses correlated with that in the element's usual binary oxide produced in air. The same correlation also applied to the f elements in the sol–gel glasses after they had been heated to 200–400°C. The authors only observed Bk(III) in the three glasses and reasoned that without the added stability afforded by the fluorite lattice in BkO_2, Bk(III) was the more stable oxidation state in these glasses (Haire *et al.*, 1998). The anomalous dependence on excitation power of the emission profile of Bk(III) in the 850°C silicate-based glass (Assefa *et al.*, 1998) has been discussed in Section 10.5.3.

10.7.4 Halides

The only reported binary Bk(IV) halide is BkF_4 (Asprey and Keenan, 1968; Keenan and Asprey, 1969; Asprey and Haire, 1973; Haug and Baybarz, 1975), prepared by fluorination of BkO_2 or BkF_3. Although these researchers agree that it exhibits the UF_4-type monoclinic structure, there is some variance in the reported lattice parameters. This could result from the complexity of the X-ray powder diffraction pattern of BkF_4. A molecular volume of 7.07×10^7 pm^3 is calculated from the lattice constants given in Table 10.2, in contrast to those of 7.148×10^7 pm^3 (Asprey and Haire, 1973) and 7.28×10^7 pm^3 (Asprey and Keenan, 1968; Keenan and Asprey, 1969) derived from the other reported lattice parameters. The solid-state absorption spectrum of BkF_4 was obtained

by Ensor *et al.* (1981). Mixed alkali metal (M)–Bk(IV) fluoride compounds of the types $MBkF_5$, M_2BkF_6, M_3BkF_7, and $M_7Bk_6F_{31}$, although at present unreported, should be readily prepared. The structural systematics of such actinide fluoride complexes have been discussed elsewhere (Thoma, 1962; Penneman *et al.*, 1973).

In addition to $[N(CH_3)_4]_2BkCl_6$ (discussed in Section 10.7.7), one other Bk(IV) halide compound, Cs_2BkCl_6, has been characterized by its crystallographic properties (Morss and Fuger, 1969). This orange compound precipitated upon dissolution of Bk(IV) hydroxide in chilled, concentrated HCl solution containing CsCl, and was found to crystallize in the Rb_2MnF_6-type hexagonal structure with $a_0 = 0.7451$ nm and $c_0 = 1.2097$ nm. Using a separated halogen atom model, the lattice energy of this compound has been calculated to be 1295 kJ mol^{-1} and the average radius of the $BkCl_6^{2-}$ ion to be 0.270 nm (Jenkins and Pratt, 1979).

The trihalides of berkelium can be prepared by hydrohalogenation of BkO_2, Bk_2O_3, or a lighter berkelium halide. BkF_3 (Peterson and Cunningham, 1968b; Ensor *et al.*, 1981), $BkCl_3$ (Peterson and Cunningham, 1968a; Young *et al.*, 1978; Peterson *et al.*, 1981, 1986), and $BkBr_3$ (Burns *et al.*, 1975; Peterson *et al.*, 1977b) have been shown by X-ray powder diffraction and absorption spectrophotometric studies to be dimorphic. Berkelium is the lightest actinide whose trifluoride exhibits the YF_3-type orthorhombic structure as the room-temperature alpha phase and the LaF_3-type trigonal structure as the high-temperature phase (Peterson and Cunningham, 1968b).

In the case of dimorphic $BkCl_3$, the UCl_3-type hexagonal structure (Peterson and Cunningham, 1968a) represents the low-temperature form, while the $PuBr_3$-type orthorhombic structure is exhibited by the high-temperature modification (Peterson *et al.*, 1981, 1986). The phase-transition temperature appears to be close (Peterson *et al.*, 1981, 1986) to the $BkCl_3$ melting point (876 K) (Peterson and Burns, 1973). The volatilization behavior of many of the binary actinide chlorides including $BkCl_3$ has been studied and correlated with the oxidation state and atomic number ($Z < 92$ or $Z \geq 92$) of the actinide (Merinis *et al.*, 1970). More recent thermochromatographic studies of berkelium chloride using ^{250}Bk confirmed these early results, in that under non-oxidizing conditions, only one deposition peak was observed, corresponding to $BkCl_3$ (Yakushev *et al.*, 2003). With oxidizing conditions (Cl_2 or $Cl_2/SOCl_2$), however, a lower temperature deposition peak grows slowly over time and was assigned to more volatile $BkCl_4$. The adsorption enthalpies were calculated via a Monte Carlo simulation method (Zvara, 1985) and found to be $-(201 \pm 6)$ and $-(154 \pm 6)$ kJ mol^{-1} for $BkCl_3$ and $BkCl_4$, respectively (Yakushev *et al.*, 2003). White $Cs_2NaBkCl_6$ was crystallized from aqueous CsCl–HCl solution by increasing the HCl concentration and cooling to -23°C, and it was found to exhibit an fcc structure in which the Bk(III) ions (O_h site symmetry) are octahedrally coordinated by chloride ions (Morss and Fuger, 1969). The unique properties of such compounds stimulated the synthesis and study of an

isostructural set of Cs_2NaMCl_6 compounds containing trivalent cations (including M = U, Np, Pu, Am, and Cf) whose ionic radii ranged from 0.065 to 0.106 nm (Morss *et al.*, 1970; Schoebrechts *et al.*, 1989).

X-ray diffraction from a powder sample of $BkCl_3 \cdot 6H_2O$ showed that it is isostructural with $AmCl_3 \cdot 6H_2O$, whose structure was refined by single-crystal diffraction methods (Burns and Peterson, 1971). By analogy, the basic units of the berkelium structure are $BkCl_2(OH_2)_6^+$ cations and Cl^- anions, the latter being octahedrally coordinated by water molecules.

From X-ray powder diffraction patterns of $BkBr_3$ obtained as a function of the sample's thermal treatment, it was concluded that the $PuBr_3$-type orthorhombic structure is the low-temperature form of $BkBr_3$, and the $AlCl_3$-type monoclinic structure is the high-temperature form (Burns *et al.*, 1975). Because these two crystallographic modifications differ by 2 in the Bk(III) CN, absorption spectrophotometric analysis easily distinguishes between them (Peterson *et al.*, 1977b). The possibility of a third polymorph of $BkBr_3$ has been suggested on the basis of eight lines of low intensity in one powder pattern (Burns *et al.*, 1975). If it does exist, it would be the form intermediate between the $PuBr_3$- and $AlCl_3$-type structures and would exhibit the $FeCl_3$-type rhombohedral structure with $a_0 = 0.766$ nm and $\alpha = 56.6°$ (Burns *et al.*, 1975). There is one additional report (Cohen *et al.*, 1968) with lattice parameters for the orthorhombic form of $BkBr_3$ and for BiI_3-type hexagonal BkI_3.

Samples of berkelium trifluoride, trichloride, tribromide, and triiodide have been studied over time to ascertain the physicochemical effects of beta decay in the bulk-phase solid state (Young *et al.*, 1984). In each case Bk^{3+} was found to transform to Cf^{3+}, and the crystal structure of the solid remained unchanged. Maintenance of oxidation state would seem to be a chemical effect of this transformation, whereas maintenance of crystal structure is more of a physical effect, the structure of the progeny being controlled by its environment. Details of the characterization and study of dimorphic $BkCl_3$, via X-ray powder diffraction and absorption spectrophotometry, have been published (Peterson *et al.*, 1986). The results of monitoring each of the crystal forms of $BkCl_3$ over a period of almost 3 years are included. Justification (and some limitations) for the use of electronic f→f absorption peaks in the spectra of berkelium (and other actinide) compounds for the elucidation of the crystal structures of these compounds (crystal-field effects) has been published (Peterson *et al.*, 1990). In addition to absorption spectrophotometry, phonon Raman spectroscopy has been shown to be an effective way to elucidate the structure of a solid-state compound. Each crystal type possesses a unique set of fundamental crystal vibrations resulting from the positions, coordinations, bonding, and masses of its atoms. A catalog of phonon Raman spectral data for selected actinide compounds, including both crystallographic and spectroscopic parameters for each individual crystal structure exhibited, is available (Wilmarth and Peterson, 1991). A discussion of the comparative science of the lanthanide and actinide halides, mainly focusing on the trivalent chlorides and

bromides, provides the systematics into which berkelium fits as expected (Peterson, 1995).

10.7.5 Chalcogenides and pnictides

The only other crystallographic result reported for a berkelium chalcogenide besides those summarized in Table 10.2 is a cubic lattice parameter of 0.844 nm for Bk_2S_3 (Cohen *et al.*, 1968). The microscale synthesis of the brownish-black sesquisulfide was carried out by treatment of berkelium oxide at 1400 K with a mixture of H_2S and CS_2 vapors. In a later work (Damien *et al.*, 1979, 1981), the higher chalcogenides were prepared on the 20–30 μg scale in quartz capillaries by direct combination of the elements. These were then thermally decomposed *in situ* to yield the lower chalcogenides. The stoichiometries of these compounds have not been determined directly.

The berkelium monopnictides have been prepared on the multi-microgram scale by direct combination of the elements (Damien *et al.*, 1980). In all cases the lattice constants of the NaCl-type cubic structures were smaller than those of the corresponding curium monopnictides but comparable to those of the corresponding terbium compounds. This supports the semimetallic classification for these compounds. One additional report of BkN has appeared (Stevenson and Peterson, 1979). The lattice parameter derived from the sample exhibiting a single phase was (0.5010 ± 0.0004) nm, whereas that extracted from the mixed-phase sample of BkN resulting from incomplete conversion of a hydride was (0.4948 ± 0.0003) nm. Additional samples of BkN should be prepared to establish more firmly its lattice constant.

10.7.6 Other inorganic compounds

BkOCl (Peterson and Cunningham, 1967b), BkOBr (Cohen *et al.*, 1968), and BkOI (Cohen *et al.*, 1968; Fellows *et al.*, 1977) have been synthesized and are found to exhibit the PbFCl-type tetragonal structure. Although presently unreported, BkOF certainly can be prepared and probably exhibits polymorphism.

Both the oxysulfate (body-centered orthorhombic) and the oxysulfide (trigonal) of Bk(III) have been studied by X-ray powder diffraction (Haire and Fahey, 1977). $Bk_2O_2SO_4$ resulted from the decomposition of $Bk_2(SO_4)_3 \cdot nH_2O$ in an argon atmosphere (to prevent oxidation to BkO_2) at about 875 K, whereas Bk_2O_2S was formed upon thermal decomposition the sulfate hydrate in a 4% H_2/96% Ar atmosphere. No decomposition of the oxysulfide was observed up to 1300 K in the H_2/Ar gas mixture (Haire and Fahey, 1977). Both $Bk_2O_2SO_4$ and Bk_2O_2S are isostructural with the corresponding lanthanide and actinide compounds.

Berkelium(III) orthophosphate has been prepared and characterized by X-ray powder diffraction and solid-state absorption and Raman spectroscopies (Haire *et al.*, 1983; Hobart *et al.*, 1983). Analysis of the X-ray data has shown

this compound to be isostructural with samarium and europium ortho-phosphates and to exhibit similar lattice parameters (Haire *et al.*, 1983). The structure type was confirmed by the direct correlation of the Raman spectrum of $BkPO_4$ with those of the isostructural lanthanide orthophosphates (Hobart *et al.*, 1983).

The preparation of berkelium(III) sesquioxalate decahydrate has been reported, along with its monoclinic unit cell parameters and its absorption and Raman spectra. It was observed that the Bk(III) compound underwent oxidation in about 24 h to a non-stoichiometric Bk(IV) oxalate complex, presumably the result of its self-irradiation (Morris *et al.*, 2005).

10.7.7 Coordination compounds

A β-diketonate compound of Bk(III) has been prepared and reported to be stable when volatilized. The possibility of using this volatile compound in transport and subsequent separation of berkelium from other actinides has been proposed (Fedoseev *et al.*, 1983).

More recently $[N(CH_3)_4]_2BkCl_6$ samples were prepared from cold, concentrated HCl(aq) on the milligram scale and studied via X-ray powder diffraction and optical spectroscopy in KBr and KCl pellets (Morss *et al.*, 1991). The powder patterns were indexed on fcc symmetry, with $a_0 = 1.308(2)$ nm, although from systematics a smaller lattice parameter was expected. No fluorescence attributable to Bk^{4+} was found under several modes of excitation. Strong f-center absorptions, due to radiation damage, and several very weak absorptions, presumably due to transitions to the first excited state of Bk^{4+}, were noted (Morss *et al.*, 1991).

10.7.8 Organometallic compounds

Two cyclopentadienylberkelium(III) compounds have been reported, but only one of them, $Bk(C_5H_5)_3$, has been characterized crystallographically (Laubereau and Burns, 1970). In addition to the data given in Table 10.2, the formula volume of this compound is 2.98×10^8 pm^3. The amber-colored tris (cyclopentadienyl)berkelium(III) was isolated from a reaction mixture of $BkCl_3$ and molten $Be(C_5H_5)_2$ by sublimation in vacuum at 475–495 K. It decomposes to an orange melt at 610 K (Laubereau and Burns, 1970).

During vacuum sublimation from a mixture of $BkCl_3$ and molten $Be(C_5H_5)_2$ at temperatures above 500 K (up to 600 K), a second berkelium fraction was obtained (Laubereau, 1970). Its identity was established to be bis(cyclopenta-dienyl)berkelium(III) chloride dimer, $[Bk(C_5H_5)_2Cl]_2$, based on the similarities of its X-ray powder diffraction pattern and sublimation behavior to those of known $[Sm(C_5H_5)_2Cl]_2$. The solid-state absorption spectrum of $[Bk(C_5H_5)_2Cl]_2$ was obtained and noted to be very similar to that of $Bk(C_5H_5)_3$ (Laubereau, 1970).

