

CHAPTER THIRTEEN

FERMIUM, MENDELEVIUM, NOBELIUM, AND LAWRENCIUM

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13.1 GENERAL

Because of conflicting claims, the International Union of Pure and Applied Chemistry (IUPAC) recently reviewed the names of all the trans-fermium elements; Münzenberg (1999) has published a detailed discussion of the problems and the resolution. First, a Transfermium Working Group decided the priority of discoveries. Next, the discoverers proposed names to the IUPAC and names were officially accepted by that body. The names for the elements mendeleevium, nobelium, and lawrencium were retained as originally proposed at the time of their discoveries.

As of this writing, the number of known isotopes of Fm, Md, No, and Lr is 58, ranging in half-life from as short as 0.25 ms for ^{250}No to as long as 100.5 days for ^{257}Fm . Relativistic effects have been predicted to affect ground state electronic configurations, ionic radii, and oxidation state for the heavier actinides. While the 3+ oxidation state remains a dominant feature of the heavier actinides, a tendency toward the formation of lower oxidation states has emerged. Divalency had been observed in solution for fermium through nobelium, in fact, the elements Fm, Md, and No are divalent in the metallic state. Due to increased 5f electron binding of the filled $5f^{14}$ shell, the 2+ oxidation state is the most stable in aqueous solution for nobelium. However, lawrencium, the last member of the actinide series, returns to the 3+ oxidation state as the most stable in aqueous solution, as predicted (Seaborg, 1949).

Due to the short half-lives and low production yields of Fm–Lr, all available chemical information has been obtained from experiments with tracer quantities. In fact, in many cases, chemical experiments were performed with only a few atoms or even one atom at a time. These experiments have necessarily been rather simple in principle, aimed primarily at making comparative studies with elements of known chemical properties. Nevertheless, all available experimental and theoretical evidence supports the original prediction of an actinide series (Seaborg, 1945) involving filling of the 5f electron shell, analogous to the lanthanide series resulting from the filling of the 4f electron shell, and that element 103 is the last member of this series of elements (Seaborg, 1949). The next element, atomic number 104, would be expected to fall into the next chemical group, i.e. Group IVB, of the periodic table.

13.2 FERMIUM

13.2.1 Introduction

The first isotope of element 100 was discovered in heavy-element samples obtained after the ‘Mike’ thermonuclear explosion of 1952, during the same set of experiments that resulted in the discovery of element 99. A joint effort by the researchers from the Lawrence Berkeley National Laboratory, the Argonne National Laboratory, and the Los Alamos National Laboratory resulted in the chemical isolation and identification of the 20 h half-life isotope ^{255}Fm (Ghiorso *et al.*, 1955a). The production involved rapid, multiple neutron capture by uranium nuclei in the nuclear device to form neutron-rich uranium isotopes of heavy mass followed by beta decay to elements of higher atomic number. The ^{255}Fm in the samples, produced from the beta decay of the longer-lived ^{255}Es , was purified and chemically identified by cation-exchange chromatography and detected through the use of alpha particle energy analysis. The name, fermium, was proposed in 1955 in honor of the leader in nuclear science, Enrico Fermi, and the name was subsequently accepted by the IUPAC.

13.2.2 Isotopes of fermium

As can be seen in Table 13.1, there are 19 known isotopes of element 100, ranging from atomic masses 242 through 260. Isotopes with masses 254 through 257 have been identified in samples of plutonium or elements of higher atomic number following neutron irradiation in nuclear reactors. All the other isotopes can only be produced by charged-particle bombardments of targets of elements of lower atomic number at charged-particle accelerators, e.g. cyclotrons, linear accelerators, etc.

The isotope that can be produced in largest quantities on an atomic basis is ^{257}Fm . This isotope is also the nuclide of highest atomic and mass number ever

Table 13.1 Nuclear properties of fermium isotopes.

Mass number	Half-life	Mode of decay	Main radiations (MeV)	Method of production
242	0.8 ms	SF		$^{204}\text{Pb}(^{40}\text{Ar},2\text{n})$
243	0.18 s	α	α 8.546	$^{206}\text{Pb}(^{40}\text{Ar},3\text{n})$
244	3.3 ms	SF		$^{206}\text{Pb}(^{40}\text{Ar},2\text{n})$
245	4.2 s	α	α 8.15	$^{233}\text{U}(^{16}\text{O},5\text{n})$
246	1.1 s	α 92% SF 8%	α 8.24	$^{233}\text{U}(^{16}\text{O},4\text{n})$ $^{235}\text{U}(^{16}\text{O},5\text{n})$
247 ^a	35 s	$\alpha \geq 50\%$ EC $\leq 50\%$	α 7.93 (~30%) 7.87 (~70%)	$^{239}\text{Pu}(^{12}\text{C},5\text{n})$ $^{239}\text{Pu}(^{12}\text{C},4\text{n})$
247 ^a	9.2 s	α	α 8.18	$^{239}\text{Pu}(^{12}\text{C},4\text{n})$
248	36 s	α 99.9% SF 0.1%	α 7.87 (80%) 7.83 (20%)	$^{240}\text{Pu}(^{12}\text{C},4\text{n})$
249	2.6 min	α	α 7.53	$^{238}\text{U}(^{16}\text{O},5\text{n})$ $^{249}\text{Cf}(\alpha,4\text{n})$
250	30 min	α SF $5.7 \times 10^{-4}\%$	α 7.43	$^{249}\text{Cf}(\alpha,3\text{n})$ $^{238}\text{U}(^{16}\text{O},4\text{n})$
250 m	1.8 s	IT		$^{249}\text{Cf}(\alpha,3\text{n})$
251	5.30 h	EC 98.2% α 1.8%	α 6.834 (87%) 6.783 (4.8%)	$^{249}\text{Cf}(\alpha,2\text{n})$
252	25.39 h	α SF $2.3 \times 10^{-3}\%$	α 7.039 (84.0%) 6.998 (15.0%)	$^{249}\text{Cf}(\alpha,\text{n})$
253	3.0 d	EC 88% α 12%	α 6.943 (43%) 6.674 (23%) γ 0.272	$^{252}\text{Cf}(\alpha,3\text{n})$
254	3.240 h	$\alpha > 99\%$ SF 0.0592%	α 7.192 (85.0%) 7.150 (14.2%)	$^{254\text{m}}\text{Es}$ daughter
255	20.07 h	α SF $2.4 \times 10^{-5}\%$	α 7.022 (93.4%) 6.963 (5.0%)	^{255}Es daughter
256	2.63 h	SF 91.9% α 8.1%	α 6.915	^{256}Md daughter ^{256}Es daughter
257	100.5 d	α 99.79% SF 0.21%	α 6.695 (3.5%) 6.520 (93.6%) γ 0.241	multiple n capture
258	0.37 ms	SF		$^{257}\text{Fm}(\text{d},\text{p})$
259	1.5 s	SF		$^{257}\text{Fm}(\text{t},\text{p})$
260	4 ms	SF		^{260}Md daughter

^a Not known whether ground-state nuclide or isomer.

isolated from either reactor or thermonuclear-produced materials. The neutron capture production chain essentially terminates at mass 257 owing to the very short spontaneous fission half-lives of the heavier isotopes. The current annual reactor production rate is in the picogram range (Porter *et al.*, 1997). However, in the thermonuclear explosion of 1969 called ‘Hutch,’ about 10^8 higher production was achieved (Hoff and Hulet, 1970), but only one

part in 10 million of the total number of atoms of ^{257}Fm imbedded in tons of geologic debris was recovered, i.e. a 10 kg sample of debris yielded about 10^{10} atoms.

Though ^{257}Fm is produced in larger amounts, ^{255}Fm has been more available on a regular basis from the beta decay of reactor-produced ^{255}Es ($t_{1/2} = 38.3$ days) and is more frequently used for chemical studies at the tracer level. Radioactivity levels in excess of 10^8 alpha disintegrations per minute of ^{255}Fm can be obtained from periodic chemical separations of Fm, 'milking,' from purified Es samples.

13.2.3 Preparation and purification

Because of their strong chemical similarity, the only satisfactory methods of separation of the trivalent actinides are by cation exchange or solvent extraction chromatography. The procedure most often selected is separation by elution from a cation-exchange resin column, e.g. Dowex 50×8 or $\times 12$ resin, using an aqueous solution of the chelating agent ammonium α -hydroxyisobutyrate (α -HIB) as eluant. This combination, developed in 1956 (Choppin *et al.*, 1956) primarily for the isolation and identification of new actinide elements, remains the main process method for the separation of trivalent actinides (Porter *et al.*, 1997). The actinides exhibit increasing complexation strength with the organic ligand with increasing atomic number, attributed to the decreasing ionic radii due to the actinide contraction (Katz *et al.*, 1986) and are eluted from the column in a regular sequence with the higher atomic number elements eluting first. Fig. 13.1 shows a typical separation of trace amounts of trivalent actinides using this method.

Vobecký *et al.* (1991) have obtained similar sequential elution and separation of 3+ actinides from a column of the spheroidal cation exchanger OSTION using a solution of ammonium α -hydroxy- α -methylbutyrate as the eluant.

Porter *et al.* (1997) have described a process method for the isolation and purification of fermium from other actinides and from rare earth fission produce from reactor target material. In addition to the standard series of transcurium actinide separations through the use of ammonium α -HIB eluant and cation-exchange resin, final purification of the fermium from small amounts of rare earth impurities that could contribute to the mass of the sample was accomplished using a solvent extraction chromatographic resin (the quaternary amine, Aliquat-336, impregnated into Amberchrom CG-71 ms support resin) that is marketed under the trade name TEVA.

