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CHEMICAL PROPERTIES OF THE HEAVIER ACTINIDES AND TRANSACTINIDES

E. K. HULET

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CHEMICAL PROPERTIES OF THE HEAVIER ACTINIDES AND TRANSACTINIDES

E. K. Hulet
University of California
Lawrence Livermore National Laboratory
P. O. Box 808, Livermore, California 94550

ABSTRACT

The chemical properties of each of the elements 99 (Es) through 105 are reviewed and their properties correlated with the electronic structure expected for 5f and 6d elements. A major feature of the heavier actinides, which differentiates them from the comparable lanthanides, is the increasing stability of the divalent oxidation state with increasing atomic number. The divalent oxidation state first becomes observable in the anhydrous halides of californium and increases in stability through the series to nobelium, where this valency becomes predominant in aqueous solution. In this range of elements, the II → III oxidation potential decreases from ~+1.5 to -1.5 volts. These observations lead to the conclusion that, in comparison with the analogous 4f electrons, the 5f electrons in the latter part of the series are more tightly bound. Thus, there is a lowering of the 5f energy levels with respect to the Fermi level as the atomic number increases.

The metallic state of the heavier actinides has not been investigated except from the viewpoint of the relative volatility among members of the series. In aqueous solutions, ions of these elements behave as "normal" trivalent actinides and lanthanides (except for nobelium). Their ionic radii decrease with increasing nuclear charge which is moderated because of increased screening of the outer 6p electrons by the 5f electrons. These relative ionic radii have been obtained from comparisons of the elution position in chromatographic separations.

The actinide series of elements is completed with the element lawrencium (Lr) in which the electronic configuration is $5f^{14}7s^{2}7p$. From Mendeleev's periodicity and Dirac-Fock calculations, the next group of elements is expected to be a d-transition series corresponding to the elements Hf through Hg. The chemical properties of elements 104 and 105 only have been studied and they indeed appear to show the properties expected of eka-Hf and eka-Ta. However, their nuclear lifetimes are so short and so few atoms can be produced that a rich variety of chemical information is probably unobtainable.

KEYWORDS

Review, solution chemistry, atomic properties, actinide compounds, metallic properties, separations.

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INTRODUCTION

The detailed chemistry of the heavier actinides has only become discernable within the past 12-14 years when berkelium, californium, and einsteinium first became available in appreciable quantities. Micro- to milligram quantities of these elements were necessary for service as target isotopes in producing tracer amounts of even heavier actinides by charged particle bombardments. In addition, these quantities permitted progress in understanding the chemical properties of the transcurium elements (Bk-Es) beyond that gathered from tracer-scale experiments. However, with each step in atomic number above that of Es (element 99), we know less and less of each element's chemistry because of the increasingly shorter lifetimes of the nuclides and because of the difficulties in synthesizing sufficient numbers of atoms.

Because of the nuclear instabilities of these man-made elements, the range of atomic and chemical properties that are accessible to experimental study are indeed limited in comparison with the vastly wider spectrum of information obtainable from the naturally occurring elements. Among the basic chemical properties of the heavier actinides which have been investigated are the behavior of these ions in solution which includes separation chemistries, complex-ion formation, oxidation-reduction reactions, electrochemistry, hydration, and absorbtion spectra. Our experimentally derived knowledge becomes scantier for other chemical forms and states of these elements as, for example, the organometallic compounds and the elemental and solid states. Atomic and physical-chemical properties are almost entirely unknown for the elements heavier than einsteinium, except where derived by theoretical extrapolations. Nevertheless, all of the small bits of knowledge so far obtained allow us to piece together a rather clear picture of the basic chemistry of these elements.

A condensed scheme that summarizes the valence states and numbers of 5f electrons in each state is shown for the actinides in Fig. 1. Elements within the first half of the series are stable in the IV, V, and VI valence states, while the divalent state is almost unknown in this group. However, one of the major features uncovered in the investigations of the heavier actinides was a finding of increasing stability of the divalent state with progressive increases in atomic number. This trend, like the high and stable valences in the lighter members of the series, sets the actinides apart from the comparable lanthanide series and can be generally interpreted on the basis of subtle changes in electronic structure. The most important change occurring with increasing Z is a marked lowering of the 5f energy levels with respect to the Fermi level and a widening separation between the 5f ground states and the first excited states in the 6d or 7p levels. Thus, removing an outer 5f valence electron becomes increasingly difficult until divalency predominates in the next to last actinide element in the series. These and other general features of the chemistry of the heavier actinides are summarized after the review of lawrencium.