10.7.9 Magnetic behavior of berkelium ions

In order to improve upon the precision ($\pm 10\%$) of the initial measurements of the magnetic susceptibility of Bk(III) ions (Cunningham, 1959) and to extend the range of measurements to lower temperatures, single beads of cation-exchange resin were saturated with Bk(III) and subjected to susceptibility measurements over the temperature range 9–298 K (Fujita, 1969). The magnetic behavior of Bk(III) over the entire temperature range was described well by the Curie–Weiss relationship with $\mu_{\text{eff}} = (9.40 \pm 0.06)\ \mu_{\text{B}}$ and $\Theta = (11.0 \pm 1.9)$ K. The magnetic susceptibility of Bk(III) in an octahedral environment of host matrix Cs_2Na-$LuCl_6$ was measured; temperature-independent paramagnetism was observed over the temperature range 10–40 K, with the lowest level of Bk(III) determined to be Γ_1 and with a Γ_1–Γ_4 separation of $8.5 \times 10^3\ \text{m}^{-1}$ (Hendricks *et al.*, 1974).

Results of electron paramagnetic resonance (Boatner *et al.*, 1972) and magnetic susceptibility (Karraker, 1975) studies of Bk(IV) in ThO_2 have been reported. The eight-line hyperfine pattern confirmed that the nuclear spin of ^{249}Bk is 7/2; the estimated nuclear moment was $(2.2 \pm 0.4)\ \mu_{\text{N}}$ (Boatner *et al.*, 1972). Two regions of temperature-dependent paramagnetism of BkO_2 in ThO_2 were observed over the temperature range 10–220 K; the possibility of an antiferromagnetic transition at 3 K was noted (Karraker, 1975).

The first measurements of the magnetic susceptibilities of bulk-phase samples of some berkelium compounds (BkO_2, BkF_3, BkF_4, and BkN) were made in 1981. The effective moments were found to agree with the calculated free-ion values, assuming Bk(IV) or Bk(III) cores and LS coupling (Nave *et al.*, 1981). The paramagnetic effective moments for BkF_4 and BkO_2 were determined from a Curie–Weiss fit to the data displayed in Fig. 10.5. The experimentally determined μ_{eff} values for BkF_4 and BkO_2 of $(7.93 \pm 0.03)\ \mu_{\text{B}}$ and $(7.92 \pm 0.1)\ \mu_{\text{B}}$, respectively, are in good agreement with a localized $5f^7$ ionic model where μ_{eff} (theory) $= 7.94\ \mu_{\text{B}}$ (Nave *et al.*, 1983).

10.8   IONS IN SOLUTION

10.8.1   Oxidation states

Berkelium exhibits both III and IV oxidation states in solution, as would be expected from the oxidation states displayed by its lanthanide counterpart, terbium. Evidence has been offered for the existence of Bk(II), but there is only speculation on the possible existence of Bk(V). Bk(III) is the most stable oxidation state in non-complexing aqueous solutions. Bk(IV) is reasonably stable in solution in the absence of reducing agents because of the stabilizing influence of the half-filled $5f^7$ subshell. Bk(III) and Bk(IV) exist in aqueous solution as simple hydrated ions, $Bk^{3+}(aq)$ and $Bk^{4+}(aq)$, respectively, unless complexed by ligands. Bk(III) is green in most mineral acid solutions. Bk(IV) is yellow in HCl solution and orange-yellow in H_2SO_4 solution.
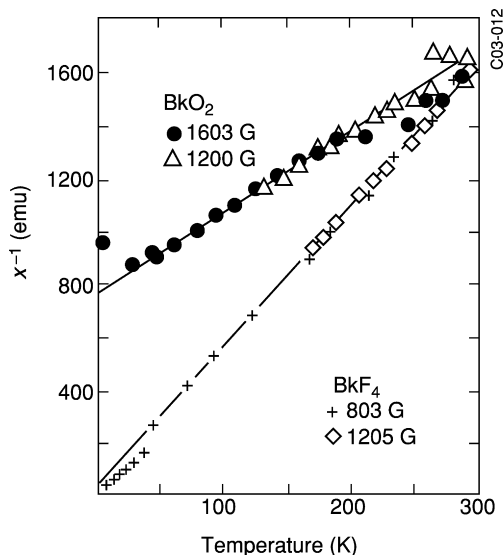
Fig. 10.5 *Inverse magnetic susceptibility of BkF₄ at 803 and* 1205 G *and BkO₂ at* 1200 *and* 1603 G *as a function of temperature.* (*The solid lines are least-squares fits of the data to the Curie–Weiss law.*) (*Reprinted figure with permission from Nave* et al. (1983). *Copyright* 1983 *by the American Physical Society.*)

The possible existence of divalent berkelium was studied by polarography in acetonitrile solution. Because of high background currents, caused by radiolysis products obscuring the polarographic wave, evidence for Bk(II) was not obtained (Friedman and Stokely, 1976). Divalent berkelium has been reported to exist in mixed lanthanide chloride–strontium chloride melts. The claim is based on the results of the distribution of trace amounts of berkelium between the melt and a solid crystalline phase (co-crystallization technique) (Mikheev *et al.*, 1979; D'yachkova *et al.*, 1980). As discussed in Section 10.8.2, additional evidence for the transient existence of Bk(II), generated via pulse radiolysis of an aqueous bicarbonate–ethanol solution, has been reported (Sullivan *et al.*, 1988).

10.8.2   Spectra in solution

The first attempts to measure the absorption spectrum of Bk(III) involved the use of a single ion-exchange resin bead (Cunningham, 1959). Later the spectrum of a 3.6×10^{-3} M Bk(III) solution was recorded in a microcell (Gutmacher *et al.*, 1967). Sixteen absorption bands of Bk(III) were identified in the solution spectrum recorded in a 'suspended-drop' microcell over the wavelength range 320–680 nm (Peterson, 1967, 1980). The results of additional observations identified a total of 23 absorption bands in the 280–1500 nm wavelength region (Fujita, 1969).

The first attempts to record the Bk(IV) solution absorption spectrum were hindered by the presence of cerium impurities (Gutmacher *et al.*, 1967). The positions of the Bk(IV) absorption bands, superimposed on the strong Ce(IV) bands, suggested the assignment of $5f^7$ for the electronic configuration of Bk(IV), which is in agreement with the actinide hypothesis.

The absorption spectra of Bk(III) and Bk(IV) have been recorded in a variety of solutions (Baybarz *et al.*, 1972). New absorption bands were reported as the result of using larger quantities of ^{249}Bk of higher purity. Observations of the spectrum of Bk(III) were extended further into the UV wavelength region (to 200 nm), and nine new absorption bands were reported (Gutmacher *et al.*, 1973). An interpretation of the low-energy bands in the solution absorption spectra of Bk(III) and Bk(IV) was published (Carnall *et al.*, 1971). Later experimental work using larger quantities of berkelium than had been available previously, coupled with a new technique for rapidly separating small quantities of daughter ^{249}Cf, has resulted in a Bk(III) solution absorption spectrum with minimal interference from radiolysis products and significantly higher resolution than those of previously published spectra (Carnall *et al.*, 1984). A parametric fit of the data was performed in order to obtain the energy-level structure of the Bk^{3+} aquo ion. The band intensities were analyzed using the Judd–Ofelt theory, and fluorescent branching ratios were computed from theoretical parameters (Carnall *et al.*, 1984).

The spectra of Bk(III) and Bk(IV) in complexing, concentrated aqueous carbonate solutions have been reported (Hobart *et al.*, 1990). Bk(III) rapidly oxidizes in strongly basic carbonate solutions, and thus the Bk(III) spectrum could only be obtained by electrochemically reducing Bk(IV) in such solutions in a semi-micro cell. The stable Bk(IV) carbonate solution spectrum exhibited a strong charge transfer band peaking at 282 nm in 2 M carbonate solution and at 274 nm in 5 M carbonate solution. The Bk(III) carbonate spectrum showed characteristic f–f transitions superimposed on remnants of the Bk(IV) spectrum. The spectra of Bk(III) in 0.1 M citrate solution at pH values of 1 and 4 have also been reported (Hobart *et al.*, 1990).

The solution absorption spectra of 1×10^{-4} M solutions of yellow Bk(IV) nitrate- and brown Bk(IV) perchlorate–triphenylarsine oxide adducts in acetonitrile were recorded as a result of ozonolysis of initial Bk(III) adduct solutions. Both Bk(IV) spectra exhibited a charge transfer UV cutoff around 300 nm (Payne and Peterson, 1987).

Fluorescence X-ray absorption near-edge spectra (XANES) and the L_3-edge fluorescence X-ray absorption fine structure (XAFS), and their Fourier transforms, of Bk(III) and Bk(IV) aquo ions have been published (Antonio *et al.*, 2002).

Although there have been a number of elegant solid-state studies that provided indirect evidence for the existence of the divalent state of berkelium (e.g. Young *et al.*, 1981), an attempt was made to generate Bk(II) in an aqueous bicarbonate–ethanol solution via pulse radiolysis (Sullivan *et al.*, 1988). The absorption
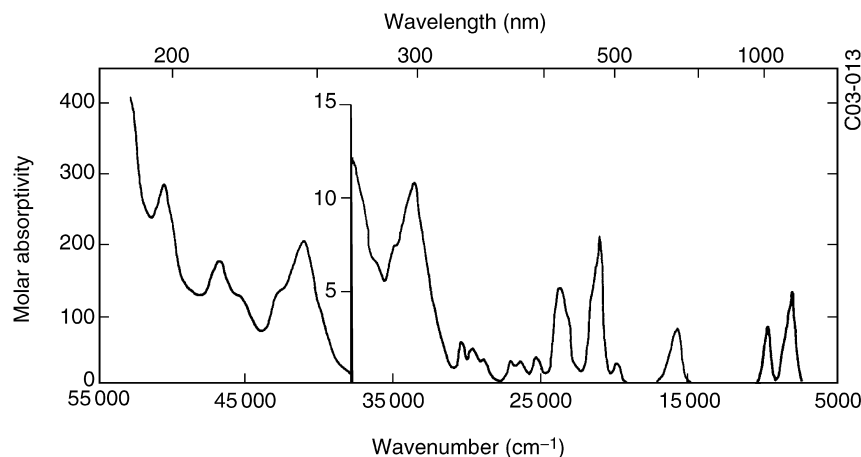
Fig. 10.6 *Solution absorption spectrum of Bk(III) in 0.2 M HClO₄ (DCl solutions were used for portions of the infrared spectrum)* (*Carnall* et al., 1984).

spectrum of Bk(II), obtained by subtracting out the contributions of the ethanol radical, yielded a peak with a maximum at 310 nm and a molar absorptivity of $(2.3 \pm 0.2) \times 10^3$ cm^{-1} M^{-1}. Bk(II) is unstable in this medium, and the rate of its disappearance was reported to be $(1.53 \pm 0.25) \times 10^5$ s^{-1} (Sullivan *et al.*, 1988).

The solution absorption spectrum of non-complexed Bk(III) is shown in Fig. 10.6. This spectrum is characterized by sharp absorption bands of low molar absorptivity attributed to 'Laporte-forbidden' f–f transitions and by intense absorption bands in the UV region attributed to f–d transitions (Gutmacher *et al.*, 1973). The spectra of Bk(IV) shown in Fig. 10.7 are dominated by a strong absorption band at 250–290 nm, the peak position of which is strongly dependent on the degree of complexation of Bk(IV) by the solvent medium. This dominant band is attributed to a charge transfer mechanism (Gutmacher *et al.*, 1973).

Electronic spectra of Bk(III) (Varga *et al.*, 1973b; Carnall *et al.*, 1984) and Bk(IV) (Varga *et al.*, 1973c) and a prediction of the electronic spectrum of Bk(II) (Varga *et al.*, 1973a) have been published. Spin–orbit coupling diagrams for these berkelium ions, based on a free-ion interpretation of the f–f spectra, were proposed. Further discussion of the absorption spectra of berkelium ions in solution can be found in Chapter 18.

10.8.3 Hydrolysis and complexation behavior

Although Bk(IV) is well known in solution, only stability constants of complexes with Bk(III) have been reported, most of which were determined during investigations of separation procedures. A compilation of the stability constants of Bk(III) complexes with various anions is given in Table 10.3. In most cases the
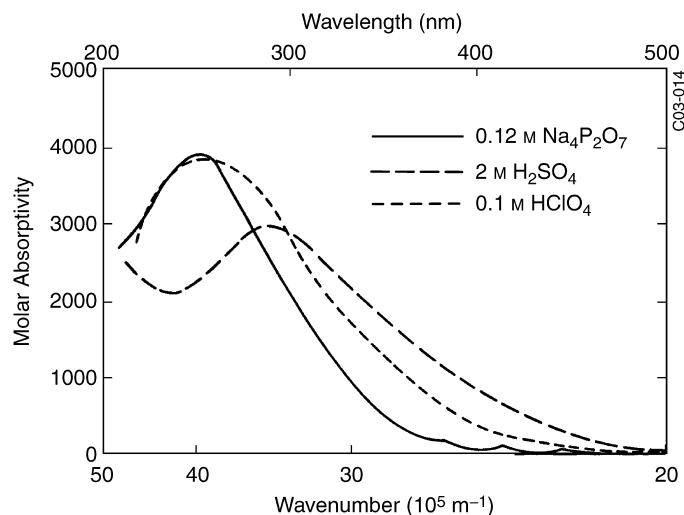
Wavelength (nm)

Fig. 10.7 *Solution absorption spectra of Bk(IV) in various media (Gutmacher et al., 1973).*

lack of replicate results precludes an assessment of the accuracy of the reported values. The reader should consult the original sources for any information regarding the precision of the stability constant values. Although the number of directly measured stability constants for complexes of Bk(III) is rather small, a number of additional, reasonably accurate values for other complexes of Bk(III) can be obtained by interpolation of the stability constant data for the corresponding complexes of Am(III), Cm(III), and Cf(III).

