ADVANCES IN INORGANIC CHEMISTRY AND RADIOCHEMISTRY, VOL. 28

THE CHEMISTRY OF BERKELIUM

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I. Introduction

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

ISBN 0-12-023628-1

formed by the bombardment of ^{241}Am with accelerated α particles provided a new electron-capture activity eluting just ahead of curium (*1, 2*). This activity was assigned to an isotope (mass number 243) of element 97. The new element was named berkelium after Berkeley, California, 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), but 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 (*2, 3*).

Since 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) to provide macro amounts of berkelium (*4*). 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) (*4*). 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 absorption by Bk(III) 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 Bohr magnetons (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 (*5*). Four X-ray diffraction lines were obtained from 4 ng of BkO_2 and indexed on the basis of a face-centered cubic structure with $a_0 = 0.533 \pm 0.001$ nm.

II. Nuclear Properties, Availability, and Applications

Selected nuclear properties of the principal isotopes of berkelium are listed in Table I (*6*). In addition to these isotopes, ranging from mass numbers 240 to 251, there are spontaneously fissioning isomers known for berkelium mass numbers 242, 243, 244, and 245, all with half-lives of less than 1 μsec. Only ^{249}Bk is available in bulk quantities for chemical studies, as a result of prolonged neutron irradiation of Pu, Am, or Cm (*7*). About 0.66 g of this isotope has been isolated from

TABLE I

NUCLEAR PROPERTIES OF BERKELIUM ISOTOPES *(6)*

Mass number	Half-life	Decay mode[a]	Decay energy[b]	Ground-state spin, parity[c]	Representative production method
240	5.0 min	EC			^{232}Th(^{14}N,6n)
242	7.0 min	EC			^{235}U(^{11}B,4n)
243	4.5 hr	EC(99.85%) α(0.15%)	 6.758 g, 6.574	(3/2−)	^{241}Am(α,2n)
244	4.35 hr	EC(99+%) α(0.006%)	 6.667, 6.625		^{243}Am(α,3n)
245	4.90 days	EC(99.88%) α(0.12%)	 6.349 g, 6.145	3/2−	^{243}Am(α,2n)
246	1.80 days	EC		(2−)	^{244}Cm(α,pn)
247	1380 years	α	5.794 g, 5.531	(3/2−)	^{244}Cm(α,p) $^{247}\mathrm{Cf}\xrightarrow{EC}$
248	23.5 hr	β (70%) EC(30%)	0.65 g	(1−)	^{247}Bk(n,γ)
248	>9 years >1 × 10^4 years (β)			(6+)	^{246}Cm(α,pn)
249	325 days 1.87 × 10^9 years (SF)	β (99+%) α(0.00145%)	0.125 g 5.437 g, 5.417	7/2+	$^{248}\mathrm{Cm}(n,\gamma)\xrightarrow{\beta^-}$
250	3.22 hr	β	1.76 g, 0.725	2−	^{249}Bk(n,γ) $^{254}\mathrm{Es}\xrightarrow{\alpha}$
251	55.6 min	β	~1.0, ~0.5	(3/2−)	$^{255}\mathrm{Es}\xrightarrow{\alpha}$

[a] EC, Electron capture; $\alpha = {}_2^4\mathrm{He}^{2+}$; $\beta^- = {}_1^0e^1$; percentage of decays via particular mode given in parentheses.

[b] Energy in MeV of ground state (g) and most intense transitions.

[c] Values in parentheses are tentative.

target rods irradiated with neutrons in the High Flux Isotope Reactor (Oak Ridge, Tennessee) over the period 1967 through 1983 (*8–10*). The relative atomic mass of berkelium-249 is given as 249.075 by the International Union of Pure and Applied Chemistry (IUPAC) (*11*).

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 (0.2% 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 (*12, 13*).

There have been no reports of practical applications for any of the isotopes of berkelium.

III. Separation and Purification

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

Since berkelium can be readily oxidized to Bk(IV), it can be separated from other, nonoxidizable 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 (*14*). The resultant Bk(IV) was then extracted with hydrogen di(2-ethylhexyl)orthophosphoric 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 (*15–19*), the use of CrO_4^{2-} (*16, 20*), $Cr_2O_7^{2-}$ (*20–22*), Ag(I)–$S_2O_8^{2-}$ (*20, 23*), PbO_2 (*21, 24, 25*), BiO_3^- (*21*), O_3 (*24*), and photochemical oxidation (*24*) has also been reported. Separation of the oxidized berkelium has been accomplished by the use of (1) liquid–liquid extraction with HDEHP (*14, 16, 19, 26*), trioctylphosphine oxide (*27*), alkylpyrocatechol (*28*), 2-thenoyltrifluoroacetone (*22*), primary, tertiary, or quaternary amines (*20, 23, 29–31*), or tributyl phosphate (*32, 33*); (2) extraction chromatography with HDEHP (*18, 34–36*), zirconium phosphate adsorbant (*21, 24, 25*); (3) precipitation of the iodate (*15, 17*); or (4) ion exchange (*18, 37, 38*), 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. Since berkelium and cerium exhibit nearly identical redox behavior, most redox separation procedures include a Bk–Ce separation step (*21, 27, 37–41*). Separation of Bk(III) from Ce(III) and other trivalent lanthanide and actinide elements can also be accomplished without the use of redox procedures (*37, 39–47*).

Personnel in the Transuranium Processing Plant (TRU) at the Oak Ridge National Laboratory have isolated and purified 0.66 g of ^{249}Bk during the period 1967 through 1983 (*9, 10*), using the procedure outlined in Fig. 1 (*48*). 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 (BUT) solution. The berkelium fraction is oxidized and extracted into HDEHP–dodecane from HNO_3–$NaBrO_3$ solution. The organic fraction

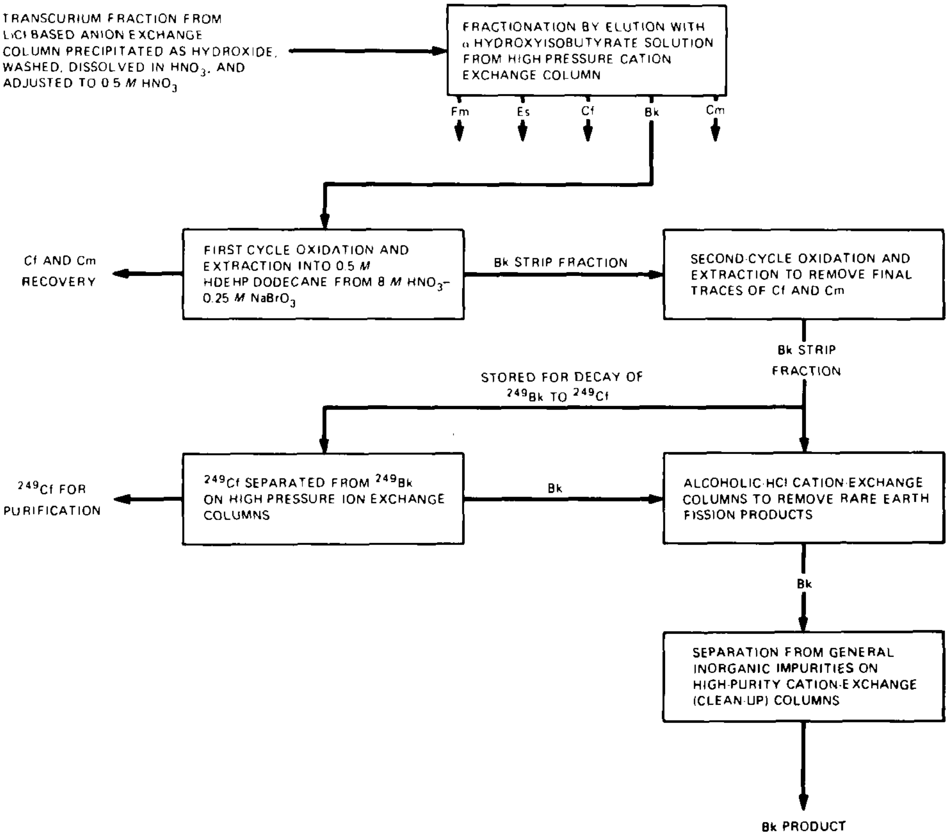

FIG. 1. Schematic diagram of procedures used in the final isolation and purification of berkelium in the Transuranium Processing Plant (TRU) at the Oak Ridge National Laboratory (ORNL). Adapted from (*48*).

containing Bk(IV) is treated with 2,5-di-*tert*-butylhydroquinone (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 and another reduction–back-extraction cycle are carried out. The solution at this point is radiochemically pure except for 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 (*48*).

An innovative procedure for the rapid separation of berkelium from other actinides, lanthanides, and fission products has been reported

(*49*). Expediency was required in order to measure the decay properties of short-lived isotopes. Berkelium and cerium were first separated from the other elements via solvent extraction of Bk(IV) and Ce(IV), using HDEHP in the usual way. Then the two-element mixture [as Bk(III) and Ce(III)] was separated in the heated cation-exchange column of a high-pressure liquid chromatograph (HPLC), using α-hydroxyisobutyrate as the eluant. The total separation time for berkelium from the initial complex mixture was about 8 min, half of the time being required for the operation of the HPLC column (*49*). Procedures for fast separations of berkelium from beryllium foil targets and gold catcher foils resulting from nuclear bombardment reactions have also been published (*50*).

For additional discussion of berkelium separation procedures, the reader is referred to several reviews and comprehensive texts on the subject (*51–58*).

