ADVANCES IN INORGANIC CHEMISTRY, VOL. 31

PREPARATION AND PURIFICATION OF ACTINIDE METALS

J. C. SPIRLET,* J. R. PETERSON,** and L. B. ASPREY†

*Commission of the European Communities,
Joint Research Centre, Karlsruhe Establishment,
European Institute for Transuranium Elements,
D-7500 Karlsruhe 1, Federal Republic of Germany
**Department of Chemistry, University of Tennessee,
Knoxville, Tennessee 37996-1600 and Transuranium Research Laboratory,
Chemistry Division, Oak Ridge National Laboratory,
Oak Ridge, Tennessee 37831
†Isotope and Nuclear Chemistry Division,
Los Alamos National Laboratory,
University of California,
Los Alamos, New Mexico 87545

I. Introduction

The first actinide metals to be prepared were those of the three members of the actinide series present in nature in macro amounts, namely, thorium (Th), protactinium (Pa), and uranium (U). Until the discovery of neptunium (Np) and plutonium (Pu) and the subsequent manufacture of milligram amounts of these metals during the hectic World War II years (i.e., the early 1940s), no other actinide element was known. The demand for Pu metal for military purposes resulted in rapid development of preparative methods and considerable study of the chemical and physical properties of the other actinide metals in order to obtain basic knowledge of these unusual metallic elements.

These early studies were carried out on metals of typically 90–99% purity, which sufficed to determine at least their gross properties. During the 1960s, interest diminished somewhat in actinide metallurgy due in part to the increasing use of ceramic rather than metallic fuel elements in nuclear reactors. The bulk of actinide metal research was for secret military purposes and only a fraction of the fundamental research was published.

Interest was rekindled during the 1970s due to advances in solid-state physics and a growing realization of the unusual properties of the lighter actinide metals due to the behavior of their $5f$ electrons.

Demand for high-purity metals, on the order of 99.9 to 99.999 atomic percent (at %) purity, resulted in renewed study of actinide metallurgy with emphasis on improved methods for preparation, refining, and growth of single crystals. Increased interest in the properties of highly symmetric binary compounds of actinides such as chalcogenides, pnictides, carbides, etc., which are made by direct combination of the elements, demanded yet further development of new and improved synthesis and crystal-growing techniques.

The actual situation with regard to the purity of most of the actinide metals is far from ideal. Only thorium (*99*), uranium (*11, 17*), neptunium (*20*), and plutonium (*60*) have been produced at a purity ≥ 99.9 at %. Due to the many grams required for preparation and for accurate analysis, it is probable that these abundant and relatively inexpensive elements (Table I) are the only ones whose metals can be prepared and refined to give such high purities, and whose purity can be verified by accurate analysis. The purity levels achieved for some of the actinide metals are listed in Table II. For actinium (Ac), berkelium (Bk), californium (Cf),

TABLE I

AVAILABILITY AND PRICE OF SELECTED ACTINIDE ISOTOPES

Element	Isotope	Available quantity	Price ($/g)	Limited handling quantity[a]	Hazardous radiation
Ac	227	mg	—	<mg	α (21.8 years) γ (daughters)
Th	232	kg	—	—	—
Pa	231	g	50,000	g	γ (daughters)
U	Natural	kg	20[b]	kg	—
	235	g	150	kg	*n*
	238	kg	100	—	—
Np	237	kg	500[b]	kg	γ (daughters)
Pu	238	g	5,000	g	α (87.7 years)
	239	kg	500[b]	250 g	γ (daughters), *n*
	242	g	15,000	10 g	*n*
Am	241	kg	2,000	mg	γ
	243	g	100,000	mg	γ (daughters)
Cm	244	g	100,000	mg	*n*,γ
	248	mg	[c]	mg	*n*
Bk	249	mg	[c]	mg	*n*,γ (daughters)
Cf	249	mg	[c]	mg	α (351 years); *n*,γ

[a] Maximum quantity of the isotope which can be handled in a standard gloved box without special shielding.

[b] Electrorefined metal.

[c] Not available commercially.

TABLE II

PURITY OF SOME ACTINIDE METALS

Element	Purity (atom %)
Thorium	99.99
Protactinium	99.7
Uranium	99.9
Neptunium	99.9
Plutonium	99.9
Americium	99.5
Curium	99.5

and einsteinium (Es) metals, only limited data on metallic impurities exist, so no values are given in Table II. The values for thorium, uranium, neptunium, and plutonium are very reliable. Complete analysis of the impurities in these metals requires at least 5 g of metal and is very expensive. Metals of ultrahigh purity are analyzed indirectly by determining the ratio of their electrical resistivity at 300 K to that at 4.2 K, a measurement which relates only to the total quantity of impurities (see footnote 1, Section III,D).

Improvements in preparative techniques are expected to increase the quality of the rarer metals, but complete analysis to establish the purity will probably remain unavailable and such work will be very time consuming and costly.

The preparation, refining, and growth of single crystals of actinide metals is a very difficult task for a number of reasons. One is that the physical properties of the metals vary enormously. They range from those typical of the transition elements for the lighter actinides to those typical of rare earth metals for Am, Cm, and beyond. Their vapor pressures vary over 10 orders of magnitude, their melting points cover the range from 913 to 2028 K, and they exhibit from none to five phase transitions (some with large density differences) with increasing temperature or pressure.

Another difficulty arises from the chemical properties of the actinide metals. They are chemically reactive, rapidly corroded by moist air, pyrophoric, and, when in the molten state, dissolve common crucible materials. The radioactivity of short-lived isotopes of Am and Cm makes their long-term storage difficult; small amounts can be stored successfully under ultrahigh vacuum. Large amounts of isotopes such as ^{238}Pu with a $\tau_{1/2}$ of only 87.7 years are best stored under a pure inert gas such as argon in order to remove the heat generated by the radioactive decay. To further complicate matters, the radioactivity and toxicity of these metals make it mandatory to carry out all procedures in gloved boxes or hot cells, whether the preparation is on a microgram or multigram scale, making contamination of the product metal more difficult to avoid. Thus, sophisticated techniques are necessary to prepare, refine, and grow single crystals of actinide metals. These techniques must be compatible with highly radioactive and chemically reactive materials. Due to the varying availability and cost of the actinide isotopes (Table I), these techniques must be applicable to submilligram up to multigram quantities of actinides. By far the biggest difficulty associated with the preparation of high-purity metals is determining the purity of the product metal. Adequate analytical methods are usually not available and must be developed.

This article presents a general discussion of actinide metallurgy, including advanced methods such as levitation melting and chemical vapor-phase reactions. A section on purification of actinide metals by a variety of techniques is included. Finally, an element-by-element discussion is given of the most satisfactory metallurgical preparation for each individual element: actinium (included for completeness even though not an actinide element), thorium, protactinium, uranium, neptunium, plutonium, americium, curium, berkelium, californium, and einsteinium.

The transeinsteinium actinides, fermium (Fm), mendelevium (Md), nobelium (No), and lawrencium (Lr), are not available in weighable ($> \mu$g) quantities, so these elements are unknown in the condensed bulk phase and only a few studies of their physicochemical behavior have been reported. Neutral atoms of Fm have been studied by atomic beam magnetic resonance (*47*). Thermochromatography on titanium and molybdenum columns has been employed to characterize some metallic state properties of Fm and Md (*61*). This article will not deal with the preparation of these transeinsteinium metals.

II. Preparation of Actinide Metals

A. METALLOTHERMIC REDUCTION OF ACTINIDE HALIDES OR OXIDES

Metallothermic reduction of an actinide halide was the first method applied to the preparation of an actinide metal. Initially, actinide chlorides were reduced by alkali metals, but then actinide fluorides, which are much less hygroscopic than the chlorides, were more generally used. On the milligram scale, the anhydrous fluorides are reduced by alkali (usually Li) or alkaline earth (usually Ba) metal vapor in a covered tantalum or ceramic crucible. The excess reductant and the fluoride salt by-product are eliminated by vaporization through an effusion hole in the crucible cover.

The vapor pressures at 1473 K of a few of the actinide elements and other materials of interest are given in Table III. All of the actinide (An) elements through einsteinium can be obtained by this process:

$$\mathrm{AnF_3 + 3Li \longrightarrow 3LiF + An} \quad \text{or} \quad \mathrm{AnF_4 + 4Li \longrightarrow 4LiF + An}$$

although significant losses of Am, Cf, and Es metals result because of their high volatilities (Fig. 1). A review of this topic has been published (*53*).

This method has also been successfully adapted to the pilot-plant and industrial-scale production of Th, U, Np, and Pu metals. In these cases, calcium metal is preferred as the reductant, and the reaction is:

$$\mathrm{AnF_4 + 2Ca \longrightarrow 2CaF_2 + An}$$

This Ca reduction technique is used widely to produce commercially available actinide metals. However, this method is not well suited to the preparation on the laboratory scale of pure (>99.9 at %) actinide

TABLE III

APPROXIMATE VAPOR PRESSURES OF SELECTED ELEMENTS AND COMPOUNDS

Metal or compound	Vapor pressure (Pa)[a]
Zn	1.3×10^{6}
Mg	$>1.3 \times 10^{5}$
Ca	1.2×10^{4}
Am	1.3×10
Pu	1.3×10^{-2}
La	1.3×10^{-4}
U	1.3×10^{-6}
Pt	1.3×10^{-8}
Th	1.3×10^{-8}
$MgCl_2$	2.7×10^{4}
PuF_4	1.3×10^{2}
$CaCl_2$	1.3×10^{-1}
CaF_2	1.3×10^{-4}

[a] At 1473 K.

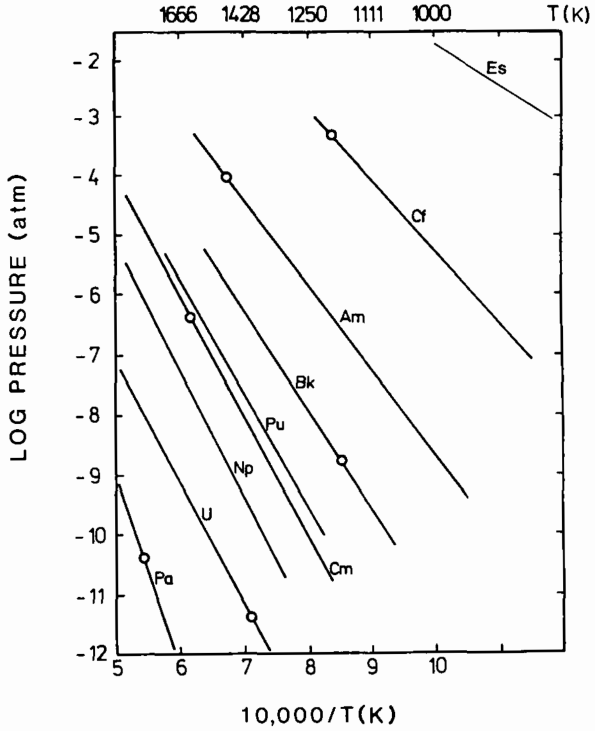

FIG. 1. Vapor pressures and some melting points of actinide metals Pa–Es. ○, melting point.

metals for solid-state physics investigations. Preparation of anhydrous actinide fluorides by treatment of the corresponding oxides with HF or F_2 gas is a source of operating difficulties. The personnel exposure to neutrons resulting from the (α,n) reaction on fluorine nuclei is high when working on the multigram scale of operation. Yield of the metallothermic reduction is somewhat irregular, and recovery of the actinide metal from the crucible and/or slag (CaF_2) can be difficult. All nonvolatile impurities present in the reductant metal as well as corrosion products from the crucible frequently end up in the product metal. If great care is taken to prepare pure anhydrous halides and to refine the reductants by successive distillation, the metal product can be >99 at % pure. Further refining steps are necessary to obtain metal of higher purity.

The fluoride reduction technique is being replaced in production plants by the metallothermic reduction of an oxide (*24*). Direct oxide reduction (DOR) is used for preparation of U, Np, and Pu on the kilogram or larger scale (*24*). The dioxide is added to molten $CaCl_2$ in the presence of excess Ca metal. The molten solvent serves to dissolve the CaO produced in the reduction reaction:

$$AnO_2 + 2Ca(xs) \longrightarrow 2CaO\ (soln) + An$$

Excellent quality metal, comparable to that from the halide reduction, can be prepared by this technique. A big advantage is that no neutrons are present from (α,n) reactions on fluorine nuclei, in marked contrast to the case with actinide fluorides.