Attempts to obtain thermodynamic data for solvent extraction of Bk(III) by thenoyltrifluoroacetone (TTA) in benzene and for complexation of Bk(III) by hydroxide and citrate ions were unsuccessful (Hubert *et al.*, 1976). The high extractibility and complexibility of the easily accessible tetravalent state of berkelium probably accounts for the difficulty encountered in this study. However, TTA was used successfully to determine the first hydrolysis constant (Désiré *et al.*, 1969; Hussonnois *et al.*, 1973) and citrate complexation constants (Aly and Latimer, 1970; Stepanov, 1971) of Bk(III).

Although no complexation constant values have been reported for Bk(IV), one study is worth noting (Makarova *et al.*, 1979). The electromigration behavior of Bk(IV), Ce(IV), and other actinide(IV) ions was studied in perchloric and nitric acid solutions and mixtures of these acids. In pure 6 M $HClO_4$ both Bk(IV) and Ce(IV) have equal mobilities of $(13.0 \pm 1.0) \times 10^{-5}$ cm^2 V^{-1} s^{-1} and behave as free hydrated ions. As HNO_3 is added to $HClO_4$ solution, keeping the total acid concentration constant at 6 M, the mobility of both ions decreases, with the Bk(IV) mobility decreasing more sharply and then remaining constant (4×10^{-5} cm^2 V^{-1} s^{-1}) between 3 and 6 M HNO_3 (Makarova *et al.*, 1979). The decreased mobility is attributed to changes in the charge of the berkelium species, possibly

Table 10.3 *Stability constants of Bk(III) complexes with various anions.*

Ligand	Conditions[a]	Stability constants[b]	References
fluoride ion, F^-	solv. extrn., 298 K, $\mu = 1.0$, pH = 2.72	$\beta_1 = 7.8 \times 10^2$	Choppin and Unrein (1976)
chloride ion, Cl^-	solv. extrn., 298 K, $\mu = 1.0$ pH = 2	$\beta_1 = 0.96$	Harmon et al. (1972a)
bromide ion, Br^-	solv. extrn., ca. 293 K, $\mu = 3.0$, pH = 0.82	$\beta_1 = 0.59$, $\beta_2 = 0.25$	Fukasawa et al. (1982)
	solv. extrn., ca. 293 K, $\mu = 3.0$, pH = 0.82	$\beta_1 = 0.15$, $\beta_2 = 0.29$	Fukasawa et al. (1982)
hydroxide ion, OH^-	solv. extrn., 293 K, $\mu = 0.1$	$\beta_1 = 2.2 \times 10^8$	Désiré et al. (1969), Hussonnois et al. (1973)
sulfate ion, SO_4^{2-}	solv. extrn., 298 K, calc. values for $\mu = 0$ (meas. $\mu \leq 0.5$)	$\beta_1 = 5.1 \times 10^3$, $\beta_2 = 3.9 \times 10^5$, $\beta_3 = 1.1 \times 10^5$	McDowell and Coleman (1972)
thiocyanate ion, SCN^-	solv. extrn., 298 K, $\mu = 5.0$	$\beta_1 = 7.21$	Kinard and Choppin (1974)
	$\mu = 1.0$, pH = 2	$\beta_1 = 3.11$, $\beta_2 = 0.31$, $\beta_3 = 2.34$	Harmon et al. (1972b)
oxalate ion, $C_2O_4^{2-}$	electromigrn. rates, 298 K, $\mu = 0.1$, pH ~ 1.8	$\beta_1 = 2.8 \times 10^5$, $\beta_2 = 1.4 \times 10^9$	Stepanov (1971)
acetate ion, CH_3COO^-	solv. extrn., 298 K, 2.0 M $NaClO_4$	$\beta_1 = 1.11 \times 10^2$	Choppin and Schneider (1970)
glycolate ion, $CH_2(OH)COO^-$	solv. extrn., 298 K, 2.0 M $NaClO_4$	$\beta_1 = 4.4 \times 10^2$, $\beta_2 = 5.0 \times 10^4$, $\beta_3 = 7.9 \times 10^5$ (est.)	Choppin and Degischer (1972)
lactate ion, $CH_3CH(OH)COO^-$	ion exch., $\mu = 0.5$		Stary (1966)
2-methyllactate ion, $(CH_3)_2C(OH)COO^-$	solv. extrn., 10^{-2} to 1 M	$\beta_1 = 6.39 \times 10^3$	Aly and Latimer (1970)
α-hydroxyisobutyrate ion, $CH_3CH_2CHOHCOO^-$	ion exch., $\mu = 0.5$	$\beta_3 = 4.0 \times 10^6$ (est.)	Stary (1966)

Table 10.3 (*Contd.*)

Ligand	*Conditions*[a]	*Stability constants*[b]	*References*
malate ion, $CH(OH)(COO)CH_2COO^{2-}$	solv. extrn., 10^{-2}–1 M	$\beta_1 = 1.07 \times 10^7$	Aly and Latimer (1970)
tartrate ion, $[CH(OH)COO]_2^{2-}$	solv. extrn., 10^{-2} to 1 M	$\beta_1 = 6.80 \times 10^5$	Aly and Latimer (1970)
citrate ion, $C(OH)(COO)(CH_2COO)_2^{3-}$	electromigrn. rates, 298K, $\mu = 0.1$	$\beta_1 = 7.8 \times 10^7$ $\beta_2 = 1.5 \times 10^{11}$	Stepanov (1971)
	solv. extrn., 10^{-2}–1 M	$\beta_1 = 3.00 \times 10^{11}$	Aly and Latimer (1970)
ethylenediamine-tetraacetate ion (EDTA) $C_2H_4N_2(CH_2COO)_4^{4-}$	ion exch., 298K, $\mu = 0.1$	$\beta_1 = 7.59 \times 10^{18}$	Fuger (1961)
trans-1,2-diaminecyclohexane-tetraacetate ion (DCTA) $C_6H_{10}N_2(CH_2COO)_4^{4-}$	ion exch., 298K, $\mu = 0.1$	$\beta_1 = 1.44 \times 10^{19}$	Baybarz (1966)
diethylenetriamine-pentaacetate ion (DTPA) $C_4H_8N_3(CH_2COO)_5^{5-}$	ion exch., 298K, $\mu = 0.1$	$\beta_1 = 6.2 \times 10^{22}$	Baybarz (1965)

[a] Solv. extrn. = solvent extraction; calc. = calculated; meas. = measured; electromigrn.= electromigration; exch.= exchange.
[b] Overall stability constants, e.g.

$$\beta_1 = \frac{\left[BkL^{(3-n)+}\right]}{\left[Bk^{3+}\right]\left[L^{n-}\right]}, \quad \beta_2 = \frac{\left[BkL_2^{(3-2n)+}\right]}{\left[Bk^{3+}\right]\left[L^{n-}\right]^2}, \text{ and } \beta_3 = \frac{\left[BkL_3^{(3-3n)+}\right]}{\left[Bk^{3+}\right]\left[L^{n-}\right]^3}.$$

forming $[Bk(H_2O)_x(NO_3)_3]^+$ between 3 and 6 M HNO_3. It was also reported that Bk(IV) does not form negatively charged species up to 10 M HNO_3. This study provides an explanation for the differences observed in the ion-exchange and solvent extraction behavior of Bk(IV) as compared to that of Ce(IV), Th(IV), Np(IV), and Pu(IV) (Makarova *et al.*, 1979).

The extraction of Bk(III) by organophosphorus acids has been studied, and activity coefficients for Bk(III) in nitric acid solution were estimated (Chudinov *et al.*, 1976). In addition a mechanism for the extraction of Bk(IV) by HDEHP from nitric acid solution was proposed. The self-diffusion coefficients (D) of Bk(III) ion in perchloric acid media were measured using the open-end capillary method (Latrous and Oliver, 1999). The limiting value, D_0, at zero ionic strength was reported to be $5.95 \times 10^{-6} \, cm^2 \, s^{-1}$. This value is in good agreement with $D_0 = 5.81 \times 10^{-6} \, cm^2 \, s^{-1}$, calculated by using a microscopic version of the Stokes–Einstein law (Mauerhofer *et al.*, 2003). Both reported values correlate well with experimentally determined values for neighboring trivalent actinide and analog lanthanide ions.

The kinetics of exchange of Bk(III) with $EuEDTA^-$ (EDTA = ethylenediaminetetraacetic acid) in aqueous acetate solutions of 0.1 M ionic strength has been studied (Williams and Choppin, 1974). The exchange was found to be first order with both acid-dependent and acid-independent rate terms. Rate values were calculated and compared to other actinide reaction rates.

The aqueous solubilities of Bk(III) oxalate and Bk(IV) iodate have been reported to be 1.5 and 10 mg L^{-1}, respectively (Erin *et al.*, 1977).

10.8.4 Redox behavior and potentials

Berkelium(III) in solution can be oxidized by strong oxidizing agents such as BrO_3^- (Knauer and Weaver, 1968; Weaver, 1968; Fardy and Weaver, 1969; Overman, 1971; Erin *et al.*, 1979b; Malikov *et al.*, 1980), AgO (Erin *et al.*, 1976), $Ag(I)S_2O_8^{2-}$ (Milyukova *et al.*, 1977, 1978, 1980), perxenate (Lebedev *et al.*, 1975), and ozone (Myasoedov *et al.*, 1973, 1974, 1975; Myasoedov, 1974).

Oxidation of green Bk(III) hydroxide as a suspension in 1 M NaOH to yellow Bk(IV) hydroxide was performed by bubbling ozone through the slurry (Cohen, 1976). In hydroxide solution, Bk(III) is unstable toward oxidation by radiolytically produced peroxide (Cohen, 1976). This 'self-oxidation' has also been observed in carbonate solutions (Baybarz *et al.*, 1972; Timofeev *et al.*, 1987; Hobart *et al.*, 1990; Morris *et al.*, 1990). Bk(III) can be stabilized in these solutions, however, by the presence of a reducing agent such as hydrazine hydrate (Cohen, 1976).

$BkCl_3$ is reported to be soluble in acetonitrile saturated with tetraethylammonium chloride (Nugent *et al.*, 1971). A colorless 7.6×10^{-4} M $BkCl_6^{3-}$ solution was formed that could be completely oxidized to red-orange $BkCl_6^{2-}$ by treatment with chlorine gas. The color of this Bk(IV) solution was quite similar to that observed for crystalline Cs_2BkCl_6 (Morss and Fuger, 1969).

Investigation of the amalgamation behavior of actinides in aqueous acetate and citrate solutions by treatment with sodium amalgam showed that berkelium and the lighter actinides do not readily form the amalgam. Those lanthanides that are known to exist only in the trivalent or the tetravalent state in solution also do not readily amalgamate. This behavior is in contrast to that of the heavier actinides californium, einsteinium, fermium, and mendelevium, and those lanthanides that exhibit stable divalent states, all of which readily amalgamate (Malý, 1967, 1969). This has been extensively studied as a basis for lanthanide/actinide and actinide/actinide separations and for determining redox reactions, kinetics, potentials, and other thermodynamic parameters (David *et al.*, 1990).

Bk(IV) is a strong oxidizing agent, comparable to Ce(IV) (Weaver and Stevenson, 1971). It can be coprecipitated with cerium iodate (Weaver, 1968) or zirconium phosphate (Cunningham, 1959). The stability of Bk(IV) solutions is a function of the degree of complexation of Bk(IV) by the solvent medium (Baybarz *et al.*, 1972). Bk(IV) is reduced by radiolytically generated peroxide in acidic and neutral solutions. The rate of reduction of Bk(IV) can be accelerated by the introduction of a reducing agent such as hydrogen peroxide (Peppard *et al.*, 1957; Kazakova *et al.*, 1975), hydroxylamine hydrochloride (Kazakova *et al.*, 1975), or ascorbic acid (Kazakova *et al.*, 1975).

Potentials of berkelium redox couples are summarized in Table 10.4. Replicate values for the Bk(IV)/Bk(III) couple under various conditions are in reasonable agreement with one another. The first estimate of the Bk(IV)/Bk(III) potential was made in 1950, only a short time after the discovery of the element. A value of 1.6 V was reported, based on tracer experiments (Thompson *et al.*, 1950a). Later, a refined value of (1.62 ± 0.01) V was reported for the couple, based on the results of experiments with microgram quantities of berkelium (Cunningham, 1959). The potential of the Bk(IV)/Bk(III) couple has subsequently been determined by several workers using direct potentiometry (Stokely *et al.*, 1969; Propst and Hyder, 1970; Nugent *et al.*, 1973b; Simakin *et al.*, 1977a; Kulyako *et al.*, 1981) or indirect methods (Musikas and Berger, 1967; Weaver and Fardy, 1969; Weaver and Stevenson, 1971). A recent, novel determination of the Bk(IV)/Bk(III) potential in $HClO_4$ solution, using *in situ* X-ray absorption spectroelectrochemistry, was reported to be (1.595 ± 0.005) V (Antonio *et al.*, 2002), in close agreement with some of the other values in perchloric acid solution listed in Table 10.4.