Mikheev *et al.* (1983) have developed a rapid method for the separation of fermium from californium, einsteinium, and lanthanide elements based on the cocrystallization of reduced $^{254}\text{Fm(II)}$ with sodium chloride in aqueous ethanol solutions containing Yb(II) . The coefficient of separation of Fm

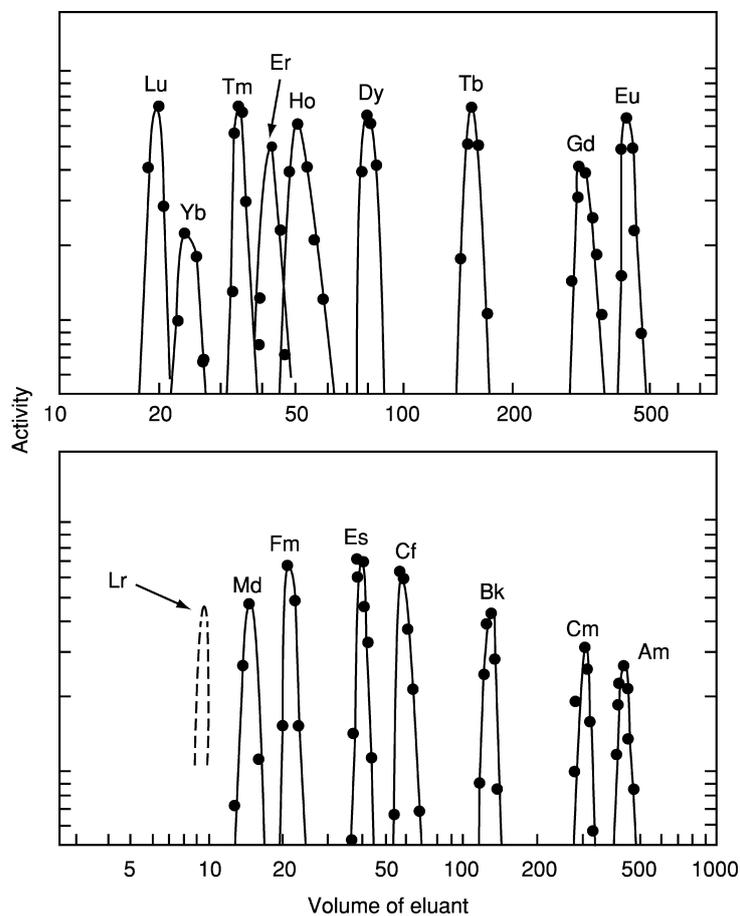


Fig. 13.1 Elution of homologous trivalent actinides and lanthanides from a Dowex 50 cation-exchange resin column at 87°C with ammonium α -hydroxyisobutyrate as eluant. The broken curve for element 103 (Lr) is an estimate based on its predicted radius.

from its elemental analogs in one cocrystallization step is 10^3 to 10^4 and the separation takes about 10 min.

Fermium has also been separated rapidly from the other transplutonium elements via chromatography using strongly basic anion-exchange resin and mixtures of nitric acid and methyl alcohol at elevated temperatures for the elutions (Usuda *et al.*, 1987).

Volatile hexafluoroacetylacetonates of Md and Fm have been prepared and could be the bases for chemical isolation by thermochromatography (Fedoseev *et al.*, 1990).

13.2.4 Atomic properties

Goodman *et al.* (1971) have used the atomic-beam magnetic resonance technique, adapted to the measurement of radioactive samples, to determine the magnetic moment, g_j , of the atomic ground state of neutral atoms of ^{254}Fm to be 1.16052 ± 0.00014 . A comparison of the experimentally measured value with values obtained from intermediate coupling calculations for several likely electron configurations was made. The measured value of g_j was found to be in close agreement only with that calculated for the $^3\text{H}_6$ level of the $5f^{12}7s^2$ electronic configuration. This agreement was taken as a conclusive evidence for the assignment of this configuration to the ground state of fermium.

The inner-shell binding energies and X-ray energies for the heavy elements have been estimated from total energies obtained from a Dirac–Fock computer code of Desclaux by Carlson and Nestor (1977). In these calculations, small empirical corrections were added as a result of comparing calculations with experimentally determined binding energies for elements of $Z > 95$. Where comparisons have been made for higher Z elements, the results of the calculations have agreed well with the experimentally measured values. Fricke *et al.* (1972) have also published electron binding energies in fermium obtained from Dirac–Fock calculations and compared them to the values of Porter and Freedman (1971) measured experimentally via spectroscopic measurements of internal conversion electrons emitted following the beta decay of $^{254\text{m}}\text{Es}$ to ^{254}Fm . Das (1981) calculated the binding energies in fermium by using a relativistic local density functional theory. Porter and Freedman (1978) have recommended atomic binding energies of the K, L, M, N, O, and P shells for heavy elements from $Z = 84$ to 103. A table of electron binding energies based on the latter is given by Firestone *et al.* (1996). The values for Fm differ slightly from their earlier experimental values (Porter and Freedman, 1971). The results of the three theoretical calculations are compared with the recommended values of Porter and Freedman in Table 13.2. The agreement is quite good and demonstrates that these types of theoretical calculations are consistent and quite useful for predictive purposes.

Dittner *et al.* (1971) have measured the K-series X-rays of ^{251}Fm emitted following the alpha decay of ^{255}No . The K-series X-ray energies derived experimentally from these studies are compared with the values calculated using the binding energies of Porter and Freedman (1978) in Table 13.2.

13.2.5 The metallic state

Fermium metal has not been prepared, however, measurements have been performed on alloys with rare earth metals and a number of predictions about it have been made.

Johansson and Rosengren (1975) have correlated the measured and predicted cohesive energies of the lanthanide and actinide elements in both the divalent and trivalent metallic states. They concluded that the gain in energy of binding

Table 13.2 Comparison of calculated and measured electron binding and X-ray energies for fermium.

Shell	Binding energy (–eV)				Transition	X-ray energy (keV)	
	Calc. ^a	Calc. ^b	Calc. ^c	Meas. ^d		Calc. ^e	Meas. ^f
1s	1 41 943	1 41 953	1 42 573	1 41 962			
2s	27 584	27 581	27 503	27 573			
2p _{1/2}	26 643	26 646	26 608	26 644	K _{α2} (2p _{1/2} → 1s _{1/2})	115.285	115.280
2p _{3/2}	20 872	20 869	20 783	20 868	K _{α1} (2p _{3/2} → 1s _{1/2})	122.058	121.070
3s	7 206	7 213	7 127	7 200			
3p _{1/2}	6 783	6 783	6 710	6 779	K _{β3} (3p _{1/2} → 1s _{1/2})	135.150	135.2
3p _{3/2}	5 414		5 341	5 408	K _{β1} (3p _{3/2} → 1s _{1/2})	136.521	136.6
3d _{3/2}	4 757		4 726	4 746			
3d _{5/2}	4 497		4 460	4 484			
4s	1 954		1 904	1 940			
4p _{1/2}	1 753		1 712	1 743	K _{β2} (4p _{1/2} → 1s _{1/2})	140.177	140.1
4p _{3/2}	1 383		1 340	1 371			
4d _{3/2}	1 071		1 046	1 059			
4d _{5/2}	1 005		979	989			
4f _{5/2}			591				
4f _{7/2}			572				
5s			440				
5p _{1/2}			361				
5p _{3/2}			264				
5d _{3/2}			150				
5d _{5/2}			144				

^a Carlson and Nester (1977).^b Fricke *et al.* (1972).^c Das (1981).^d Porter and Freedman (1971).^e Porter and Freedman (1978).^f Dittner *et al.* (1971).

of the $5f^n 6d^1 7s^2$ (trivalent) configuration over the $5f^{n+1} 7s^2$ (divalent configuration) is less than the energy necessary to promote one 5f electron to the 6d state in the final members of the actinide series. Therefore, Es, Fm, Md, and No prefer a divalent metallic state similar to Eu and Yb rather than a trivalent one. However the energy difference is small for Es and Fm and, at modest compression, the divalent metallic state may convert to the trivalent one.

The sublimation enthalpy, a fundamental metallic property, is connected directly with the valence electronic structure of the metal. The enthalpy of sublimation of fermium has been determined directly by measuring the partial pressure of Fm over Fm–Sm and Fm, Es–Yb alloys for the temperature range 642–905 K (Haire and Gibson, 1989). Based on their combined second law and third law measured values for the enthalpy of sublimation of Fm, they reported a value of (142 ± 13) kJ mol^{–1} for ΔH_{298} . Because the enthalpy of sublimation

of Fm was similar to those of divalent Es, Eu, and Yb, it was concluded that Fm is divalent in the metallic state. Comparisons with radii and melting points of Eu, Yb, and Es metals have yielded estimated values of 0.198 nm and 1125 K for Fm by these authors. David *et al.* (1978) have estimated a divalent metallic radius of 0.194 nm for Fm, in close agreement.

Because the heaviest actinides are available only in trace amounts, innovative experimental approaches must be used in order to characterize their elemental state properties. Zvara and coworkers (Zvara *et al.*, 1976) compared the evaporation rates of trace amounts of Es, Fm, and Md from molten La with those of Ce, Eu, Yb, Am, and Cf to obtain information on their metallic states. Hübener (1980) compared the thermochromatographic behavior of Es, Fm, and Md evaporated from molten La in titanium columns with those of Na, Sc, Sm, Eu, Yb, Bk, and Cf. The conclusion reported in both of these papers supported the idea that Es, Fm, and Md prefer the divalent metallic state. The adsorption behavior of Cf, Es, Fm, and Md on titanium and molybdenum thermochromatographic columns was compared to a number of monovalent, divalent, and trivalent elements and enthalpies of adsorption determined (Hübener and Zvara, 1982). From the data, the authors also concluded that Es, Fm, and Md are divalent in the metallic state and that the position of the f-energy levels relative to the Fermi-energy is lower than in the cases of Cf and Yb. A nearly linear correlation was found between the experimental enthalpies of adsorption of the heavy actinides and their predicted enthalpies of sublimation.