B. METALLOTHERMIC REDUCTION OF ACTINIDE OXIDES FOLLOWED BY DISTILLATION

The metallothermic reduction of an oxide is a useful preparative method for an actinide metal when macro quantities of the actinide are available. A mixture of the actinide oxide and reductant metal is heated in vacuum at a temperature which allows rapid vaporization of the actinide metal, leaving behind an oxide of the reductant metal and the excess reductant metal, in accord with the following equations:

$$An_2O_3 + 2La \longrightarrow La_2O_3 + 2An \quad \text{and} \quad 2An_2O_3 + 3Th \longrightarrow 3ThO_2 + 4An$$

The reductant metal must have the following properties: (1) the free energy of formation of the oxide of the reductant has to be more negative than that of the actinide oxide; and (2) the vapor pressure of the reductant metal needs to be smaller by several orders of magnitude than that of the actinide metal. This difference in vapor pressure should be at least five orders of magnitude to keep the contamination level of the co-evaporated reductant metal in the product actinide metal below the 10 ppm level.

Americium, californium, and einsteinium oxides have been reduced by lanthanum metal, whereas thorium has been used as the reductant metal to prepare actinium, plutonium, and curium metals from their respective oxides. Berkelium metal could also be prepared by Th reduction of BkO_2 or Bk_2O_3, but the quantity of berkelium oxide available for reduction at one time has not been large enough to produce other than thin foils by this technique. Such a form of product metal can be very difficult to handle in subsequent experimentation. The rate and yield of Am from the reduction at 1525 K of americium dioxide with lanthanum metal are given in Fig. 2.

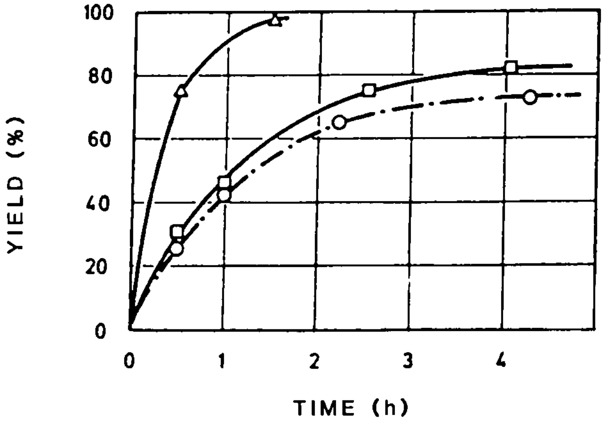

FIG. 2. Metallothermic reduction at 1525 K of AmO_2 by La metal as a function of time: ○ and □, mixtures of AmO_2 powder and La metal turnings; △, pelletized mixture of AmO_2 powder and ground La metal turnings.

Actinide metals with lower vapor pressures (Th, Pa, and U) cannot be obtained by this method since no reductant metal exists which has a sufficiently low vapor pressure and a sufficiently negative free energy of formation of its oxide. For the large-scale production of U, Np, and Pu metals, the calciothermic reduction of the actinide oxide (Section II,A) followed by electrorefining of the metal product is preferred (*24*). In this process the oxide powder and solid calcium metal are vigorously stirred in a $CaCl_2$ flux which dissolves the by-product CaO. Stirring is necessary to keep the reactants in intimate contact.

C. METALLOTHERMIC REDUCTION OF ACTINIDE CARBIDES

Transition metals like Ti, Zr, Nb, and Ta are able to reduce actinide carbides to metals according to the following generic reaction:

$$AnC + Ta \longrightarrow TaC + An$$

The free energies of formation of the transition metal carbides are somewhat more negative than the free energies of formation of the actinide carbides. To facilitate separation of the actinide metal from the reaction products and excess transition metal reductant, a transition metal with the lowest possible vapor pressure is chosen as the reductant. Tantalum metal and tantalum carbide have vapor pressures which are low enough (at the necessary reaction temperature) to avoid contamination of the actinide metal by co-evaporation.

Actinide carbides are prepared by carbothermic reduction of the corresponding dioxides according to the reaction:

$$AnO_2 + 3C \longrightarrow AnC + 2CO$$

In practice, a mixture of actinide dioxide and graphite powder is first pelletized and then heated to 2275 K in vacuum in a graphite crucible until a drop in the system pressure indicates the end of CO evolution. The resulting actinide carbide is then mixed with tantalum powder, and the mixture is pressed into pellets. The reduction occurs in a tantalum crucible under vacuum. At the reduction temperature, the actinide metal is vaporized and deposited on a tantalum or water-cooled copper condenser.

The yield and rate of the tantalothermic reduction of plutonium carbide at 1975 K are given in Fig. 3. Producing actinide metals by metallothermic reduction of their carbides has some interesting advantages. The process is applicable in principle to all of the actinide metals, without exception, and at an acceptable purity level, even if quite impure starting material (waste) is used. High decontamination factors result from the selectivities achieved at the different steps of the process. Volatile oxides and metals are eliminated by vaporization during the carboreduction. Lanthanides, Y, Ti, Zr, Hf, V, Nb, Ta, Mo, and W form stable carbides, whereas Rh, Os, Ir, Pt, and Pd remain as nonvolatile metals in the actinide carbides. Thus, these latter elements

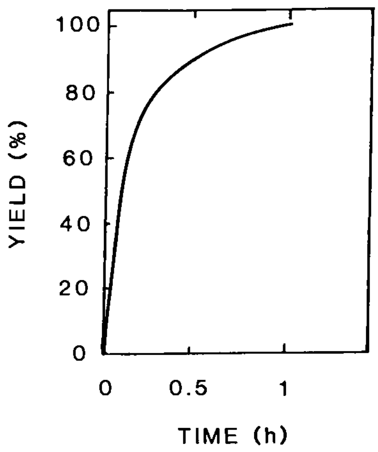

FIG. 3. Metallothermic reduction at 1975 K of PuC with Ta metal as a function of time.

$$PuC + Ta \rightarrow TaC + Pu(\uparrow)$$

will contaminate the actinide carbides if they are present in the starting materials. The carbides of Zr, Hf, Nb, and W are not reduced by Ta and remain as stable carbides in the reaction products during the tantalothermic reduction. The other elements are eliminated during selective vaporization and deposition of the actinide metal (Section III,B).

This process is particularly useful for the preparation of pure plutonium metal from impure oxide starting material (*111*). It should also be applicable to the preparation of Cm metal. Common impurities such as Fe, Ni, Co, and Si have vapor pressures similar to those of Pu and Cm metals and are difficult to eliminate during the metallothermic reduction of the oxides and vaporization of the metals. They are eliminated, however, as volatile metals during preparation of the actinide carbides.

The light actinide metals (Th, Pa, and U) have extremely low vapor pressures. Their preparation via the vapor phase of the metal requires temperatures as high as 2375 K for U and 2775 K for Th and Pa. Therefore, uranium is more commonly prepared by calciothermic reduction of the tetrafluoride or dioxide (Section II,A). Thorium and protactinium metals on the gram scale can be prepared and refined by the van Arkel–De Boer process, which is described next.

D. IODIDE TRANSPORT (VAN ARKEL–DE BOER) PROCESS

The van Arkel–De Boer process is widely used to refine metals. A transporting agent such as I_2 reacts with the metal (M) to be refined to form a volatile iodide. This iodide is then decomposed at a higher temperature into the refined metal and I_2, which becomes available again to react with the impure metal, thus sustaining the process:

$$\mathrm{M} + 2\mathrm{I}_2 \longrightarrow \mathrm{MI}_4 \qquad \text{(low temperature)}$$

$$\mathrm{MI}_4 \longrightarrow \mathrm{M} + 2\mathrm{I}_2 \qquad \text{(high temperature)}$$

For successful use of the van Arkel–De Boer process starting with an actinide compound, it is necessary that the original actinide compound react readily with I_2 to yield a volatile actinide iodide. Both ThC and PaC, easily prepared from the corresponding metal oxides by carboreduction (Section II,C), react with I_2 at 625 K to yield volatile iodides and carbon. Above 1475 K these iodides are unstable and decompose into the respective metals and iodine.

Expressed in chemical equations for Th,

$$\mathrm{ThC} + 2\mathrm{I}_2 \longrightarrow \mathrm{ThI}_4 + \mathrm{C} \qquad \text{(625 K)}$$

$$\mathrm{ThI}_4 \longrightarrow \mathrm{Th} + 2\mathrm{I}_2 \qquad \text{(above 1475 K)}$$

Using Pyrex ampoules with resistively heated tungsten wire or strip filaments, protactinium metal has been prepared on the milligram scale (*9, 13, 15*). An improved technique is to use a quartz van Arkel–De Boer bulb with an inductively heated W sphere which solves the previous problem of filament breaking and considerably improves the deposition rate of Pa metal (*109*).

Proceeding from thorium to plutonium along the actinide series, the vapor pressure of the corresponding iodides decreases and the thermal stability of the iodides increases. The melting point of U metal is below 1475 K and for Np and Pu metals it is below 975 K. The thermal stabilities of the iodides of U, Np, and Pu below the melting points of the respective metals are too great to permit the preparation of these metals by the van Arkel–De Boer process.

E. MOLTEN SALT ELECTROLYSIS

Methods have been developed (*75*) to prepare actinide metals directly from actinide oxides or oxycompounds by electrolysis in molten salts (e.g., LiCl/KCl eutectic). Indeed, the purest U, Np, and Pu metals have been obtained (*19, 24*) by oxidation of the less pure metal into a molten salt and reduction to purer metal (electrorefining, Section III,D).

III. Purification (Refining) of Actinide Metals

A. VACUUM MELTING WITHOUT DISTILLATION OF THE PRODUCT METAL

The metal to be refined is melted in high vacuum. The melt is kept at the highest possible temperature at which the vapor pressure of the liquid metal is still acceptably low in order to facilitate rapid evaporation of the volatile impurities. Vacuum melting is used to eliminate traces of iodides and iodine in metals prepared by the van Arkel–De Boer process (Th and Pa). Th, U, Np, and Pu metals obtained by the metallothermic reduction of the halides (Section II,A) are vacuum melted to eliminate traces of the reductant metals (Li, Ca, or Ba) and of the reaction by-products (alkali metal or alkaline earth halide salts). Electrolyte inclusions in molten salt-electrorefined metals (U, Np, Pu) can be eliminated by vacuum melting. Melting the metal in ultrahigh vacuum is necessary due to the reactive nature of the actinide metals. Melting of actinides in W or Ta crucibles results in some contamination from the crucible material. In the case of Pu metal at 1000 K, the contamination is slight (less than 50 atomic ppm when W crucibles are used). It is less than 10 atomic ppm when Ta crucibles coated with tantalum oxide are used (*60*). Levitation melting techniques (*86, 95*) have been used to avoid contamination of the actinide metal by the crucible material (*1*).

B. SELECTIVE VAPORIZATION

Efficient refining of the more volatile actinide metals (Pu, Am, Cm, Bk, and Cf) is achieved by selective vaporization for those (Pu, Am, Cm) available in macro quantities. The metal is sublimed at the lowest possible temperature to avoid co-evaporation of the less volatile impurities and then deposited at the highest possible temperature to allow vaporization of the more volatile impurities. Deposition occurs below the melting point of the metal to avoid potential corrosion of the condenser by the liquid metal. Very good decontamination factors can be obtained for most metallic impurities. However, Ag, Ca, Be, Sn, Dy, and Ho are not separated from Am metal nor are Co, Fe, Cr, Ni, Si, Ge, Gd, Pr, Nd, Sc, Tb, and Lu from Cm and Pu metals.

Nonmetallic impurities, mostly oxygen, found in actinide metals distilled under a vacuum of 0.1 mPa range from 4000 to 7000 atomic ppm. In a vacuum of 0.1 μPa the nonmetallic impurity content decreases to between 400 and 880 atomic ppm (*51, 52*).