All of the above-mentioned determinations were performed in media of relatively low complexing capability. The potential of the Bk(IV)/Bk(III) couple is significantly shifted to less positive values in media containing anions that strongly complex Bk(IV). Values of 1.36 V (Stokely *et al.*, 1969; Kulyako *et al.*, 1981) and 1.12 V (Stokely *et al.*, 1972) have been reported for the couple in sulfuric and phosphoric acid solutions, respectively. Carbonate ions, apparently forming the strongest complex with Bk(IV) of the anions listed in Table 10.4, provide conditions for the least positive potential, 0.26 V (Stokely *et al.*, 1972), as compared to the potential of 1.6 V for the couple in non-complexing

Table 10.4 *Potentials of berkelium redox couples.*

Redox couple	Potential (V versus *NHE*)	Conditions[a]	References
Bk(IV)–Bk(III)	1.6 ± 0.2	calc.	Nugent *et al.* (1973b, 1976)
	1.664	calc.	Simakin *et al.* (1977b)
	1.54 ± 0.1	1 M HClO$_4$, dir. pot.	Stokely *et al.* (1972)
	1.597 ± 0.005	1 M HClO$_4$, dir. pot.	Simakin *et al.* (1977a)
	1.595 ± 0.005	1 M HClO$_4$, spectroelectro.	Antonio *et al.* (2002)
	1.735 ± 0.005	9 M HClO$_4$, dir. pot.	Simakin *et al.* (1977a)
	1.54 ± 0.1	1 M HNO$_3$, dir. pot.	Stokely *et al.* (1972)
	1.562 ± 0.005	1 M HNO$_3$, dir. pot.	Simakin *et al.* (1977a)
	1.56	6 M HNO$_3$, solv. extrn.	Musikas and Berger (1967)
	1.6	3–8 M HNO$_3$, coprecip.	Thompson *et al.* (1950a)
	1.543 ± 0.005	8 M HNO$_3$, dir. pot.	Simakin *et al.* (1977a)
	1.43	0.1 M H$_2$SO$_4$, dir. pot.	Propst and Hyder (1970)
	1.44	0.25 M H$_2$SO$_4$, solv. extrn.	Musikas and Berger (1967)
	1.38	0.5 M H$_2$SO$_4$, dir. pot.	Stokely *et al.* (1969)
	1.42	0.5 M H$_2$SO$_4$, solv. extrn.	Musikas and Berger (1967)
	1.37	1 M H$_2$SO$_4$, dir. pot.	Stokely *et al.* (1969), Kulyako *et al.* (1981)
	1.36	2 M H$_2$SO$_4$, dir. pot.	Stokely *et al.* (1969), Kulyako *et al.* (1981)
	1.12 ± 0.1	7.5 M H$_3$PO$_4$, dir. pot.	Stokely *et al.* (1972)
	0.85	0.006 M K$_{10}$P$_2$W$_{17}$O$_{61}$, pH = 0, dir. pot.	Baranov *et al.* (1981)
	0.65	0.006 M K$_{10}$P$_2$W$_{17}$O$_{61}$, pH > 4, dir. pot.	Baranov *et al.* (1981)
	0.24	1 M Na$_2$CO$_3$, dir. pot.	Timofeev *et al.* (1987)
	0.26 ± 0.1	2 M K$_2$CO$_3$, dir. pot.	Stokely *et al.* (1972)
Bk(III)–Bk(II)	−2.8 ± 0.2	calc.	Nugent *et al.* (1976)
	−2.75	calc.	Lebedev (1978)
Bk(III)–Bk(0)	−2.03 ± 0.05	calc.	Nugent (1975)
	−2.4	calc.	Krestov (1965)
	−1.99 ± 0.09	calc.	David *et al.* (1976)
	−2.18 ± 0.09	0.1 M LiCl, radiopol.	Samhoun and David (1976, 1979)
	−2.01 ± 0.03	calc.	Fuger *et al.* (1981)

[a] Calc. = calculated value; dir. pot. = direct potentiometry; spectroelectro. = spectroelectrochemistry; solv. extrn. = solvent extraction; coprecip. = coprecipitation; radiopol. = radiopolarography.

perchlorate solutions (Stokely *et al.*, 1972; Simakin *et al.*, 1977a). Other studies of the Bk(IV)/Bk(III) couple in complexing concentrated carbonate solutions also yielded potential values significantly shifted from those in non-complexing perchloric acid media (Timofeev *et al.*, 1987; Hobart *et al.*, 1990; Morris *et al.*, 1990). This behavior closely parallels that of the Ce(IV)/Ce(III) couple. In fact the
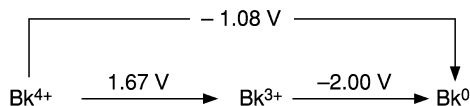
$$\text{Bk}^{4+} \xrightarrow{\;1.67\text{ V}\;} \text{Bk}^{3+} \xrightarrow{\;-2.00\text{ V}\;} \text{Bk}^{0}$$

with an overarching -1.08 V from Bk^{4+} to Bk^{0}.

Fig. 10.8 *Standard reduction potential diagram for berkelium ions in acid solution* (*Chapter* 19).

Bk(IV)/Bk(III) couple markedly resembles the Ce(IV)/Ce(III) couple in its redox chemistry.

The overall thermodynamic and electrochemical data support a value of (1.67 ± 0.07) V for the standard potential (E°) of the Bk(IV)/Bk(III) couple (Fuger and Oetting, 1976; Martinot and Fuger, 1985), which is 0.05 V less positive than the accepted value of (1.72 ± 0.02) V for the corresponding cerium couple (Morss, 1985), though within the stated uncertainties.

The potential of the Bk(III)/Bk(0) couple has been investigated using radio-polarography (Samhoun and David, 1976, 1979) and theoretical calculations (Krestov, 1965), as well as by correlation with data concerning enthalpy of formation (David *et al.*, 1976; Fuger *et al.*, 1981). Estimates of the potentials of berkelium redox couples have also been made from correlation plots of electron-transfer and f–d absorption band energies versus redox potential and by theoretical calculations (Nugent *et al.*, 1971, 1973b, 1976; Nugent, 1975). The overall data support a value of $-(2.00 \pm 0.02)$ V for the standard potential of the Bk(III)/Bk(0) couple.

Theoretical estimates of the potentials of the Bk(v)/Bk(0) and Bk(v)/Bk(IV) couples have been reported as 0.2 and 3.5 V, respectively (David *et al.*, 1976). These estimates suggest that Bk(v) would be very unstable in aqueous solution.
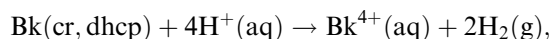
The scatter in the potential values of the Bk(III)/Bk(II) and Bk(III)/Bk(0) couples in Table 10.4 reflects the necessary requirement of making estimates of thermodynamic quantities that have not been directly determined. A standard reduction potential diagram for berkelium ions is shown in Fig. 10.8. Additional information on the redox behavior of berkelium can be found in reviews by Martinot (1978) and Martinot and Fuger (1985).

10.8.5 Thermodynamic properties

Values of thermodynamic properties for the formation of berkelium ions in solution, according to the reactions:

$$\text{Bk(cr, dhcp)} + 3\text{H}^{+}(\text{aq}) \rightarrow \text{Bk}^{3+}(\text{aq}) + 3/2\,\text{H}_2(\text{g})$$

and

$$\text{Bk(cr, dhcp)} + 4\text{H}^{+}(\text{aq}) \rightarrow \text{Bk}^{4+}(\text{aq}) + 2\text{H}_2(\text{g}),$$
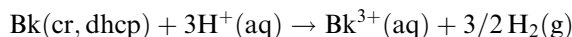
are summarized in Table 10.5. These values result from the evaluation of experimental measurements on the enthalpy of formation of $\text{Bk}^{3+}(\text{aq})$

Table 10.5 *Thermodynamic quantities for simple aqueous berkelium ions at 298 K.*[a]

Bk ion	$\Delta_f H^\circ$ (kJ mol^{-1})	$\Delta_f G^\circ$ (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
Bk^{3+}(aq)	$-(601 \pm 5)$	$-(578 \pm 7)$	$-(194 \pm 17)$
Bk^{4+}(aq)	$-(483 \pm 5)$	$-(417 \pm 7)$	$-(402 \pm 17)$

[a] Chapter 19.

(Fuger *et al.*, 1981), on the temperature dependence of the Bk(IV)/Bk(III) couple (Simakin *et al.*, 1977b), and on estimated entropies. These values are discussed in more detail in Chapter 19.

An electrostatic hydration model has been applied to the trivalent lanthanide and actinide ions in order to predict the standard Gibbs energy ($\Delta_{hydr}G_t^0$) and enthalpy ($\Delta_{hydr}H_t^0$) of hydration for these series. Assuming crystallographic and gas-phase radii for Bk(III) to be 0.096 and 0.1534 nm, respectively, and using 6.1 as the primary hydration number, $\Delta_{hydr}G_{298}^0$ was calculated to be -3357 kJ mol^{-1} and $\Delta_{hydr}H_{298}^0$ to be -3503 kJ mol^{-1} (Goldman and Morss, 1975). Later efforts to calculate semi-empirically entropy and enthalpy effects associated with hydration (David, 1986a,b), as well as an effort to intercorrelate non-complexed di-, tri-, and tetravalent actinide aquo ions based on crystallographic radii, have been published (David, 1986c). More recently the hydration enthalpy of Bk(III) has been derived by interpolation from data for the neighboring actinides attained by combining previously published thermodynamic and structural data with new data on high-symmetry elpasolites (Cs$_2$NaAnCl$_6$) using Born–Haber cycles (Schoebrechts *et al.*, 1989). The value obtained for Bk(III), $\Delta_{hydr}H_{298}^0 = -3501$ kJ mol^{-1}, is in excellent agreement with that calculated by Goldman and Morss (1975). A more comprehensive treatment of the thermodynamic properties of berkelium, including correlations of berkelium hydration enthalpies and Gibbs hydration energies with those of other actinides, can be found in Chapter 19.

Activity coefficients for Bk(III) in aqueous NaNO$_3$ solutions have been calculated from distribution data for the ion between the aqueous phase and a tertiary alkylamine organic phase (Chudinov and Pirozhkov, 1973). The activity coefficient values were reported as a function of the NaNO$_3$ concentration. Additional discussion of, and derived thermochemical properties for, a number of compounds of berkelium can be found in Chapter 19.

10.9 ANALYTICAL CHEMISTRY

The analytical determination of berkelium is dominated by radioanalytical methods, usually after separation from other radionuclides by procedures outlined in Section 10.4. ^{249}Bk, the most common isotope available, emits primarily (>99%) beta (β^-) particles up to a maximum energy of 125 keV. A proportional flow or liquid scintillation counter is used to measure this

radiation. The use of scintillators for this determination is complicated by the fact that most substances quench the weak scintillations induced by the beta particles; however, a detection limit of $\sim$0.1 Bq can be attained with an error of about 0.1% (Myasoedov, 1987). The beta decay of ^{249}Bk results in the ingrowth of daughter ^{249}Cf ($t_{1/2}$ = 351 years) at about 0.22% per day. This has been utilized for an analytical determination of the parent berkelium. After an initial Bk/Cf separation, the ingrowth decay product is measured over time (Propst and Hyder, 1970) to determine the original berkelium amount.

Methods other than radioanalytical techniques have been developed for berkelium determination. Coulometric determinations of berkelium utilizing the Bk(IV)/Bk(III) couple have been reported (Propst and Hyder, 1970; Timofeev *et al.*, 1986). A spectrophotometric titration method for determination of microgram amounts of berkelium has been proposed (Frolova *et al.*, 1986). Berkelium is electrolytically oxidized to Bk(IV) in nitric acid solution and titrated with H_2O_2 or $NaNO_2$ solution with the equivalence point determined by the disappearance of the high molar absorptivity peak of Bk(IV) at 350 nm. The error in the determination of >70 mg of Bk is reported to be 3–5% (Frolova *et al.*, 1986).

Mass spectrometric techniques that provide increased sensitivity for detection of lanthanides and other actinides in berkelium samples have been developed. In 0.1 µg of berkelium, californium can be determined at the 0.03% level with an error of 10–20% (Tikhomirov *et al.*, 1981). The ionization efficiency of ^{250}Bk has been investigated utilizing an on-line isotope separator, which may have valuable applications in analytical determinations (Asai *et al.*, 2002).

A sensitive neutron-activation method for Bk determination in mixtures of curium and californium has been developed (Ivanov *et al.*, 1979). Thermal neutron irradiation of ^{249}Bk produces ^{250}Bk ($t_{1/2}$ = 3.217 h) which emits intense gamma radiation at 989 keV that can be measured using a semiconductor detector. The absolute measurement error for Bk in a 2 µg sample was 1.8×10^{-4} %, and a detection limit for Bk of 4 pg was observed (Ivanov *et al.*, 1979).

The emission spectrum of berkelium over the range from 250 to 336 nm excited by an alternating current arc has been investigated in an effort to develop a semi-quantitative analysis method for berkelium in solutions containing large amounts of curium, cerium, and other elements. The reported detection limit for berkelium is 30 ng over the concentration range 1–100 µg of total metal per milliliter (Myasoedov, 1987).

10.10 CONCLUDING REMARKS

Berkelium is the first member of the second half of the actinide series of elements. Extended knowledge of the stability and accessibility of the various oxidation states of berkelium is important to the understanding and predictability

of its physicochemical behavior. In addition such information would enable more accurate extrapolations to the physicochemical behavior of the transberkelium elements for which experimental studies are severely limited by lack of material and/or by intense radioactivity.

Although berkelium oxidation states 0, III, and IV are known in bulk phase, further work is required to characterize more completely the solid-state and solution chemistries of this element. The synthesis of divalent berkelium in bulk should be possible via the metallothermic reduction of its trihalides, e.g.

$$Bk + 2BkBr_3 \rightarrow 3BkBr_2,$$
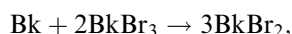
in an inert reaction vessel. It is quite possible that nature accomplishes this synthesis through alpha decay of the dihalides of ^{253}Es. A direct synthesis, however, would allow both absorption spectrophotometric and X-ray powder diffraction analyses, the results of which would aid in the identification of Bk(II) species in aged einsteinium dihalide samples that also contain Cf(II) (Peterson *et al.*, 1979; Young *et al.*, 1981).

Intermetallic compounds, various alloys, and additional semimetallic compounds of berkelium should be prepared and characterized to extend the knowledge of the physicochemical behavior of berkelium in these kinds of solids. Studies of such materials under pressure would be of interest in determining the effects of the non-berkelium component on physical properties such as bulk modulus (compressibility), pressure for the onset of 5f electron delocalization, and possible volume collapse associated with a change in the metallic valence of berkelium from three to four.

The range of oxidation states accessible to berkelium in solution should be further examined by using strong complexing agents in an effort to stabilize Bk(II), Bk(IV), and possibly Bk(V), produced chemically or electrochemically in nonaqueous or molten salt media. The complexation of Bk(III) with additional organic ligands should be studied to improve solvent extraction separation procedures. Also lacking to date, but experimentally obtainable, are stability constants of any complexes of Bk(IV). With an estimated potential of 3.5 V for the Bk(V)/Bk(IV) couple, it may be possible to prepare Bk(V) in a non-complexing molten salt solution.