IV. Atomic Properties

A. ELECTRONIC ENERGIES

The ionization potential of neutral berkelium ($5f^97s^2$) has been derived from spectroscopic data to be 6.229 ± 0.025 eV (*59*). The changes in entropy associated with the stepwise ionization of gaseous berkelium atoms have also been calculated (*60*). The energy interval between the ground ($^7H_8$) and first excited level ($^5H_7$) of singly ionized berkelium was determined to be 1.48752×10^5 m^{-1} from measurements on plates taken with a high-resolution emission spectrograph (*61*). Several authors have calculated the energies of, and energy intervals between, the lowest-lying levels of the various electronic configurations of neutral berkelium (*62–65*) and of singly, doubly, and triply ionized berkelium (*65, 66*).

From measurements of the energies of a number of internal conversion lines in berkelium-249 (produced by the α decay of einsteinium-253), the atomic electron binding energies in berkelium were calculated for the K through O shells (*67*). The K-series X-ray energies and intensities of berkelium were later measured, and the K-shell electron binding energy calculated (*68*). The measured energies and relative transition probabilities agreed well with theoretical predictions (*69, 70*). A crystal spectrometer has been used to measure precisely the berkelium K-series X-ray energies, natural line widths, and relative intensities (*71*).

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 (*72*), relativistic relaxed-orbital Hartree–Fock–Slater calculations of the neutral-atom electron binding energies in berkelium (*73*), refined K- and L-shell electron binding energies for berkelium (*74*), calculations and compilations of the electron binding energies in berkelium (*75, 76*), and single-zeta, double-zeta, and extended (triple-zeta-valence) Slater-type basis sets for berkelium in the $5f^86d7s^2$ configuration (*77*).

Relativistic Hartree–Slater values of the X-ray emission rates for the filling of K- and L-shell vacancies in berkelium have been tabulated (*78*). 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 wavefunctions (*79*).

B. EMISSION SPECTRA

Twenty emission lines, produced from 0.2 μg of berkelium in a high-voltage spark, were reported in 1965 (*80*). 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 (*81*). Many of the emission lines exhibited well-resolved eight-component hyperfine structure, which established the nuclear spin of ^{249}Bk to be 7/2 (*81*). 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 $5f^97s^2$ ($^6H_{15/2}$) and $5f^97s^1$ ($^7H_8$), respectively (*82*). A nuclear magnetic dipole moment of 1.5 nuclear magnetons (*61*) and a quadrupole moment of 4.7 barns (*83*) were determined for ^{249}Bk, based on analysis of the hyperfine structure in the berkelium emission spectrum.

The wave numbers, wavelengths, and relative intensities of 1930 of the stronger emission lines from ^{249}Bk in the 254- to 980-nm wavelength region are available (*84*). The infrared emission spectrum of ^{249}Bk from 830 to 2700 nm has been recorded (*85*). An interpretation of 8 levels in the Bk(I) spectrum ($5f^97s^2$, neutral Bk) and 10 levels in the Bk(II) spectrum ($5f^97s$, Bk^+) has been made on the basis of a generalized parametric study of the $5f^N$ and $5f^N7s$ electron configurations of the actinides (*86*).

A preliminary report on the self-luminescence of ^{249}Bk(III) in a $LaCl_3$ host lattice was published in 1963 (*87*), and the self-luminescence spectra of ^{249}Bk-doped BaF_2 and $SrCl_2$ were reported in 1978 (*88*). The absence of ultraviolet-excited sharp-line sensitized luminescence of ^{249}Bk-doped gadolinium hexafluoroacetylacetonate has been noted (*89, 90*). Such luminescence was absent also in cesium berkelium hexafluoroacetylacetonate chelate in anhydrous ethanol (*89*). 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 has been established (*91*).

C. SOLUTION ABSORPTION SPECTRA

The first attempts to measure the absorption spectrum of Bk(III) involved the use of a single ion-exchange resin bead (*4*). Later the spectrum of a 3.6×10^{-3} *M* Bk(III) solution was recorded in a microcell (*92*). 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 (*93*). The results of additional observations identified a total of 23 absorption bands in the 280- to 1500-nm wavelength region (*94*).

The first attempts to record the Bk(IV) solution absorption spectrum were hindered by the presence of cerium impurities (*92*). 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), in agreement with the actinide hypothesis.

In later work, the absorption spectra of Bk(III) and Bk(IV) were recorded in various media (*95*). New absorption bands were reported as the result of using larger quantities of berkelium-249 of higher purity than had been previously available. Observations of the spectrum of Bk(III) were extended further into the ultraviolet wavelength region (to 200 nm), and nine new absorption bands were reported (*96*). Later the absorption spectra of Bk(III) and Bk(IV) in 2 *M* perchloric and 0.5 *M* nitric acid solutions have been obtained (*97*). An interpretation of the low-energy bands in the solution absorption spectra of Bk(III) and Bk(IV) has been published (*98*).

Solution absorption spectra of Bk(III) and Bk(IV) are shown in Figs. 2 and 3, respectively. The spectrum of Bk(III) is characterized by sharp absorption bands of low molar absorptivity attributed to "Laporte-forbidden" f–f transitions and by intense absorption bands in the ultraviolet region, which are attributed to f–d transitions (*96*). The spectrum of Bk(IV) is 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 band is attributed to a charge-transfer mechanism (*96*).

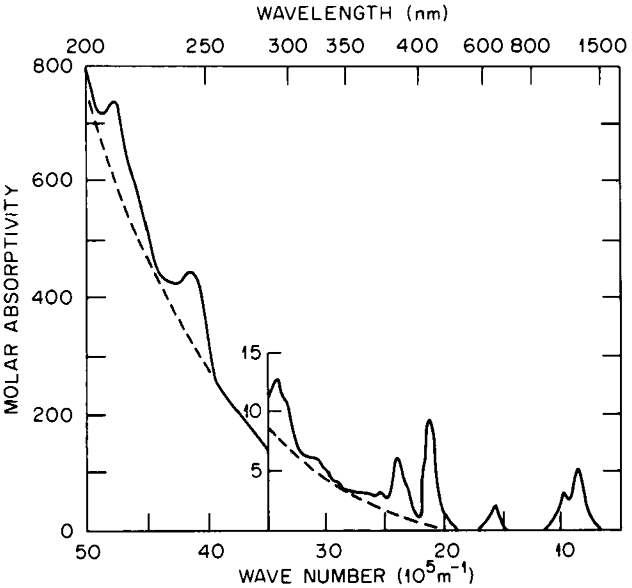

FIG. 2. Solution absorption spectrum of Bk(III) in 1 *M* $DClO_4$–99.9% D_2O. Reprinted with permission from the *J. Inorg. Nucl. Chem.* **34**, R. D. Baybarz, J. R. Stokely, and J. R. Peterson, 1972, Pergamon Press, Ltd. (*95*).

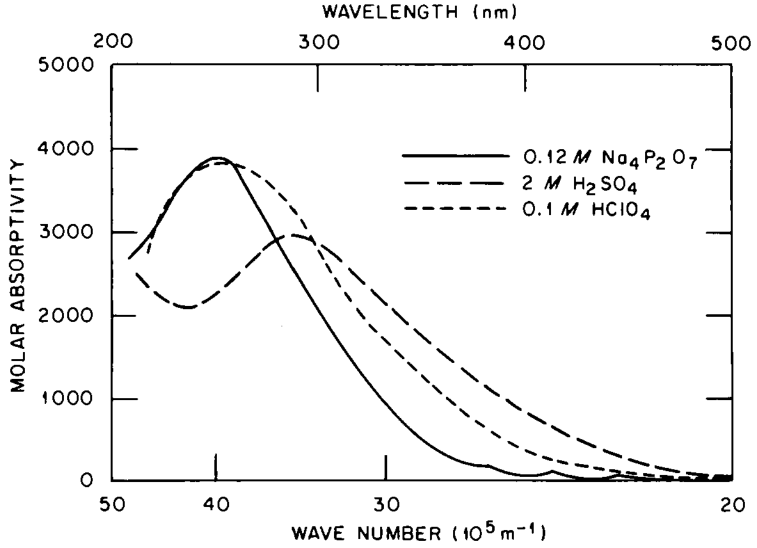

FIG. 3. Solution absorption spectra of Bk(IV) in various aqueous media. Reprinted with permission from the *J. Inorg. Nucl. Chem.* **35**, R. G. Gutmacher, D. D. Bodé, R. W. Lougheed, and E. K. Hulet, 1973, Pergamon Press, Ltd. (*96*).

Electronic spectra of Bk(III) (*99*) and Bk(IV) (*100*) and a prediction of the electronic spectrum of Bk(II) (*101*) have been published. Spin-orbit coupling diagrams for these berkelium ions, based on a free-ion interpretation of the f–f spectra, were proposed.

D. SOLID STATE ABSORPTION AND RAMAN SPECTRA

The absorption spectrum of Bk(III) in a lanthanum chloride host matrix at 77 K was first obtained in 1964 (*102*). A prediction of the energy level structure of Bk(III) was made by others the same year (*103*). Extensive, low-temperature spectroscopic studies of $BkCl_3$ showed the absence of transitions to excited $J = 0$ and $J = 1$ states (*104, 105*). This provided good evidence for a $\mu = 0$ ground level for Bk(III), consistent with that of Tb(III)–$LaCl_3$ (*106*). Experimental and theoretical studies of the crystal field parameters of Bk(III) in a $LaCl_3$ host lattice have also been reported (*107*).