Selective vaporization and deposition are performed in radiofrequency-heated tantalum distillation columns (Fig. 4). The

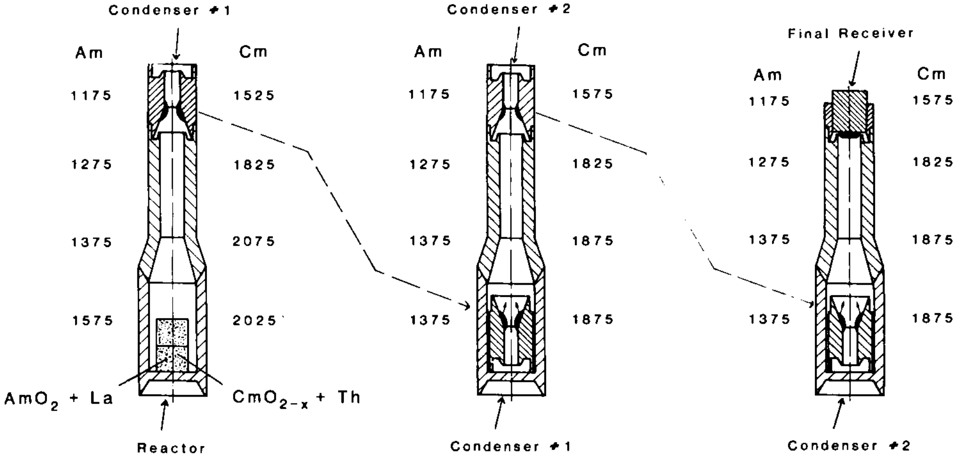

FIG. 4. Tantalum distillation columns and appropriate temperatures (K) for the preparation–purification of Am and Cm metals.

evaporation rate is maintained at the ideal value of 1–5 g of metal per hour. Americium is distilled at 1375 K and curium at 1875 K. The deposition temperatures are 1175 K for americium metal and 1575 K for curium metal (*112*).

C. IODIDE TRANSPORT

The efficiency of the van Arkel–De Boer process (Section II,D) for refining thorium and protactinium metals can be increased by repeating the process to achieve higher purity of product metal.

D. ELECTROREFINING, ZONE MELTING, AND SOLID-STATE ELECTROTRANSPORT

If an actinide metal is available in sufficient quantity to form a rod or an electrode, very efficient methods of purification are applicable: electrorefining, zone melting, and electrotransport. Thorium, uranium, neptunium, and plutonium metals have been refined by electrolysis in molten salts (*84*). An electrode of impure metal is dissolved anodically in a molten salt bath (e.g., in LiCl/KCl eutectic); the metal is deposited electrochemically on the cathode as a solid or a liquid (*19, 24*). To date, the purest Np and Pu metals have been produced by this technique.

In zone melting, a narrow molten zone is passed several times along a thin metal rod. Metallic impurities and carbon dissolve in the liquid and move with the molten zone to the end of the rod, whereas oxygen and nitrogen move to the opposite end.

If the metal is kept just below its melting temperature, refining in an electric field [solid-state electrotransport processing (SSEP)] is possible for actinide metals with low vapor pressures (Th, Pa, U, Np, and Pu). Oxygen, nitrogen, and carbon are carried with the electron flow, while metallic impurities move in the opposite direction, resulting in purification of the central part of the rod. Both zone melting and SSEP require a very high vacuum. Refining of Th by SSEP (1875 K, $\sim 2 \times 10^3$ A/cm^2, 0.1 mPa) resulted in metal with a resistivity ratio (Sections I and V,B) of 200;[1] improving the vacuum to 0.3 nPa yielded Th metal with a resistivity ratio of about 2000 (*99*). A Th metal rod was then made from four segments of this best, once-processed Th and reprocessed by SSEP at 0.3 nPa to produce the world's purest Th metal, that with a resistivity ratio of 4200 (*99*).

---

[1] The *resistivity ratio* is defined as the resistivity of the metal at 300 K divided by its resistivity at 4.2 K. The resistivity at 4.2 K is assumed to be due entirely to impurities.

IV. Growth of Single Crystals of Actinide Metals

Actinide solid-state research progress depends upon the availability of single crystals of the highest possible purity and perfection level. Due to spin–orbit coupling, the properties of actinide compounds are very anisotropic. The unusually large anisotropic field (10^6 0e or higher) cannot be explained by orbital anisotropy alone. Investigation of this phenomenon (bonding anisotropy) can only be carried out on good single crystals by magnetization measurements, neutron scattering, and angular- and energy-resolved photoemission spectroscopy.

Single crystals of the actinide metals are particularly difficult to grow. The light actinide metals (U, Np, and Pu) exhibit multiple crystallographic phases. Methods of crystal growth from the liquid state (zone melting, Czochralski) are therefore not usually applicable. More delicate crystal growth techniques (*64*) like recrystallization in the solid state using grain coarsening (*39*), strain annealing (*16, 116*), solid-state electrotransport (*99*), or phase transformation (*49, 90, 105*) techniques at normal or high pressure (*70, 71*) have to be employed. The various methods used to grow single crystals of actinide metals are summarized in Table IV. The van Arkel–De Boer process (chemical vapor transport) has facilitated the preparation of single crystals of thorium and protactinium metals (Fig. 5) (*108, 109*). The best single crystals of actinide metals available in macro quantities are obtained by solid-state electrotransport under ultrahigh vacuum ($\leqslant 0.5$ nPa).

TABLE IV

METHODS USED TO GROW SINGLE CRYSTALS OF ACTINIDE METALS

Element	Method	Reference
Thorium	Strain anneal	*116*
	Phase change	*49, 90*
	van Arkel–De Boer (chemical vapor transport)	*108*
	Solid-state electrotransport	*99*
Protactinium	van Arkel–De Boer (chemical vapor transport)	*109*
Uranium	Strain anneal	*16*
	Phase change	*105*
	Grain coarsening	*39*
	High pressure	*71*
	Electrodeposition in molten salts	*17*
Neptunium	—	None reported
Plutonium	High pressure	*70*
Americium	Physical vapor transport	*106*
Curium	Physical vapor transport	*83*

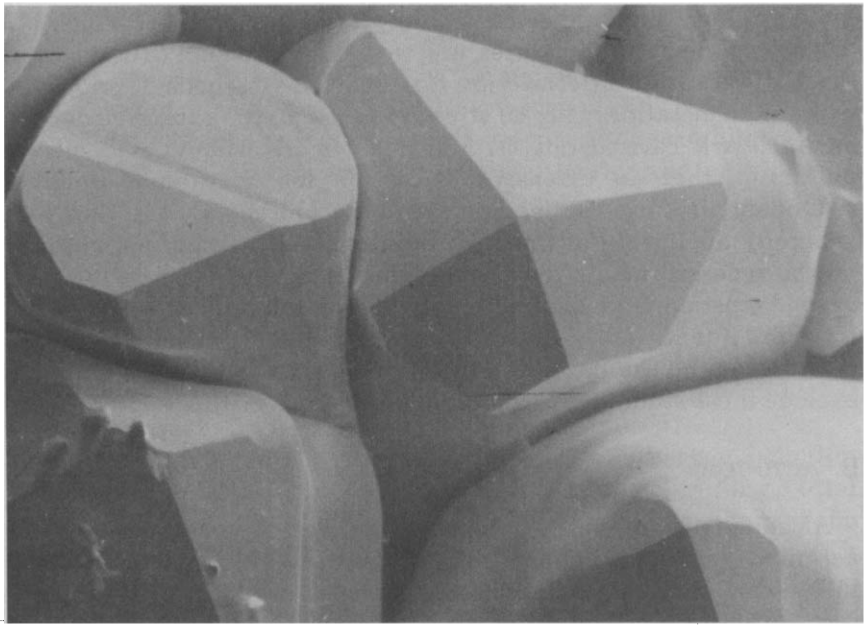

FIG. 5. Scanning electron micrograph of single crystals of Pa metal grown by iodide transport (Sections II,D and III,C); magnification = 100 × (*107*).

Large single crystals (54 mm^3) of ultrapure thorium metal have been prepared by this technique (*99*).

During the electrorefining of uranium metal in a molten salt eutectic, a low current density favors the formation of large single crystals. Up to 5-cm^3 single crystals of uranium metal have resulted from the large-scale (100 kg of U) electrorefining of uranium metal in molten LiCl/KCl eutectic (*17*).

Single crystals of elemental Am (*106*) and Cm (*83*) have been obtained during their refining by deposition of the metal vapor at 1175 K and 1575 K, respectively (Section III,B; Fig. 4).

V. Specifics of Actinide Metal Preparation

A. GENERAL COMMENTS

Differences in the availability and radioactivity of the actinides lead to a great disparity in the lengths of the following discussions of the individual elements. For instance, both thorium and uranium have been known since the nineteenth century; there seems little point in discussing their early histories, and we have chosen not to do so, which results in a rather brief section for each. The methods developed for neptunium metallurgy are so strongly based on the extensive developmental work carried out for the much more widely used element plutonium that an extensive discussion for neptunium would be redundant. In fact, the methods used for plutonium metallurgy are generally applicable to thorium, uranium, and neptunium, and need not be redescribed. At the heavy end of the actinides, the elements beyond einsteinium exist only in submicrogram or even in so little as few-atom quantities. Some fascinating techniques have been worked out to examine the nature of these elements, but we have chosen to exclude these studies as being beyond the scope of this review.

B. ACTINIUM

Although in a strict sense not a member of the actinide series, actinium is included here for completeness as lanthanum is frequently included in the lanthanide series. The longest lived isotope of actinium is ^{227}Ac with a half-life of 21.8 years. It occurs in nature from the decay of ^{235}U but also may be prepared by bombarding ^{226}Ra with neutrons. Actinium decays via a series of short-lived isotopes, eventually ending with stable lead. The presence of these radioactive daughters, particularly ^{227}Th (which is a strong γ-emitter), necessitates the use of lead-lined gloved boxes and remote control manipulators. Consequently, the metallurgy of actinium has been little studied and, due to the great expense and trouble involved, probably will not be studied extensively in the future.

The first preparation of metallic Ac was on the microgram scale and used the metallothermic reduction (Section II,A) of $AcCl_3$ with K metal vapor (*38*), which is the same method used by Klemm and Bommer (*67*) to prepare La metal. The metal produced by this method is mixed with KCl and K metal. X-Ray diffraction revealed that Ac metal was isostructural with β-La, but that the face-centered cubic cell dimension of Ac (5.311 Å) was slightly larger than that of La (5.304 Å).

A milligram-scale preparation has been reported that used AcF_3 with Li metal as the reductant (*115*). No X-ray diffraction data were obtained. The melting point was found to be 1325 ± 50 K. The metal was observed to glow in the dark with a blue color (*115*).

Reduction of Ac_2O_3 by Th metal followed by evaporation of the Ac metal (Section II,B) was used by Colson (*9, 22*); the product was re-evaporated and then collected on tantalum platelets. It was characterized by X-ray diffraction. Two different preparations gave values for the unit cell dimension of 5.317 and 5.314 Å, slightly larger than the value reported previously (*38*).

In principle, a promising method for the preparation of Ac metal is the tantalothermic reduction of AcC, as described generally in Section II,C. This method has not been tried as yet, however, so the metallothermic reduction of an actinium halide or oxide remains the only proved method.

C. THORIUM

Thorium occurs naturally primarily as the very long-lived ^{232}Th ($\tau_{1/2} > 10^{10}$ years), along with small amounts of other isotopes resulting from the radioactive decay of ^{235}U and ^{238}U. It is so weakly radioactive that very few precautions are necessary in its handling.

Thorium metal is generally prepared by the metallothermic reduction of its halides (Section II,A). Very high-quality metal containing a total of 250 ppm impurities has been prepared at the Ames Laboratory of the Department of Energy (*98, 99*). These workers reduced $ThCl_4$ with excess Mg metal to yield a Th–Mg alloy, which was then heated *in vacuo* to remove the excess Mg (*99*):

$$\mathrm{ThCl_4 + Mg(xs) \longrightarrow Th{-}Mg(alloy) + 2MgCl_2}$$

$$\mathrm{Th{-}Mg(alloy) \xrightarrow[\Delta]{vacuum} Th(sponge) + Mg(vapor)}$$

Ultrapure Th metal has been processed at the Ames Laboratory by solid-state electrotransport under very low pressures (on the order of 0.3 nPa), which has produced the purest Th metal known, that with a resistivity ratio of 4200 for doubly refined metal (*99–101*). This resistivity ratio of 4200 translates into probably <50 ppm total impurities in the metal (see footnote 1) (*87–90, 104*). Single crystals measuring 0.25 cm in diameter by 1.1 cm in length with resistivity ratios of 1700–1800 have also been grown (*99*).