Thermochromatographic studies of the adsorption of Cf, Es, and Fm on several metals were conducted by Taut *et al.* (1997) and enthalpies of sublimation inferred from the measured enthalpies of adsorption. The results support the value of the enthalpy of sublimation of Fm published by Haire and Gibson (1989).

13.2.6 Solution chemistry

The chemical properties of fermium have been studied only with trace quantities. The chemical properties of Fm have been discussed by Thompson *et al.* (1954). Under conditions not strongly reducing, fermium behaves in aqueous solution as expected for a trivalent actinide ion. Fermium coprecipitates with rare earth fluorides and hydroxides. The elution of fermium just before einsteinium from cation-exchange resin columns with hydrogen ion and the complexing ligands citric acid, lactic acid, and α -HIB is consistent with the existence of a trivalent ion (Katz and Seaborg, 1957). In concentrated hydrochloric acid, nitric acid, and ammonium thiocyanate solutions, fermium forms anion complexes with these ligands that can be adsorbed onto and subsequently eluted from anion-exchange columns (Thompson *et al.*, 1954). In this case, fermium follows einsteinium in the elution sequence. Both types of column results indicate that Fm forms a slightly stronger complex with the ligands than Es, which is due to the slightly smaller ionic radius of Fm as a result of the actinide contraction

(Katz *et al.*, 1986). Fermium also exhibits a more acidic behavior than the preceding actinides in aqueous solution, having a first hydrolysis constant of 1.6×10^{-4} (Hussonnois *et al.*, 1972).

David *et al.* (1978) have estimated some thermodynamic properties of the 5f elements obtained from theoretical considerations and empirical correlations drawn from observed trends in the 4f series. They proposed an ionic radius of 0.0922 nm for Fm^{3+} . From the linear correlation of log distribution coefficients with ionic radius obtained from elution positions from α -HIB/cation-exchange column separations, a value of 0.0911 nm was calculated for the ionic radius of Fm^{3+} (Brüchle *et al.*, 1988). Lundqvist *et al.* (1981) have studied the migration rates of Fm^{3+} in an electrical potential gradient using paper electrophoresis and reported a hydrated radius of 0.495 nm and a hydration number of 16.9 in aqueous perchlorate solutions.

Fermium readily forms complexes with a variety of organic ligands, e.g., β -diketones (Hussonnois *et al.*, 1972), hydroxycarboxylic acids (Thompson *et al.*, 1954; Choppin *et al.*, 1956; Baybarz, 1965, 1966; Ermakovl and Sary, 1967; Hubert *et al.*, 1974), organophosphorus esters (Baybarz, 1963; Sary, 1966; Horwitz *et al.*, 1969), and alkylamines (Müller, 1967). α -HIB has long been used as the eluant for inner series separation of trivalent actinides by cation-exchange chromatography as stated above. However, bis(2-ethylhexyl)phosphoric acid (HDEHP) (Horwitz and Bloomquist, 1973) and Alamine 336 (a mixed *n*-octyl and *n*-decyl tertiary amine) (Leuze *et al.*, 1963) have also been used for similar separations of Fm by solvent extraction column chromatography. Gorski *et al.* (1990) have investigated the complex formation of several transplutonium elements, including Fm, with 1,2-diaminocyclohexane tetraacetic acid (DCTA) and shown the correlation of ionic radii with the values of the log of the complex stability constants. A linear dependence is observed for lanthanides while it deviates from linearity for the heavy actinides. The author's postulate that, since the stability of chelate complexes are determined by the positive change of entropy of the reaction, the change in stability constants of the heavy actinides is due to an entropy effect rather than to the change in the ionic radii.

The behavior of Sr, Y, Sm, Eu, Am, Cf, Es, and Fm in the molten salt mixtures $\text{LiCl-NdCl}_2\text{-NdCl}_3$ and LiI-PrI_2 have been studied (Kulyukhin, 1997). In the presence of Nd^{2+} , Cf, Es, and Fm are reduced to the 2+ oxidation state. The results obtained in the LiI-PrI_2 system were ambiguous as to whether the actinides Cf-Fm were reduced to the 1+ or 2+ oxidation states.

The tendency of Fm to form a divalent ion under strong reducing conditions was first suggested by the work of Maly (1967). Mikheev *et al.* (1972) reported the reduction of Fm^{3+} to Fm^{2+} in 1972 from the results of reduction/cocrystallization experiments with SmCl_2 . The reduction of Fm^{3+} to Fm^{2+} with SmCl_2 has also been observed by Hulet *et al.* (1979). Mikheev *et al.* (1977) were able to estimate the reduction potential to be very nearly the same as the $\text{Yb}^{3+} \rightarrow \text{Yb}^{2+}$ couple or -1.15 V. This value is in reasonably good

agreement with the value of $-(1.1 \pm 0.2)$ V calculated by Nugent (1975) using refined electron-spin-pairing theory.

Using a refined radiopolarographic technique, Samhoun and David (1976) measured the half-wave potential for the $\text{Fm}^{2+} \rightarrow \text{Fm}(\text{Hg})$ reduction at a dropping mercury electrode as $-(1.47 \pm 0.01)$ V. By applying an estimated amalgamation potential correction of 0.90 V obtained from correlations of other divalent ions, a value for $E^\circ (\text{Fm}^{2+} \rightarrow \text{Fm}^0)$ of $-(2.37 \pm 0.1)$ V was reported. Using this latter value of Samhoun and David, combined with Mikheev's value of -1.15 V for the $\text{Fm}^{3+} \rightarrow \text{Fm}^{2+}$ couple, a value of $-(1.96 \pm 0.13)$ V can be calculated for $E^\circ (\text{Fm}^{3+} \rightarrow \text{Fm}^0)$. Nugent (1975) has estimated $E^\circ (\text{Fm}^{4+} \rightarrow \text{Fm}^{3+})$ to be $+4.9$ V. These values (Table 13.8) are consistent within uncertainties with those in Chapter 19 (Fig. 19.9).

Unless otherwise indicated, all electrode potentials in this chapter are with reference to the normal hydrogen electrode (NHE) and the 1969 IUPAC convention, i.e. the more positive the potential the more stable the reduced form (McGlashan, 1970).

13.3 MENDELEVIUM

13.3.1 Introduction

The first isotope of element 101 was produced in 1955 by Ghiorso *et al.* (1955b). It was synthesized in the bombardment of approximately one billion atoms of ^{253}Es with 41 MeV alpha particles and produced at a rate of only about two atoms per 3 h bombardment. A chemical identification was made on the basis of its elution position just before Fm from a cation-exchange resin column using ammonium α -HIB as eluant in a series of repetitive experiments. It was not detected directly but by the observation of spontaneous fission events arising from its electron-capture daughter ^{256}Fm . Additional analysis of the data, coupled with further experimentation, showed the isotope to have mass 256 and to decay by electron capture with a half-life of 1.5 h. The name mendelevium was proposed for the element in honor of Dimitri Mendeleev, in recognition of his contributions to the development of the chemical periodic system, and it was accepted by IUPAC.

13.3.2 Isotopes of mendelevium

Sixteen isotopes of mendelevium from mass 245 to 260 are known (see Table 13.3). All of its isotopes can only be produced through charged-particle irradiations at accelerators. Although ^{258}Md , with a half-life of 51 days, is the longest-lived isotope, ^{256}Md remains the isotope most often used in chemical experiments because it can be produced in relatively larger quantities. Using microgram amounts of ^{253}Es presently available, more than a million

Table 13.3 Nuclear properties of mendelevium isotopes.

Mass number	Half-life	Mode of decay	Main radiations (MeV)	Method of production
245	0.4 s	α	α 8.680	$^{209}\text{Bi}(^{40}\text{Ar},4\text{n})$
246	0.9 ms	SF		
247	1.0 s	α	α	$^{209}\text{Bi}(^{40}\text{Ar},3\text{n})$
247	1.12 s	α 80%	α 8.424	$^{209}\text{Bi}(^{40}\text{Ar},2\text{n})$
248	0.27 s			
248	7 s	EC \sim 80% α \sim 20%	α 8.36 (\sim 25%) 8.32 (\sim 75%)	$^{241}\text{Am}(^{12}\text{C},5\text{n})$ $^{239}\text{Pu}(^{14}\text{N},5\text{n})$
249	24 s	EC \leq 80% α \geq 20%	α 8.03	$^{241}\text{Am}(^{12}\text{C},4\text{n})$
250	52 s	EC 94% α 6%	α 7.830 (\sim 25%) 7.750 (\sim 75%)	$^{243}\text{Am}(^{12}\text{C},5\text{n})$ $^{240}\text{Pu}(^{15}\text{N},5\text{n})$
251	4.0 min	EC \geq 94% α \leq 6%	α 7.55	$^{243}\text{Am}(^{12}\text{C},4\text{n})$ $^{240}\text{Pu}(^{15}\text{N},4\text{n})$
252	2.3 min	EC $>$ 50% α $<$ 50%	α 7.73	$^{243}\text{Am}(^{13}\text{C},4\text{n})$
253	6 min		$^{238}\text{U}(^{19}\text{F},5\text{n})$	
254 ^a	10 min	EC		$^{253}\text{Es}(\alpha,3\text{n})$
254 ^a	28 min	EC		$^{253}\text{Es}(\alpha,3\text{n})$
255	27 min	EC 92% α 8%	α 7.333 γ 0.453	$^{253}\text{Es}(\alpha,2\text{n})$ $^{254}\text{Es}(\alpha,3\text{n})$
256	1.27 h	EC 90.7% α 9.9%	α 7.205 (63%) 7.139 (16%)	$^{253}\text{Es}(\alpha,\text{n})$
257	5.52 h	EC 90% α 10%	α 7.069	$^{254}\text{Es}(\alpha,\text{n})$
258 ^a	51.5 d	α	α 6.790 (28%) 6.716 (72%)	$^{255}\text{Es}(\alpha,\text{n})$
258 ^a	57 min	EC ?		$^{255}\text{Es}(\alpha,\text{n})$
259	1.60 h	SF		^{259}No daughter
260	31.8 d	SF $>$ 73% EC $<$ 15%		$^{254}\text{Es}(^{18}\text{O},^{12}\text{C})$

^a Not known whether ground-state nuclide or isomer.

atoms per hour of ^{256}Md can be produced by alpha-particle bombardments (Hulet *et al.*, 1967).