Microscale spectrophotometric techniques, using 0.5–10 μg-sized berkelium samples, have been applied for identification and characterization of berkelium halides and oxyhalides (*108*). Spectra of orthorhombic and monoclinic $BkBr_3$, trigonal and orthorhombic BkF_3 (*13*), and monoclinic BkF_4 (*13*) are shown in Figs. 4–6, respectively. The coordination number of Bk(III) in the $PuBr_3$-type orthorhombic modification of $BkBr_3$ is eight, whereas it is six in the $AlCl_3$-type monoclinic form. The two spectra are readily distinguished by their differing fine structure and relative peak intensities. The more intense f–f transitions in orthorhombic $BkBr_3$ are expected because of the lower coordination site symmetry of Bk(III) in this form compared to that of Bk(III) in the monoclinic form of $BkBr_3$. This difference in absorption intensities was exploited in a study of the solid state transformation between the two forms of $BkBr_3$ (*109*).

The spectra of dimorphic BkF_3 (see Fig. 5) indicate the sensitivity of solid state absorption spectrophotometric analysis, since both crystallographic modifications exhibit a coordination number of nine for Bk(III). Small but reproducible changes are apparent in the relative absorbance and fine structure of the bands at 440, 475, 625, and 1050 nm. The less centrosymmetric, orthorhombic BkF_3 exhibits f–f transition intensities greater than those exhibited by the more centrosymmetric, trigonal BkF_3 (*13*). The absorption spectrum of BkF_4 (see Fig. 6) is characterized by four sharp peaks between 415 and 455 nm and major absorption bands at 562 and 592–617 nm (*13*). This solid-state spectrum is similar to, but exhibits better resolution than, the solution absorption spectrum of Bk(IV) in phosphate medium (*95*).

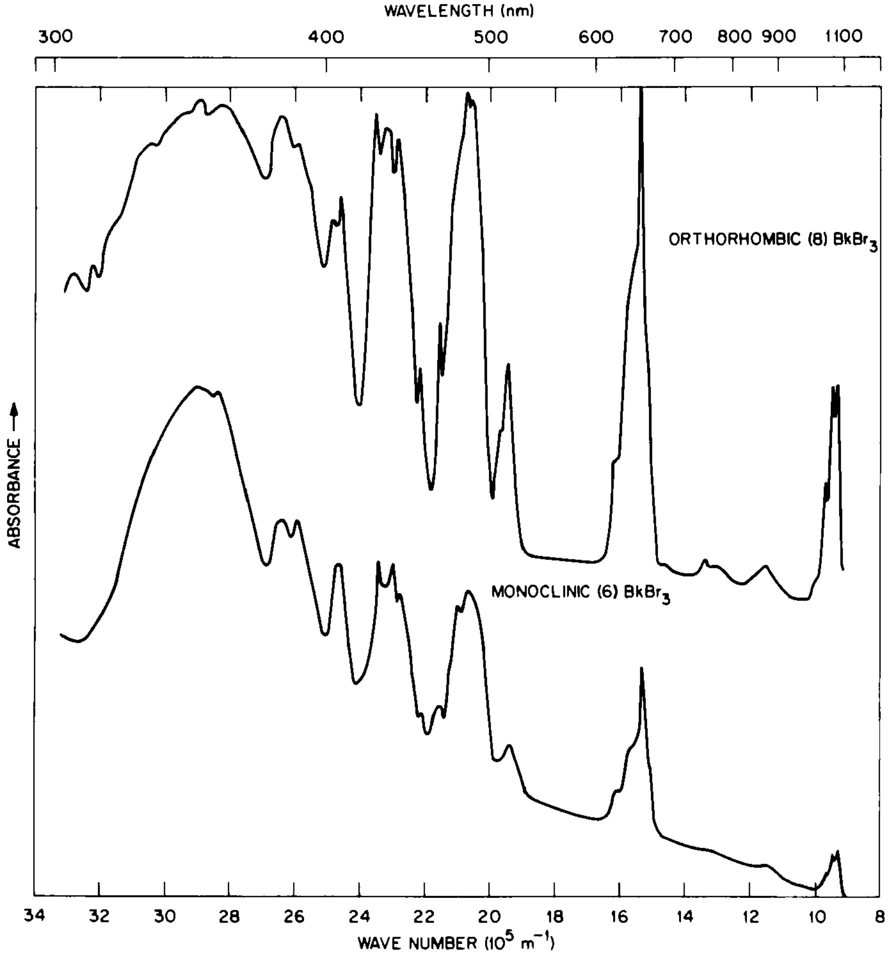

FIG. 4. Solid state absorption spectra of $BkBr_3$ in its orthorhombic and monoclinic modifications at room temperature.

This absorption spectrophotometric technique has also been applied to the study of the chemical consequences of radioactive decay in bulk-phase solid state samples (*12, 110–112*). It was found that the ^{249}Cf daughters growing into crystalline $^{249}BkBr_3$ and $^{249}BkCl_3$ exhibited the same oxidation state and crystal structure as their respective berkelium parents (*12, 112*).

The absorption spectra of Bk(III) and Bk(IV) hydroxides as suspensions in 1 *M* NaOH have been reported (*113*). The solid state absorp-

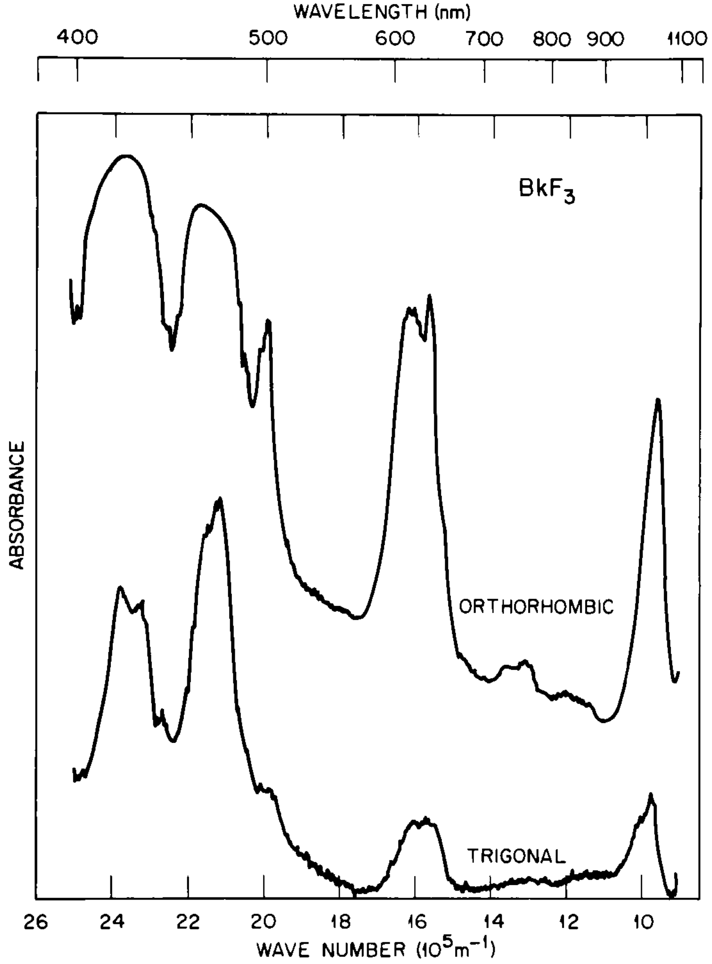

FIG. 5. Solid-state absorption spectra of BkF_3 in its orthorhombic and trigonal forms at room temperature. Reprinted with permission from the *J. Inorg. Nucl. Chem.* **43**, D. D. Ensor, J. R. Peterson, R. G. Haire, and J. P. Young, 1981, Pergamon Press, Ltd. (*13*).

tion (*111*) and Raman (*115*) spectra of berkelium(III) orthophosphate have been obtained. It was found that $BkPO_4$ fluoresced strongly when excited by the 514.5-nm emission of an argon-ion laser. By lowering the laser intensity below the fluorescence threshold, it was possible to obtain the Raman spectrum, the bands of which were assigned by direct analogy to those of the monazite-type monoclinic lanthanide orthophosphates (*115*).

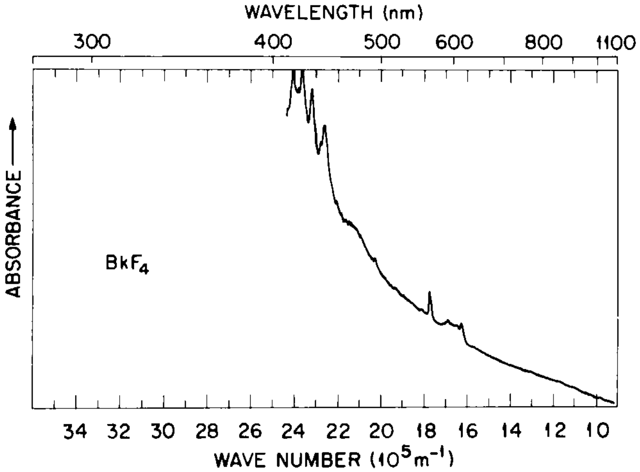

FIG. 6. Solid-state absorption spectrum of monoclinic BkF_4 at room temperature. Reprinted with permission from the *J. Inorg. Nucl. Chem.* **43,** D. D. Ensor, J. R. Peterson, R. G. Haire, and J. P. Young, 1981, Pergamon Press, Ltd. (*13*).

Line lists of the absorption bands of two organoberkelium compounds, $Bk(C_5H_5)_3$ (*116*) and $[Bk(C_5H_5)_2Cl]_2$ (*117*), have also been published. For additional information (*118*) and discussion of the development of the theoretical treatment of berkelium spectra, the reader is referred to other sources (*83, 106*).