The method of choice for the preparation of Th metal is reduction of the tetrachloride (Section II,B) by Mg (*99*), followed by refinement using electrotransport purification (Section III,D) (*87, 88, 90*).

D. PROTACTINIUM

The most common isotope of protactinium is ^{231}Pa ($\tau_{1/2} = 3.3 \times 10^4$ years), which occurs in pitchblende in the amount of 300 mg/ton, about the same as radium. The heroic efforts of British researchers resulted in the isolation of some hundred grams of ^{231}Pa from the sludge left over from uranium processing; without this supply, little or nothing would be known about Pa metal. Freshly purified Pa can be handled in gloved boxes without extra shielding. Aged Pa emits strong and intense penetrating radiation resulting from its decay products so that shielding must be provided.

Protactinium metal was first prepared in 1934 by thermal decomposition of a pentahalide on a hot filament (*50*). It has since been prepared from PaF_4 by metallothermic reduction (Section II,A) with barium (*26, 27, 34, 102*), lithium (*40*), and calcium (*73, 74*). However, the highest purity metal is achieved using the iodide transport (van Arkel–De Boer) process (Section II,D).

The method of choice for the preparation of Pa metal is a somewhat modified van Arkel–De Boer process, which uses protactinium carbide (Section II,C) as the starting material. The carbide and iodine are heated to form protactinium iodide, which is thermally dissociated on a hot filament (*12–15*). An elegant variation is to replace the filament with an inductively heated W or Pa sphere (*109*). A photograph of a 1.4-g sample of Pa metal deposited on a radiofrequency-heated W sphere is shown in Fig. 6. From the analytical data presented in Table V, the impurities present before and after application of this modified iodide transport process (Sections II,D and III,C) can be compared.

Levitation melting (Section III,A) of Pa metal in high vacuum results in a considerable increase in purity. Metallic Pa resembles Th metal in that it has a very high melting point and a low vapor pressure.

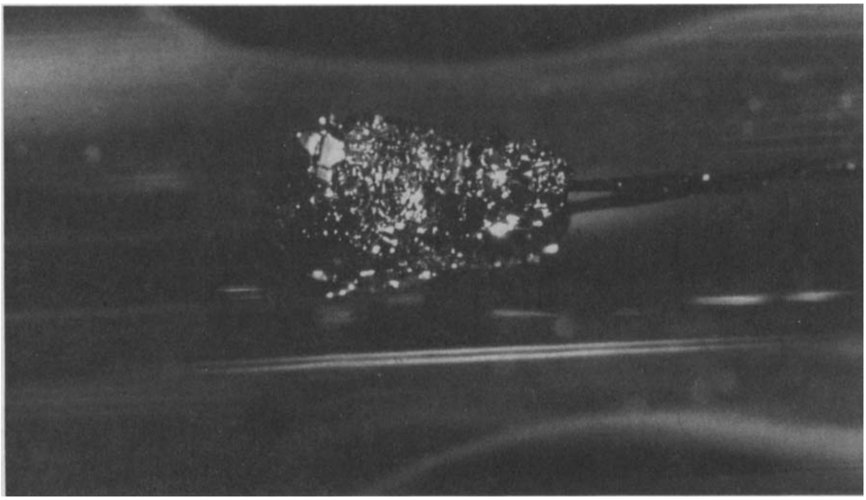

FIG. 6. A 1.4-g mass of Pa metal crystals deposited on a W sphere.

TABLE V

VAN ARKEL–DE BOER PURIFICATION OF PROTACTINIUM[a]

Element	Elemental impurities (atomic ppm)[b]	
	Starting material (oxide)	Refined metal
B	600	<1
Mg	600	25
Al	1,400	55
Si	68,000	600
Fe	2,500	100
Cu	700	6
Sr	100	<1
Nb	1,800	<1
Mo	180	5
Ag	150	1
Ba	1,600	<2
Bi	48	<1
Th	120	97
U	74	29
Am	60	<1
Ti	—	170
Total purity	93 at %	99.7 at %

[a] From ref. (*109*).

[b] All metals not listed were <100 atomic ppm. Nonmetallic elements in the refined metal were found to be 200 atomic ppm for N and 300 atomic ppm for O, with only traces of other elements.

Secondary refining processes such as zone melting and solid-state electrotransport (Section III,D) should yield ultrahigh-purity Pa metal.

E. URANIUM

Uranium is spread widely over the world but usually occurs in very low concentrations. Since the beginning of the nuclear age, the estimates of its abundance have been revised upwardly rather dramatically. Presently there is a surfeit, which is probably a temporary situation. In any event, multiton amounts are available, which affects the technology employed in its metallurgy. The radioactivity of natural uranium is so low as to present no problems in its handling. Over 99% is composed of very long-lived ^{238}U with a half-life of 4.5×10^9 years; the balance is primarily the fissionable isotope ^{235}U. The real concern associated with uranium handling probably stems more from the danger of heavy metal poisoning than from radioactivity.

It appears that Peligot in 1841 was the first to prepare U metal, using the metallothermic reduction of UCl_4 by K metal (Section II,A). At present, U metal is usually prepared by the same general method; that is, reduction of uranium halides by alkali or alkaline earth metals. The calciothermic reduction of UF_4 in either closed bombs or open crucibles is the most commonly used method for preparing U metal (*121*). The product metal is usually relatively impure. When special precautions were taken to purify the reagents, multigram quantities of very pure U metal containing only a few hundred ppm of impurities (Table VI) were obtained by bomb reduction of UF_4 with Ca metal (*7, 65*). Further refining can improve the quality of the metal. Vacuum melting (Section III,A) is used to eliminate the excess reductant metal. Electrorefining (Section III,D) in molten salts such as LiCl/KCl eutectic (*11*) is also a very effective purification method. At low current densities and on the kilogram scale, large single crystals (Section IV) of pure U metal have been obtained by this secondary purification (*17*).

As with Th and Pa metals, ultrapure U metal can in principal be obtained by such methods as zone melting and solid-state electro-

TABLE VI

AVERAGE ANALYSIS OF URANIUM METAL PRODUCED BY Ca REDUCTION OF UF_4 ON THE 250-g SCALE[a]

Element	Impurity level (ppm by wt)
Al	<2
B	<0.1
Be	<0.1
C	<25
Ca	<10
Co	<5
Cr	2
Cu	1
Fe	50
Li	<0.1
Mg	<3
Mn	6
Na	<1
Ni	8
O	<70
Si	<7
V	<10
Total	<200

[a] From ref. (*65*).

transport (Section III,D). The method of choice for the preparation of excellent-quality U metal is bomb reduction of UF_4 by Ca metal (*7, 65*).

F. NEPTUNIUM

The only isotope of Np suitable for chemical work is ^{237}Np, which has a very long $\tau_{1/2}$ of 2.14×10^6 years. It is an α-emitter with some penetrating γ radiation, and is available in kilogram amounts. The isotope is formed in nuclear reactors from both ^{235}U and ^{238}U and also results from the α-decay of ^{241}Am. Although it is the least toxic of the common transuranic isotopes, it is about 1000 times more radioactive than U and should always be handled in gloved boxes.

The metallothermic reduction of NpF_3 with Ba metal vapor (Section II,A) was used in 1948 to prepare Np metal on the 50-μg scale (*41*). The same method was used to prepare some few milligrams of elemental Np in 1951 (*124*). The metal has been prepared on the gram and multigram scales with yields up to 99% by reduction of NpF_4 with Ca metal (*4, 33, 35, 68, 76*); Li metal has also been used as the reductant (*78*). The metal obtained by these methods is not very pure, but it can be refined further by vacuum melting (Section III,A) and by electrorefining in molten salts (Section III,D). Another preparative method is electrolysis between a graphite anode and a W cathode of Np(III) dissolved in a molten LiCl/KCl eutectic (Section II,E) (*75*). Figure 7 shows 2.5 g of Np metal electrodeposited on a W electrode.

Direct oxide reduction by Ca metal (Section II,A) in a molten $CaCl_2$ solvent system (*80*) has been used for kilogram-scale production of Np metal. The product metal is further purified by electrorefining (Section III,D). This combination has been used to prepare Np metal which is 99.9 at % pure. Analyses of two preparations are given in Table VII (*20*). A

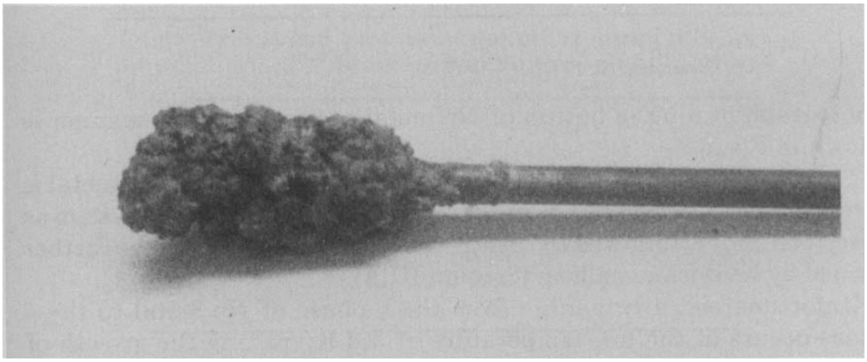

FIG. 7. Neptunium metal (2.5 g) electrodeposited on a W electrode.

TABLE VII

ANALYSIS OF ULTRAPURE NEPTUNIUM METAL[a]

Element	Impurity level (ppm by wt)	
	Preparation 1	Preparation 2
Ag	3	5
Al	30	25
Am	0.2[b]	0.2[b]
B	<5	<5
Be	<1	<1
Bi	<1	<1
C	20	5
Ca	100	300
Cd	<10	<10
Cr	<5	<5
Cu	<1	<1
Fe	<5	<5
Ir	<100	<100
Mg	<1	<1
Mn	<1	<1
Mo	<20	<20
Na	<50	<50
Ni	<5	<5
O	75	40
Pb	<5	<5
Pu	14	14.6
Si	<5	<5
Sn	<5	<5
Ta	<10	<10
U	<10	<10
W	<10	<20
Zn	<5	<5
Total purity (wt %)	99.97	99.96

[a] From ref. (*20*).

[b] On December 10, 1984.

photograph of a 500-g button of Np metal produced in this manner is shown in Fig. 8.

The method of choice for kilogram-scale preparations of Np metal is direct oxide reduction by Ca metal in a molten $CaCl_2$ solvent system as described above, followed by electrorefining. This metal can be further refined by levitation melting (Section III,A).

Unfortunately, a transition from the α phase of Np metal to the β phase occurs at the low temperature of 301 K, making the growth of single crystals of α-Np metal extremely difficult.

FIG. 8. A 500-g button of Np metal. Courtesy Los Alamos National Laboratory, Los Alamos, New Mexico.

G. PLUTONIUM

The relatively long-lived isotopes of Pu suitable for chemistry and metallurgy are those of masses 238, 239, 240, 241, 242, and 244. Plutonium formed in nuclear reactors occurs as a mixture of isotopes. A typical isotopic composition of Pu in spent fuel containing 10.4 kg of Pu/ton of fuel is given in Table VIII.

TABLE VIII

TYPICAL ISOTOPIC COMPOSITION OF PLUTONIUM IN SPENT REACTOR FUEL[a]

Mass number	Weight percent	$\tau_{1/2}$ (years)	Principal radiation
238	1	87.7	α
239	56	2.4×10^4	α
240	26	6.6×10^3	α
241	12	14.4	β
242	5	3.8×10^5	α

[a] From ref. (*18*).