EINSTEINIUM

Production

The isotopes ^{253}Es and ^{254g}Es, with half lives of 20.5 and 275.7 days, respectively, can be produced in high-flux nuclear reactors in sufficient

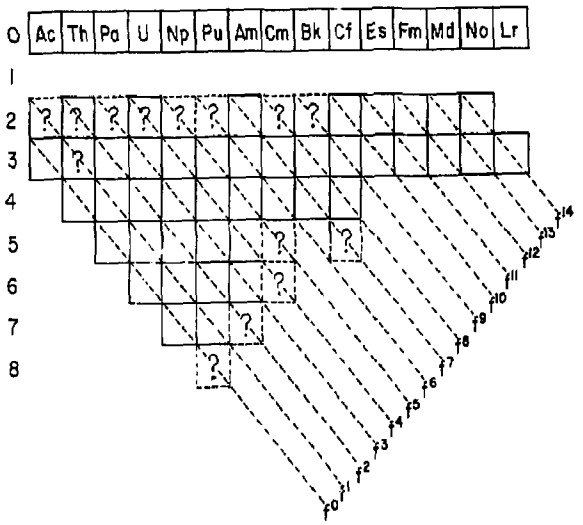

Fig. 1. Schematic of actinide oxidation states and associated 5f electronic structure.

quantities for chemical investigations. Starting with neutron capture by ^{238}U, the production of ^{253}Es proceeds through a long chain of further captures and beta decays by intermediate nuclides during long neutron irradiations. The yearly production of ^{253}Es from 1962 onward is shown in Fig. 2. The production of ^{253}Es has by now leveled off at a rate of about two milligrams per year while the amounts of ^{254g}Es and ^{255}Es are necessarily limited by the fission destruction of ^{254}Es to about 0.3 and 0.06 percent of the ^{253}Es quantities, respectively(1). Prior to 1969, einsteinium and the other transplutonium elements were produced by the individual National Laboratories but an overall U.S. production program, maintained at the Oak Ridge National Laboratory by the U.S. Department of Energy, has since superseded those individual efforts.

Atomic Properties

The electronic configurations of einsteinium in neutral and singly ionized gaseous atoms have been determined from emission spectra taken with electrodeless discharge lamps containing EsI_3. Although the first emission spectrum of einsteinium revealed only 9 lines(2), the most recent exposures using the 10-m spectrograph at the Argonne National Laboratory are expected to show some 20,000 lines(3). Unfortunately, the measurements on these photographic plates are incomplete and the electronic configurations given in Table 3 are based on term assignments to a portion of the 290 lines observed earlier by Worden et al.(4). It should be noted that not all of the lowest energy electronic configurations have been observed yet. Brewer

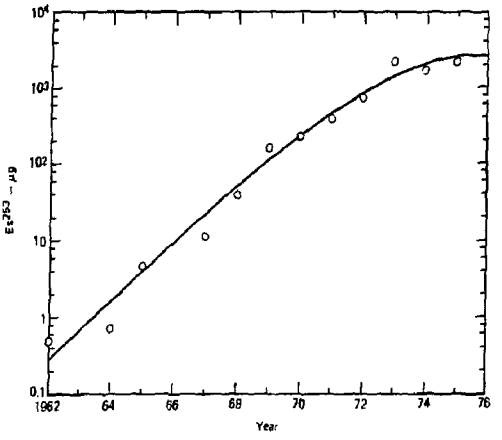

Fig. 2. Yearly production of ^{253}Es in the United States.

has tabulated his estimated energies of the lowest level of the lowest spectroscopic term for each electron configuration(5,6). For the singly ionized free atom, it is apparent from his estimates that the $f^{10}s^2$, f^{12} and $f^{11}d$ should be lower in energy than the first excited level $f^{11}p$ observed by Worden and others(4). Other atomic properties from atomic beam and x-ray measurements are listed in Table 1.