In the intervening years since the 1986 publication of the second edition of this work, a surprisingly large number of berkelium research reports have been published. This is significant because berkelium is quite rare and its longest-lived isotope has a half-life of a little less than 1 year. This continued interest must be attributed, in part, to the extensive use of ^{249}Bk as a nuclear target for creating still heavier elements. New research on this fascinating element will continue to contribute to the knowledge of the physicochemical properties of berkelium and will aid in elucidating the intricacies of the structure of the atom and in extending the limits of the periodic table.

ACKNOWLEDGMENTS

REFERENCES

[NOTE: In citations to *Sov. Radiochem.* and *Radiochem.*, both of which are English translations of *Radiokhimiya*, the year given herein is that of the original publication in Russian. This date is the same or one year later in the English translation.]

Ahmad, I. (2002) *J. Nucl. Radiochem. Sci.*, **3**, 179–82.

Aly, H. F. and Latimer, R. M. (1970) *Radiochim. Acta*, **14**, 27–31.

Antonio, M. R., Williams, C. W., and Soderholm, L. (2002) *Radiochim. Acta*, **90**, 851–6.

Asai, M., Sakama, M., Tsukada, K., Ichikawa, S., Haba, H., Nishinaka, I., Nagame, Y., Goto, S., Akiyama, K., Toyoshima, A., Kojima, Y., Oura, Y., Nakahara, H., Shibata, M., and Kawade, K. (2002) *J. Nucl. Radiochem. Sci.*, **3**, 187–90.

Asai, M., Tsukada, K., Ichikawa, S., Sakama, M., Haba, H., Nagame, Y., Nishinaka, K., Akiyama, K., Toyoshima, A., Kaneko, T., Oura, Y., Kojima, Y., Shibata, M. (2003) *Eur. Phys. J. A*, **16**, 17–19.

Asprey, L. B. and Keenan, T. K. (1968) *Inorg. Nucl. Chem. Lett.*, **4**, 537–41.

Asprey, L. B. and Haire, R. G. (1973) *Inorg. Nucl. Chem. Lett.*, **9**, 1121–8.

Assefa, Z., Haire, R. G., and Stump, N. A. (1998) *J. Alloys Compds*, **271–273**, 854–8.

Audi, G. and Wapstra, A. H. (1995) *Nucl. Phys. A*, **595**, 409–80.

Baranov, A. A., Simakin, G. A., Kosyakov, V. N., Erin, E. A., Kopytov, V. V., Timofeev, G. A., and Rykov, A. G. (1981) *Sov. Radiochem.*, **23**, 104–6.

Baybarz, R. D. (1965) *J. Inorg. Nucl. Chem.*, **27**, 1831–9.

Baybarz, R. D. (1966) *J. Inorg. Nucl. Chem.*, **28**, 1055–61.

Baybarz, R. D. (1968) *J. Inorg. Nucl. Chem.*, **30**, 1769–73.

Baybarz, R. D., Stokely, J. R., and Peterson, J. R. (1972) *J. Inorg. Nucl. Chem.*, **34**, 739–46.

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

Baybarz, R. D., Knauer, J. B., and Orr, P. B. (1973) *Final Isolation and Purification of the Transplutonium Elements from the Twelve Campaigns Conducted at TRU During the Period August 1967–December 1971*, U.S. Atomic Energy Commission Document ORNL-4672, Oak Ridge National Laboratory.

Behera, B. R., Jena, S., Satpathy, M., Kailas, S., Mahata, K., Shrivastava, A., Chatterjee, A., Roy, S., Basu, P., Sharan, M. K., and Datta, S. K. (2001) *Phys. Rev. C*, **64**, 041602 (R)1–3.

Beitz, J. V., Carnall, W. T., Wester, D. W., and Williams, C. W. (1981) in *Actinides – 1981*, Pacific Grove, California, September 1981, Abstracts Volume (ed. N. M. Edelstein), U.S. Department of Energy Document LBL-12441, University of California, Lawrence Berkeley Laboratory, pp. 108–9.

Benedict, U., Peterson, J. R., Haire, R. G., and Dufour, C. (1984) *J. Phys. F: Met. Phys.*, **14**, L43–7.

Bigelow, J. E. (1974) in *Gmelin Handbuch der Anorganischen Chemie*, System No. 71, *Transurane*, New Suppl. Ser., vol. 7b, part A1, II, *The Elements*, Springer-Verlag, New York, pp. 326–36.

Bigelow, J. E., Corbett, B. L., King, L. J., McGuire, S. C., and Sims, T. M. (1981) in *Transplutonium Elements – Production and Recovery* (eds. J. D. Navratil and W. W. Schulz) (ACS Symp. Ser. 161), American Chemical Society, Washington, DC, pp. 3–18.

Bigelow, J. E. (1985) Oak Ridge National Laboratory, personal communication.

Boatner, L. A., Reynolds, R. W., Finch, C. B., and Abraham, M. M. (1972) *Phys. Lett. A*, **42**, 93–4.

Brewer, L. (1971a) *J. Opt. Soc. Am.*, **61**, 1101–11.

Brewer, L. (1971b) *J. Opt. Soc. Am.*, **61**, 1666–82.

Brito, H. F. and Liu, G. K. (2000) *J. Chem. Phys.*, **112**, 4334–41.

Britt, H. C. and Wilhelmy, J. B. (1979) *Nucl. Sci. Eng.*, **72**, 222–9.

Brüchle, W., Schädel, M., Scherer, U. W., Kratz, J. V., Gregorich, K. E., Lee, D., Nurmia, M., Chasteler, R. M., Hall, H. L., Henderson, R. A., and Hoffman, D. C. (1988) *Inorg. Chim. Acta*, **146**, 267–76.

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

Burns, J. H., Peterson, J. R., and Stevenson, J. N. (1975) *J. Inorg. Nucl. Chem.*, **37**, 743–9.

Campbell, D. O. (1981) in *Transplutonium Elements – Production and Recovery* (eds. J. D. Navratil and W. W. Schulz) (ACS Symp. Ser. 161), American Chemical Society, Washington, DC, pp. 189–201.

Carlson, T. A., Nestor, C. W. Jr, Malik, F. B., and Tucker, T. C. (1969) *Nucl. Phys. A*, **135**, 57–64.

Carlson, T. A. and Nestor, C. W. Jr (1977) *At. Data Nucl. Data Tables*, **19**, 153–73.

Carnall, W. T., Sjoblom, R. K., Barnes, R. F., and Fields, P. R. (1971) *Inorg. Nucl. Chem. Lett.*, **7**, 651–7.

Carnall, W. T., Fried, S., Wagner, F. Jr, Barnes, R. F., Sjoblom, R. K., and Fields, P. R. (1972) *Inorg. Nucl. Chem. Lett.*, **8**, 773–4.

Carnall, W. T. (1973) in *Gmelin Handbuch der Anorganischen Chemie*, System No. 71, *Transurane*, New Suppl. Ser., vol. 8, part A2, *The Elements*, Springer-Verlag, New York, pp. 35–80.

Carnall, W. T., Fried, S., and Wagner, F. Jr (1973) *J. Chem. Phys.*, **58**, 3614–24.

Carnall, W. T. and Fried, S. (1976) in *Proc. Symp. Commemorating the 25th Anniversary of Elements 97 and 98*, January 20, 1975, U.S. Energy Research and Development Administration Document LBL–4366, University of California, Lawrence Berkeley Laboratory, pp. 61–9.

Carnall, W. T., Crosswhite, H. M., Crosswhite, H., Hessler, J. P., Aderhold, C., Caird, J. A., Paszek, A., and Wagner, F. W. (1977) in *Proc. 2nd Int. Conf. on the Electronic Structure of the Actinides,* Wrocław, Poland, September 1976 (eds. J. Mulak, W. Suski, and R. Troć), Ossolineum, Wrocław, pp. 105–10.

Carnall, W. T., Beitz, J. V., and Crosswhite, H. (1984) *J. Chem. Phys.*, **80**, 2301–8.

Chen, M. H., Crasemann, B., Huang, K., Aoyagi, M., and Mark, H. (1977) *At. Data Nucl. Data Tables*, **19**, 97–151.

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

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

Choppin, G. R. and Unrein, P. J. (1976) in *Transplutonium Elements 1975* (eds. W. Müller and R. Lindner), *Proc. 4th Int. Transplutonium Element Symp.*, Baden-Baden, September 1975, North-Holland, Amsterdam, pp. 97–107.

Chudinov, E. G. and Pirozhkov, S. V. (1972) *J. Radioanal. Chem.*, **10**, 41–6.

Chudinov, E. G. and Pirozhkov, S. V. (1973) *Sov. Radiochem.*, **15**, 195–9.

Chudinov, E. G., Kosyakov, V. N., Shvetsov, I. K., and Vereshchaguin, Yu. I. (1976) in *Transplutonium 1975* (eds. W. Müller and R. Lindner), *Proc. 4th Int. Transplutonium Element Symp.*, Baden-Baden, September 1975, North-Holland, Amsterdam, pp. 49–56.

Cohen, D., Fried, S., Siegel, S., and Tani, B. (1968) *Inorg. Nucl. Chem. Lett.*, **4**, 257–60.

Cohen, D. (1976) *J. Inorg. Nucl. Chem.*, Suppl., 41–9.

Collins, E. D., Benker, D. E., Chattin, F. R., Orr, P. B., and Ross, R. G. (1981) in *Transplutonium Elements – Production and Recovery* (eds. J. D. Navratil and W. W. Schulz) (ACS Symp. Ser. 161), American Chemical Society, Washington, DC, pp. 147–60.

Conway, J. G. (1976) in *Proc. Symp. Commemorating the 25th Anniversary of Elements 97 and 98*, January 20, 1975, U.S. Energy Research and Development Administration Document LBL-4366, University of California, Lawrence Berkeley Laboratory, pp. 70–5.

Conway, J. G., Worden, E. F., Blaise, J., Camus, P., and Vergès, J. (1977) *Spectrochim. Acta*, **32B**, 101–6.

Cunningham, B. B. (1959) *J. Chem. Edn.*, **36**, 32–7.

Cunningham, B. B. (1963) in *Proc. Robert A. Welch Foundation Conf. on Chemical Research*, vol. VI, *Topics in Modern Inorganic Chemistry*, Houston, Texas, November 1962, (ed. W. O. Milligan), The Robert A. Welch Foundation, Houston, pp. 237–59.

Damien, D. A., Haire, R. G., and Peterson, J. R. (1979) *J. Physique*, **40** (C4), 95–100.

Damien, D., Haire, R. G., and Peterson, J. R. (1980) *J. Inorg. Nucl. Chem.*, **42**, 995–8.

Damien, D., Haire, R. G., and Peterson, J. R. (1981) Oak Ridge National Laboratory, unpublished results.

David, F., Samhoun, K., Guillaumont, R., and Nugent, L. J. (1976) in *Heavy Element Properties* (eds. W. Müller and H. Blank), *Proc. Joint Session, 4th Int. Transplutonium Element Symp. & 5th Int. Conf. on Plutonium and Other Actinides*, Baden-Baden, September 1975, North-Holland, Amsterdam, pp. 97–104.

David, F. (1986a) *J. Less Common Metals*, **121**, 27–42.

David, F. (1986b) *J. Chim. Phys.*, **83**, 393–401.

David, F. (1986c) in *Handbook on the Physics and Chemistry of the Actinides*, vol. 4 (eds. A. J. Freeman and C. Keller), North-Holland, Amsterdam, pp. 97–128.

David, F., Maslennikov, A. G., and Peretrukhin, V. P. (1990) *J. Radioanal. Nucl. Chem.*, **143**, 415–26.

Désiré, B., Hussonnois, M., and Guillaumont, R. (1969) *C. R. Acad. Sci. Paris C*, **269**, 448–51.

Dittner, P. F. and Bemis, C. E. Jr (1972) *Phys. Rev. A*, **5**, 481–4.

D'yachkova, R. A., Auérman, L. N., Mikheev, N. B., and Spitsyn, V. I. (1980) *Sov. Radiochem.*, **22**, 234–8.

Eichler, R., Brüchle, W., Dressler, R., Düllmann, Ch. E., Eichler, B., Gäggler, H. W., Gregorich, K. E., Hoffman, D. C., Hübener, S., Jost, D. T., Kirbach, U. W., Laue, C. A., Lavanchy, V. M., Nitsche, H., Patin, J. B., Piguet, D., Schädel, M., Shaughnessy, D. A., Strellis, D. A., Taut, S., Tobler, L., Tsyganov, Y. S., Türler, A. Vahle, A., Wilk, P. A., and Yakushev, A. B. (2000) *Nature*, **407**, 63–5.

Ensor, D. D., Peterson, J. R., Haire, R. G., and Young, J. P. (1981) *J. Inorg. Nucl. Chem.*, **43**, 1001–3.

Ensor, D. D. and Shah, A. H. (1984) *Solvent Extr. Ion Exch.*, **2**, 591–605.

Erdmann, N., Nunnemann, M., Eberhardt, K., Herrmann, G., Huber, G., Köhler, S., Kratz, J. V., Passler, G., Peterson, J. R., Trautmann, N., and Waldek, A. (1998) *J. Alloys Compds*, **271–273**, 837–40.

Erin, E. A., Kopytov, V. V., and Vityutnev, V. M. (1976) *Sov. Radiochem.*, **18**, 446–8.

Erin, E. A., Kopytov, V. V., Vasil'ev, V. Ya., and Vityutnev, V. M. (1977) *Sov. Radiochem.*, **19**, 380–2.

Erin, E. A., Vityutnev, V. M., Kopytov, V. V., and Vasil'ev, V. Ya. (1979a) *Sov. Radiochem.*, **21**, 85–8.