The isotope ^{238}Pu is of special value as a heat source to make electricity for various esoteric uses, mainly in space. Plutonium-244, with a $\tau_{1/2}$ of 8.1×10^7 years, is the longest lived Pu isotope available in multigram quantities. It is formed from various Pu isotopes by successive neutron capture. Unfortunately, it is very rare and expensive due to the fact that long irradiations are necessary to produce significant amounts and that it has to be separated from the mixture of Pu isotopes formed in nuclear reactors. Long-lived ^{242}Pu can be prepared by extremely long-term neutron irradiation of reactor Pu so that the isotopes of mass numbers 239–241 are burned up or converted to ^{242}Pu. This isotope can be made 99% isotopically pure by neutron irradiation of ^{241}Am to produce ^{242}Am, which has a 17% electron capture decay branch to ^{242}Pu. It is available in multigram quantities and thus is extremely valuable, although very expensive, for research purposes.

It should be emphasized that all isotopes of Pu are sufficiently radioactive so that they must be handled in gloved boxes. However, Pu is formed as a mixture of isotopes, many of which emit neutrons and/or form daughters that emit penetrating radiation resulting from their decay. Neutron emission rates of various Pu isotopes are given in Table IX (*103*).

Because of the wide variations in the neutron emission rates shown in Table IX, it is obviously necessary to know the isotopic composition of any particular batch of Pu in order to know how much and what kind of shielding is demanded for biologic safety.

The first Pu metal ever made was prepared in late November 1943 by metallothermic reduction of about 35 μg of PuF_4 with Ba metal (Section II,A) (*42*). This method, modified to use Ca as the reductant for PuF_4, has been widely used and is very successful; yields of more than 98% and purities of the order of 99.8 at % are obtained (*2, 5, 62, 81, 96*). The Pu

TABLE IX

NEUTRON EMISSION RATES FOR VARIOUS PLUTONIUM ISOTOPES[a]

Isotope	From spontaneous fission (n sec^{-1} g^{-1})	From (α,n) reactions in PuF_4 (n sec^{-1} g^{-1})
^{238}Pu	3.4×10^3	2.1×10^6
^{239}Pu	0.02	4.3×10^3
^{240}Pu	1.0×10^3	1.6×10^3
^{242}Pu	1.7×10^3	1.7×10^2

[a] From ref. (*103*).

metal from the calciothermic reduction can be refined by vacuum melting (Section III,A) or by electrorefining in molten salts (Section III,D) to give metal of 99.9+ at % purity.

Another approach used to prepare massive amounts of Pu metal is reduction of PuO_2 with Ca metal (Section II,A) in a molten $CaCl_2$ flux. The molten $CaCl_2$ dissolves the CaO and separates the metallic phases (*118*). The yield and purity of the product Pu metal are excellent. This method was further developed and then used to prepare massive amounts of elemental ^{238}Pu for isotopic power sources (*84*). This DOR method (*6, 19, 21, 24, 84*) is now competitive with the metallothermic reduction of PuF_4 described above. A photograph of a typical Pu metal product from this DOR process is shown in Fig. 9. Electrorefining of this metal routinely yields Pu of 99.9 at % purity. A photograph of a cylinder of ultrapure Pu metal produced by electrorefining is given in Fig. 10. An analysis of ultrapure Pu metal (99.995% by weight) furnished to the United States Bureau of Standards as a primary standard is given in Table X (*60*).

The method of choice for the preparation of Pu metal on the multigram to kilogram scale is metallothermic reduction of PuF_4 or PuO_2 by Ca metal (*69*), followed by electrorefining with TaC electrodes and vacuum casting. This method produces metal 99.9 at % pure. An

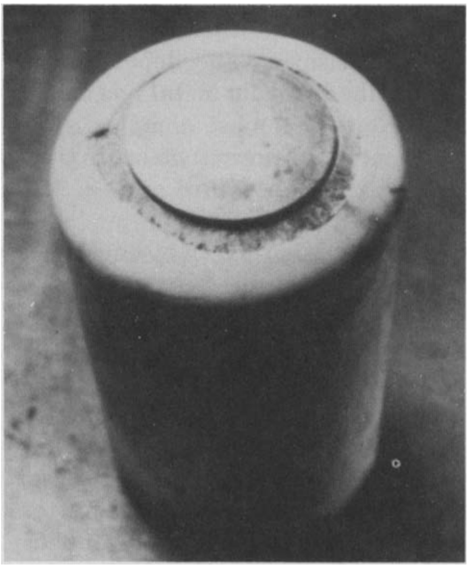

FIG. 9. Photograph of a typical Pu metal product from the DOR process.

FIG. 10. 5.3 kg of ultrapure (99.99% by wt) Pu metal produced by electrorefining in a molten salt.

alternative method is the tantalothermic reduction of PuC (*111*) followed by selective vaporization and deposition (Section III,B). A review of preparative methods for Pu metal has been published (*69*).

Plutonium metal exhibits the most complex series of crystalline phases of any known element. At normal pressure there are six metallic phases of Pu between room temperature and its 913 K melting point (*60*).

Single crystals of α-Pu have been grown by holding polycrystalline Pu metal at 675 K under a hydrostatic pressure of 5.5 GPa for several days (*70*).

H. AMERICIUM

The isotopes of Am useful for metallurgical studies are ^{241}Am and ^{243}Am, both of which are available in multigram or even kilogram amounts. The lighter isotope, ^{241}Am, has the shorter $\tau_{1/2}$ of only 432 years, which results in self-heating and consequent corrosion of the metal. It is thus less desirable for metallurgical studies. This isotope is formed by β-decay of ^{241}Pu ($\tau_{1/2} = 14$ years), which itself is formed by

TABLE X

IMPURITY LEVELS IN PLUTONIUM[a,b]

Element	Concentration[c]	Element	Concentration[c]
Li	<0.005	Cd	<1
Be	<0.001	Sn	<1
B	<0.5	Ba	<0.5
Na	<1	La	<1
Mg	2	Hf	<1
Al	<0.5	Re	<1
K	<0.5	Pb	<1
Ca	<4	Bi	<1
Ti	<0.5	Fe	5
V	<0.5	Am	7
Cr	<0.5	Si	2
Mn	<0.5	C	10
Co	<1	U	11
Ni	<0.5	Ta	6
Cu	<0.5	Th	<0.5
Zn	<5	Ga	<1
Sr	<0.5	W	<2.5
Y	<1	O	10
Zr	<1	H	<5
Mo	<1	N	3

[a] Casting made for the United States Bureau of Standards.
[b] From ref. (*60*).
[c] Expressed in parts per million of plutonium by weight.

successive neutron captures in a nuclear reactor. The second, heavier isotope, ^{243}Am, has a $\tau_{1/2}$ of 7380 years, 17 times longer than that of ^{241}Am, a fact which makes it much more suitable for metallurgical studies. This heavier isotope is formed by successive neutron captures in a nuclear reactor; its immediate precursor is 16-hour ^{242}Am. Both isotopes emit α- and γ-radiation and must be handled in shielded gloved boxes.

Metallothermic reduction of AmF_3 with elemental Ba (Section II,A) was used for the early, mostly microgram scale, preparations of Am metal (*48, 72, 122, 123*). Although the Am was not of high purity, the studies of these early Am metal products yielded valuable information about the basic thermodynamic, magnetic, and crystallographic properties of Am metal. In 1960, the first milligram quantities of Am metal were prepared using this method (*79*). At that time, workers at Los Alamos developed a new preparative method (*79*) based on the greater volatility of Am metal versus that of elemental La. Reduction of AmO_2

with La metal at elevated temperature resulted in the preparation and separation of the more volatile Am metal, which was then deposited on a fused silica fiber (Section II,B). The less-volatile by-product, La_2O_3, and excess La metal reductant were left behind in the Ta crucible. The size of the Am metal unit cell was then determined by X-ray diffraction of the metal deposited on the fiber.

Much effort was expended in improving techniques for both the metallothermic reduction of the halide (*77*), usually with Ba metal, and by reduction of the oxide with La metal (*63, 77, 110, 117*). Two significant improvements have been reported (*110*), which improved both yield and purity. The first was to pelletize intimate mixtures of La metal and AmO_2 powders (Section II,B; Fig. 2). The second was to eliminate the use of quartz for collection of Am vapor and ceramic crucibles for melting, since both quartz and ceramics were shown to introduce several thousand ppm oxygen. Use of Ta for these operations yielded Am metal containing <250 ppm by weight of oxygen.

Other methods for the preparation of elemental Am, mostly variations on the above two, have been studied (*1, 23, 63*). Thermal decomposition of the intermetallic compound Pt_5Am has also been used to prepare Am metal (*36, 82, 110*).

At the present time, when gram to kilogram amounts of either Am isotope are available, the method of choice for the preparation of Am metal is the metallothermic reduction of AmO_2 with La (or Th) using a pressed pellet of the oxide and the reductant metal. An oxide reduction–metal distillation still system is shown schematically in Fig. 11. Yields of Am metal are typically $>90\%$ and purity levels equal or exceed 99.5 at %. Further purification of the product Am metal can be achieved by repeated sublimations under high vacuum in a Ta apparatus (Section III,B; Fig. 4). A photograph of 2 g of Am metal distilled in a Ta apparatus is given in Fig. 12.

I. CURIUM

The isotopes of Cm available in multigram quantities are ^{242}Cm with a $\tau_{1/2}$ of only 163 days and ^{244}Cm with a longer $\tau_{1/2}$ of 18.1 years, still inconveniently short for chemical studies. These isotopes are made by successive neutron captures of ^{239}Pu in a nuclear reactor. The two relatively long-lived isotopes of Cm, available only in few-mg amounts, are ^{246}Cm with a $\tau_{1/2}$ of 4730 years and ^{248}Cm with a $\tau_{1/2}$ of 3.4×10^5 years. The cost of these two isotopes, measured in terms of neutrons used in their formation, is so great that it is probable that only milligram quantities will ever be available for study. The isotope ^{248}Cm is obtained in $>90\%$ isotopic purity from the α-decay of ^{252}Cf. All of

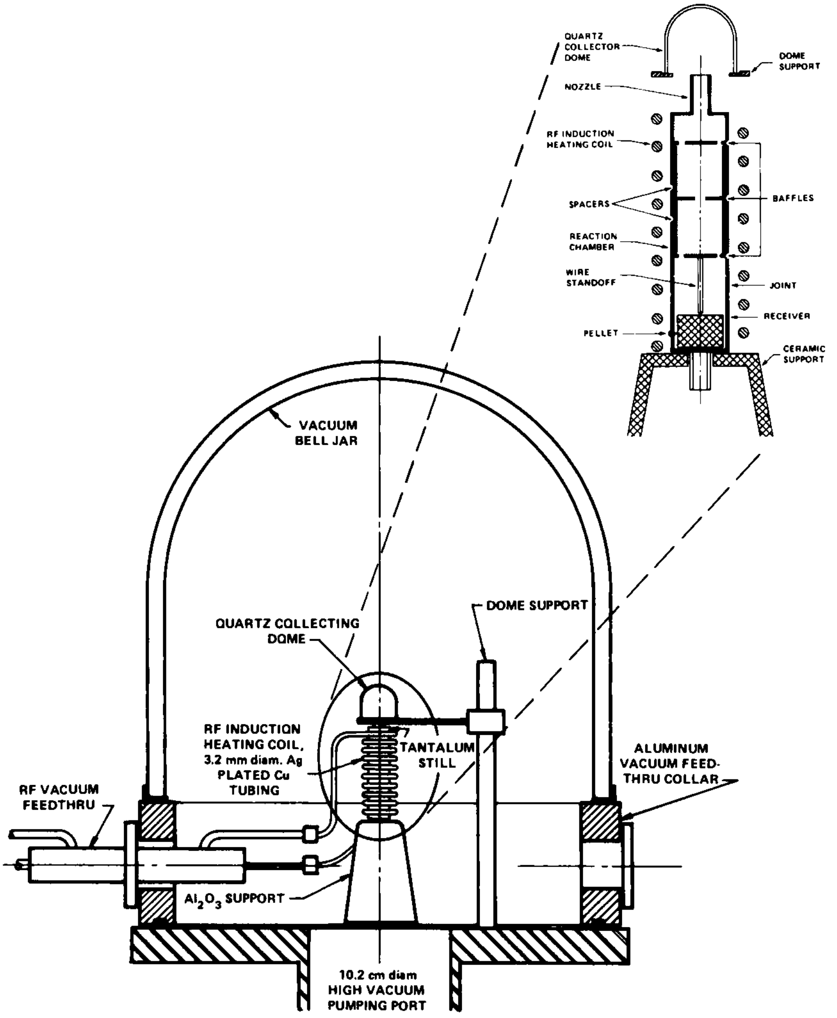

FIG. 11. An oxide reduction–metal distillation still system.

these curium isotopes are primarily α-emitters; however, the neutron emission rate accompanying spontaneous fission becomes more significant the larger the quantity of curium involved and/or the higher the mass number of the curium isotope. Also, the (*α*,*n*) reaction on the flourine nuclei in CmF_3 or CmF_4 produces neutrons which can be neglected with submilligram quantities of curium but which cause a serious problem with grams or more of curium.