Metallic State

The high specific radioactivity of einsteinium has greatly limited the investigations of the metal. Of the two attempts to prepare the metal and determine its structure, the successful method employed electron diffraction rather than x-ray diffraction. The latter was largely inconclusive because of degradation of the metal's crystallinity caused by self-irradiation. The electron diffraction lines from eleven samples were indexed on the basis of a face-centered cubic structure with $a_0 = 0.575 \pm 0.001$ nm(11). This fcc form of einsteinium metal is believed to be divalent because it has the same lattice parameter as reported for the divalent form of californium metal.

A melting point for the metal was also noted while heating the samples in the electron microscope used for the diffraction measurements. Micro puddles of the metal formed during the heating and, after calibrating with metals of known melting points, a temperature of 860 ± 50°C was established as the melting point of einsteinium metal.

Further evidence for divalency in Es metal has come from studies comparing the condensation temperatures of elemental lanthanides and actinides in thermochromatographic columns(12). The trivalent metals Sc, La, and Bk were

TABLE 1 Atomic Properties of Einsteinium (^{253}Es)

	Ground Level	Other Levels	Energy (cm^{-1})
Neutral, I	$5f^{11}7s^2$, $^4I^\circ_{15/2}$	$5f^{11}7s7p$, $^6I_{15/2}$	17 802.89
		$5f^{10}6d7s^2$, $^6I_{17/2}$	19 367.93
		$5f^{11}7s8s$, $^4I_{15/2}$, $^3S_1$	33 829.35
Singly Ionized, II	$5f^{11}7s$, $^5I^\circ_8$	$5f^{11}7p$, $^5I_7$	27 751.12
		$5f^{10}6d7s$	32 897.77*

Property	Value	Reference
First ionization potential	6.42 ± 0.03 eV (calculated)	(7,8)
Nuclear spin	7/2	(4)
Nuclear dipole moment	$\mu_I = 4.10 \pm 0.07 \mu_N$	(9)
Nuclear quadrupole moment	$Q_s = 6.7 \pm 0.8$ barns	(9)
K x-ray energies	$K\alpha_2$ 112.501 ± 0.01 keV $K\alpha_1$ 118.018 ± 0.01 $K\alpha_3$ 131.848 ± 0.02 $K\alpha_1$ 133.188 ± 0.02	(10)

* May not be the lowest level of this configuration.

not volatilized at the initial temperature of 1425°K, whereas the metals of Yb, Es, Fm, and Md were vaporized and later condensed at the same temperature (~700°K). The behavior of divalent Eu, Sm, and Ca metals was intermediate between those extremes. Since volatilities are correlated with promotional energies and the number and energy of the valence bonds, the more volatile actinides are associated with the divalent metals. The estimates of Nugent et al.(13) for the enthalpy of sublimation of lanthanide and actinide metals closely agree with the relative volatilities found in the thermochromatographic study reported above. Furthermore, Ward and colleagues (14) have recently completed detailed analyses of the cohesive energy of the actinide metals (entropies and heats of sublimation), in which they also indicate that einsteinium is a divalent metal.

The thermal conductivity of einsteinium has been estimated to be 10 W m^{-1} K^{-1} at 300°K(15).

Compounds

Only a few simple compounds of einsteinium have been prepared and structurally identified. Aside from self-destruction of the crystal structures, there is a rapid in-growth of the α-daughter ^{249}Bk; the L, M, and N x-rays, emitted following α-decay blacken the x-ray film used in Debye-Scherrer cameras within 10 to 20 minutes with microgram samples of ^{253}Es or ^{254g}Es. A synchrotron radiation source may be the only way of overwhelming this sample background source of radiation with sufficient intensity of monochromatic radiation to permit diffraction measurements.

The known compounds of einsteinium are listed in Table 2 together with the rather sparse information detailing their properties. Divalent compounds were not identified by their crystal structure, but by adsorption spectra of their halides, taken with crystallites or of samples first melted and then quenched. These spectra show a sharp difference in the f-f absorption bands when compared to the corresponding spectra of the trivalent halides (Fig. 3). We emphasize that the apparent stability of the divalent oxidation state in einsteinium was not realized until a decade ago and that this feature in the heavier actinides clearly sets this series of elements apart from the later elements in the 4f series.