13.3.3 Preparation and purification

The isotope ^{256}Md can best be produced for chemical study by the $^{253}\text{Es}(\alpha,\text{n})$ or $^{254}\text{Es}(\alpha,2\text{n})$ reactions at cyclotrons or linear accelerators. The isotope ^{254}Es would be the target material of choice if available. It has a half-life of 276 days compared to only 20.5 days for ^{253}Es and thus it would have a longer usable target lifetime.

The discovery experiments on mendelevium were the first in which the recoil momentum imparted by the bombarding ion to a product atom during its formation was used to carry out an instantaneous physical separation of the product atom from the target material (Seaborg, 1963). The recoil atoms were collected on a thin metal foil placed behind the target in an evacuated reaction chamber. This eliminated the time needed to separate the product atoms from the target atoms, previously accomplished by chemical means, and made it possible to use the same valuable target in repeated bombardments. A few years later, it was found that the recoil atoms could be slowed down and stopped in a gaseous atmosphere, frequently helium. The gas could be pumped out of the reaction chamber through a small orifice to form a 'gas-jet.' If this jet was impinged onto the surface of a foil, some fraction (frequently 75% or more) of the nonvolatile product atoms carried along with the gas were deposited permanently on the foil surface (Ghiorso, 1959; Macfarlane and Griffioen, 1963). The foil could be removed periodically for processing and a new foil installed. A good description of this system has been given by Hoffman (1994).

After removal of the Md atoms from the collector foil by acid etching or following total dissolution of the thin metal foil, they can be purified and isolated from other product activities by several other techniques.

Md can be separated from the dissolved 'catcher' foil material, e.g. Be, Al, Pt, or Au, and most fission-product activities by coprecipitation with lanthanum fluoride. Subsequent separation of trivalent actinides from lanthanide fission products and La carrier can be accomplished with a cation-exchange resin column using a 90% water/10% ethanol solution saturated with HCl as eluant (Thompson *et al.*, 1954). When a very thin gold foil is used as the 'catcher' foil, after dissolution with aqua regia, a rapid separation of the Md from the Au can be made by anion-exchange chromatography using 6 M HCl as eluant. The gold remains on the column while the Md and other actinides pass through.

Final isolation of Md³⁺ from other trivalent actinides can be accomplished by selective elution from a cation-exchange resin column using ammonium α -HIB (Choppin *et al.*, 1956). When using the gas-jet system, the first two steps can frequently be eliminated.

In more recent years, it was found that, using the 'gas-jet' method, the recoil product atoms could be transported many meters with the stopping gas through a long capillary tube to the chemistry/counting area (Macfarlane and McHarris, 1974). In this case, effective transport over long distances requires the presence of large clusters, frequently KCl aerosols, in the 'carrier' gas. By this method, it is possible to transport and collect individual product atoms in a fraction of a second some tens of meters away from the target area. This method is quite generally used nowadays in the production and isolation of transeinsteinium elements.

A good separation of Md and Fm has been performed on a spheroidal cation-exchanger OSTIN using ammonium α -hydroxy- α -methylbutyrate (Vobecký *et al.*, 1991). The isotope ²⁵⁶Md is most easily detected through the measurement

of the spontaneous fission activity of its daughter ^{256}Fm ; however, in the presence of other fissioning nuclides, the detection of alpha particles of the characteristic energy of ^{256}Md associated with the 10% alpha decay branch can be used for identification.

Intragroup separation of the 3+ actinides has also been achieved by solvent extraction chromatography using HDEHP as the stationary organic phase and HNO_3 as the mobile aqueous phase (Horwitz and Bloomquist, 1969). Here, the actinide elution sequence is reversed from that of the cation-exchange resin column. This method gives a somewhat better final separation of Md from Fm than the cation-exchange resin column. It has the advantage that the final solution containing the Md is free of organic complexing agents compared to the resin column but has the disadvantage that Md elutes after Fm late in the sequence.

Following the discovery that Md can form a divalent state, extraction chromatography using HDEHP was used to show that the elution behavior of Md^{2+} is dissimilar to that of Es^{3+} and Fm^{3+} (Hulet *et al.*, 1967). This became the basis for a rapid separation method for the isolation of Md (Hulet *et al.*, 1979; Lundqvist *et al.*, 1981). After the initial steps of dissolution from the 'catcher' foil and coprecipitation with terbium fluoride, the mendelevium and 50 mg of Cr (added as a holding reductant) in 0.1 M HCl are co-reduced with Zn(Hg). The solution is passed through a solvent extraction column containing HDEHP on an inert support as the stationary organic phase. The actinides in the trivalent and tetravalent states as well as the trivalent lanthanides are extracted by the HDEHP and are retained on the column while the divalent Md is not appreciably extracted and appears in the 0.1 M HCl washes of the column. After reoxidation of the Md and Cr to the trivalent states with H_2O_2 , the residual impurities, including the Cr, are separated from the Md by selective elution with 2 M (to remove the impurities) and 6 M HCl (to remove the Md) from a small column of Dowex 50 \times 12 colloidal resin. Guseva *et al.* (1988) have reported a similar method for isolating Md where, using one column with cationite and zinc amalgam and a solution of 1 M HCl as the eluant, Md is reduced and washes through the column with the alkaline earth elements.

Volatile hexafluoroacetylacetonates of Md and Fm have been prepared and could be the bases for chemical isolation by thermochromatography (Fedoseev *et al.*, 1990).

13.3.4 Atomic properties

The electronic structure of the ground state of gaseous mendelevium atoms has been predicted to be the $^2\text{F}_{7/2}$ level of the $5f^{13}7s^2$ configuration (Martin *et al.*, 1974). An experimental confirmation has not yet been made. No experimental measurements of inner-shell binding energies or X-ray energies have been reported but estimated values have been reported by Firestone *et al.* (1996)

Table 13.4 Estimated electron binding and X-ray energies for mendelevium, nobelium, and lawrencium.

Shell	Binding energy (–eV)			Transition	X-ray energy (keV)		
	Md	No	Lr		Md	No	Lr
1s	1 46 526	1 49 208	1 52 970	$K_{\alpha 1} (2p_{3/2} \rightarrow 1s)$	125.17	127.36	130.61
				$K_{\alpha 2} (2p_{1/2} \rightarrow 1s)$	119.09	120.95	123.87
2s	28 387	29 221	30 083	$K_{\alpha 3} (2s \rightarrow 1s)$	118.14	119.99	122.89
2p _{1/2}	27 438	28 255	29 103				
2p _{3/2}	21 356	21 851	22 359	$K_{\beta 1} (3p_{3/2} \rightarrow 1s)$	140.97	143.51	147.11
				$K_{\beta 2} (4p_{3/2,1/2} \rightarrow 1s)$	144.91	147.53	151.23
3s	7 440	7 678	7 930	$K_{\beta 3} (3p_{1/2} \rightarrow 1s)$	139.53	141.98	145.50
3p _{1/2}	7 001	7 231	7 474	$K_{\beta 4} (4d_{5/2,3/2} \rightarrow 1s)$	145.46	148.10	151.82
3p _{3/2}	5 552	5 702	5 860	$K_{\beta 5} (3d_{3/2,1/2} \rightarrow 1s)$	141.77	144.32	147.94
3d _{3/2}	4 889	5 028	5 176				
3d _{5/2}	4 615	4 741	4 876	$L_{\alpha 1} (3d_{5/2} \rightarrow 2p_{3/2})$	16.74	17.10	17.48
				$L_{\alpha 2} (3d_{3/2} \rightarrow 2p_{3/2})$	16.47	16.82	17.18
4s	2 024	2 097	2 180				
4p _{1/2}	1 816	1 885	1 963	$L_{\beta 1} (3d_{3/2} \rightarrow 2p_{1/2})$	22.55	23.23	23.93
4p _{3/2}	1 424	1 469	1 523	$L_{\beta 2} (4d_{5/2,3/2} \rightarrow 2p_{3/2})$	20.29	20.74	21.21
4d _{3/2}	1 105	1 145	1 192	$L_{\beta 3} (3p_{3/2} \rightarrow 2s)$	22.84	23.52	24.22
4d _{5/2}	1 034	1 070	1 112	$L_{\beta 4} (3p_{1/2} \rightarrow 2s)$	21.39	21.99	22.61
4f _{5/2}	618	645	680	$L_{\beta 5} (5d_{5/2,1/2} \rightarrow 2p_{3/2})$	21.21	21.70	22.20
4f _{7/2}	597	624	658	$L_{\beta 6} (4s \rightarrow 2p_{3/2})$	19.33	19.75	20.18
5s	471	490	516	$L_{\gamma 1} (4d_{3/2} \rightarrow 2p_{1/2})$	26.33	27.11	27.91
5p _{1/2}	389	406	429	$L_{\gamma 2} (4p_{1/2} \rightarrow 2s)$	26.57	27.34	28.12
5p _{3/2}	272	280	296	$L_{\gamma 3} (4p_{3/2} \rightarrow 2s)$	26.96	27.75	28.56
5d _{3/2}	154	161	174	$L_{\nu} (3s \rightarrow 2p_{3/2})$	13.92	14.17	14.43
5d _{5/2}	137	142	154	$L_{\nu} (3s \rightarrow 2p_{1/2})$	20.00	20.58	21.17
5f _{5/2}	12.9	13.6	19.9				
5f _{7/2}	10.5	11.1	17.0				

based on the values recommended by Porter and Freedman (1978). The results are given in Table 13.4.