V. Metallic State

A. PREPARATION

The first bulk samples of berkelium metal were prepared in early 1969 by the reduction at about 1300 K of BkF_3 with lithium metal vapor (*119*). The BkF_3 samples were suspended in a tungsten wire spiral above a charge of Li metal in a tantalum crucible. A photomicrograph of the first isolated bulk (1.7 μg) sample of berkelium metal is shown in Fig. 7.

Later berkelium metal samples of up to 0.5 mg each have been prepared via the same chemical procedure (*120*). 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. The latter reduction process is better suited to the preparation of thin metal foils unless multimilligram quantities of berkelium are available.

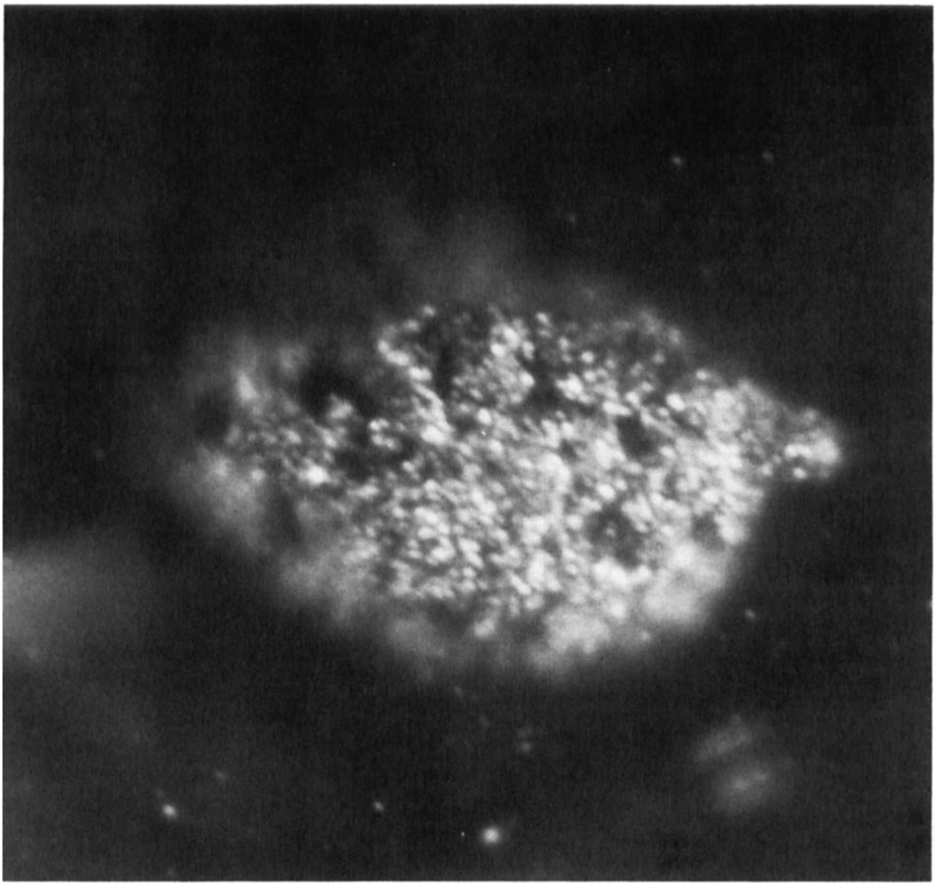

FIG. 7. A photomicrograph of the first isolated bulk (1.7 μg) sample of berkelium metal in a quartz X-ray capillary.

B. PHYSICAL PROPERTIES

Berkelium metal exhibits two stable crystallographic modifications, double hexagonal closest packed (dhcp) and face-centered cubic (fcc). Thus it is isostructural with the two preceding elements, all of which exhibit the fcc structure at high temperature. The room-temperature lattice constants of the dhcp form are $a_0 = 0.3416 \pm 0.0003$ nm and $c_0 = 1.1069 \pm 0.0007$ nm, yielding a calculated density of 1.478×10^4 kg/m^3 and a metallic radius (CN = 12) of 0.170 nm (*119*). The room-temperature fcc lattice parameter is $a_0 = 0.4997 \pm 0.0004$ nm from which the

X-ray density and the metallic radius (CN = 12) are calculated to be 1.325×10^4 kg/m^3 and 0.177 nm, respectively (*119*). The metallic radius of berkelium, assuming a metallic valence of 3- and 12-fold coordination, has been calculated to be 0.1739 nm (*121*). On the other hand, the radii (CN = 12) of berkelium were predicted to be 0.184 nm for trivalent metal and 0.1704 nm for tetravalent metal, so that the observed dhcp form would correspond to tetravalent metal, while the fcc form would represent a metallic valence of 3.5 (*122*).

Although berkelium metal is dimorphic, the transformation temperature is now 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 → fcc phase transformation, which should be accompanied by a 12% change in the volume of the sample (*123*). The melting point of berkelium metal has been determined to be 1259 ± 25 K from measurements on two samples (*123*). The melting and boiling points of elemental berkelium have been estimated to be 1323 ± 50 and 2900 ± 50 K, respectively (*124*).

The first data on berkelium metal under pressure were obtained with a diamond anvil pressure cell, using silicone oil as the pressure medium, ruby fluorescence to determine the applied pressure, and energy-dispersive X-ray powder diffraction analysis (*125*). Three metallic phases were observed with increasing pressure to 57 GPa: the normal-pressure dhcp modification was transformed to fcc at about 8 GPa; this fcc form was transformed to the α-uranium-type orthorhombic structure at ~22 GPa (*125*). Accompanying this latter transition was a shrinkage in volume of ~12% (see Fig. 8), which was associated with delocalization of the 5f electrons, i.e., with the onset of 5f-electron participation in the metallic bonding in berkelium (*126*). A bulk modulus of 30 ± 10 GPa was estimated for berkelium metal below 22 GPa (*125*). Thus berkelium metal under pressure behaves similarly to americium, californium, and some of the light lanthanide metals and does not appear to undergo an isostructural phase transition (corresponding to a change in metallic valence from three to four) before delocalization of its 5f electrons (*127*).

In the first experiments to measure the vapor pressure of metallic Bk, 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 ΔH°_{298} was calculated to be 382 ± 18 kJ/mol (*128*). The crystal entropy of berkelium metal at 298 K (S°_{298}) had been estimated earlier to be 76.2 ± 1.3 J K^{-1} mol^{-1} (*129*), and later, to be 78.2 ± 1.3 J K^{-1} mol^{-1} (*124*).

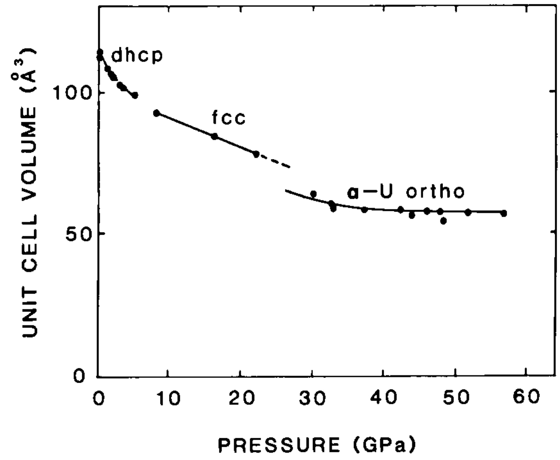

FIG. 8. Unit-cell volume of berkelium metal as a function of pressure. Adapted and reprinted with permission from the *J. Phys. F: Met. Phys.* **14**, U. Benedict, J. R. Peterson, R. G. Haire, and C. Dufour, 1984, The Institute of Physics, London (*126*).

Later data on the vapor pressure of berkelium metal over the temperature range 1100–1500 K, obtained by using combined Knudsen effusion mass spectrometric and target collection techniques, have been published in 1982 (*124*). The vaporization equations obtained were

$$\log P(\text{atm}) = (5.78 \pm 0.21) - (15{,}718 \pm 253)/T$$

for solid Bk between 1107 and 1319 K and

$$\log P(\text{atm}) = (5.14 \pm 0.17) - (14{,}902 \pm 244)/T$$

for liquid Bk between 1345 and 1528 K. The enthalpy of fusion was calculated to be 7.92 kJ/mol, and the enthalpy associated with the dhcp → fcc phase transition was calculated to be 3.66 kJ/mol (*124*). An average of the second and third law data yielded 310 ± 6 kJ/mol for its enthalpy of vaporization, ΔH°_{298} (*124*). Correlation systematics have suggested that the standard enthalpy of sublimation of berkelium metal [ΔH°_fBk(g)] is 280 kJ/mol and that the standard enthalpy of formation of aqueous Bk(III) [ΔH°_fBk^{3+}(aq)] is −615 kJ/mol (*130, 131*). A later modification of the systematics (*130*) led to values of 320 ±

8 kJ/mol and −590 ± 21 kJ/mol for ΔH_f°Bk(g) and $\Delta H_f^\circ$$Bk^{3+}$(aq), respectively (*132*).

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 ± 25 kJ/mol (*120*). 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 ± 5.1 kJ/mol (*133*). From this value $\Delta H_f^\circ$$Bk^{3+}$(aq) was derived to be −601 ± 5 kJ/mol, and using reasonable entropy estimates, the standard potential of the Bk(III)–Bk(0) couple was calculated to be −2.01 ± 0.03 V.

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 atom % Cf) indicated a transition to antiferromagnetic behavior at about 34 K and paramagnetic behavior between 70 and 250 K (*134*). 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 $\mu_{\text{eff}} = 9.69\ \mu_B$ 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 L–S 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 (*94, 135*).

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 because of the formation of a "protective" oxide film on the metal surface (*135*). Berkelium is a chemically reactive metal, and berkelium hydride (*123*), some chalcogenides (*123, 136, 137*) and pnictides (*138, 139*) 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 (*120, 133*). Undoubtedly it forms alloys and/or intermetallic compounds with a number of other metals.