Erin, E. A., Vityutnev, V. M., Kopytov, V. V., and Vasil'ev, V. Ya. (1979b) *Sov. Radiochem.*, **21**, 487–9.

Fahey, J. A., Peterson, J. R., and Baybarz, R. D. (1972) *Inorg. Nucl. Chem. Lett.*, **8**, 101–7.

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

Fardy, J. J. and Weaver, B. (1969) *Anal. Chem.*, **41**, 1299–302.

Farrar, L. G., Cooper, J. H., and Moore, F. L. (1968) *Anal. Chem.*, **40**, 1602–4.

Fedoseev, E. V., Ivanova, L. A., Travnikov, S. S., Davidov, A. V., and Myasoedov, B. F. (1983) *Sov. Radiochem.*, **25**, 343–7.

Fellows, R. L., Young, J. P., and Haire, R. G. (1977) in *Physical–Chemical Studies of Transuranium Elements* (Progress Report April 1976–March 1977) (ed. J. R. Peterson), U.S. Energy Research and Development Administration Document ORO-4447-048, University of Tennessee, Knoxville, pp. 5–15.

Ferguson, D. E. and Bigelow, J. E. (1969) *Actinides Rev.*, **1**, 213–21.

Fields, P. R., Wybourne, B. G., and Carnall, W. T. (1964) *The Electronic Energy Levels of the Heavy Actinides* $Bk^{3+}(5f^8)$, $Cf^{3+}(5f^9)$, $Es^{3+}(5f^{10})$, and $Fm^{3+}(5f^{11})$, U.S. Atomic Energy Commission Document ANL-6911, Argonne National Laboratory.

Finch, C. B., Fellows, R. L., and Young, J. P. (1978) *J. Lumin.*, **16**, 109–15.

Firsova, L. A., Chuveleva, E. A., and Kharitonov, O. V. (1996) *Radiochemistry*, **38**, 407–9.

Firsova, L. A., Chuveleva, E. A., and Kharitonov, O. V. (1998a) *Radiochemistry*, **40**, 254–6.

Firsova, L. A., Chuveleva, E. A., and Kharitonov, O. V. (1998b) *Radiochemistry*, **40**, 257–61.

Fournier, J. M. (1976) *J. Phys. Chem. Solids*, **37**, 235–44.

Freeman, A. J. and Koelling, D. D. (1974) in *The Actinides: Electronic Structure and Related Properties,* vol. 1 (eds. A. J. Freeman and J. B. Darby Jr), Academic Press, New York, pp. 51–108.

Friedman, H. A. and Stokely, J. R. (1976) *Inorg. Nucl. Chem. Lett.*, **12**, 505–13.

Frolova, L. M., Vityutnev, V. M., Vasil'ev, V. Ya. (1986) *Sov. Radiochem.*, **28**, 349–53.

Fuger, J. (1961) *J. Inorg. Nucl. Chem.*, **18**, 263–9.

Fuger, J., Peterson, J. R., Stevenson, J. N., Noé, M., and Haire, R. G. (1975) *J. Inorg. Nucl. Chem.*, **37**, 1725–8.

Fuger, J. and Oetting, F. L. (1976) in *The Chemical Thermodynamics of Actinide Elements and Compounds,* part 2, *The Actinide Aqueous Ions.* (eds. V. Medvedev, M. H. Rand, E. F. Westrum Jr and F. L. Oetting), IAEA, Vienna, pp. 50–3.

Fuger, J., Haire, R. G., and Peterson, J. R. (1981) *J. Inorg. Nucl. Chem.*, **43**, 3209–12.

Fuger, J. (1982) in *Actinides in Perspective, Proc. Actinides – 1981*, Pacific Grove, California, September 1981 (ed. N. M. Edelstein), Pergamon Press, New York, pp. 409–31.

Fujita, D. K. (1969) *Some Magnetic, Spectroscopic, and Crystallographic Properties of Berkelium, Californium, and Einsteinium*, PhD Thesis, U.S. Atomic Energy Commission Document UCRL-19507, University of California, Lawrence Berkeley Radiation Laboratory.

Fukasawa, T., Kawasuji, I., Mitsugashira, T., Satô, A., and Suzuki, S. (1982) *Bull. Chem. Soc. Jpn.*, **55**, 726–9.

Gavron, A., Britt, H. C., Goldstone, P. D., Schoenmackers, R., Weber, J., and Wilhelmy, J. B. (1977) *Phys. Rev. C*, **15**, 2238–40.

Gibson, J. K. and Haire, R. G. (1985) *J. Less Common Metals*, **109**, 251–9.

Gibson, J. K. and Haire, R. G. (2001a) *Radiochim. Acta*, **89**, 363–9.

Gibson, J. K. and Haire, R. G. (2001b) *Radiochim. Acta*, **89**, 709–19.

Gobrecht, J., Zehnder, A., Kubik, P., Kettle, P.-R., Junker, K., Herlach, D., and Gaeggler, H. (1999) *Particles and Matter*, vol. 1, Paul Sherrer Institute Scientific Report INIS-CH-019.

Goldman, S. and Morss, L. R. (1975) *Can. J. Chem.*, **53**, 2695–700.

Gregorich, K. E., Henderson, R. A., Lee, D. M., Nurmia, M. J., Chasteler, R. M., Hall, H. L., Bennett, D. A., Gannet, C. M., Chadwick, R. B., Leyba, J. D., Hoffman, D. C., and Hermann, G. (1988) *Radiochim. Acta*, **43**, 223–31.

Guseva, L. I., Gregor'eva, S. I., and Tikhomirova, G. S. (1971) *Sov. Radiochem.*, **13**, 802–4.

Guseva, L. I. and Stepushkina, V. V. (1987) *Sov. Radiochem.*, **29**, 611–14.

Guseva, L. I., Tikhomirova, G. S., and Stepushkina, V. V. (1987) *Sov. Radiochem.*, **29**, 733–9.

Guseva, L. I., Tikhomirova, G. S., and Stepushkina, V. V. (1991) *Sov. Radiochem.*, **33**, 193–8.

Gutmacher, R. G., Hulet, E. K., Worden, E. F., and Conway, J. G. (1963) *J. Opt. Soc. Am.*, **53**, 506.

Gutmacher, R. G. (1964) *Atomic Spectroscopy of Berkelium* (Abstract), U.S. Atomic Energy Commission Document UCRL-12275-T, University of California, Lawrence Livermore Radiation Laboratory.

Gutmacher, R. G., Hulet, E. K., and Lougheed, R. (1965) *J. Opt. Soc. Am.*, **55**, 1029–30.

Gutmacher, R. G., Hulet, E. K., Lougheed, R., Conway, J. G., Carnall, W. T., Cohen, D., Keenan, T. K., and Baybarz, R. D. (1967) *J. Inorg. Nucl. Chem.*, **29**, 2341–5.

Gutmacher, R. G., Bodé, D. D., Lougheed, R. W., and Hulet, E. K. (1973) *J. Inorg. Nucl. Chem.*, **35**, 979–94.

Haire, R. G. (1973) in *Proc. 10th Rare Earth Research Conf.,* Carefree, AZ, April–May 1973, vol. II (eds. C. J. Kevane and T. Moeller), National Technical Information Service, U.S. Department of Commerce, Springfield, VA, pp. 882–91.

Haire, R. G. and Baybarz, R. D. (1973) *J. Inorg. Nucl. Chem.*, **35**, 489–96.

Haire, R. G. and Fahey, J. A. (1977) *J. Inorg. Nucl. Chem.*, **39**, 837–41.

Haire, R. G., Hellwege, H. E., Hobart, D. E., and Young, J. P. (1983) *J. Less Common Metals*, **93**, 358–9.

Haire, R. G., Peterson, J. R., Benedict, U., and Dufour, C. (1984) *J. Less Common Metals*, **102**, 119–26.

Haire, R. G., Benedict, U., Peterson, J. R., Dufour, C., and Dabos, S. (1986) *Physica*, **144B**, 19–22.

Haire, R. G., Assefa, Z., and Stump, N. (1998) *Mat. Res. Soc. Symp. Proc.*, **506**, 153–60.

Haire, R. G. and Raison, P. E. (2000) *AIP Conf. Proc.*, **532**, 173–4. (Plutonium Futures – The Science, Santa Fe, NM, July 10–13, 2000.)

Haire, R. G., Raison, P. E., and Assefa, Z. (2002) *J. Nucl. Sci. Technol.*, Suppl. 3, 616–19.

Harbour, R. M. (1972) *J. Inorg. Nucl. Chem.*, **34**, 2680–1.

Harmon, H. D., Peterson, J. R., and McDowell, W. J., (1972a) *Inorg. Nucl. Chem. Lett.*, **8**, 57–63.

Harmon, H. D., Peterson, J. R., McDowell, W. J., and Coleman, C. F. (1972b) *J. Inorg. Nucl. Chem.*, **34**, 1381–97.

Haug, H. O. and Baybarz, R. D. (1975) *Inorg. Nucl. Chem. Lett.*, **11**, 847–55.

Heathman, S. and Haire, R. G. (1998) *J. Alloys Compds*, **271–273**, 342–6.

Hendricks, M. E., Jones, E. R. Jr, Stone, J. A., and Karraker, D. G. (1974) *J. Chem. Phys.*, **60**, 2095–103.

Herbst, J. F., Watson, R. E., and Lindgren, I. (1976) *Phys. Rev. B*, **14**, 3265–72.

Hessler, J. P., Caird, J. A., Carnall, W. T., Crosswhite, H. M., Sjoblom, R. K., and Wagner, F. Jr (1978) in *The Rare Earths in Modern Science and Technology* (eds. G. J. McCarthy and J. J. Rhyne), Plenum, New York, pp. 507–12.

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

Hobart, D. E. and Peterson, J. R. (1986) in *The Chemistry of the Actinide Elements,* 2nd edn (eds. J. J. Katz, G. T. Seaborg, and L. R. Morss), Chapman & Hall, London, pp. 989–1024.

Hobart, D. E., Morris, D. E., Palmer, P. D., Haire, R. G., and Peterson, J. R. (1990) *Radiochim. Acta*, **49**, 119–24.

Hollander, J. M., Holtz, M. D., Novakov, T., and Graham, R. L. (1965) *Ark. Fys.*, **28**, 375–9.

Holley, C. E. Jr, Mulford, R. N. R., Ellinger, F. H., Koehler, W. C., and Zachariasen, W. H. (1955) *J. Phys. Chem.*, **59**, 1226–8.

Horwitz, E. P., Bloomquist, C. A. A., Henderson, D. J., and Nelson, D. E. (1969) *J. Inorg. Nucl. Chem.*, **31**, 3255–71.

Horwitz, E. P. and Bloomquist, C. A. A. (1973) *J. Inorg. Nucl. Chem.*, **35**, 271–84.

Huang, K., Aoyagi, M., Chen, M. H., Crasemann, B., and Mark, H. (1976) *At. Data Nucl. Data Tables*, **18**, 243–91.

Hübener, S., Taut, S., Vahle, A., Eichler, B., Trautmann, N., and Peterson, J. R. (2000) in *Annual Report 1999*, Laboratory for Radio- and Environmental Chemistry, University of Bern and Paul Scherrer Institute, Switzerland, p. 16.

Hubert, S., Hussonnois, M., Brillard, L., and Guillaumont, R. (1976) in *Transplutonium 1975* (eds. W. Müller and R. Lindner), *Proc. 4th Int. Transplutonium Element Symp.*, Baden-Baden, September 1975, North-Holland, Amsterdam, pp. 109–18.

Hussonnois, M., Hubert, S., Brillard, L., and Guillaumont, R. (1973) *Radiochem. Radioanal. Lett.*, **15**, 47–56.

Ionova, G. V., Spitsyn, V. I., and Mikheev, N. B. (1977) in *Proc. 2nd Int. Conf. on the Electronic Structure of the Actinides,* Wrocław, Poland, September 1976 (eds. J. Mulak, W. Suski, and R. Troć), Ossolineum, Wrocław, pp. 39–47.

Itié, J. P., Peterson, J. R., Haire, R. G., Dufour, C., and Benedict, U. (1985) *J. Phys. F: Met. Phys.*, **15**, L213–19.

Ivanov, O. I., Krainov, E. V., and Sviridov, A. F. (1979) *Sov. At. Energ.*, **45**, 924–6.

Jenkins, H. D. B. and Pratt, K. F. (1979) *Prog. Solid State Chem.*, **12**, 125–76.

Johansson, B. and Rosengren, A. (1975) *Phys. Rev. B*, **11**, 1367–73.

Johansson, B., Skriver, H. L., and Andersen, O. K. (1981) in *Physics of Solids Under High Pressure* (eds. J. S. Schilling and R. N. Shelton), North-Holland, Amsterdam, pp. 245–62.

Jullien, R., Galleani d'Agliano, E., and Coqblin, B. (1972) *Phys. Rev. B*, **6**, 2139–55.

Jursich, G. M., Beitz, J. V., Carnall, W. T., Goodman, G. L., Williams, C. W., and Morss, L. R. (1987) *Inorg. Chim. Acta*, **139**, 273–4.

Karalova, Z. K., Myasoedov, B. F., Rodionova, L. M., and Kuznetsov, V. S. (1983) *Sov. Radiochem*, **25**, 175–9.

Karraker, D. G. (1975) *J. Chem. Phys.*, **62**, 1444–6.

Kazakova, G. M., Kosyakov, V. N., and Erin, E. A. (1975) *Sov. Radiochem.*, **17**, 315–18.

Keenan, T. K. and Asprey, L. B. (1969) *Inorg. Chem.*, **8**, 235–8.

Keller, C. (1971) *The Chemistry of the Transuranium Elements,* Verlag Chemie, Weinheim, pp. 553–66.

Khopkar, P. K. and Mathur, J. N. (1980) *J. Radioanal. Chem.*, **60**, 131–40.

Kinard, W. F. and Choppin, G. R. (1974) *J. Inorg. Nucl. Chem.*, **36**, 1131–4.