13.3.5 The metallic state

While mendelevium metal has not been prepared, Johansson and Rosengren (1975) predicted that, for the same reasons as discussed above for Fm, Md would prefer a divalent metallic state similar to Eu and Yb rather than a trivalent one.

As was the case with Fm, thermochromatographic studies conducted with trace amounts of Md by Zvara *et al.* (1976), Hübener (1980), and Hübener and Zvara (1982) led to the conclusion that Md forms a divalent metal. If the enthalpies of sublimation determined for Es and Fm from alloys are accepted, then, using the measured enthalpies of adsorption and the established correlation between the sublimation and adsorption enthalpies, Haire and Gibson (1990) estimated that Md has an enthalpy of sublimation in the range of

134–142 kJ mol⁻¹. Using empirical correlation methods, David *et al.* (1978) have estimated a divalent metallic radius of (0.194 ± 0.010) nm.

13.3.6 Solution chemistry

Before mendelevium was discovered, the trivalent state was predicted to be the most stable in aqueous solution and, therefore, it was expected to exhibit a chemical behavior similar to the other 3+ actinides and lanthanides (Seaborg and Katz, 1954). The elution of Md just before Fm in the elution sequence of trivalent actinides from a cation-exchange resin column observed in the discovery experiments appeared to confirm this prediction. Later, Md was indeed found to form insoluble hydroxides and fluorides that are quantitatively coprecipitated with trivalent lanthanides (Hulet *et al.*, 1967). Both the cation-exchange resin column (Choppin *et al.*, 1956) and HDEHP solvent extraction column (Horwitz and Bloomquist, 1969) elution data are consistent with a trivalent state for Md and an ionic radius slightly smaller than Fm.

Using empirical correlations, David *et al.* (1978) have estimated an ionic radius of 0.0912 nm (coordination number (CN) 6) for Md³⁺. In addition to the ionic radius, a number of enthalpies and entropies of formation and sublimation were also estimated for Md. Hoffman *et al.* (1988) and Brüchle *et al.* (1988) compared the distribution coefficients for Lr, Md, and Fm with those of Tm, Er, and Ho obtained from ammonium α -HIB elutions from cation-exchange resin columns. Using the known ionic radii for the trivalent rare earths and the linear correlation of log distribution coefficient with ionic radius (for the same coordination number), an average ionic radius of 0.0896 nm was estimated for Md³⁺ and a heat of hydration of $-(3654 \pm 12)$ kJ mol⁻¹ calculated using empirical models and the Born–Haber cycle.

Gorski *et al.* (1990) have studied the extraction behavior of Md with trioctylphosphine oxide in the presence of complexing agents and compared it to other transplutonium elements. They have also investigated the complex formation of several transplutonium elements, including Md, with DCTA and shown the correlation of ionic radii with the values of the log of the complex stability constants. The observed deviation from linearity by the heavy actinides is discussed in Section 13.2.5.

Hulet *et al.* (1967) first observed an anomalous chemical behavior for Md in certain chemical systems involving reducing conditions. With 10⁵ to 10⁶ atoms per experiment, coprecipitation with BaSO₄ and solvent extraction chromatography experiments using HDEHP were carried out in the presence of a number of different reducing agents. These experiments showed that Md³⁺ could be easily reduced to a stable Md²⁺ in aqueous solution. An estimate was made for the standard potential of the half-reaction $E^\circ(\text{Md}^{3+} \rightarrow \text{Md}^{2+})$ of approximately -0.2 V. Maly and Cunningham (1967) also produced the divalent state of Md and, from experiments similar to Hulet *et al.*, estimated $E^\circ(\text{Md}^{3+} \rightarrow \text{Md}^{2+})$ at -0.1 V. David (1986a) estimated $E^\circ(\text{Md}^{3+} \rightarrow \text{Md}^0)$ to be -1.74 V. David

et al. (1981, 1990a) measured $-(1.51 \pm 0.01)$ V for the polarographic $E_{1/2}$ of the couple $\text{Md}^{2+} \rightarrow \text{Md}^0$ which (with correction for amalgamation potential of 1.0 V) yields an estimated $E^\circ(\text{Md}^{2+} \rightarrow \text{Md}^0) = -2.5$ V (SHE). These values (Table 13.8) are consistent with those in Chapter 19 (Fig. 19.9).

Guseva *et al.* (1988) compared the elution behavior of Md^{2+} with Sr^{2+} and Eu^{2+} from a cationite and zinc amalgam ion-exchange column using 1 M HCl. On the basis of the elution peak position of Md relative to the Sr and Eu and the known ionic radii of the latter two elements, a value for the ionic radius of Md^{2+} was estimated to be 0.115 nm. Using this value for the radius, the enthalpy of hydration of Md^{2+} was calculated to be -1413 kJ mol $^{-1}$.

In 1973, Mikheev *et al.* reported that a stable monovalent Md ion could be produced in neutral water–ethanol solutions and that it cocrystallized with CsCl (Mikheev *et al.*, 1973). However, studies of the overall reduction of Md^{3+} to Md^0 (Hg) using controlled potential radiocoulometry (Samhoun *et al.*, 1979) and radiopolarography (David *et al.*, 1981) led to the conclusion that Md could not be considered as a cesium-like element and no evidence was obtained consistent with the formation of a monovalent state. Electrode reduction proceeded in two steps, $3+ \rightarrow 2+$ and $2+ \rightarrow 0$. Hulet *et al.* (1979) repeated some of the cocrystallization experiments of Mikheev and performed a series of new experiments in an attempt to prepare Md^+ by reduction with Sm^{2+} in ethanol solutions and also in fused KCl. In these experiments, the coprecipitation behavior of Md was compared to tracer quantities of Es, Fm, Eu, Sr, Y, and Cs. Md consistently followed the behavior of Fm^{2+} , Eu^{2+} , and Sr^{2+} rather than Cs^+ . They concluded that Md could not be reduced to a monovalent state with Sm^{2+} as claimed by Mikheev. However, on the basis of the results of further thermodynamic studies of the cocrystallization process of mendelevium with chlorides of alkali metals, the Russian investigators maintain that Md can be reduced to the monovalent state in water–ethanol solutions and that the cocrystallization of Md^+ with salts of divalent ions can be explained as being due to the formation of mixed crystals (Mikheev *et al.*, 1980, 1981a; Spitsyn *et al.*, 1982). An ionic radius of 0.117 nm was calculated for Md^+ from the results of the cocrystallization studies (Mikheev *et al.*, 1981b, 1982).

Unsuccessful attempts have been made to oxidize Md^{3+} to Md^{4+} using the strong oxidant sodium bismuthate (Hulet *et al.*, 1967). Thus, Md^{3+} is not readily oxidized as would be expected from the value of +5.4 V predicted by Nugent (1975) for the $E^\circ(\text{Md}^{4+} \rightarrow \text{Md}^{3+})$ couple.

13.4 NOBELIUM

13.4.1 Introduction

The discovery of element 102 was first reported in 1957 by an international research team working at the Nobel Institute in Stockholm, Sweden (Fields *et al.*, 1957). During the bombardment of a ^{244}Cm target with ^{13}C ions from the

Nobel Institute cyclotron, an 8.5 MeV alpha particle activity was produced which decayed with a half-life of approximately 10 min. The alpha activity eluted just before Es and Fm from a cation-exchange resin column using ammonium α -HIB as eluant and also appeared in the trivalent actinide fraction along with Cf and Fm, also produced in the irradiations, from a cation-exchange resin column using 6 M HCl as eluant. This behavior was taken as chemical evidence for the production of an isotope of element 102. From half-life systematics and reaction energetics, an isotope with a mass number of 253 or 255 was thought to have been produced. The name, nobelium, was proposed in honor of Alfred Nobel, in recognition of his support of the natural sciences, and in honor of the Nobel Institute where the experiments were conducted.

During the following 10 years, researchers at both the Lawrence Berkeley National Laboratory and the Dubna Research Center, Russia, attempted to repeat the Nobel Institute experiments, but were unsuccessful. However, the Berkeley group did succeed in identifying an alpha-emitting isotope of element 102 in 1958 using a newly developed method called the 'double recoil technique' (Ghiorso *et al.*, 1958) and assigned a mass of 254. Where the same isotopes have been studied, the Dubna and Berkeley groups are in substantial agreement (Ghiorso and Sikkeland, 1967). The results of the efforts of both groups exclude the likelihood of any isotope of element 102 having a half-life of 10 min with the emission of 8.5 MeV alpha particles. Further, chemical studies by Maly *et al.* (1968) showed that, because of its divalency in aqueous solutions, element 102 could not have exhibited the trivalent cation-exchange column elution behavior attributed to the 10 min activity. On the basis of their 1958 and later work, the Berkeley group claimed discovery of element 102 and, because of the wide use of the name over many years, suggested that nobelium be retained as the name of element 102 (Ghiorso and Sikkeland, 1967).

Because No is normally a divalent ion in aqueous solution and is difficult to oxidize and hold in the trivalent state, it has not been possible to make a chemical identification of the atomic number in the same manner as the preceding 3+ actinides, i.e. identification by their unique positions in the elution sequence from a cation-exchange resin column. However, in 1971, the atomic number of ^{255}No was unequivocally determined through the observance of characteristic K-series X-rays from the daughter isotope ^{251}Fm in coincidence with the alpha particles from the decay of the parent, ^{255}No (Dittner *et al.*, 1971).