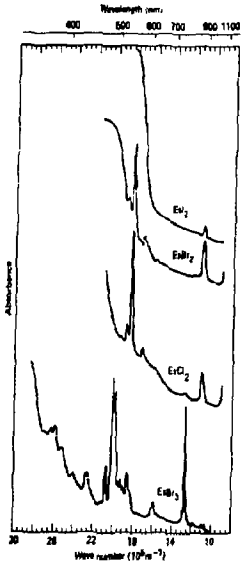

Fig. 3. Absorption spectra of the divalent einsteinium halides and trivalent $EsBr_3$. Reprinted with the permission of the J. Phys. Colloq. (Ref. 25).

Electron paramagnetic-resonance spectra of divalent einsteinium have been recorded in single-crystal hosts of CaF_2(16), BaF_2, and SrF_2(17). Reduction of Es^{3+} to Es^{2+} was spontaneous from electron displacement caused by the α-radiation. A $5f^{11}$ configuration with a ground state close to the $^4I_{15/2}$ level, but with a small admixture of the $^2K_{15/2}$, was found, which indicated the cubic crystal-field only slightly perturbs the inner 5f orbitals.

A possible tetravalent compound EsF_4 may also exist, as judged by comparing the volatility of an einsteinium fluoride with PuF_4, AmF_4, CmF_4, BkF_4, and CfF_4(18). The f-f electronic spectrum of the Es^{4+} free ion has been calculated by Varga and coworkers(19). Nugent et al.(20) and Lebedev(21) estimated a III→IV oxidation potential of -4.6 V which Nugent thought might allow the synthesis of the compound Cs_3EsF_7.

TABLE 2 Simple Compounds of Di- and Trivalent Einsteinium Characterized by Either Structural or Spectroscopic Analysis

Compound	Structural Type*	Lattice Parameters (a_o, b_o, c_o in nm; β in °) a_o	b_o	c_o	β	Major Absorption Bands ($10^5 m^{-1}$)	Reference
Es_2O_3	Mn_2O_3-bcc	1.0766±0.0006				---	22
$EsCl_3$	UCl_3-hex	0.740±0.002		0.407±0.002		(see Ref 23)	23,24
$EsCl_2$	---					11.1,18.5,24.5	25,26
EsOCl	PbFCl-tetra	0.3948±0.0004		0.6702±0.0019		---	23,24
$EsBr_3$	$AlCl_3$-mono	0.727±0.002	1.259±0.003	0.681±0.002	110.8±.2	12.6,19.8	27
$EsBr_2$	---					11.2,18.3	25
EsOBr	---					(no published data)	23
EsI_3	BiI_3-hex	0.753		2.084		(see Ref 23)	23,28
EsI_2	---					11.2,18.5	25
EsOI	---					(no published data)	23
EsF_3	---					13.2,20.3	23

* bcc = body-centered cubic
hex = hexagonal
tetra = tetragonal
mono = monoclinic

Separation and Purification

The chemical recovery of einsteinium (and Bk, Cf, and Fm) after irradiation is performed remotely in large shielded cells. Details of the chemical separation processes used in the United States and by the Soviets at the Kurchatov Institute of Atomic Energy have been reviewed by Hulet and Bodé (29) and by Kosyakov and coworkers(30), respectively. Nearly all of the separation steps used in these large-scale processes were developed earlier for applications in laboratory separations, but extensive modifications were were required to adapt them to the special and nearly always adverse conditions encountered in remote operations with very high levels of radioactivity present. These separation processes are unlikely to be scaled up further as, for instance, for the recovery of transplutonium elements during the reprocessing of fuel from power reactors. This is largely because they were born in the laboratory where corrosive chemicals could be easily contained in glass apparatus and where the chemist could oversee the difficult chromatographic separations.

Purification of einsteinium requires two difficult separations: 1) from lanthanide fission products and 2) from adjacent actinides. The main difficulty arises from the great similarity in the chemical properties of their trivalent ions. Fortunately, the contraction in size of the aqueous ions with increasing atomic number can be exploited with complexing ligands to offer slight variations in complex strengths between members of either series of f elements. Chromatographic methods then exploit these small chemical differences many times over to give useful separation factors for the tripositive elements.