Two preparations of Cm metal by the metallothermic reduction of CmF_3 with Ba metal (Section II,A) have been reported (*29, 119*). The

FIG. 12. Distilled Am metal (2 g) (center, front) and associated parts of the Ta still.

first, in 1951, resulted in the preparation of a few micrograms of a silvery metal which rapidly tarnished, presumably due to the high radioactivity of the ^{242}Cm employed. Thirteen years later, a similar reduction scheme using a double Ta crucible with an effusion hole resulted in the preparation of 0.25–0.50 mg of silvery ^{244}Cm metal. The contaminant found in the greatest concentration in this metal product was oxygen, at 4000 ppm.

To avoid the problems arising from excessive neutron production via (α,n) reactions when using a fluoride of Cm, a scheme employing reduction of the oxide by an Mg–Zn alloy in a flux of $MgCl_2$–MgF_2 was developed to produce up to gram quantities of elemental Cm (*37*). This method has the distinct disadvantage of concentrating any nonvolatile impurity originally present in the reagents in the product Cm metal.

Two other methods have been used successfully to prepare very pure Cm metal. A rather unique one is thermal decomposition of the intermetallic compound Pt_5Cm produced by hydrogen reduction of curium oxide in the presence of Pt (*36, 82*). The second method, the method of choice for gram-scale preparations of very pure Cm metal, involves reduction of curium oxide with Th metal (*8, 83*) in an apparatus like those shown schematically in Fig. 4 (Section III,B) and Fig. 11 (Section V,H). An intimate mixture of excess thorium metal and curium oxide is pelletized, outgassed, and then heated initially to 1925 K and finally to 2300 K (*8*). Yields of Cm metal of 74% (*8*) and about 90% (*83*) have been obtained. Extensions of this method, including multiple distillations and depositions at controlled temperatures (Section III,B; Fig. 4), resulted in the preparation of very high-purity Cm metal, with total cationic impurities at <50 ppm, O at 250 ppm, N at 20 ppm, and H at 10 ppm (*83*). A photograph of the Cm metal obtained by this method is shown in Fig. 13.

The method of choice for preparing up to 10 mg of metal, when using the rare ^{248}Cm, is metallothermic reduction (Section II,A) of anhydrous, oxygen-free CmF_4 (from treatment of CmF_3 with F_2 or ClF_3) with Ba metal vapor (*31, 58, 113, 114*).

J. BERKELIUM

The only isotope of Bk available in weighable quantities is ^{249}Bk, which is obtained by long-term neutron irradiation of Pu, Am, or Cm in

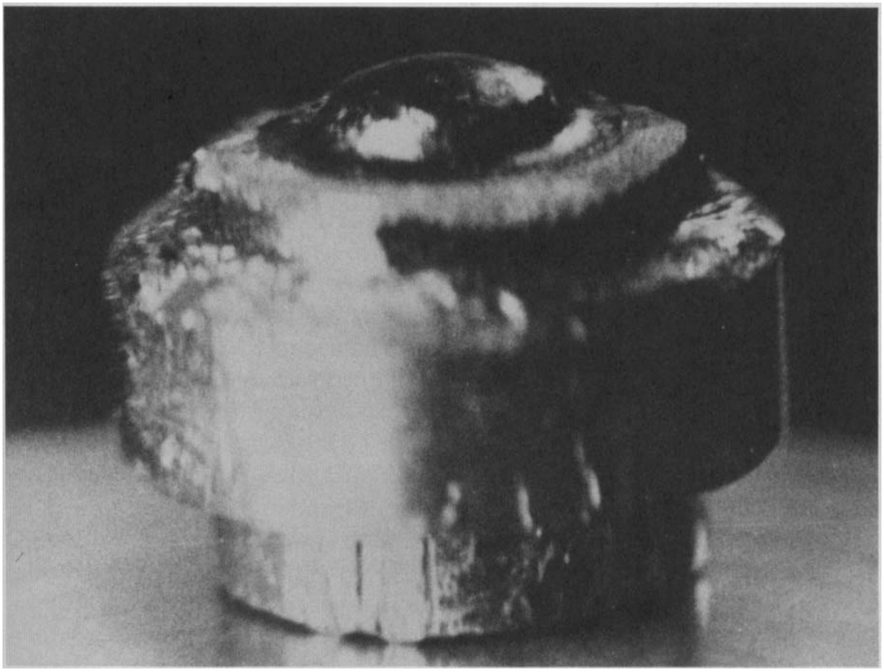

FIG. 13. A mass of Cm metal produced by distillation and deposition in a Ta still.

high-flux nuclear reactors. This isotope is a weak β-emitter, 126 keV maximum, which makes it difficult to identify when in the presence of other radioactivities, but which means that it poses little biologic danger until it decays (with a $\tau_{1/2}$ of 320 days) to the α-emitting ^{249}Cf. This decay daughter is so biologically dangerous that ^{249}Bk must be handled in gloved boxes.

Metallothermic reduction of BkF_3 by Li metal vapor (Section II,A) was used in 1968 for the first preparation of Bk metal on the few-microgram scale (*94*). This difficult task was accomplished by developing some unique microchemical techniques. Microgram quantities of Bk(III) were collected and manipulated by employing the single-bead ion-exchange resin technique (*25*). A W wire spiral holding the spherically shaped sample of BkF_3 was suspended from a Ta "chair," and it and the Li reductant were enclosed in a Ta crucible fitted with a cap having an effusion hole to permit the escape of by-product LiF and excess Li (*92, 93*).

The next preparation of Bk metal was in 1975 (*43*) and was on the much larger scale of 0.25–0.50 mg. The much improved yields resulted by lowering the heat capacity of the reduction system (*113*) to minimize vaporization losses of the relatively volatile Bk metal. This reduction system is shown schematically in Fig. 14. The most recent preparations of Bk metal (*44, 53, 59*) have been on the multimilligram scale and have used BkF_4 (instead of BkF_3) prepared by F_2 or ClF_3 treatment of BkO_2 or BkF_3. This method has the advantage of completely removing oxygen.

In principle, the DOR process using La or Th metal as the reductant (Section II,B) should be an excellent method for preparing Bk metal. However, the limited amount of Bk available (< 50 mg/year) precludes

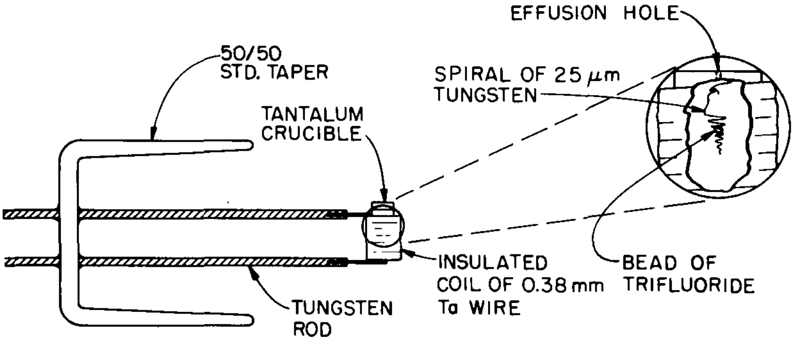

FIG. 14. Apparatus of low heat capacity used for preparation of Bk metal.

the use of this method due to the difficulty in handling the thin metal foils produced. The method of choice for the preparation of Bk metal is still metallothermic reduction of the tetrafluoride by an alkali or alkaline earth metal (Section II,A).

K. CALIFORNIUM

The only isotope of Cf suitable for chemical study is ^{249}Cf, an α-emitter with a $\tau_{1/2}$ of 351 years, which results from the β-decay of ^{249}Bk ($\tau_{1/2}$ = 320 days). This Cf isotope is an α-emitter and requires the usual precautions, such as working in gloved boxes, to avoid ingestion.

Initial attempts to prepare Cf metal using metallothermic reduction methods (Section II,A) were less than successful due to the high vapor pressure of Cf metal (*28, 46*). Reduction of californium oxide with La metal (Section II,B) and collection of the product Cf metal on a fused silica fiber (in the apparatus shown schematically in Fig. 15), were found to give metal with usable X-ray diffraction patterns (*3*). Later, the same method was used to collect Cf metal both on a fused silica fiber for X-ray diffraction analysis and on an electron microscopy grid for electron diffraction analysis (*56*). As more ^{249}Cf became available, preparations via this method were carried out on 0.4–1.0-mg samples of californium oxide (*55*), using fibers of quartz, Be, or C (suitable for direct X-ray diffraction analysis) to collect the product Cf metal.

A thorough study of the metallothermic reduction of CfF_3 with Li metal vapor (Section II,A) was reported in 1976 (*85*). From these studies, the three crystal structures of Cf metal and the temperature relationships between them were elucidated, but uncertainties still remained due to the lack of adequate analytical data concerning the level of impurities in the Cf metal studied (*85*).

All subsequent preparations of Cf metal have used the method of choice, that is, reduction of californium oxide by La metal and deposition of the vaporized Cf metal (Section II,B) on a Ta collector (*10, 30, 32, 45, 91, 97, 120*). The apparatus used in this work is pictured schematically in Fig. 16. Complete analysis of Cf metal for cationic and anionic impurities has not been obtained due to the small (milligram) scale of the metal preparations to date. Since Cf is the element of highest atomic number available for measurement of its bulk properties in the metallic state, accurate measurement of its physical properties is important for predicting those of the still heavier actinides. Therefore, further studies of the metallic state of californium are necessary.

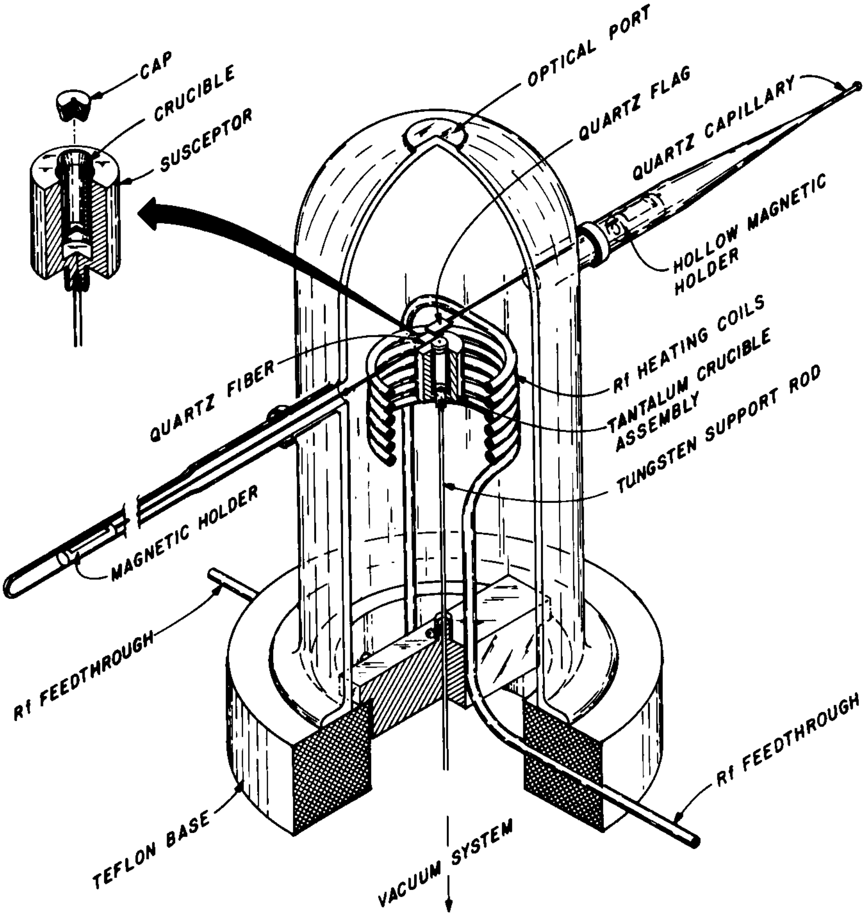

FIG. 15. Apparatus used for preparing early samples of californium metal.