13.4.2 Isotopes of nobelium

The known isotopes of nobelium range from mass 250 through 262, with the exception of 261 (Table 13.5). The isotope ^{259}No is the longest-lived with a half-life of 58 min. However, the isotope ^{255}No has a considerably higher production rate and is most often used for chemical studies.

Table 13.5 Nuclear properties of nobelium isotopes.

Mass number	Half-life	Mode of decay	Main radiations (MeV)	Method of production
250	0.25 ms	SF		$^{233}\text{U}(^{22}\text{Ne},5\text{n})$
251	0.8 s	α	α 8.68 (20%) 8.60 (80%)	$^{244}\text{Cm}(^{12}\text{C},5\text{n})$
252	2.27 s	α 73% SF 27%	α 8.415 (~ 75%) 8.372 (~ 25%)	$^{244}\text{Cm}(^{12}\text{C},4\text{n})$ $^{239}\text{Pu}(^{18}\text{O},5\text{n})$
253	1.62 min	α	α 8.01	$^{246}\text{Cm}(^{12}\text{C},5\text{n})$ $^{242}\text{Pu}(^{16}\text{O},5\text{n})$
254	51 s	α	α 8.086	$^{246}\text{Cm}(^{12}\text{C},4\text{n})$ $^{242}\text{Pu}(^{16}\text{O},4\text{n})$
254 m	0.28 s	IT		$^{246}\text{Cm}(^{12}\text{C},4\text{n})$ $^{249}\text{Cf}(^{12}\text{C},\alpha 3\text{n})$
255	3.1 min	α 61.4% EC 38.6%	α 8.121 (46%) 8.077 (12%)	$^{248}\text{Cm}(^{12}\text{C},5\text{n})$ $^{249}\text{Cf}(^{12}\text{C},\alpha 2\text{n})$
256	2.91 s	α ~ 99.7% SF ~ 0.3%	α 8.43	$^{248}\text{Cm}(^{12}\text{C},4\text{n})$
257	25 s	α	α 8.27 (26%) 8.22 (55%)	$^{248}\text{Cm}(^{12}\text{C},3\text{n})$
258	1.2 ms	SF		$^{248}\text{Cm}(^{13}\text{C},3\text{n})$
259	58 min	α ~ 75% EC ~ 25%	α 7.551 (22%) 7.520 (25%)	$^{248}\text{Cm}(^{18}\text{O},\alpha 3\text{n})$
260	106 ms	SF, α		$^{254}\text{Es}(^{18}\text{O},x)$
262	5 ms	SF		^{262}Lr daughter

13.4.3 Preparation and purification

The isotope ^{255}No can be produced for chemical study via the $^{249}\text{Cf}(^{12}\text{C},\alpha 2\text{n})$ reaction; about 1200 atoms were produced in a 10 min irradiation of a $350 \mu\text{g cm}^{-2}$ target of ^{249}Cf with 3×10^{12} particles per second of 73 MeV ^{12}C ions (Dittner *et al.*, 1971).

As with Md, the physical separation of the nobelium atoms from the target material can be made using the recoil-atom catcher foil technique. It is preferable to combine this with the 'gas-jet' technique since the product atoms can be deposited on the 'catcher' foil in a chemistry area separate from the bombardment area. The nearly monolayer of collected atoms can then be easily rinsed off the surface of the foil with dilute acid without dissolution of the foil. Isolation of the No from other actinides produced in the bombardment and from any target material transferred to the foil can be readily made using schemes based on the separation of divalent ions from trivalent ones, e.g. selective elution by solvent extraction chromatography using HDEHP as the stationary organic phase and 0.05 M HCl as the mobile aqueous phase (Silva *et al.*, 1969). Under these conditions, No passes through the column in the first few column volumes while the trivalent actinides are strongly adsorbed on the column. Selective

elution from a cation-exchange resin column, e.g. Dowex 50 \times 4, can also be made using 3 M HCl as eluant. Here, No again elutes in a few column volumes and the trivalent actinides remain on the column (Silva *et al.*, 1973). When using a direct 'catcher' foil, e.g. gold, a more elaborate scheme involving separation of the gold by anion-exchange chromatography is necessary (David *et al.*, 1990b). This can be followed by selective isolation of the No from contaminants by elution from a chromatographic extraction column using HDEHP.

13.4.4 Atomic properties

The electronic ground state of gaseous nobelium atoms has been predicted to be the 1S_0 level of the $5f^{14}7s^2$ configuration (Martin *et al.*, 1974). No experimental information is available. No experimental measurements of inner-shell binding energies have been reported but estimated values have been published by Firestone *et al.* (1996), along with X-ray energies, based on the values recommended by Porter and Freedman (1978). The results are given in Table 13.4.

The characteristic K-series X-rays of ^{253}No emitted following the alpha decay of ^{257}Rf have been measured in alpha/X-ray coincidence experiments by Bemis *et al.* (1973). Values for $K_{\alpha 2}$ and $K_{\alpha 1}$ were reported as (120.9 ± 0.3) and (127.2 ± 0.3) keV, respectively.

13.4.5 The metallic state

Nobelium metal has not been prepared; however Johansson and Rosengren (1975) predicted that, for the same reasons as discussed above for Fm, No would prefer a divalent metallic state similar to Eu and Yb rather than a trivalent one. An estimate of 126 kJ mol^{-1} for the enthalpy of sublimation of No has been reported (David, 1986a). This value is similar to that of Es, Fm, and Md and supports the suggestion that No would form a divalent metal (Haire and Gibson, 1990). David (1986a) estimated a divalent metallic radius of 0.197 nm.

13.4.6 Solution chemistry

Before discovery, nobelium was expected to be a trivalent ion in aqueous solution and to exhibit a chemical behavior similar to the elements preceding it in the actinides series. However, in 1949, Seaborg (1949) predicted that a relatively stable $2+$ state might exist for element 102 due to the special stability of the filled $5f^{14}$ shell in the $5f^{14}7s^2$ electronic configuration. Twenty years later, this prediction was confirmed.

In over 600 experiments, Maly *et al.* (1968) subjected about 50000 atoms of ^{255}No to cation-exchange chromatography and coprecipitation experiments. These tracer experiments showed that nobelium exhibits a chemical behavior substantially different from the trivalent actinides but similar to the divalent alkaline earth elements, Sr, Ba, and Ra. Thus, the divalent ion of nobelium was

shown to be the most stable species in aqueous solution in the absence of strong oxidizing agents.

Chuburkov *et al.* (1967) have compared the behavior of nobelium to those of Tb, Cf, and Fm during experiments where the atoms were first chlorinated and subsequently were carried by gas along a tube with a thermal gradient. From the position of deposition of atoms along the tube, they concluded that the chloride of No undergoes strong adsorption on solid surfaces and therefore is not very volatile; its volatility is close to the chlorides of Tb, Cf, and Fm. The chloride of either divalent or trivalent nobelium would be expected to exhibit a low volatility.

Silva *et al.* (1974) have conducted solvent extraction and cation-exchange chromatography studies of nobelium. Its complexing ability with chloride ions were compared with that of divalent mercury, cadmium, copper, cobalt, and barium in a tri-*n*-octylamine chloride/HCl liquid extraction system, and it was found to be most similar to the relatively weakly complexed alkaline earth element. The elution behavior of nobelium was also compared with that of Be, Mg, Ca, Sr, Ba, and Ra in a cation-exchange resin column/4 M HCl system and found to elute with Ca^{2+} . Further, comparison with these alkaline earth elements in an HDEHP/HCl liquid chromatography system showed nobelium to elute between Ca^{2+} and Sr^{2+} . The ionic radius of No^{2+} was estimated as 0.11 nm from a linear correlation of ionic radius with log distribution coefficient for several divalent ions obtained using an HDEHP/ HNO_3 liquid-liquid extraction system. Using a similar correlation, a value of 0.10 nm was obtained from the cation-exchange chromatography data. From the results of relativistic Hartree-Fock-Slater calculations (Lu *et al.*, 1971), a value of 0.11 nm was suggested for the ionic radius of No^{2+} . The single-ion heat of hydration, calculated using an empirical form of the Born equation (Phillips and Williams, 1966) was 1486 kJ mol^{-1} . From correlations of ionic radii of actinides and lanthanides with atomic number, an ionic radius for No^{3+} of 0.90 and 1.02 Å for CNs 6 and 8, respectively, have been estimated. (David *et al.*, 1978; David, 1986b).

The formation of divalent nobelium complexes with citrate, oxalate, and acetate ions in aqueous solution of 0.5 M NH_4NO_3 have been studied by McDowell *et al.* (1976) using solvent extraction techniques. In general, the complexing tendency of nobelium with these ligands is between that of Ca and Sr, being somewhat more like Sr.

Silva *et al.* (1969) have studied the reduction potential of the $\text{No(III)}-\text{No(II)}$ couple in aqueous solution with 50–100 atoms per experiment using HDEHP extraction column chromatography to distinguish between No^{2+} and No^{3+} . By comparing the extraction of nobelium from dilute acid solutions containing oxidants of differing potentials with the extraction behavior of tracer quantities of Cf, Cm, Ra, Tl, and Ce, the standard potential $E^\circ(\text{No}^{3+} \rightarrow \text{No}^{2+})$ was estimated to be between +1.4 and +1.5 V.