Separation of einsteinium from the lanthanides is usually accomplished by elution with either 13 M HCl or 20 vol % ethanol saturated with HCl from an ion-exchange column containing a strongly acidic cation exchange resin(31). Einsteinium and the other actinides are rapidly eluted in a band while the trivalent lanthanides are retained and eluted somewhat later. The purification of einsteinium from many milligrams of lanthanides necessitates an anion-exchange procedure using 10 M LiCl as an eluant(32). With this elution method, Cf, Es, and Fm are separated from all lanthanides, Pu, Am, and Cm with separation factors ranging from 4 to 23.

The intragroup separation of einsteinium from adjacent actinides can be performed by either of two chromatographic methods. In the ion-exchange method the trivalent actinides are eluted with a complexing agent such as 2-hydroxy-2-methylpropanoic acid (α-hydroxyisobutyric acid or αHIB) from a heated column of cation exchange resin containing a strongly acidic, highly cross-linked resin(33). Such columns are often run at pressures up to 17.2 MPa to force the eluant through the very fine particles of ion-exchange resin (34). The second method employs extraction chromatography in which the extractants, either bis(2-ethylhexyl) phosphoric acid (HDEHP) or 2-ethylhexylphenyl phosphonic acid (HEHØP), are absorbed on an inert support material(29). An eluant of approximately 0.3 to 0.4 M HCl or HNO_3 provides distribution coefficients appropriate for Es-Fm separations. Table 3 summarizes the separation factors (ratio of distribution coefficients) obtainable by each of these methods. Clearly, the purification of Cf from Es is the poorest; hence, the cation exchange method is preferred because of the larger separation factor. The major difference between the two methods of chromatographic separation lies in a reversal of the elution sequence with atomic number.

TABLE 3 Separation Factors ($S = K_{d(z)}/K_{d(z+1)}$) for Es/Fm and Cf/Es Obtained with Acidic Extractants and by Cation-Exchange. Average Values from Ref. 29, p. 11, and Ref. 35 are Listed

Elements	αHIB (87°C)	HDEHP (60°C)		HEHØP (25°C)
		(HCl)	(HNO_3)	HCl
	S	S	S	S
Cf				
	1.5	0.99	1.02	1.3
Es				
	1.7	2.04	2.20	2.5
Fm				

Solution Chemistry

Trivalent ions. Across the actinide series from Pu to Lr, the solution properties of the An^{3+} ion vary only slowly and in a regular manner. Thus, much of the behavior described in prior chapters for trivalent actinide ions can be safely extrapolated to estimate that of Es^{3+}. Bonding with ligands is almost entirely attributed to electrostatic forces, but with some second-order contribution from covalent sharing of electrons due to the relatively large radial extension of the 5f orbitals. The ionic radius of Es^{3+} has been calculated from the six-coordinated sesquioxide to give a value of 0.0928 nm(22), or about 1 pm smaller than the radius of Cf^{3+}. Einsteinium is stable only as the trivalent ion in aqueous solution.

A number of measurements of the absorption spectrum of $^{253}Es^{3+}$ have been made over the energy range of 9430 to 34,000 cm^{-1} (36-39). The band structure (12 peaks) observed could be reasonably well fitted in both energy and intensity by assuming Es^{3+} behaved as a free ion and that the f-f transition arose from eigenstates which were strongly mixed because of coupling that is intermediate between L-S and j-j(37-40). These assumptions follow closely those used in fitting calculated levels to identified absorption bands in preceeding members of the actinide (and lanthanide) series.

Studies of the complex-ion chemistry of Es^{3+} have been made in conjunction with measurements of the stability constants of other trivalent actinides. A summary of the known stability constants for einsteinium complexes is shown in Table 4. Figure 4 is illustrative of the trend of greater complex formation with increasing atomic number for the trivalent actinides. The step-wise increase in β_3 between Cm and Bk, often seen as part of the tetrad effect, is related to the first pairing of a 5f electron at Bk after half filling the 5f shell in Cm. With the possible exception of the two lower thiocyanate complexes, the chloride is the only outer-sphere complex in which waters of hydration lie between the ligand and einsteinium ion. The remaining complexes are believed to be inner-sphere as inferred from the increase of a given stability constant with an increase in atomic number and from the enthalpy and entropy of formation of the complex.