D. THEORETICAL TREATMENT

In 1972 a hybridized nondegenerate 6d and 5f virtual-bound-states model was used to describe the properties of the actinide metals, including berkelium (*140*). It accounted for the occurrence of localized magnetism in Bk metal. In 1974 a review of the understanding of the electronic properties of berkelium metal, as derived from electronic band theory, was published (*141*). Included were the relativistic energy-band structure of face-centered cubic Bk metal ($5f^86d^17s^2$) and the conclusion 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 (*142*). An energy difference of 0.92 eV was calculated between the $5f^97s^2$ ground state and the $5f^86d^17s^2$ first excited state. The enthalpy of sublimation of trivalent Bk metal was calculated to be 2.99 eV (288 kJ/mol), reflecting the fact that berkelium metal is more volatile than curium metal. It was also concluded that the metallic valence of the face-centered cubic form of berkelium metal is less than that of the double hexagonal closest packed modification (*142*).

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 (*143*). 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.

Predictions based on electronic structure calculations have been made for the pressures at which the 5f electrons in the heavier actinide metals will delocalize. For berkelium metal, such calculations indicated a delocalization pressure higher than 45 GPa (*127*). In addition, it was suggested that a change in metallic valence (corresponding to the change from a localized $5f^8$ to a localized $5f^7$ electron configuration) might occur at a pressure below 45 GPa. Such a change in metallic valence would be accompanied by a sudden and significant volume decrease and could possibly appear as an isostructural phase transition (*127*).

VI. Compounds

A. 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, and Cs_2BkCl_6. Selected crystallographic data for Bk metal and a number of berkelium compounds are collected in Table II. In cases where there have been multiple reports of lattice parameters for a particular compound, the later values or the ones considered more reliable by the present authors are given in Table II. 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" berkelium-249 compounds concerns the ingrowth of daughter californium-249 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 (this assumes, of course, that the lattice parameters of the isostructural "pure" californium compound are known).

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 anion, have been calculated (*114*). 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, based on the same anion radii (*114*). Other self-consistent sets of trivalent and tetravalent lanthanide and actinide ionic radii, based on isomorphous series of oxides (*145, 157*) and fluorides (*148, 157*), 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 (*158*). It is important to note, however, that meaningful comparisons of ionic radii can be made only if the values compared are calculated in like fashion from the same type of compound, both with respect to composition and crystal structure.

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,

TABLE II

SELECTED CRYSTALLOGRAPHIC DATA FOR BERKELIUM METAL AND COMPOUNDS

Substance	Structure type	Crystal system	Lattice parameters[a]				Other[b]	Reference
			a_0 (nm)	b_0 (nm)	c_0 (nm)	β (deg)		
Metal								
Bk	α-La	Hexagonal (dhcp)	0.3416		1.1069		ρ14.78 V27.96	*119*
Bk	Cu(A1)	Cubic (fcc)	0.4997				ρ13.25 V31.19	*119*
Oxides								
BkO_2	CaF_2	Cubic (fcc)	0.53315					*144*
Bk_2O_3	$(Fe, Mn)_2O_3$	Cubic (bcc)	1.0887					*145*
Bk_2O_3	Sm_2O_3	Monoclinic	1.4197	0.3606	0.8846	100.23		*146*
Bk_2O_3	La_2O_3	Hexagonal	0.3754		0.5958		V72.7	*146*
Halides								
BkF_4	UF_4	Monoclinic	1.2396	1.0466	0.8118	126.33	V70.7	*147*
BkF_3	LaF_3	Trigonal	0.697		0.714		ρ10.15	*148*
BkF_3	YF_3	Orthorhombic	0.670	0.709	0.441		ρ9.70	*148*
$BkCl_3$	UCl_3	Hexagonal	0.7382		0.4127			*149*
Cs_2BkCl_6	Rb_2MnF_6	Hexagonal	0.7451		1.2097		ρ4.155	*150*
$Cs_2NaBkCl_6$	$(NH_4)_3AlF_6$	Cubic (fcc)	1.0805				ρ3.952	*150*
$BkCl_3 \cdot 6H_2O$	$GdCl_3 \cdot 6H_2O$	Monoclinic	0.966	0.654	0.797	93.77	ρ3.06	*151*
$BkBr_3$	$PuBr_3$	Orthorhombic	0.403	1.271	0.912		V116.8	*152*
$BkBr_3$	$AlCl_3$	Monoclinic	0.723	1.253	0.683	110.6	V144.8	*152*
BkI_3	BiI_3	Hexagonal	0.7584		2.087			*153*

Oxyhalides							
BkOCl	PbFCl	Tetragonal	0.3966		0.6710	ρ9.45	*154*
BkOBr	PbFCl	Tetragonal	0.395		0.81		*155*
BkOI	PbFCl	Tetragonal	0.3986		0.9149		*153*
Pnictides							
BkN	NaCl	Cubic (fcc)	0.4951				*138*
BkP	NaCl	Cubic (fcc)	0.5669				*138*
BkAs	NaCl	Cubic (fcc)	0.5829				*138*
BkSb	NaCl	Cubic (fcc)	0.6191				*138*
Chalcogenides							
BkS_{2-x}	Anti-Fe_2As	Tetragonal	0.3902		0.792		*137*
Bk_2S_3	Deficit Th_3P_4	Cubic (bcc)	0.8358				*137*
$BkSe_{2-x}$	Anti-Fe_2As	Tetragonal	0.404		0.828		*137*
Bk_2Se_3	Deficit Th_3P_4	Cubic (bcc)	0.8712				*137*
$BkTe_3$	$NdTe_3$	Orthorhombic	0.4318	0.4319	2.5467		*136* *137*
$BkTe_{2-x}$	Anti-Fe_2As	Tetragonal	0.4314		0.8945		*137*
Bk_2Te_3	Sc_2S_3	Orthorhombic	1.226	0.8685	2.605		*137*
Miscellaneous							
BkH_{2+x}	CaF_2	Cubic (fcc)	0.523				*123*
$Bk_2O_2SO_4$	$La_2O_2SO_4$	Orthorhombic	0.4195	0.4083	1.3110		*156*
Bk_2O_2S	Pu_2O_2S	Trigonal	0.3861		0.6686		*156*
$Bk(C_5H_5)_3$	$Pr(C_5H_5)_3$	Orthorhombic	1.411	1.755	0.963	ρ2.47 V298	*116*

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[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).

argon, and H_2–Ar atmospheres and compared to that of the corresponding hydrates of cerium, gadolinium, and terbium (*159*). In air or Ar, the final berkelium product was BkO_2; in H_2–Ar, it was Bk_2O_3.

B. OXIDES

The first compound of berkelium identified on the basis of its characteristic X-ray powder diffraction pattern was BkO_2 (*5*). Other workers have since confirmed its CaF_2-type face-centered cubic structure with $a_0 = 0.533$ nm (*144–146, 160, 161*). The thermal expansion of BkO_2 in 1 atm oxygen was determined and shown to be reversible with temperature (*144*). 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°C (298 K) and 900°C (1173 K) were calculated to be 8.25×10^{-6}/°C and 13.2×10^{-6}/°C, respectively (*144*).

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 (*162*). The valence-band XPS spectrum, which was limited in resolution by photon broadening, was dominated by 5f-electron emission.

A capacitance manometer system was used to measure the equilibrium oxygen decomposition pressures over nonstoichiometric BkO_x ($1.5 < x < 2.0$) (*163*). Three broad nonstoichiometric phases were defined: $BkO_{1.50-1.77}$, $BkO_{1.81-1.91}$, and $BkO_{1.93-2.00}$. Later an X-ray diffraction investigation of this BkO_x system under equilibrium conditions was undertaken to correlate the above data with structural behavior (*164*). A phase diagram was suggested, showing above 673 K two widely nonstoichiometric phases: body-centered cubic for $1.5 < 0/Bk < {\sim}1.70$ and face-centered cubic for ${\sim}1.78 < 0/Bk < 2.00$. 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.

This same BkO_2 sample (*164*) was used in a later study to investigate, under controlled conditions of temperature and oxygen activity, the redox behavior of the daughter californium-249 at compositions of $Bk_{0.76}Cf_{0.24}O_x$ and $Cf_{0.64}Bk_{0.36}O_x$ (*165*). Based on measured lattice parameters, the former ternary compound cooled in oxygen produced MO_2 and the latter produced $MO_{1.8}$, in contrast to the behavior of pure CfO_x, which produces $CfO_{1.71}$ (Cf_7O_{12}). Another observation was that oxidation of the californium to Cf(IV) or reduction of the californium to Cf(III) occurred at much lower temperatures in these ternary oxides than those in pure CfO_x (*165*).

The stable room-temperature form of berkelium sesquioxide exhibits the bixbyite-type body-centered cubic structure with $a_0 = 1.0887$ nm (*145*). This has been corroborated by an independent worker (*146, 160*). The cubic sesquioxide has also been analyzed by electron diffraction (*166*). 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 (*146*). 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 body-centered cubic (C form) to monoclinic (B form) to hexagonal (A form).

The possibility of the existence of BkO has been raised (*123*). The true identity of the brittle, gray material exhibiting a face-centered cubic structure with $a_0 = 0.4964$ nm is still in doubt. Not to be excluded from consideration is that this phase represents a nitride or an oxide nitride.