Meyer *et al.* (1976) used a modified radiopolarographic technique and ^{255}No to measure the half-wave potential for the reduction of nobelium at a mercury electrode and reported a value for $E^\circ(\text{No}^{2+} \rightarrow \text{No}^0(\text{Hg}))$ of -1.6 V . After

applying an estimated amalgamation potential correction, a value of -2.6 V was calculated for the standard potential of the $\text{No}^{2+} \rightarrow \text{No}^0$ couple. More recently David *et al.* (1990b) have measured amalgamation potentials of nobelium using radiocoulometry with the isotope ^{259}No . From the data, they estimated the $\text{No}^{2+} \rightarrow \text{No}^0$ couple standard potential as $-(2.49 \pm 0.06)$ V. This couple, combined with the measured $3+ \rightarrow 2+$ potential of 1.45 V (Silva *et al.*, 1969) resulted in an estimated value for $E^\circ(\text{No}^{3+} \rightarrow \text{No}^0)$ of -1.18 V by David *et al.* (1990b). David (1986a, 1986b) estimated $E^\circ(\text{No}^{3+} \rightarrow \text{No}^0)$ to be -1.26 V, which leads to a calculated $E^\circ(\text{No}^{2+} \rightarrow \text{No}^0) = -2.61$ V; these values were selected for Table 13.8 and Fig. 19.9 because of the consistent systematics (David, 1986a, 1986b) among many actinide species. David *et al.* (1990b) also estimated Gibbs energies of formation of -480 and -342 kJ mol^{-1} for No^{2+} (aq) and No^{3+} (aq), respectively. From a semiempirical technique for the linearization of actinide and lanthanide electrode potentials, Nugent (1975) has calculated a value of $+6.5$ V for $E^\circ(\text{No}^{4+} \rightarrow \text{No}^{3+})$.

13.5 LAWRENCIUM

13.5.1 Introduction

In 1961, Ghiorso, Sikkeland, Larsh, and Latimer of the Lawrence Berkeley National Laboratory reported the discovery of element 103 (Ghiorso *et al.*, 1961). An alpha particle activity of 8.5 MeV energy with a half-life of 8 s was produced in bombardments of a Cf target with both ^{10}B and ^{11}B ions. Owing to the short half-life, a chemical identification was not possible but the alpha activity was attributed to an isotope of element 103 on the basis of convincing nuclear evidence, i.e. the results of cross-bombardments with other targets and projectiles. However, because the target consisted of a mixture of californium isotopes, masses 249 through 252, an unambiguous mass assignment was not possible. Though isotopes of masses 255–259 could have been produced, based on cross-section considerations, the highest yield was expected for mass 257. The discoverers suggested the name lawrencium, symbol Lw, for the new element in honor of E. O. Lawrence, inventor of the cyclotron and founder of the Lawrence Berkeley National Laboratory. The name was accepted by IUPAC, but the symbol was changed to Lr.

The results of subsequent studies on the production and identification of ^{255}Lr , ^{256}Lr , and ^{257}Lr by researchers at the Joint Institute for Nuclear Research (JINR) at Dubna, Russia, appeared to conflict with the Berkeley mass assignment because none of the above isotopes had the decay properties of the original Berkeley alpha activity (Druin, 1971). However, in 1971, six alpha particle emitting isotopes of lawrencium, masses 255–260, were identified at Berkeley in bombardments of nearly isotopically pure targets of ^{248}Cm with ^{14}N and ^{15}N and ^{249}Cf with ^{10}B and ^{11}B ions, respectively, and an explanation for the discrepancy was suggested (Eskola *et al.*, 1971). From the Berkeley experiments, ^{257}Lr was found to emit

alpha particles of 8.8 MeV with a half-life of only 0.6, but ^{258}Lr was found to have a half-life of 4.2 s with the emission of 8.62 MeV alpha particles. Thus, Ghiorso and associates considered that the mass assignment made in 1961 should have been 258. The difference in the new half-life value compared to the 1961 value was attributed to relatively poor counting statistics resulting from the small number of alpha particle events observed in the earlier work.

13.5.2 Isotopes of lawrencium

Twelve isotopes of lawrencium are known with masses ranging from 252 through 262 (Table 13.6). The longest-lived isotope is ^{262}Lr , with a half-life of 3.6 h. The isotope ^{256}Lr , half-life of 26 s, was used in the early chemical studies; however, the longer-lived isotope ^{260}Lr ($t_{1/2} = 3$ min) has been used in more recent experiments.

13.5.3 Preparation and purification

The production of ^{256}Lr is best accomplished through the $^{249}\text{Cf}(^{11}\text{B},4n)$ reaction using 70 MeV boron ions while ^{260}Lr is produced via the $^{249}\text{Bk}(^{18}\text{O},\alpha 3n)$ reaction using 117 MeV oxygen ions.

As with Md and No, the physical separation of the Lr atoms from the target material and subsequent rapid collection is best accomplished using a recoil-atom gas-jet system coupled to a capillary transport system of some type (Hoffman *et al.*, 1988).

Because of their short half-lives, there is insufficient time to obtain a rigorous chemical purification of ^{256}Lr or ^{260}Lr . The isotope, ^{256}Lr was first isolated from

Table 13.6 Nuclear properties of lawrencium isotopes.

Mass number	Half-life	Mode of decay	Main radiations (MeV)	Method of production
252	0.36 s	α	α 9.018 (75%)	^{256}Db daughter
253 m	1.5 s	α	α 8.722	^{257}Db daughter
253	0.57 s	α	α 8.794	^{257}Db daughter
254	13 s	α	α 8.460 (64%)	^{258}Db daughter
255	21.5 s	α	α 8.43 (40%) 8.37 (60%)	$^{243}\text{Am}(^{16}\text{O},4n)$ $^{249}\text{Cf}(^{11}\text{B},5n)$
256	25.9 s	α	α 8.52 (19%) 8.43 (37%)	$^{243}\text{Am}(^{18}\text{O},5n)$ $^{249}\text{Cf}(^{11}\text{B},4n)$
257	0.65 s	α	α 8.86 (85%) 8.80 (15%)	$^{249}\text{Cf}(^{11}\text{B},3n)$ $^{249}\text{Cf}(^{14}\text{N},\alpha 2n)$
258	3.9 s	α	α 8.621 (25%) 8.595 (46%)	$^{248}\text{Cm}(^{15}\text{N},5n)$ $^{249}\text{Cf}(^{15}\text{N},\alpha 2n)$
259	6.2 s	α	α 8.45	$^{248}\text{Cm}(^{15}\text{N},4n)$
260	3.0 min	α	α 8.03	$^{248}\text{Cm}(^{15}\text{N},3n)$
261	39 min	SF		$^{254}\text{Es}(^{22}\text{Ne},x)$
262	3.6 h	SF, EC		$^{254}\text{Es}(^{22}\text{Ne},x)$

reaction products by a rapid solvent extraction technique using the chelating agent thenoyltrifluoroacetone (TTA) dissolved in methyl isobutyl ketone (MIBK) as the organic phase and buffered acetate solutions as the aqueous phase (Silva *et al.*, 1970). This method did not separate individual trivalent actinides so identification of Lr was made on the basis of its unique alpha particle energy of 8.24 MeV.

When the capillary transport system is used, the longer-lived isotope, ^{260}Lr , can be washed from the 'catcher' foil along with the small amount of aerosol carrier particles with 0.05 M HCl. Kept to a few drops of volume, this solution can be placed on the top of a cation-exchange resin column and isolation of Lr^{3+} from other trivalent actinides can be accomplished by selective elution with ammonium α -HIB (Hoffman *et al.*, 1988). An automated system called Automated Rapid Chemistry Apparatus (ARCA) has been developed and used to carry out this separation (Brüchle *et al.*, 1988).

13.5.4 Atomic properties

The electronic structure of the ground state of neutral atoms of Lr was predicted in 1970 as the $^2\text{D}_{3/2}$ level of the $5f^{14}6d^{17}s^2$ configuration (Moeller, 1970) similar to the rare earth homolog Lu, $4f^{14}5d^16s^2$, as one would expect from a simple extrapolation from the chemical periodic table. This prediction was brought into question in 1971 by Brewer who calculated, by a semiempirical method, a configuration of $5f^{14}7s^27p^1$ (Brewer, 1971). Later the results of relativistic Dirac–Hartree–Fock calculations by Nugent *et al.* (1974) concluded that the energy difference between these two configurations was quite small and either configuration could be the ground state. On the basis of the results of multiconfiguration Dirac–Fock calculations, Desclaux and Fricke (1980) predicted the $5f^{14}7s^27p^1$ configuration as the ground state. Later, multiconfiguration Dirac–Hartree–Fock calculations by Wijesundera *et al.* (1995) and relativistic Fock-space coupled-cluster method by Eliav *et al.* (1995) led to a similar conclusion, i.e. the s^2p $J = 1/2$ is energetically favored over the s^2d $J = 3/2$ state. This result is due to the relativistic mass increase of the electrons that are strongly accelerated near the highly charged nucleus. This effect is strongest for the spherical s and $p_{1/2}$ orbitals that have high densities near the nucleus.

In 1988, Eichler and coworkers proposed gas adsorption chromatography experiments to distinguish between the two ground state configurations s^2d and s^2p . They calculated that there should be a measurable difference in the enthalpies of adsorption on metal surfaces for the two different configurations (Eichler *et al.*, 1988). The s^2p was predicted to be less volatile, perhaps similar to the p-element Pb, than the s^2d configuration with estimated sublimation energies of about 134 and 400 kJ mol^{-1} , respectively. Online gas chromatography was applied to study the volatility of Lr by Jost *et al.* (1988) and to determine the enthalpy of adsorption. No evidence for Lr as a volatile element was found under reducing conditions at a temperature of about 1000°C. Their

Table 13.7 Comparison of calculated and measured L-series X-rays for Lr.