King, L. J., Bigelow, J. E., and Collins, E. D. (1981) in *Transplutonium Elements – Production and Recovery* (eds. J. D. Navratil and W. W. Schulz) (ACS Symp. Ser. 161), American Chemical Society, Washington, DC, pp. 133–45.

Knauer, J. B. and Weaver, B. (1968) *Separation of Berkelium from Trivalent Actinides by Chromate Oxidation and HDEHP Extraction*, U.S. Atomic Energy Commission Document ORNL-TM-2428, Oak Ridge National Laboratory.

Knauer, J. B. Jr (2002) Oak Ridge National Laboratory, personal communication.

Kohler, S., Deissenberger, R., Eberhardt, K., Erdmann, N., Herrmann, G., Huber, G., Kratz, J. V., Nunnemann, M., Passler, G., Rao, P. M., Riegel, J., Trautmann, N., and Wendt, K. (1997) *Spectrochim. Acta Part B*, **52**, 717–26.

Kooi, J. and Boden, R. (1964) *Radiochim. Acta*, **3**, 226.

Kooi, J., Boden, R., and Wijkstra, J. (1964) *J. Inorg. Nucl. Chem.*, **26**, 2300–2.

Korkisch, J. (1966) *Oesterr. Chem. Ztg.*, **67**, 273–9.

Korpusov, G. V., Patrusheva, E. N., and Dolidze, M. S. (1975) *Sov. Radiochem.*, **17**, 230–6.

Kosyakov, V. N., Yakovlev, N. G., Kazakova, G. M., Erin, E. A., and Kopytov, V. V. (1977) *Sov. Radiochem.*, **19**, 397–400.

Kosyakov, V. N. and Yakovlev, N. G. (1983) *Sov. Radiochem.*, **25**, 172–5.

Kratz, J. V., Gober, M. K., Zimmerman, H. P., Schädel, M., Brüchle, W., Schimpf, E., Gregorich, K. E., Türler, A., Hannink, N. J., Czerwinski, K. R., Kadkhodayan, B., Lee, D. M., Nurmia, M. J., Hoffman, D. C., Gäggeler, H., Jost, D., Kovacs, J., Scherer, U. W., and Weber, A. (1992) *Phys. Rev. C*, **45**, 1064–9.

Krause, M. O., Haire, R. G., Keski-Rahkonen, O., and Peterson, J. R. (1988) *J. Electron. Spectrosc. Relat. Phenom.*, **47**, 215–26.

Kreek, S. A., Hall, H. L., Gregorich, K. E., Henderson, R. A., Leyba, J. D., Czerwinski, K. R., Kadkhodayan, B., Neu, M. P., Kacher, C. D., Hamilton, T. M., Lane, M. R., Sylwester, E. R., Türler, A., Lee, D. M., Nurmia, M. J., and Hoffman, D. C. (1994) *Phys. Rev. C,* **49**, 1859–66.

Krestov, G. A. (1965) *Sov. Radiochem.*, **7**, 69–77.

Krestov, G. A. (1966) *Sov. Radiochem.*, **8**, 200–3.

Kulyako, Yu. M., Frenkel, V. Ya., Lebedev, I. A., Trofimov, T. I., Myasoedov, B. F., and Mogilevskii, A. N. (1981) *Radiochim. Acta*, **28**, 119–22.

Latrous, H. and Oliver, J. (1999) *J. Mol. Liq.*, **81**, 115–21.

Laubereau, P. G. (1970) *Inorg. Nucl. Chem. Lett.*, **6**, 611–16.

Laubereau, P. G. and Burns, J. H. (1970) *Inorg. Chem.*, **9**, 1091–5.

Lebedev, I. A., Chepovoy, V. I., and Myasoedov, B. F. (1975) *Radiochem. Radioanal. Lett.*, **22**, 239–42.

Lebedev, I. A. (1978) *Sov. Radiochem.*, **20**, 556–62.

Liu, Y.-F., Luo, C., von Gunten, H. R., and Seaborg, G. T. (1981) *Inorg. Nucl. Chem. Lett.*, **17**, 257–9.

Liu, Y.-F., Luo, C., Moody, K. J., Lee, D., Seaborg, G. T., and von Gunten, H. R. (1983) *J. Radioanal. Chem.*, **76**, 119–24.

Liu, G. K., Carnall, W. T., Jursich, G., and Williams, C. W. (1994a) *J. Chem. Phys.*, **101**, 8277–89.

Liu, G. K., Jursich, G., Huang, J., Beitz, J. V., and Williams, C. W. (1994b) *J. Alloys Compds*, **213–214**, 207–11.

Lu, C. C., Malik, F. B., and Carlson, T. A. (1971) *Nucl. Phys. A*, **175**, 289–99.

Makarova, T. P., Fridkin, A. M., Kosyakov, V. N., and Erin, E. A. (1979) *J. Radioanal. Chem.*, **53**, 17–24.

Malikov, D. A., Almasova, E. V., Milyukova, M. S., and Myasoedov, B. F. (1980) *Radiochem. Radioanal. Lett.*, **44**, 297–305.

Malikov, D. A., Milyukova, M. S., Kuzovkina, E. V., and Myasoedov, B. F. (1983) *Sov. Radiochem.*, **25**, 293–6.

Malý, J. (1967) *Inorg. Nucl. Chem. Lett.*, **3**, 373–81.

Malý, J. (1969) *J. Inorg. Nucl. Chem.*, **31**, 1007–17.

Manson, S. T. and Kennedy, D. J. (1974) *At. Data Nucl. Data Tables*, **14**, 111–20.

Martinot, L. (1978) in *Encyclopedia of Electrochemistry of the Elements* (ed. A. J. Bard), Marcel Dekker, New York, ch. VIII-2, pp. 196–8.

Martinot, L. and Fuger, J. (1985) in *Standard Potentials in Aqueous Solution* (eds. A. J. Bard, R. Parsons, and J. Jordan), Marcel Dekker, New York, ch. 21, pp. 631–73.

Maruyama, T., Kaji, D., Kaneko, T., Goto, S., Tsukada, K., Haba, H., Asai, M., Ichikawa, S., Nagame, Y., and Kudo, H. (2002) *J. Nucl. Radiochem. Sci.*, **3**, 155–8.

Mathur, J. N. and Khopkar, P. K. (1982) *Sep. Sci. Technol.*, **17**, 985–1002.

Mauerhofer, E., Zhernosekov, K., and Rösch, F. (2003) *Radiochim. Acta*, **91**, 473–7.

McDowell, W. J. and Coleman, C. F. (1972) *J. Inorg. Nucl. Chem.*, **34**, 2837–50.

Merinis, J., Legoux, Y., and Bouissières, G. (1970) *Radiochem. Radioanal. Lett.*, **3**, 255–61.

Mikheev, N. B., D'yachkova, R. A., and Spitsyn, V. I. (1979) *Dokl. Chem.*, **244**, 18–20.

Milyukova, M. S., Malikov, D. A., and Myasoedov, B. F. (1977) *Radiochem. Radioanal. Lett.*, **29**, 93–101.

Milyukova, M. S. and Myasoedov, B. F. (1978) *Sov. Radiochem.*, **20**, 324–30.

Milyukova, M. S., Malikov, D. A., and Myasoedov, B. F. (1978) *Sov. Radiochem.*, **20**, 762–8.

Milyukova, M. S., Malikov, D. A., and Myasoedov, B. F. (1980) *Sov. Radiochem.*, **22**, 267–72.

Milyukova, M. S., Malikov, D. A., Kuzovkina, E. V., and Myasoedov, B. F. (1981) *Radiochem. Radioanal. Lett.*, **48**, 355–61.

Moore, F. L. (1966) *Anal. Chem.*, **38**, 1872–6.

Moore, F. L. (1967) *Anal. Chem.*, **39**, 1874–6.

Moore, F. L. and Jurriaanse, A. (1967) *Anal. Chem.*, **39**, 733–6.

Moore, F. L. (1969) *Anal. Chem.*, **41**, 1658–61.

Morris, D. E., Hobart, D. E., Palmer, P. D., Haire, R. G., and Peterson, J. R. (1990) *Radiochim. Acta*, **49**, 125–34.

Morris, D. E., Hobart, D. E., Palmer, P. D., Begun, G. M., Young, J. P., and Haire, R. G. (2005) *Structural characterization of berkelium and californium oxalates*, U.S. Department of Energy Document LA-UR-05-4597, University of California, Los Alamos National Laboratory.

Morss, L. R. and Fuger, J. (1969) *Inorg. Chem.*, **8**, 1433–9.

Morss, L. R., Siegal, M., Stenger, L., and Edelstein, N. (1970) *Inorg. Chem.*, **9**, 1771–5.

Morss, L. R. (1985) in *Standard Potentials in Aqueous Solution* (eds. A. J. Bard, R. Parsons, and J. Jordan), Marcel Dekker, New York, ch. 20, pp. 587–629.

Morss, L. R., Carnall, W. T., Williams, C. W., Fahey, J. A., Fuger, J., Meyer, G., and Irmler, M. (1991) *J. Less Common Metals*, **169**, 1–8.

Müller, W. (1967) *Actinides Rev.*, **1**, 71–119.

Musikas, C. and Berger, R. (1967) in *Lanthanide/Actinide Chemistry* (eds. P. R. Fields and T. Moeller) (ACS Adv. Chem. Ser. 71), American Chemical Society, Washington, DC, pp. 296–307.

Myasoedov, B. F., Barsukova, K. V., and Radionova, G. N. (1971) *Radiochem. Radioanal. Lett.*, **7**, 269–74.

Myasoedov, B. F., Chepovoy, V. I., and Lebedev, I. A. (1973) *Radiochem. Radioanal. Lett.*, **15**, 39–45.

Myasoedov, B. F. (1974) *Sov. Radiochem.*, **16**, 716–21.

Myasoedov, B. F., Guseva, L. I., Lebedev, I. A., Milyukova, M. S., and Chmutova, M. K. (1974) in *Analytical Chemistry of Transplutonium Elements* (ed. D. Slutzkin), John Wiley, New York, pp. 122–32.

Myasoedov, B. F., Chepovoy, V. I., and Lebedev, I. A. (1975) *Radiochem. Radioanal. Lett.*, **22**, 233–8.

Myasoedov, B. F. (1987) *Talanta*, **34**, 31–40.

Myasoedov, B. F. and Lebedev, I. A. (1991) *J. Radioanal. Nucl. Chem.*, **147**, 5–26.

Nave, S. E., Huray, P. G., and Haire, R. G. (1980) in *Crystalline Electric Field and Structural Effects in f-Electron Systems* (eds. J. E. Crow, R. P. Guertin, and T. W. Mihalisin), Plenum, New York, pp. 269–74.

Nave, S. E., Haire, R. G., and Huray, P. G. (1981) in *Actinides – 1981,* Pacific Grove, California, September 1981, Abstracts Volume (ed. N. M. Edelstein), U.S. Department of Energy Document LBL-12441, University of California, Lawrence Berkeley Laboratory, pp. 144–6.

Nave, S. E., Haire, R. G., and Huray, P. G. (1983) *Phys. Rev. B*, **28**, 2317–27.

Nugent, L. J., Burnett, J. L., Baybarz, R. D., Werner, G. K., Tanner, S. P., Tarrant, J. R., and Keller, O. L. Jr (1969) *J. Phys. Chem.*, **73**, 1540–9.

Nugent, L. J., Baybarz, R. D., Werner, G. K., and Friedman, H. A. (1970) *Chem. Phys. Lett.*, **7**, 179–82.

Nugent, L. J. and Vander Sluis, K. L. (1971) *J. Opt. Soc. Am.*, **61**, 1112–5.

Nugent, L. J., Baybarz, R. D., Burnett, J. L., and Ryan, J. L. (1971) *J. Inorg. Nucl. Chem.*, **33**, 2503–30.

Nugent, L. J., Burnett, J. L., and Morss, L. R. (1973a) *J. Chem. Thermodyn.*, **5**, 665–78.

Nugent, L. J., Baybarz, R. D., Burnett, J. L., and Ryan, J. L. (1973b) *J. Phys. Chem.*, **77**, 1528–39.

Nugent, L. J. (1975) *J. Inorg. Nucl. Chem.*, **37**, 1767–70.

Nugent, L. J., Baybarz, R. D., Burnett, J. L., and Ryan, J. L. (1976) *J. Inorg. Nucl. Chem.*, Suppl., 37–9.

Okamoto, H. (1999) *J. Phase Equilib.*, **20**, 351.

Overman, R. F. (1971) *Anal. Chem.*, **43**, 600–1.

Passler, G., Nunnemann, M., Huber, G., Deissenberger, R., Erdmann, N., Köhler, S., Kratz, J. V., Trautmann, N., Waldek, A., and Peterson, J. R. (1998) *AIP Conf. Proc.*, **454**, 183–8. (Resonance Ionization Spectroscopy, Manchester, UK, June 21–25, 1998)

Paulus, W., Kratz, J. V., Strub, E., Zauner, S., Brüchle, W., Pershina, V., Schädel, M., Schausten, B., Adams, J. L., Gregorich, K. E., Hoffman, D. C., Lane, M. R., Laue, C., Lee, D. M., McGrath, C. A., Shaughnessy, D. A., Strellis, D. A., and Sylwester, E. R. (1999) *Radiochim. Acta*, **84**, 69–77.

Payne, G. F. and Peterson, J. R. (1987) *Inorg. Chim. Acta*, **139**, 111–12.

Penneman, R. A., Ryan, R. R., and Rosenzweig, A. (1973) *Struct. Bond.*, **13**, 1–52.

Peppard, D. F., Moline, S. W., and Mason, G. W. (1957) *J. Inorg. Nucl. Chem.*, **4**, 344–8.

Peterson, J. R. (1967) *The Solution Absorption Spectrum of Bk^{3+} and the Crystallography of Berkelium Dioxide*, *Sesquioxide*, *Trichloride*, *Oxychloride*, *and Trifluoride*, PhD Thesis, U.S. Atomic Energy Commission Document UCRL-17875, University of California, Lawrence Berkeley Radiation Laboratory.