C. HALIDES AND OXYHALIDES

The only reported binary Bk(IV) halide is BkF_4 (*147, 167, 168*), prepared by fluorination of BkO_2 or BkF_3. Although these workers agree that it exhibits the UF_4-type monoclinic structure, there is some variance in the reported lattice parameters. This stems 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 II in contrast to those of 7.148×10^7 pm^3 (*167*) and 7.28×10^7 pm^3 (*168*) derived from the other reported lattice parameters. The solid state absorption spectrum of BkF_4 was reported in 1981 (*13*). 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 unreported, should be readily prepared. The structural systematics of such actinide fluoride complexes have been discussed elsewhere (*169, 170*).

One other Bk(IV) halide compound, Cs_2BkCl_6, has been characterized by its crystallographic properties (*150*). 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 $a_0 = 0.7451$ 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 and the average radius of the $BkCl_6^{2-}$ ion to be 0.270 nm (*171*).

The trihalides of berkelium can be prepared by hydrohalogenation of BkO_2, Bk_2O_3, or a lighter halide of berkelium. BkF_3 (*13, 148*), $BkCl_3$ (*108, 112, 149*), and $BkBr_3$ (*152, 172*) have been shown by X-ray powder diffraction and absorption spectrophotometric studies to be dimorphic. Berkelium is the first actinide whose trifluoride exhibits the YF_3-type orthorhombic structure as the room-temperature, α phase and the LaF_3-type trigonal structure as the high-temperature phase (*148*).

In the case of dimorphic $BkCl_3$, the UCl_3-type hexagonal structure (*149*) represents the low-temperature form, while the $PuBr_3$-type orthorhombic structure is exhibited by the high-temperature modification (*112*). The phase transition temperature appears to be close (*112*) to the $BkCl_3$ melting point, 876 K (*173*). 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 (<92 or ≥ 92) of the actinide (*174*). White $Cs_2NaBkCl_6$ was crystallized from aqueous CsCl–HCl solution by increasing the HCl concentration and cooling and found to exhibit a face-centered cubic structure in which the Bk(III) ions (0_h site symmetry) are octahedrally coordinated by chloride ions (*150*). The unique properties of such compounds stimulated the synthesis and study of an isostructural set of Cs_2NaMCl_6 compounds containing trivalent cations (M) whose ionic radii ranged from 0.065 to 0.106 nm (*175*).

X-Ray diffraction by 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 (*151*). By analogy, the basic units of the berkelium structure are $BkCl_2(OH_2)_6^+$ cations and Cl^- anions, the latter ones 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 (*152*). Since these two crystallographic modifications differ by two in the Bk(III) coordination number, absorption spectrophotometric analysis easily distinguishes between them (*172*). 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 (*152*). If it does exist, it would be the form intermediate between the $PuBr_3$- and $AlCl_3$-type structures and exhibit the $FeCl_3$-type rhombohedral structure with a_0 = 0.766 nm and α = 56.6° (*152*). There is one additional report (*155*) with lattice parameters for the orthorhombic form of $BkBr_3$ and for BiI_3-type hexagonal BkI_3.

BkOCl (*154*), BkOBr (*155*), and BkOI (*153, 155*) have been synthesized and found to exhibit the PbFCl-type tetragonal structure. Although presently unreported, BkOF certainly can be prepared and probably exhibits polymorphism.

D. PNICTIDES, CHALCOGENIDES, AND OTHER COMPOUNDS

The berkelium monopnictides have been prepared on the multimicrogram scale by direct combination of the elements (*138*). 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 (*139*). 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. Clearly, additional samples of BkN should be prepared to establish more firmly its lattice constant.

The only other crystallographic result reported for a berkelium chalcogenide besides those summarized in Table II is a cubic lattice parameter of 0.844 nm for Bk_2S_3 (*155*). 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 later work (*136, 137*), the higher chalcogenides were prepared on the 20- to 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 preparation of only one sample of berkelium hydride has been reported and that was by treatment of berkelium metal at 500 K with H_2 gas derived from thermal decomposition of UH_3 (*123*). The product exhibited a face-centered cubic structure with $a_0 = 0.523 \pm 0.0001$ nm, determined from nine observed X-ray powder diffraction lines. By analogy with the behavior of the lanthanide hydrides (*176*), the superdihydride stoichiometry, $BkH_{2+x}(0 < x < 1)$, was assigned. The stoichiometric dihydride should exhibit the largest cubic unit cell. One would anticipate also the existence of BkH_3, which should exhibit a hexagonal unit cell. Additional work is required to characterize fully the berkelium–hydrogen system.

Both the oxysulfate (body-centered orthorhombic) and oxysulfide (trigonal) of Bk(III) have been studied by X-ray powder diffraction (*156*). $Bk_2O_2SO_4$ 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 formed upon thermal decomposition of 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 (*156*). Both $Bk_2O_2SO_4$ and Bk_2O_2S are isostructural with the corresponding lanthanide and actinide compounds.

Berkelium(III) orthophosphate has been characterized both by X-ray powder diffraction and by solid state absorption and Raman spectroscopies (*111, 115*). The X-ray data confirm the hypothesis that $BkPO_4$ is isostructural (monazite-type monoclinic) with the lighter lanthanide orthophosphates (*177*) and exhibits unit-cell dimensions similar to those of $SmPO_4$ and $EuPO_4$ (*111*).

Two organoberkelium compounds have been reported, but only one of them, $Bk(C_5H_5)_3$, has been characterized crystallographically (*116*). In addition to the data given in Table II, the formula volume of this compound is 2.98×10^8 pm^3. The amber-colored tricyclopentadienylberkelium(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. By vacuum sublimation at temperatures above 500 K (up to 600 K), a second berkelium fraction was obtained (*117*). Its identity was established to be dicyclopentadienylberkelium(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 $Bk(C_5H_5)_3$ (*117*).

E. MAGNETIC BEHAVIOR OF BERKELIUM IONS

In order to improve upon the precision (±10%) of the initial measurements of the magnetic susceptibility of Bk(III) ions (*4*) 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 (*94*). The magnetic behavior of Bk(III) over the entire temperature range was described well by the Curie–Weiss relationship with $\mu_{\text{eff}} = 9.40 \pm 0.06$ μ_B and $\theta = 11.0 \pm 1.9$ K. The magnetic susceptibility of Bk(III) in an octahedral environment of host matrix $Cs_2NaLuCl_6$ was measured, and temperature-independent paramagnetism was observed over the temperature range 10–40 K; the lowest level of Bk(III) was determined to be Γ_1, and a $\Gamma_1 - \Gamma_4$ separation of 8.5×10^3 m^{-1} was derived (*178*).

Results of electron paramagnetic resonance (*179*) and magnetic susceptibility (*180*) studies of Bk(IV) in ThO_2 have been reported. The eight-line hyperfine pattern confirmed the hypothesis that the nuclear spin of ^{249}Bk is 7/2; the estimated nuclear moment was 2.2 ± 0.4 μ_N (*179*). 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 (*180*).

The first measurements of the magnetic susceptibilities of bulk-phase samples of some berkelium compounds (BkO_2, BkF_3, BkF_4, and BkN) have been made (*181*). The effective moments were found to agree with the calculated free-ion values, assuming Bk(III) or Bk(IV) cores and L–S coupling. Of particular note was the apparent agreement between the measured moment (7.8 μ_B) for BkN and that calculated (7.9 μ_B) for Bk(IV). However, the interpretation of this result is complicated by the unknown magnitudes of the covalency and conduction electron polarization effects (*181*).

VII. Solution Chemistry

A. Ionic Species

Berkelium exhibits both the III and IV oxidation states, as would be expected from the oxidation states displayed by its lanthanide counterpart, terbium. Bk(III) is the most stable oxidation state in noncomplexing aqueous solution. Bk(IV) is reasonably stable in solution, undoubtedly because of the stabilizing influence of the half-filled $5f^7$ electronic configuration. Bk(III) and Bk(IV) exist in aqueous solution as the 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 is orange-yellow in H_2SO_4 solution. A discussion of the absorption spectra of berkelium ions in solution can be found in Section IV,C.

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 (*182*). 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 (cocrystallization technique) (*183, 184*).

B. THERMODYNAMIC QUANTITIES

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

$$\mathrm{Bk(c,\alpha) + 3H^{+}(aq) \longrightarrow Bk^{3+}(aq) + \tfrac{3}{2}H_2(g)}$$

and

$$\mathrm{Bk(c,\alpha) + 4H^{+}(aq) \longrightarrow Bk^{4+}(aq) + 2H_2(g)}$$

are summarized in Table III.

An electrostatic hydration model has been applied to the trivalent lanthanide and actinide ions in order to predict the standard free energy (ΔG_t°) and enthalpy (ΔH_t°) 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, ΔG_{298}° was calculated to be −3357 kJ/mol, and ΔH_{298}° was calculated to be −3503 kJ/mol (*187*).

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 (*188*). The activity coefficient values were reported as a function of the $NaNO_3$ concentration.

C. STABILITY CONSTANTS AND OTHER PROPERTIES

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 IV. In most cases, the lack of replicate results precludes an assessment here 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).