Transition	X-ray energy (keV)	
	Calculated ^a	Measured ^b
L _{γ1} (4d _{3/2} → 2p _{1/2})	27.91	27.97 (15) ^c
L _{β1} (3d _{3/2} → 2p _{1/2})	23.93	24.03 (14)
L _{β4} (3p _{1/2} → 2s)	22.61	22.61 (18)
L _{β2} (4d _{5/2} → 2p _{3/2})	21.21	21.35 (20)
L _{α1} (3d _{5/2} → 2p _{3/2})	17.48	17.57 (12)
L ₁ (3s → 2p _{3/2})	14.43	14.43 (20)

^a Firestone *et al.* (1996).

^b Bemis *et al.* (1977).

^c Error in last two digits.

results gave a lower limit for the adsorption enthalpy for Lr on quartz and Pt surfaces at 290 kJ mol⁻¹, significantly higher than the estimated values for Lr (s²p). The configuration of the ground state of lawrencium is still in doubt.

No experimental measurements of inner-shell binding energies have been reported but estimated values have been published by Firestone *et al.* (1996), along with X-ray energies, based on the values recommended by Porter and Freedman (1978). The results are given in Table 13.4.

The characteristic L-series X-rays of ²⁵⁶Lr have been observed in coincidence with alpha particles of the parent ²⁶⁰Db by Bemis *et al.* (1977). The results are presented in Table 13.7. They agree very well with those given by Firestone *et al.* (1996).

13.5.5 Metallic state

Lawrencium metal has not been prepared. An estimate of 352 kJ mol⁻¹ for the enthalpy of sublimation of Lr has been reported (David *et al.*, 1978). This value is similar to that of Lu and supports the suggestion that Lr would prefer the formation of a trivalent metal as expected for the last member of the actinide series. Systematic properties of heats of vaporization, bulk modulus, and atomic volumes suggest that Lr would be a trivalent metal with a volume similar to that of Lu (Haire and Gibson, 1990). David *et al.* (1978) estimated a trivalent metallic radius of 0.171 nm.

13.5.6 Solution chemistry

In 1949, element 103 was predicted by Seaborg (1949) to be the last member of the proposed actinide or 5f series of elements and to be similar to lutetium with respect to the stability of the 3+ oxidation state in aqueous solution. It required nearly 20 years to finally synthesize this element and to conduct chemical experiments to confirm this prediction.

Silva *et al.* (1970) employed a fast solvent extraction procedure using MIBK containing the chelating agent TTA as the organic phase and buffered acetate solutions of differing pH as the aqueous phase to distinguish between the 2+, 3+, and 4+ oxidation states. In over 200 separate experiments, approximately 1500 atoms of ^{256}Lr were produced for study and the extraction behavior of Lr was compared with a number of tetravalent (Th, Pu), trivalent (Fm, Cf, Cm, Am, Ac), and divalent ions (No, Ba, Ra). In these experiments, lawrencium was found to extract into the organic phase over the pH range of 3+ ions along with Fm and Cf. Thus, it was concluded that the 3+ oxidation state is the most stable oxidation state for Lr in aqueous solution. Unfortunately, because of the short half-life, there was insufficient time to perform a cation-exchange resin column separation to confirm its predicted elution position just ahead of Md^{3+} .

From studies comparing the retention times of chlorinated atoms of several different actinides and transactinides as they passed through a heated glass column, Chuburkov *et al.* (1969) concluded that the chloride of element 103 has an adsorbability on solid surfaces, and hence volatility, similar to the chlorides of Cm, Fm, and No and to be much less volatile than the chlorides of element 104, Rf.

Because Lr is a trivalent ion in aqueous solution, it should exhibit a chemical behavior similar to the other 3+ actinides and lanthanides, e.g. insoluble fluoride and hydroxide. One would expect Lr^{3+} to have a slightly smaller ionic radius than Md^{3+} , due to the actinide contraction, and to elute just before Md from a cation-exchange resin column using ammonium α -HIB as eluant (see Fig. 13.1). From correlations of ionic radius with atomic number for actinide and lanthanide elements, David *et al.* (1978) estimated an ionic radius of 0.0893 nm for Lr^{3+} .

By 1987, a longer-lived isotope of lawrencium, ^{260}Lr , with a half-life of 3 months and alpha particle energy of 8.03 MeV, was available for chemical studies. Hoffman *et al.* (1988) repeated the solvent extraction experiments of Silva *et al.* (1970) and confirmed the trivalent nature of Lr in aqueous solution. Further, elutions of Lr from a cation-exchange resin columns using ammonium α -HIB as eluant were conducted and compared with the elution behavior of Md and the rare earths Tm, Er, and Ho (Hoffman *et al.*, 1988). Lr was found to elute between Ho and Tm, and approximately with the Er tracer. Seven alpha events attributable to Lr^{260} were detected. The distribution coefficients were determined from the elution positions and, using the linear correlation of ionic radius with log distribution coefficient, an ionic radius was calculated for each Lr event. The average Lr^{3+} radius was found to be 0.0886 ± 0.0003 nm assuming an ionic radius of 0.0881 nm for Er for CN 6 (Templeton and Dauben, 1954). This result was surprising to the authors because it gave a difference of only 0.0015 nm for the step of 2 in atomic number between Md, with an ionic radius of 0.0896 nm, and Lr. This is substantially smaller than the $2Z$ difference of 0.0021 for the analogous trivalent rare earth ions Tm and Lu and indicates

an ionic radius for Lr larger than expected. Therefore, Lr elutes later than predicted in Fig. 13.1.

In later experiments, a German–American collaboration (Brüchle *et al.*, 1988) used the ARCA (Automated Rapid Chemistry Apparatus) system to check the earlier results of Hoffman *et al.* (1988) and to increase the number of Lr atoms studies and thus the statistical significance. The earlier work was confirmed and a value of 0.0881 ± 0.0001 nm was obtained from the elution data for Lr. A heat of hydration of $-(3685 \pm 13)$ kJ mol⁻¹ was calculated from the radius using empirical models and the Born–Haber cycle. Brüchle *et al.* (1988) pointed out that the difference between the radii of Md³⁺, Fm³⁺, and Es³⁺ is 0.0016 nm while this difference is 0.0012 nm for the analogous lanthanide ions. This suggests that the contraction at the end of the actinides series is larger than the analogous lanthanide contraction, perhaps due to relativistic effects (Seth *et al.*, 1994), with the exception of the last member of the actinide series, Lr.

It is possible that relativistic effects could stabilize the 7s² closed shell so that only the 7p_{1/2} or 6d electron would be ionized under reducing conditions to give a monovalent Lr. Several attempts have been made to reduce Lr³⁺ to a divalent or monovalent ion in aqueous solution. Hoffman *et al.* (1988) used a solvent extraction column with HDEHP as the stationary organic phase and dilute HCl as the mobile aqueous phase to separate 1+ and 2+ ions from 3+ and 4+ ions, the former passing through the column while the latter remain fixed. Solutions containing ²⁶⁰Lr³⁺ were passed through the column where the Lr remained fixed. The reducing agent hydroxylamine hydrochloride was added to the HCl and the resulting solution passed through the column for 20 s at 80°C in an attempt to reduce and elute any Lr. The attempt was unsuccessful, however, as the authors noted, the kinetics of the reduction are slow. In companion experiments, Scherer *et al.* (1988) used the HDEHP solvent extraction column

Table 13.8 Summary of chemical properties of elements 100–103.

Element	100	101	102	103
electronic configuration ^a	5f ¹² 7s ²	5f ¹³ 7s ²	5f ¹⁴ 7s ²	5f ¹⁴ 6d ¹ (7p ¹)7s ²
stable oxidation states ^b	<u>3</u> , 2	<u>3</u> , 2	3, <u>2</u>	<u>3</u>
ionic radius of indicated ion (nm)	0.0911(3+)	0.0896(3+)	0.105(2+)	0.0886(3+)
standard electrode potentials (V) ^c				
3+ → 2+	-1.15	-0.15	+1.45	<-0.44
3+ → 0	-1.96	-1.74	-1.26	-2.06
2+ → 0	-2.37	-2.5	-2.61	
first ionization potential (V) ^d	6.50	6.58	6.65	

^a Free neutral atom + Rn core.

^b Most stable state in aqueous solution underlined.

^c Values in italics are estimates.

^d From Martin *et al.* (1974).

method, with the ARCA system, to attempt reductions of Lr to di- or monovalent ions (Scherer *et al.*, 1988). In a series of experiments using the reducing agents V^{2+} and Cr^{2+} in the dilute HCl-eluting solutions, there was no evidence for the reduction of Lr^{3+} to either the 2+ or 1+ oxidation state. From the results, a limit of <-0.44 V was estimated for the $Lr^{3+} \rightarrow Lr^{2+}$, 1+ reduction potential. Using the newly discovered Lr^{262} ($t_{1/2} = 3.6$ h), Lougheed *et al.* (1988) attempted to reduce Lr with Sm^{2+} , $E^\circ(Sm^{3+} \rightarrow Sm^{2+}) = -1.55$ V, and coprecipitate Lr^{1+} with Rb using sodium tetraphenylborate or chloroplatinic acid but were unsuccessful. The 2+ and 3+ actinide ions do not coprecipitate under these conditions. On the basis of 20 Lr events, they calculated an upper limit of -1.56 V for $E^\circ(Lr^{3+} \rightarrow Lr^{1+})$ and concluded that it is unlikely that Lr^{1+} can exist in aqueous solutions. Nugent (1975) has calculated values of -2.06 V for $E^\circ(Lr^{3+} \rightarrow Lr^0)$ and $+7.9$ V for $E^\circ(Lr^{4+} \rightarrow Lr^{3+})$.

A summary of some of the chemical properties of fermium, mendelevium, nobelium, and lawrencium is given in Table 13.8.

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