TABLE 4 The Stability Constants of Es^{3+} Complexes

Complex	Stability Constant			Reference
	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	
$EsCl^{2+}$	-0.18			(41)
$EsOH^{2+}$	8.86			(42)
$Es(SO_4)_n^{3-2n}$	-2.19	-4.3	-4.93	(43)
$Es(SCN)_n^{3-n}$	0.559	-1.4	0.468	(44)
$EsHCit^{2-}$	10.6			(45)
$Es(Cit)_2^{3-}$	12.1			
$Es(HIB)^{2+}$	4.29			(46)
$Es(tartrate)^{+}$	5.86			
$Es(malate)^{+}$	7.06			
$EsDETPA^{2-}$	22.62			(47)
$EsDACTA^{-}$	19.43			
EsEDTA	19.11			

Cit = citrate ion
αHIB = 2-hydroxy-2-methylpropanoate ion
DEPTA = diethylenetriaminepentaacetate ion
DACTA = 1,2-diaminecyclohexanetetraacetate ion
EDTA = ethylenediaminetetraacetate ion

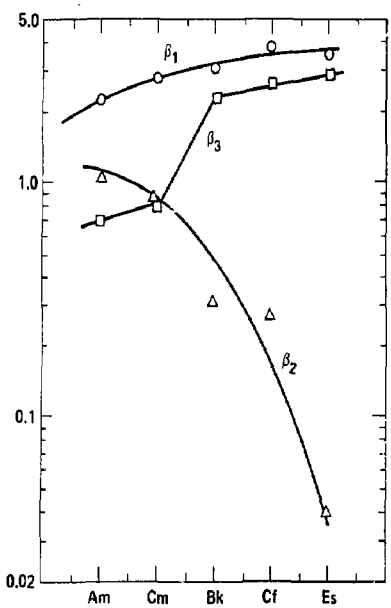

Fig. 4. First three stability constants of the actinide (III) thiocyanate complexes as a function of atomic number. Redrawn from the data of Harmon and Peterson (44).

Hydrated radii and hydration numbers for the An^{3+} ions have recently been derived from migration rates in an electric field and from Stokes' Law(48). The hydrated ions of einsteinium and fermium are the largest in the series Am^{3+} to Md^{3+}; the hydrated radius of einsteinium is 0.492 nm which would allow 16.6 molecules of water in the total hydration sphere. Several parameters of thermodynamic interest have been measured or estimated; e.g. the molar activity coefficient of Es^{3+} in $NaNO_3$ solution(49) and the free energy, enthalpy, and entropy of formation of Es^{3+} in aqueous solution(21), 50,52). The values $\Delta H_f^\circ = 595.8 \pm 21$ kJ mole^{-1}, $\Delta S_f^\circ = 76.1$ J mole^{-1} K^{-1}, and $\Delta F_f^\circ = 573 \pm 17$ kJ mole^{-1} given by David and colleagues(50) were obtained from an entropy prescription and the standard reduction potential, III→0, described in the following paragraph.

For the purpose of measuring the electropotential, reduction of the trivalent einsteinium ion to the metal (Hg amalgam) has been performed by polarographic methods. A single half-wave representing the III → 0 reduction potential was observed(53). The potential found for the combined reactions of reduction and amalgamation was -1.460 ± 0.005 V. After correcting for the amalgamation energy by an empirical method suggested by Nugent(52), the standard potential derived was -1.98 V relative to the standard hydrogen

potential. Because the amalgamation energy represents a large correction, caution should be exercised in using the standard potential in thermodynamic calculations.

Divalent ions. The divalent state is of major importance and has attracted the interest of many experimenters since 1967 when the appreciable stability of this state was first recognized in the actinides. The III→II reduction potential of einsteinium was first estimated to be -1.6 V from the lowest energy electron-transfer band(55). A later estimate of -1.21 V was obtained for chloroaluminate melts(56) as well as another estimate of the standard potential of -1.18 V(54). Mikheev and coworkers identified Es(II) from the the cocrystallization of einsteinium tracer with $SmCl_2$ in an ethanol solution(57). Einsteinium was only partially reduced to the (II) state by $SmCl_2$, which allowed them to conclude that the standard reduction potential of Es^{3+} was close to that of Sm^{3+}, or -1.55 ± 0.06 V(58). An ionic radius of 0.105 nm was estimated from the radius of maximum electron density obtained in Hartree-Fock calculations, which was then corrected to obtain the crystalline radius by an empirical proportionality constant(59).