L. EINSTEINIUM

The only isotope of Es available in at least multimicrogram quantities is ^{253}Es, whose half-life is 20.5 days. Considering the 6.6-MeV α-particles it emits at the rate of about 6×10^{10} min^{-1} μg^{-1}, the α-decay energy alone amounts to some 1.5×10^4 kJ mol^{-1} min^{-1}. This explains why there have been very few attempts to prepare Es metal!

The first attempted preparation of elemental Es was made on the 1-μg scale by distilling Li metal *in vacuo* onto an unheated sample of EsF_3 (Section II,A), followed by quickly raising the temperature of the Li-

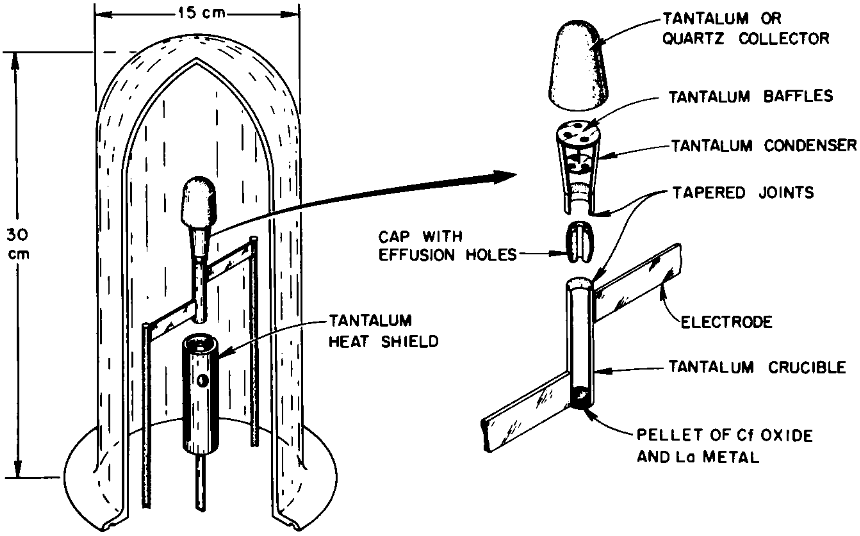

FIG. 16. Cf metal preparation apparatus.

coated EsF_3 to about 1075 K to promote reduction (*28*). The product obtained by quenching (to prevent complete loss of the volatile Es metal) exhibited four diffraction lines consistent with a face-centered cubic structure. These workers noted the high volatility of Es metal and suggested that it be exploited as a basis for quickly and efficiently separating and purifying Es from the lighter and less-volatile actinide metals. With the later availability of multimicrogram quantities of ^{253}Es, 20-μg pieces of Es_2O_3 were reduced with La metal (Section II,B) at about 1325 K; the evaporated metal was collected on carbon-coated, 3-mm diameter, electron microscopy grids (*57*). The thin film deposits were then analyzed by electron diffraction. The diffraction data were consistent with a face-centered cubic cell with a lattice parameter of 5.75 Å. Multimicrogram deposits of Es metal on Pt and Ta substrates have been obtained at Oak Ridge National Laboratory by distillation from Es_2O_3–La mixtures (*54*). The intense radiation and limited quantity of Es have precluded to date the preparation of bulk Es metal free of any supporting substrate.

The high volatility of metallic Es makes it an ideal candidate for preparation by metallothermic reduction of its oxide (Section II,B), but the scarcity of ^{253}Es prohibits its preparation in pure bulk form. Vaporization thermodynamics of Es metal have been determined, assuming that Henry's Law applies, using alloys of Es with divalent lanthanide metals (*66*). See Fig. 1 (Section II,A) for a comparison of the vapor pressures of many of the actinide metals, including Es.

VI. Some Physical Properties of Actinide Metals

Table XI gives the room-temperature, atmospheric pressure crystal structures, densities, and atomic volumes, along with the melting points and standard enthalpies of vaporization (cohesive energies), for the actinide metals. These particular physical properties have been chosen as those of concern to the preparative chemist who wishes to prepare an actinide metal and then characterize it via X-ray powder diffraction. The numerical values have been selected from the literature by the authors.

TABLE XI

PHYSICAL PROPERTIES OF ACTINIDE METALS

Actinide metal	Crystal structure	Density (g/cm^3)	Atomic volume (Å^3)	Melting point (K)	Enthalpy of vaporization ΔH°_{298} (kJ/mol)
Ac	Face-centered cubic	10.1	37.4	1325	(420)[a]
Th	Face-centered cubic	11.72	32.85	2028	597
Pa	Body-centered tetragonal	15.42	24.89	1840	570
U	Orthorhombic	19.05	20.75	1405	531
Np	Orthorhombic	20.48	19.22	913	465
Pu	Monoclinic	19.86	20.00	913	343
Am	Double-hexagonal close packed	13.67	29.27	1448	284
Cm	Double-hexagonal close packed	13.51	29.98	1620	387
Bk	Double-hexagonal close packed	14.78	27.96	1260	310
Cf	Double-hexagonal close packed	15.1	27.4	1173	196
Es	Face-centered cubic	8.84	47.5	1133	131

[a] Estimated value only; no measured value available.

ACKNOWLEDGMENTS

The authors wish to thank the following colleagues for their cooperation and assistance in preparing this chapter: J. Reavis, J. Ward, C. Herrick, D. Christensen, and L. Mullins of the Los Alamos National Laboratory, Los Alamos, New Mexico; F. Schmidt and J. Smith of the Ames Laboratory, Iowa State University, Ames, Iowa; R. Haire of the Oak Ridge National Laboratory, Oak Ridge, Tennessee; and J. Fuger of the European Institute for Transuranium Elements, Karlsruhe, FRG.

This research has been sponsored in part by the Commission of the European Communities and in part by the Division of Chemical Sciences, United States Department of Energy under contracts DE-AS05-76ER04447 with the University of Tennessee (Knoxville), DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc., and W-7405-ENG-36 with the University of California.

REFERENCES

1. Adair, H. L., *J. Inorg. Nucl. Chem.* **32,** 1173 (1970).

2. Anselin, F., *in* "Extractive and Physical Metallurgy of Plutonium and its Alloys" (W. D. Wilkinson, ed.), p. 61. Wiley (Interscience), New York, 1960.

3. Asprey, L. B., paper presented at the Third International Transplutonium Element Symposium, Argonne National Laboratory, Argonne, IL, October 20–22, 1971.

4. Baaso, D. L., Conner, W. V., and Burton, D. A., Doc. No. RFP-1032, Dow Chemical Co., Rocky Flats Div., U.S. Atomic Energy Commission, 1967.

5. Baker, R. D., and Maraman, W. J., *in* "Extractive and Physical Metallurgy of Plutonium and its Alloys" (W. D. Wilkinson, ed.), p. 43. Wiley (Interscience), New York, 1960.

6. Baldwin, C. E., and Navratil, J. D., *ACS Symp. Ser.* **216,** 369 (1983).

7. Bard, R. J., *et al.*, Doc. No. LA-1652, University of California, Los Alamos Scientific Laboratory, U.S. Atomic Energy Commission, Los Alamos, NM, 1954.

8. Baybarz, R. D., and Adair, H. L., *J. Inorg. Nucl. Chem.* **34,** 3127 (1972).

9. Baybarz, R. D., Bohet, J., Buijs, K., Colson, L., Müller, W., Reul, J., Spirlet, J. C., and Toussaint, J. C., *Transplutonium 1975, Proc. Int. Transplutonium Elem. Symp. 4th, 1975*, p. 61 (1976).

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

11. Blumenthal, B., and Noland, R. A., *Prog. Nucl. Energy Ser. 5* **1,** 62 (1956).

12. Bohet, J., Rep. EUR 5882 FR, Commission of the European Communities, 1977.

13. Bohet, J., and Müller, W., *J. Less-Common Met.* **57,** 185 (1978).

14. Brown, D., Tso, T. C., and Whittaker, B., Rep. No. AERE-R 8638, United Kingdom Atomic Energy Research Establishment, 1976.

15. Brown, D., Tso, T. C., and Whittaker, B., *J. Chem. Soc., Dalton Trans.*, p. 2291 (1977).

16. Cahn, R. W., Acta Metall. **1,** 176 (1953).

17. Chauvin, G., Coriou, H., and Hure, J., *Met. Corros.-Ind.* **37,** 112 (1962).

18. Choppin, G. R., and Rydberg, J., *in* "Nuclear Chemistry, Theory and Applications," p. 511. Pergamon, New York, 1980.

19. Christensen, D. C., and Mullins, L. J., *ACS Symp. Ser.* **216,** 409 (1983).

20. Christensen, D. C., unpublished results, University of California, Los Alamos National Laboratory, Los Alamos, NM, 1985.

21. Christensen, E. L., Grey, L. W., Navratil, J. D., and Schulz, W. W., *ACS Symp. Ser.* **216,** 349 (1983).

22. Colson, L., Ph.D. Thesis, University of Liège, Belgium, 1975.

23. Conner, W. V., Doc. No. RFP-1188, Dow Chemical Co., Rocky Flats Div., U.S. Atomic Energy Commission, 1968.

24. Coops, M. S., Knighton, J. B., and Mullins, L. J., *ACS Symp. Ser.* **216,** 381 (1983).

25. Cunningham, B. B., *Microchem. J. Symp. Ser.* **1,** 55 (1961).

26. Cunningham, B. B., *Colloq. Int. CNRS* **154,** 45 (1966).

27. Cunningham, B. B., *Proc. Int. Protactinium Conf., 3rd, Schloss Elmau, 1969,* BMBW-FBK 71–17, 14.1, 1971.

28. Cunningham, B. B., and Parsons, T. C., Doc. No. UCRL-20426, p. 239, University of California, Lawrence Radiation Laboratory, U.S. Atomic Energy Commission, Berkeley, CA, 1971.

29. Cunningham, B. B., and Wallmann, J. C., *J. Inorg. Nucl. Chem.* **26,** 271 (1964).

30. Damien, D. A., Haire, R. G., and Peterson, J. R., *J. Phys. Colloq.* **40,** C4–95 (1979).

31. Damien, D., Haire, R. G., and Peterson, J. R., *J. Less-Common Met.* **68,** 159 (1979).

32. Damien, D., Haire, R. G., and Peterson, J. R., *Inorg. Nucl. Chem. Lett.* **16,** 537 (1980).

33. Damien, M. D., Rep. CEA-N-816, p. 374, French Atomic Energy Commission, Fontenay-aux-Roses, 1967.

34. Dod, R. L., Ph.D. Thesis, University of California; Doc. No. LBL-659, Lawrence Berkeley Laboratory, U.S. Atomic Energy Commission, Berkeley, CA, 1972.

35. Eldred, V. W., and Curtis, G. C., *Nature (London)* **179,** 910 (1957).

36. Erdmann, B., and Keller, C., *Inorg. Nucl. Chem. Lett.* **7,** 675 (1971); *J. Solid State Chem.* **7,** 40 (1973).

37. Eubanks, I. D., and Thompson, M. C., *Inorg. Nucl. Chem. Lett.* **5,** 187 (1969).

38. Farr, J. D., Giorgi, A. L., Bowman, M. G., and Money, R. K., *J. Inorg. Nucl. Chem.* **18,** 42 (1961).

39. Fisher, E. S., *Trans. Met. Soc. AIME* **209,** 882 (1957).

40. Fowler, R. D., Matthias, B. T., Asprey, L. B., Hill, H. H., Lindsay, J. D. G., Olsen, C. E., and White, R. W., *Phys. Rev. Lett.* **15,** 860 (1965).