TABLE III

THERMODYNAMIC QUANTITIES FOR AQUEOUS BERKELIUM IONS AT 298 K

	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° ($J\ K^{-1}\ mol^{-1}$)	Reference
$Bk^{3+}(aq)$	−601 ± 5	−581 ± 7	−188 ± 17	*133, 185*
$Bk^{4+}(aq)$	−483 ± 5	−417 ± 13	−406 ± 42	*185, 186*

TABLE IV

STABILITY CONSTANTS OF Bk(III) COMPLEXES WITH VARIOUS ANIONS

Ligand	Conditions[a]	Stability constants[b]	Reference
Fluoride ion, F^-	Solv. extrn., 298 K, $\mu = 1.0$, pH = 2.72	$\beta_1 = 7.8 \times 10^2$	*189*
Chloride ion, Cl^-	Solv. extrn., 298 K, $\mu = 1.0$, pH = 2	$\beta_1 = 0.96$	*190*
	Solv. extrn., ca. 293 K, $\mu = 3.0$, pH = 0.82	$\beta_1 = 0.59$ $\beta_2 = 0.25$	*239*
Bromide ion, Br^-	Solv. extrn., ca. 293 K, $\mu = 3.0$, pH = 0.82	$\beta_1 = 0.15$ $\beta_2 = 0.29$	*239*
Hydroxide ion, OH^-	$\mu = 0.1$	$\beta_1 = 7.9 \times 10^8$	*191*
Sulfate ion, SO_4^{2-}	Solv. extrn., 298 K, Calc. values for $\mu = 0$ (meas. $\mu \leq 0.5$)	$\beta_1 = 5.1 \times 10^3$ $\beta_2 = 3.9 \times 10^5$ $\beta_3 = 1.1 \times 10^5$	*192*
Thiocyanate ion, SCN^-	Solv. extrn., 298 K, $\mu = 5.0$	$\beta_1 = 7.21$	*193*
	$\mu = 1.0$, pH = 2	$\beta_1 = 3.11$, $\beta_2 = 0.31$ $\beta_3 = 2.34$	*194*
Oxalate ion, $C_2O_4^{2-}$	Electromigrn. rates, 298 K, $\mu = 0.1$, pH $\simeq$ 1.8	$\beta_1 = 2.8 \times 10^5$ $\beta_2 = 1.4 \times 10^9$	*195*
Acetate ion, CH_3COO^-	Solv. extrn., 298 K, 2.0 *M* $NaClO_4$	$\beta_1 = 1.11 \times 10^2$	*196*
Glycolate ion, $CH_2(OH)COO^-$	Solv. extrn., 298 K, 2.0 *M* $NaClO_4$	$\beta_1 = 4.4 \times 10^2$ $\beta_2 = 5.0 \times 10^4$	*197*
Lactate ion, $CH_3CH(OH)COO^-$	Ion exch., $\mu = 0.5$	$\beta_3 = 7.9 \times 10^5$ (est.)	*198*
2-Methyllactate ion, $(CH_3)_2C(OH)COO^-$	Solv. extrn., 10^{-2}–1 *M*	$\beta_1 = 6.39 \times 10^3$	*47*
α-Hydroxyisobutyrate ion, $(CH_3)_2C(OH)COO^-$	Ion exch., $\mu = 0.5$	$\beta_3 = 4.0 \times 10^6$ (est.)	*198*
Malate ion, $CH(OH)(COO)CH_2COO^{2-}$	Solv. extrn., 10^{-2}–1 *M*	$\beta_1 = 1.07 \times 10^7$	*47*
Tartrate ion, $[CH(OH)COO]_2^{2-}$	Solv. extrn., 10^{-2}–1 *M*	$\beta_1 = 6.80 \times 10^5$	*47*

(continued)

TABLE IV (*continued*)

Ligand	Conditions[a]	Stability constants[b]	Reference
Citrate ion, $C(OH)(COO)(CH_2COO)_2^{3-}$	Electromigrn. rates, 298 K, $\mu = 0.1$	$\beta_1 = 7.8 \times 10^7$ $\beta_2 = 1.5 \times 10^{11}$	*195*
	Solv. extrn., 10^{-2}–1 *M*	$\beta_1 = 3.00 \times 10^{11}$	*47*
Ethylenediamine-tetraacetate ion (EDTA), $C_2H_4N_2(CH_2COO)_4^{4-}$	Ion exch., 298 K, $\mu = 0.1$	$\beta_1 = 7.59 \times 10^{18}$	*199*
1,2-Diaminecyclohexane-tetraacetate ion (DACTA), $C_6H_{10}N_2(CH_2COO)_4^{4-}$	Ion exch., 298 K, $\mu = 0.1$	$\beta_1 = 1.44 \times 10^{19}$	*200*
Diethylenetriamine-pentaacetate ion (DTPA), $C_4H_8N_3(CH_2COO)_5^{5-}$	Ion exch., 298 K, $\mu = 0.1$	$\beta_1 = 6.2 \times 10^{22}$	*201*

[a] Solv. extrn., solvent extraction; calc., calculated; electromigrn., electromigration; exch., exchange; meas., measured.

[b] Overall stability constants, e.g., $\beta_1 = \frac{[BkL^{(3-n)+}]}{[Bk^{3+}][L^{n-}]}$, $\beta_2 = \frac{[BkL_2^{(3-2n)+}]}{[Bk^{3+}][L^{n-}]^2}$, and $\beta_3 = \frac{[BkL_3^{(3-3n)+}]}{[Bk^{3+}][L^{n-}]^3}$.

Attempts to obtain thermodynamic data for solvent extraction of Bk(III) by thenoyltrifluoroacetone in benzene and for complexation of Bk(III) by hydroxide and citrate ions were unsuccessful (*202*). The high extractability and complexability of the easily accessible tetravalent state of berkelium probably accounts for the difficulty encountered in this work.

Aside from the fact that no quantitative information was reported for a Bk(IV) complex with nitrate ions, a 1979 report is worthy of note (*203*). The hexanitrato complexes of Bk(IV) were studied in nitric acid solution by electromigration. An ionic mobility corresponding to a negatively charged Bk(IV) ion was evident only at HNO_3 concentrations higher than 10 *M*. The data indicated that at concentrations between 3 and 6 *M* HNO_3, Bk(IV) exists mainly as $[Bk(H_2O)_x(NO_3)_3]^+$. 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), and Np(IV) (*203*).

The extraction of Bk(IV) from sulfuric acid solutions by decylamine in chloroform has been studied. The extraction mechanism, the optimized extraction parameters, and the identity of the extracted species have been reported (*31*).

The extraction of Bk(III) by phosphoorganic acids has been studied, and activity coefficients for Bk(III) in nitric acid solution were estimated (*204*). In addition, a mechanism for the extraction of Bk(IV) by hydrogen di(2-ethylhexyl)orthophosphoric acid (HDEHP) from nitric acid solutions was proposed.

Mixtures of the linear polyether 1,13-bis[8-quinolyl]-1,4,7,10,13-pentaoxatridecane (K-5) and thenoyltrifluoroacetone (HTTA) were found to exhibit synergism in Bk(III) extraction from 0.5 *M* $NaNO_3$ solution. The stability constant for the $Bk(TTA)_3 \cdot K5$ species in HTTA–chloroform mixtures was calculated (*205*). Berkelium(III) hexafluoroacetylacetonate, Bk(III) and Bk(IV) thenoyltrifluoroacetonates, and Bk(IV) pivaloyltrifluoroacetonate have been obtained in tracer quantities by extraction of Bk(III) or Bk(IV) from aqueous solutions with xylene solutions of the respective fluorine-containing β-diketones (*206*). Thermoradiometric studies carried out in a stream of carrier gas saturated with hexafluoroacetylacetone indicated substantial volatilities for these berkelium species in the temperature range 413–483 K. Although the identities of the gas-phase berkelium species are unknown, it was suggested that they consist mainly of Bk(III) hexafluoroacetylacetonate, the first reported volatile compound of berkelium (*206*).

The kinetics of exchange of Bk(III) with $EuEDTA^-$ in aqueous acetate solutions of 0.1 *M* ionic strength has been studied (*207*). 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 (*207*).

The solubilities of Bk(III) oxalate and Bk(IV) iodate have been reported to be 1.5 and 10 mg/liter, respectively (*208*).

D. OXIDATION–REDUCTION BEHAVIOR AND POTENTIALS

Berkelium(III) in solution can be oxidized by strong oxidizing agents such as BrO_3^- (*15–19, 209*), AgO (*210*), $Ag(I)/S_2O_8^{2-}$ (*20, 23, 211*), perxenate (*212*), and ozone (*24, 213, 214*).

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 (*113*). In basic solution, Bk(III) is unstable toward oxidation by radiolytically produced peroxide. This "auto-oxidation" had been previously observed in carbonate solution (*95*). Bk(III) can be stabilized in alkaline media by the presence of a reducing agent such as hydrazine hydrate (*113*).

$BkCl_3$ is reported to be soluble in acetonitrile saturated with tetraethylammonium chloride (*215*). The colorless, 7.6×10^{-4} *M* $BkCl_6^{3-}$ solution formed 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 (*150*).

Investigation of the amalgamation behavior of trivalent actinides in acetate and citrate solutions by treatment with sodium amalgam showed that Bk(III) does not readily form an amalgam. This behavior is in contrast to that of the heavier actinides californium, einsteinium, and fermium, which readily amalgamate (*216, 217*).

Bk(IV) is a strong oxidizing agent, comparable to Ce(IV) (*218*). It can be coprecipitated with cerium iodate (*17*) or zirconium phosphate (*4*). The stability of Bk(IV) solutions is a function of the degree of complexation of Bk(IV) by the solvent medium (*95*). Bk(IV) is reduced by radiolytically generated peroxide in acidic and neutral solutions (*14, 97, 219*). The rate of reduction of Bk(IV) can be accelerated electrochemically (*220*) or by the introduction of a reducing agent such as hydrogen peroxide (*14, 219*), hydroxylamine hydrochloride (*219*), or ascorbic acid (*219*).