Peterson, J. R. and Cunningham, B. B. (1967a) *Inorg. Nucl. Chem. Lett.*, **3**, 327–36.

Peterson, J. R. and Cunningham, B. B. (1967b) *Inorg. Nucl. Chem. Lett.*, **3**, 579–83.

Peterson, J. R. and Cunningham, B. B. (1968a) *J. Inorg. Nucl. Chem.*, **30**, 823–8.

Peterson, J. R. and Cunningham, B. B. (1968b) *J. Inorg. Nucl. Chem.*, **30**, 1775–84.

Peterson, J. R., Fahey, J. A., and Baybarz, R. D. (1970) *Nucl. Metall.*, **17**, 20–34.

Peterson, J. R., Fahey, J. A., and Baybarz, R. D. (1971) *J. Inorg. Nucl. Chem.*, **33**, 3345–51.

Peterson, J. R. and Burns, J. H. (1973) *J. Inorg. Nucl. Chem.*, **35**, 1525–30.

Peterson, J. R. (1976) in *Gmelin Handbuch der Anorganischen Chemie,* New Suppl. Ser., vol. 31 (ed. G. Koch), Springer-Verlag, New York, pp. 72–6.

Peterson, J. R., Fellows, R. L., Young, J. P., and Haire, R. G. (1977a) in *Proc. 2nd Int. Conf. on the Electronic Structure of the Actinides,* Wrocław, Poland, September 1976 (eds. J. Mulak, W. Suski, and R. Troć), Ossolineum, Wrocław, pp. 111–16.

Peterson, J. R., Fellows, R. L., Young, J. P., and Haire, R. G. (1977b) *Rev. Chim. Minér.*, **14**, 172–7.

Peterson, J. R., Ensor, D. D., Fellows, R. L., Haire, R. G., and Young, J. P. (1979) *J. Physique*, **40**(C4), 111–13.

Peterson, J. R. (1980) in *Lanthanide and Actinide Chemistry and Spectroscopy* (ed. N. M. Edelstein) (ACS Symp. Ser. 131), American Chemical Society, Washington, DC, pp. 221–38.

Peterson, J. R., Young, J. P., Ensor, D. D., and Haire, R. G. (1981) in *Actinides – 1981,* Pacific Grove, California, September 1981, Abstracts Volume (ed. N. M. Edelstein), U.S. Department of Energy Document LBL-12441, University of California, Lawrence Berkeley Laboratory, pp. 118–20.

Peterson, J. R. and Hobart, D. E. (1984) in *Adv. Inorg. Chem. Radiochem.,* vol. 28 (eds. H. J. Emeléus and A. G. Sharpe), Academic Press, New York, pp. 29–72.

Peterson, J. R., Young, J. P., Ensor, D. D., and Haire, R. G. (1986) *Inorg. Chem.*, **25**, 3779–82.

Peterson, J. R., Haire, R. G., Benedict, U., and Young, J. P. (1987) *J. Less Common Metals*, **33**, 143–53.

Peterson, J. R., Young, J. P., Wilmarth, W. R., and Haire, R. G. (1990) *Appl. Spectrosc.*, **44**, 461–5.

Peterson, J. R. (1995) *J. Alloys Compds*, **223**, 180–4.

Popov, Yu. S. and Timofeev, G. A. (1999) *Radiochem.*, **41**, 26–30, and references therein.

Propst, R. C. and Hyder, M. L. (1970) *J. Inorg. Nucl. Chem.*, **32**, 2205–16.

Ronen, Y. (1998) *Ann. Nucl. Energy*, **25**, 983–5.

Samhoun, K. and David, F. (1976) in *Transplutonium Elements 1975* (eds. W. Müller and R. Lindner), *Proc. 4th Int. Transplutonium Element Symp.*, Baden-Baden, September 1975, North-Holland, Amsterdam, pp. 297–304.

Samhoun, K. and David, F. (1979) *J. Inorg. Nucl. Chem.*, **41**, 357–63.

Sarkisov, E. S. (1966) *Dokl. Akad. Nauk SSSR*, **166**, 627–30.

Scherer, U. W., Kratz, J. V., Schädel, M., Brüchle, W., Gregorich, K. E., Henderson, R. A., Lee, D., Nurmia, M., and Hoffman, D. C. (1988) *Inorg. Chim. Acta*, **146**, 249–54.

Schoebrechts, J.-P., Gens, R., Fuger, J., and Morss, L. R. (1989) *Thermochim. Acta*, **139**, 49–66.

Scofield, J. H. (1974) *At. Data Nucl. Data Tables*, **14**, 121–37.

Shafiev, A. I. and Efremov, Yu. V. (1972) *Sov. Radiochem.*, **14**, 754–6.

Shafiev, A. I., Efremov, Yu. V., and Yakovlev, G. N. (1974) *Sov. Radiochem.*, **16**, 31–4.

Shannon, R. D. and Prewitt, C. T. (1969) *Acta Crystallogr. B*, **25**, 925–46.

Shannon, R. D. (1976) *Acta Crystallogr. A*, **32**, 751–67.

Simakin, G. A., Kosyakov, V. N., Baranov, A. A., Erin, E. A., Kopytov, V. V., and Timofeev, G. A. (1977a) *Sov. Radiochem.*, **19**, 302–7.

Simakin, G. A., Baranov, A. A., Kosyakov, V. N., Timofeev, G. A., Erin, E. A., and Lebedev, I. A. (1977b) *Sov. Radiochem.*, **19**, 307–9.

Smentek, L., Wybourne, B. G., and Kobus, J. (2001) *J. Phys. B*, **34**, 1513–22.

Spirlet, J. C., Peterson, J. R., and Asprey, L. B. (1987) in *Advances in Inorganic Chemistry,* vol. 31 (eds. H. J. Emeléus and A. G. Sharpe), Academic Press, Orlando, FL, pp. 1–41.

Stary, J. (1966) *Talanta*, **13**, 421–37.

Stepanov, A. V. (1971) *Russ. J. Inorg. Chem.*, **16**, 1583–6.

Stevenson, J. N. and Peterson, J. R. (1979) *J. Less Common Metals*, **66**, 201–10.

Stokely, J. R., Baybarz, R. D., and Shults, W. D. (1969) *Inorg. Nucl. Chem. Lett.*, **5**, 877–84.

Stokely, J. R., Baybarz, R. D., and Peterson, J. R. (1972) *J. Inorg. Nucl. Chem.*, **34**, 392–3.

Sudakov, L. V., Erin, E. A., Kopytov, V. V., Baranov, A. Yu., Shimbarev, E. V., Vasil'ev, V. Ya., and Kapshukov, I. I. (1977) *Sov. Radiochem.*, **19**, 394–6.

Sugar, J. (1974) *J. Chem. Phys.*, **60**, 4103.

Sullivan, J. C., Schmidt, K. H., Morss, L. R., Pippin, C. G., and Williams, C. (1988) *Inorg. Chem.*, **27**, 598–9.

Taut, S., Hübener, S., Eichler, B., Türler, A., Gäggeler, H. W., Timokhin, S. N., and Zvara, I. (1998) *J. Alloys Compds*, **271–273**, 316–21.

Taut, S., Vahle, A., Hübener, S., Eichler, B., Jost, D., and Türler, A. (2000) in *Annual Report 1999,* Laboratory for Radio- and Environmental Chemistry, University of Bern and Paul Scherrer Institute, Switzerland, p. 17.

Thoma, R. E. (1962) *Inorg. Chem.*, **1**, 220–6.

Thompson, S. G., Cunningham, B. B., and Seaborg, G. T. (1950a) *J. Am. Chem. Soc.*, **72**, 2798–801.

Thompson, S. G., Ghiorso, A., and Seaborg, G. T. (1950b) *Phys. Rev.*, **77**, 838–9.

Thompson, S. G., Ghiorso, A., and Seaborg, G. T. (1950c) *Phys. Rev.*, **80**, 781–9.

Tikhomirov, V. V., Chetverikov, A. P., and Gabeskiriya, V. Ya. (1981) *Sov. Radiochem.*, **23**, 722–5.

Timofeev, G. A., Chistyakov, V. M., and Erin, E. A. (1986) *Sov. Radiochem.*, **28**, 454–8.

Timofeev, G. A., Chistyakov, V. M., Erin, E. A., and Baranov, A. A. (1987) *Sov. Radiochem.*, **29**, 147–51.

Turcotte, R. P., Chikalla, T. D., and Eyring, L. (1971) *J. Inorg. Nucl. Chem.*, **33**, 3749–63.

Turcotte, R. P., Chikalla, T. D., Haire, R. G., and Fahey, J. A. (1980) *J. Inorg. Nucl. Chem.*, **42**, 1729–33.

Ulstrup, J. (1966) *At. Energy Rev.*, **4**, 3–82.

Vander Sluis, K. L. and Nugent, L. J. (1972) *Phys. Rev. A*, **6**, 86–94.

Vander Sluis, K. L. and Nugent, L. J. (1974) *J. Opt. Soc. Am.*, **64**, 687–95.

Varga, L. P., Baybarz, R. D., Reisfeld, M. J., and Asprey, L. B. (1973a) *J. Inorg. Nucl. Chem.*, **35**, 2775–85.

Varga, L. P., Baybarz, R. D., Reisfeld, M. J., and Volz, W. B. (1973b) *J. Inorg. Nucl. Chem.*, **35**, 2787–94.

Varga, L. P., Baybarz, R. D., and Reisfeld, M. J. (1973c) *J. Inorg. Nucl. Chem.*, **35**, 4313–7.

Veal, B. W., Lam, D. J., Diamond, H., and Hoekstra, H. R. (1977) *Phys. Rev. B*, **15**, 2929–42.

Waldek, A., Erdmann, N., Grüning, C., Huber, G., Kunz, P., Kratz, J. V., Lassen, J., Passler, G., and Trautmann, N. (2001) *AIP Conf. Proc.*, **584**, 219–24. (Resonance Ionization Spectroscopy, Knoxville, TN, October 8–12, 2000.)

Ward, J. W. and Hill, H. H. (1976) in *Heavy Element Properties* (eds. W. Müller and H. Blank), *Proc. Joint Session, 4th Int. Transplutonium Element Symp. & 5th Int. Conf. on Plutonium and Other Actinides,* Baden-Baden, September 1975, North-Holland, Amsterdam, pp. 65–79.

Ward, J. W., Kleinschmidt, P. D., Haire, R. G., and Brown, D. (1980) in *Lanthanide and Actinide Chemistry and Spectroscopy* (ed. N. M. Edelstein) (ACS Symp. Ser. 131), American Chemical Society, Washington, DC, pp. 199–220.

Ward, J. W., Kleinschmidt, P. D., and Haire, R. G. (1982) *J. Chem. Phys.*, **77**, 1464–8.

Weaver, B. (1968) *Anal. Chem.*, **40**, 1894–6.

Weaver, B. and Fardy, J. J. (1969) *Inorg. Nucl. Chem. Lett.*, **5**, 145–6.

Weaver, B. and Stevenson, J. N. (1971) *J. Inorg. Nucl. Chem.*, **33**, 1877–81.

Wilk, P. A., Gregorich, K. E., Türler, A., Laue, C. A., Eichler, R., Ninov, V., Adams, J. L., Kirbach, U. W., Lane, M. R., Lee, D. M., Patin, J. B., Shaughnessy, D. A., Strellis, D. A., Nitsche, H., and Hoffman, D. C. (2000) *Phys. Rev. Lett.*, **85**, 2697–700.

Williams, K. R. and Choppin, G. R. (1974) *J. Inorg. Nucl. Chem.*, **36**, 1849–53.

Wilmarth, W. R. and Peterson, J. R. (1991) in *Handbook on the Physics and Chemistry of the Actinides,* vol. 6 (eds. A. J. Freeman and C. Keller), North-Holland, New York, pp. 1–38.

Worden, E. F., Hulet, E. K., Lougheed, R., and Conway, J. G. (1967) *J. Opt. Soc. Am.*, **57**, 550.

Worden, E. F., Gutmacher, R. G., Conway, J. G., and Mehlhorn, R. J. (1969) *J. Opt. Soc. Am.*, **59**, 1526.

Worden, E. F., Gutmacher, R. G., Lougheed, R. W., and Conway, J. G. (1970) *J. Opt. Soc. Am.*, **60**, 1555.

Worden, E. F. and Conway, J. G. (1978) *At. Data Nucl. Data Tables*, **22**, 329–66.

Yakovlev, N. G., Kosyakov, V. N., and Kazakova, G. M. (1982) *J. Radioanal. Chem.*, **75**, 113–20.

Yakovlev, N. G. and Kosyakov, V. N. (1983) *Sov. Radiochem.*, **25**, 687–92.

Yakushev, A., Eichler, B., Türler, A., Gäggeler, H. W., and Peterson, J. (2003) *Radiochim. Acta*, **91**, 123–6.

Young, J. P., Haire, R. G., Fellows, R. L., and Peterson, J. R. (1978) *J. Radioanal. Chem.*, **43**, 479–88.

Young, J. P., Haire, R. G., Peterson, J. R., Ensor, D. D., and Fellows, R. L. (1980) *Inorg. Chem.*, **19**, 2209–12.

Young, J. P., Haire, R. G., Peterson, J. R., Ensor, D. D., and Fellows, R. L. (1981) *Inorg. Chem.*, **20**, 3979–83.

Young, J. P., Haire, R. G., Peterson, J. R., and Ensor, D. D. (1984) in *Geochemical Behavior of Disposed Radioactive Waste* (eds. G. S. Barney, J. D. Navratil, and W. W. Schulz) (ACS Symp. Ser. 246), American Chemical Society, Washington, DC, pp. 335–46.

Zachariasen, W. H. (1973) *J. Inorg. Nucl. Chem.*, **35**, 3487–97.

Zvara, I. (1985) *Radiochim. Acta*, **38**, 95–101.