41. Fried, S., and Davidson, N., *J. Am. Chem. Soc.* **70,** 3539 (1948).

42. Fried, S., Westrum, E. F., Baumbach, H. L., and Kirk, P. L., *J. Inorg. Nucl. Chem.* **5,** 182 (1958).

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

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

45. Fuger, J., Haire, R. G., and Peterson, J. R., *J. Less-Common Metals* **98,** 315 (1984).

46. Fujita, D. K., Ph.D. Thesis, University of California; Doc. No. UCRL-19507, Lawrence Radiation Laboratory, U.S. Atomic Energy Commission, Berkeley, CA, 1969.

47. Goodman, L. S., Diamond, H., Stanton, H. E., and Fred, M. S., *Phys. Rev. A* **4,** 473 (1971).

48. Graf, P., Cunningham, B. B., Dauben, C. H., Wallmann, J. C., Templeton, D. H., and Ruben, H., *J. Am. Chem. Soc.* **78,** 2340 (1956).

49. Greiner, J. D., Peterson, D. T., and Smith, J. F., *J. Appl. Phys.* 48, 3357 (1977).

50. Grosse, A. V., *J. Am. Chem. Soc.* **56,** 2200 (1934).

51. Gschneidner, K. A., *in* "Science and Technology of Rare Earth Materials" (E. C. Subbarao and W. E. Wallace, eds.), p. 25. Academic Press, New York, 1980.

52. Gschneidner, K. A., *in* "The Rare Earths in Modern Science and Technology" (G. J. McCarthy, J. J. Rhyne, and H. B. Silber, eds.), Vol. 2, p. 13. Plenum, New York, 1980.

53. Haire, R. G., *in* "Actinides in Perspective" (N. M. Edelstein, ed.), p. 309. Pergamon, New York, 1982.
54. Haire, R. G., Doc. No. ORNL-5817, p. 93, Union Carbide Corp., Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, TN, 1982.
55. Haire, R. G., and Asprey, L. B., *Inorg. Nucl. Chem. Lett.* **12,** 73 (1976).
56. Haire, R. G., and Baybarz, R. D., *J. Inorg. Nucl. Chem.* **36,** 1295 (1974).
57. Haire, R. G., and Baybarz, R. D., *J. Phys. Colloq.* **40,** C4–101 (1979).
58. Haire, R. G., Benedict, U., Peterson, J. R., Dufour, C., and Itié, J. P., *J. Less-Common Met.* **109,** 71 (1985).
59. Haire, R. G., Peterson, J. R., Benedict, U., and Dufour, C., *J. Less-Common Met.* **102,** 119 (1984).
60. Harbur, D. R., Anderson, J. W., and Maraman, W. J., *Mod. Cast.* **53(3),** 80 (1968).
61. Hübener, S., and Zvára, I., *Radiochim. Acta* **31,** 89 (1982).
62. Johnson, K. W. R., Doc. No. LA-1680, University of California, Los Alamos Scientific Laboratory, U.S. Atomic Energy Commission, Los Alamos, NM, 1954.
63. Johnson, K. W. R., and Leary, J. A., Doc. No. LA-2992, University of California, Los Alamos Scientific Laboratory, U.S. Atomic Energy Commission, Los Alamos, NM, 1964.
64. Jones, D. W., Farrant, S. P., Fort, D., and Jordan, R. G., *in* "Rare Earths and Actinides 1977" (W. D. Corner and B. K. Tanner, eds.), p. 11. Institute of Physics, London, 1978.
65. Kewish, R. W., Bard, R. J., Bertino, J. P., Fry, O. E., Hayter, S. W., Hill, F. J., Kelchner, B. L., and Savage, A. W., Jr., *Trans. Met. Soc. AIME* **215,** 425 (1959).
66. Kleinschmidt, P. D., Ward, J. W., Matlack, G. M., and Haire, R. G., *J. Chem. Phys.* **81,** 473 (1984).
67. Klemm, W., and Bommer, H., *Z. Anorg. Allg. Chem.* **231,** 138 (1937).
68. Lee, J. A., *Prog. Nucl. Energy, Ser. 5* **3,** 453 (1961).
69. Lesser, R., *in* "Gmelin Handbuch der Anorganischen Chemie" (G. Koch, ed.), System No. 71, Vol. 31, Part B1, p. 9. Springer-Verlag, Berlin and New York, 1976.
70. Liptai, R. G., and Friddle, R. J., *J. Cryst. Growth* **5,** 216 (1969).
71. Liptai, R. G., Lloyd, L. T., and Friddle, R. J., *Cryst. Growth Proc. Int. Conf. 1966,* p. 573 (1967).
72. Lohr, H. R., and Cunningham, B. B., *J. Am. Chem. Soc.* **73,** 2025 (1951).
73. Marples, J. A. C., *Acta Crystallogr.* **18,** 815 (1965).
74. Marples, J. A. C., *Colloq. Int. CNRS* **154,** 39 (1966).
75. Martinot, L., paper presented at the Journee d'etude des sels fondus, Soc. Chim. de Belgique, Liège, May 23–25, 1984.
76. McKay, H. A. C., Nairn, J. S., and Waldron, M. B., *Proc. UN Int. Conf. Peaceful Uses At. Energy 2nd* **28,** 299 (1958).
77. McWhan, D. B., Cunningham, B. B., and Wallmann, J. C., *J. Inorg. Nucl. Chem.* **24,** 1025 (1962).
78. McWhan, D., Montgomery, P. W., Stromberg, H. D., and Jura, G., Doc. No. UCRL-9808, University of California, Lawrence Radiation Laboratory, U.S. Atomic Energy Commission, Berkeley, CA, 1961.
79. McWhan, D. B., Wallmann, J. C., Cunningham, B. B., Asprey, L. B., Ellinger, F. H., and Zachariasen, W. H., *J. Inorg. Nucl. Chem.* **15,** 185 (1960).
80. Morgan, A. N., Johnson, K. W. R., and Leary, J. A., Doc. No. LAMS-2756, University of California, Los Alamos Scientific Laboratory, U.S. Atomic Energy Commission, Los Alamos, NM, 1962.

81. Mowat, J. A. S., and Yuille, W. D., *J. Less-Common Met.* **6,** 295 (1964).

82. Müller, W., Reul, J., and Spirlet, J. C., *ATW Atomwirtsch. Atomtech.* **17,** 415 (1972).

83. Müller, W., Reul, J., and Spirlet, J. C., *Rev. Chim. Miner.* **14,** 212 (1977).

84. Mullins, L. J., and Foxx, C. L., Doc. No. LA-9073, University of California, Los Alamos National Laboratory, U.S. Department of Energy, Los Alamos, NM, 1982.

85. Noé, M., and Peterson, J. R., *Transplutonium 1975, Proc. Int. Transplutonium Elem. Symp. 4th, 1975,* p. 69 (1976).

86. Okress, E. C., Wroughton, D. M., Comenetz, G., Brace, P. H., and Kelly, J. C. R., *J. Appl. Phys.* **23,** 545 (1952).

87. Peterson, D. T., Krupp, W. E., and Schmidt, F. A., *J. Less-Common Met.* **7,** 288 (1964).

88. Peterson, D. T., Schmidt, F. A., and Verhoeven, J. D., *Trans. Met. Soc. AIME* **236,** 1311 (1966).

89. Peterson, D. T., Page, D. F., Rump, R. B., and Finnemore, D. K., *Phys. Rev.* **153,** 701 (1967).

90. Peterson, D. T., and Schmidt, F. A., *J. Less-Common Met.* **24,** 223 (1971).

91. Peterson, J. R., Benedict, U., Dufour, C., Birkel, I., and Haire, R. G., *J. Less-Common Met.* **93,** 353 (1983).

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

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

94. See photomicrograph of this first isolated bulk sample of Bk metal in *Adv. Inorg. Chem. Radiochem.* **28,** 42 (1984).

95. Polonis, D. H., Butters, R. G., and Parr, J. G., *Research (London)* **7,** 273 (1954).

96. *Plutonium 1960, Proc. Int. Conf. Plutonium Metall. 2nd, 1960* (1961).

97. Raschella, D. L., Haire, R. G., and Peterson, J. R., *Radiochim. Acta* **30,** 41 (1982).

98. Schmidt, F. A., Lunde, B. K., and Williams, D. E., Doc. No. IS-4125, Iowa State University, Ames National Laboratory, U.S. Energy Research and Development Administration, Ames, IA, 1976.

99. Schmidt, F. A., Outlaw, R. A., and Lunde, B. K., Doc. No. IS-M-171, Iowa State University, Ames National Laboratory, U.S. Department of Energy, Ames, IA, 1979.

100. Schmidt, F. A., Outlaw, R. A., and Lunde, B. K., *J. Electrochem. Soc.* **126,** 1811 (1979).

101. Schmidt, F. A., Lunde, B. K., and Outlaw, R. A., *J. Spacecr. Rockets* **17,** 383 (1980).

102. Sellers, P. A., Fried, S., Elson, R. E., and Zachariasen, W. H., *J. Am. Chem. Soc.* **76,** 5935 (1954).

103. Shuck, A. B., *Plutonium React. Fuel, Proc. Symp.* 1967, p. 221 (1967).

104. Smith, J. F., Carlson, O. N., Peterson, D. T., and Scott, T. E., "Thorium: Preparation and Properties." Iowa State Univ. Press, Ames, 1975.

105. Smith, T. F., and Fisher, E. S., *J. Low Temp. Phys.* **12,** 631 (1973).

106. Spirlet, J. C., Rep. No. EUR 5412f, Commission of the European Communities, 1975.

107. Spirlet, J. C., *J. Phys. Colloq.* **40,** C4-87 (1979).

108. Spirlet, J. C., *in* "Actinides in Perspective" (N. M. Edelstein, ed.), p. 361. Pergamon, New York, 1982.

109. Spirlet, J. C., Bednarczyk, E., and Müller, W., *J. Less-Common Met.* **92,** L27 (1983).

110. Spirlet, J. C., and Müller, W., *J. Less-Common Met.* **31,** 35 (1973).

111. Spirlet, J. C., Müller, W., and van Audenhove, *J. Nucl. Instrum. Methods Phys. Res.* **A236,** 500 (1985).

112. Spirlet, J. C., and Vogt, O., *in* "Handbook on the Physics and Chemistry of the Actinides" (A. J. Freeman and G. H. Lander, eds.), p. 79. North-Holland Publ., Amsterdam, 1984.

113. Stevenson, J. N., and Peterson, J. R., *Microchem. J.* **20,** 213 (1975).

114. Stevenson, J. N., and Peterson, J. R., *J. Less-Common Met.* **66,** 201 (1979).

115. Stites, J. G., Salutsky, M. L., and Stone, B. D., *J. Am. Chem. Soc.* **77,** 237 (1955).

116. Thorsen, A. C., Joseph, A. S., and Valby, L. E., *Phys. Rev.* **162,** 574 (1967).

117. Wade, W. Z., and Wolf, T., *J. Inorg. Nucl. Chem.* **29,** 2577 (1967).

118. Wade, W. Z., and Wolf, T., *J. Nucl. Sci. Technol.* **6,** 402 (1969).

119. Wallmann, J. C., Crane, W. W. T., and Cunningham, B. B., *J. Am. Chem. Soc.* **73,** 493 (1951).

120. Ward, J. W., Kleinschmidt, P. D., and Haire, R. G., *J. Phys. Colloq.* **40,** C4-233 (1979).

121. Warner, J. C., *in* "Metallurgy of Uranium and its Alloys" (J. C. Warner, J. Chipman, and F. H. Spedding, eds.), Vol. 12A, p. 25. National Nuclear Energy Series, Division IV, 1953.

122. Westrum, E. F., Doc. No. MB-IP-96, University of California, Berkeley Radiation Laboratory, Berkeley, California, 1946. (Unavailable report referred to in reference *123* below).

123. Westrum, E. F., and Eyring, L., *J. Am. Chem. Soc.* **73,** 3396 (1951).

124. Westrum, E. F., and Eyring, L., *J. Am. Chem. Soc.* **73,** 3399 (1951).