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 (*3*). Later, in 1959, 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 (*4*). The potential of the Bk(IV)–Bk(III) couple has subsequently been determined by several workers using direct potentiometry (*220–224*) or indirect methods (*218, 225, 226*). All of the above-mentioned determinations were performed in media of relatively low complexing capability. The formal potential of the Bk(IV)–Bk(III) couple is significantly shifted to less positive values in media containing anions that strongly complex Bk(IV), such as PO_4^{3-} and CO_3^{2-} ions (*227*). This behavior closely parallels that of the Ce(IV)–Ce(III) couple (*228*). In fact, the Bk(IV)–Bk(III) couple markedly resembles the Ce(IV)–Ce(III) couple in its oxidation-reduction chemistry.

The potential of the Bk(III)–Bk(0) couple has been investigated, using radiopolarography (*229, 230*) and theoretical calculations (*231*), as well as by correlation with enthalpy of formation data (*132, 133*). 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 (*215, 221, 232, 233*).

TABLE V

POTENTIALS OF BERKELIUM REDOX COUPLES

Redox couple	Potential (V versus NHE)	Conditions[a]	Reference
Bk(IV)–Bk(III)	1.6 ± 0.2	Calc.	*221, 232*
	1.664	Calc.	*234*
	1.54 ± 0.1	1 M $HClO_4$, dir. pot.	*227*
	1.597 ± 0.005	1 M $HClO_4$, dir. pot.	*224*
	1.735 ± 0.005	9 M $HClO_4$, dir. pot.	*224*
	1.54 ± 0.1	1 M HNO_3, dir. pot.	*227*
	1.562 ± 0.005	1 M HNO_3, dir. pot.	*224*
	1.56	6 M HNO_3, solv. extrn.	*226*
	1.6	3–8 M HNO_3, coprecip.	*3*
	1.543 ± 0.005	8 M HNO_3, dir. pot.	*224*
	1.43	0.1 M H_2SO_4, dir. pot.	*222*
	1.44	0.25 M H_2SO_4, solv. extrn.	*226*
	1.38	0.5 M H_2SO_4, dir. pot.	*223*
	1.42	0.5 M H_2SO_4, solv. extrn.	*226*
	1.37	1 M H_2SO_4, dir. pot.	*220, 223*
	1.36	2 M H_2SO_4, dir. pot.	*220, 223*
	1.12 ± 0.1	7.5 M H_3PO_4, dir. pot.	*227*
	0.85	0.006 M $K_{10}P_2W_{17}O_{61}$, pH = 0, dir. pot.	*235*
	0.65	0.006 M $K_{10}P_2W_{17}O_{61}$, pH > 4, dir. pot.	*235*
	0.26 ± 0.1	2 M K_2CO_3, dir. pot.	*227*
Bk(III)–Bk(II)	−2.8 ± 0.2	Calc.	*232*
	−2.75	Calc.	*236*
Bk(III)–Bk(0)	−2.03 ± 0.05	Calc.	*233*
	−2.4	Calc.	*231*
	−1.99 ± 0.09	Calc.	*132*
	−2.18 ± 0.09	0.1 M LiCl, radiopol.	*229, 230*
	−2.01 ± 0.03	Calc.	*133*

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

Potentials of berkelium redox couples are summarized in Table V. Replicate values for the Bk(IV)–Bk(III) couple are in reasonable agreement with one another. The effect of anions that strongly complex Bk(IV) is clearly reflected in the values of the formal potential for the Bk(IV)–Bk(III) couple and can be seen in the Nernst equation plots for the couple in various media given in Fig. 9 (*227*). Values of 1.36 (*220, 223*) and 1.12 V (*227*) have been reported for the couple in sulfuric and phosphoric acid solutions, respectively. Carbonate ions, apparently

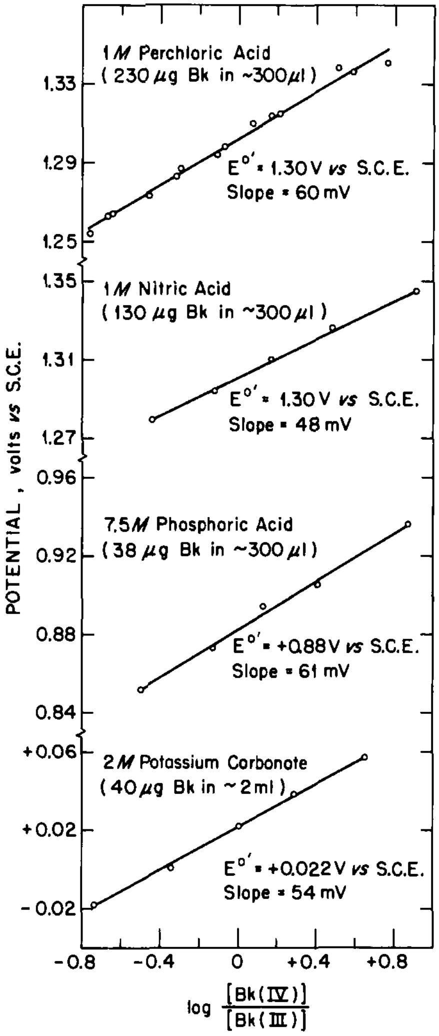

FIG. 9. Nernst equation plots for the Bk(IV)–Bk(III) couple in various aqueous media. Reprinted with permission from the *J. Inorg. Nucl. Chem.* **34**, J. R. Stokely, R. D. Baybarz, and J. R. Peterson, 1972, Pergamon Press, Ltd. (*227*).

forming the strongest complex with Bk(IV) of the anions listed in Table V, provide conditions for the least positive potential, 0.26 V (*227*), as compared to the potential of 1.6 V for the couple in noncomplexing perchlorate solution (*224, 227*). The overall thermodynamic and electrochemical data support a value of 1.67 ± 0.07 V for the standard potential ($E°$) for the Bk(IV)–Bk(III) couple, which is 0.07 V less positive than the accepted value of 1.74 V for the corresponding cerium couple (*185*). The scatter in the potential values for the Bk(III)–Bk(II) and Bk(III)–Bk(0) couples reflects the necessary requirement of making estimates of thermodynamic quantities that have not been directly determined. The potential for the Bk(III)–Bk(II) couple in mixed lanthanide chloride–strontium chloride melts has been reported to be 0.12 ± 0.02 V more positive than that for the Nd(III)–Nd(II) couple in the same media (*237*). As is the case with most nonaqueous solvent systems, it is difficult to relate this measured difference in potentials to the standard potentials in aqueous solutions that are referenced to the normal hydrogen electrode (NHE).

Theoretical estimates of the potentials for the Bk(V)–Bk(0) and Bk(V)–Bk(IV) couples have been reported as 0.2 and 3.5 V, respectively (*132*). These estimates suggest that Bk(V) is very unstable in aqueous solution.

Additional information on the oxidation-reduction behavior of berkelium can be found in a comprehensive review (*238*).

VIII. Concluding Remarks

Knowledge of both the accessibility and stability of the various oxidation states of an element is fundamental to the understanding and predictability of that element's physicochemical behavior. For element 97, oxidation states 0, III, and IV are presently known and reasonably well characterized.

The possibility of studying the physical and chemical properties of Bk(II) in bulk is intriguing. It has been suggested that this new oxidation state of berkelium is produced by nature via the α decay of einsteinium-253 dihalides (*110, 240*); however, in these absorption spectrophotometric studies, only the divalent parent species and the divalent californium-249 granddaughter species have been directly identified. Other work has shown that the β decay of berkelium-249 in the bulk-phase solid state results in the production of daughter californium-249 species exhibiting the same oxidation state and structural environment as those of the berkelium parent (*12, 13*). Direct synthesis of Bk(II) via the reaction $Bk + 2BkBr_3 \rightarrow 3BkBr_2$ should be attempted to establish with certainty the existence of Bk(II) in the bulk-phase solid state and to characterize it via absorption spectrophotometry and X-ray powder diffraction.

Studies of berkelium metal under pressure should be continued to determine more precisely its bulk modulus and to search for the existence of a distorted face-centered cubic (fcc) modification between the known fcc and α-uranium-type orthorhombic phases. An interesting extension of this research would be to investigate the behavior of BkN under pressure to see if it might undergo a sudden volume collapse corresponding to a change in metallic valence from three to four.

The preparation and characterization of intermetallic compounds and alloys of berkelium should be pursued, as well as the determination of the stability constants of Bk(IV) complexes. The range of oxidation states accessible to berkelium might be expanded by stabilizing Bk(II) and/or Bk(V) in highly complexing aqueous, nonaqueous, or even molten salt media and/or in appropriate solid-state matrices.

Further work is necessary to elucidate more completely both the solid state and solution chemistries of berkelium. Complete knowledge of its physicochemical behavior is important for more accurate extrapolations to the behavior of the still heavier elements, for which experimental studies are often precluded by intense self-irradiation and/or by lack of material.

ACKNOWLEDGMENTS

Research sponsored by the Division of Chemical Sciences, U.S. Department of Energy, under contracts DE-AS05-76ER04447 with the University of Tennessee (Knoxville), W-7405-eng-26 with Union Carbide Corporation, and W-7405-eng-36 with the University of California.

The authors gratefully acknowledge the early assistance of J. N. Stevenson and D. L. Raschella in gathering some of the references included here. The more recent cooperation of numerous colleagues in supplying and/or verifying information, identifying oversights, and in critiquing the assembled manuscript was greatly appreciated. One of the present authors (JRP) wishes to thank posthumously Professor B. B. Cunningham, whose guidance, inspiration, and personal interest during the first systematic study of the physicochemical properties of berkelium are still fondly remembered.

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Earlier reviews of the physicochemical properties of berkelium are available in several new supplement series volumes of *Gmelin Handbuch der Anorganischen Chemie* (G. Koch, editor, Springer-Verlag, New York) and in *The Chemistry of the Transuranium Elements* (C. Keller, 1971, Verlag Chemie, Weinheim).

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