FEW ATOM CHEMISTRY

Beginning with fermium and with each advancement in atomic number beyond, the amounts of these rare elements that can be made available for chemical research are measured in atoms rather than fractions of a gram. Weighable quantities cannot be synthesized and we speak of "atom chemistry" and even "one-atom-at-time chemistry" for the heaviest actinide and transactinides. These realities are illustrated in Table 5, which also points to a second grave obstacle to chemical research with the elements listed, namely, the sharply decreasing nuclear half-lives. Clearly, with these limitations on the time in which to complete an experiment and the few atoms available, many fundamental and important physical and chemical properties are outside the domain of experimental measurement.

TABLE 5 Half-Lives and Numbers of Atoms Available for the Chemical Investigations of the Heaviest Actinides

Isotope	Half-Life	Average Atoms per Experiment
^{255}Fm	20.1 h	10^{11}
^{256}Md	77 min	10^{6}
^{255}No	3.1 min	10^{3}
^{256}Lr	31 s	10

If we observe the chemical behavior of fewer than a hundred atoms, can we be reasonably certain that our observations represent the "true" chemistry of an element? A detailed answer to this troublesome question has only recently been addressed. Borg and Dienes(60) considered the rate of approach to a

thermodynamic equilibrium in an ensemble where only a few atoms of an element are present. Taking a single-step exchange reaction,

$$MX + Y \underset{k_2}{\overset{k_1}{\rightleftharpoons}} MY + X,$$

as one commonly encountered, they assume a displacement mechanism illustrated in the simple activation energy diagram of Fig. 5. If $\Delta G^{\dagger}$ was less than ~15 to 17 kcal, the residence time in each state MX or MY was calculated to be very short and an equilibrium would be rapidly (1 s) reached. This assumes a collision frequency of the same magnitude as vibration frequencies, or about 10^{14} s^{-1}. Once equilibrium is reached, the fractional average time an atom spends as MY or MX is proportional to the equilibrium value of (MY)/(MX). Thus, an experimental measurement of (MY) and (MX) with very few

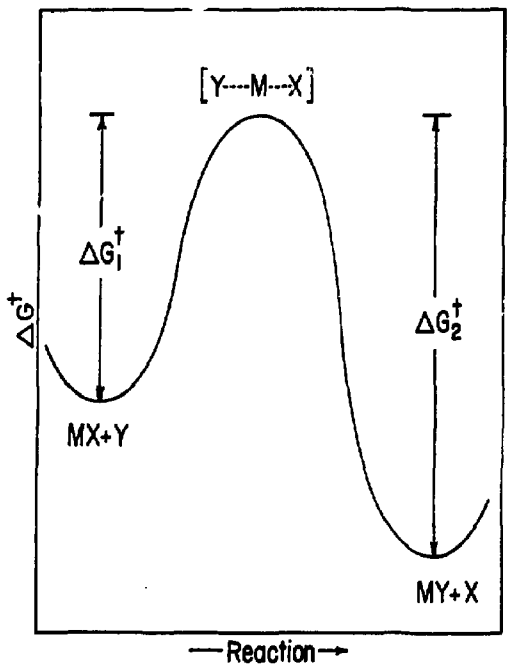

Fig. 5. Activation energy diagram for a single-step exchange reaction.

atoms of M present will yield an equilibrium constant statistically close to the "true" value provided both states are rapidly sampled. They calculated from the binomial law that with as few as 10 atoms of M, the probability of obtaining twice the most probable value was 10% or less when the fraction of either species was greater than 1%.

FERMIUM

Several Fm isotopes with half lives of nearly a day to 100 days are available in amounts of 10^9 atoms or more. The nuclides ^{255}Fm and ^{257}Fm are conveniently used for chemical investigation of Fm; they are obtainable as products from long neutron irradiations of ^{242}Pu and ^{244}Cm. The 20-h ^{255}Fm is generated by the beta decay of 40-d ^{255}Es produced in the neutron irradiations. By chemically isolating the Es and periodically reseparating Fm from its parent, one can secure a fairly long-term source of ^{255}Fm adequate for all tracer experiments.

The ground-state electronic configuration of Fm is $5f^{12}7s^2$ or an $^3H_6$ level (61). This was established by an atomic-beam measurement of the magnetic moment g_j of 3.24-h ^{254}Fm. In this elegant measurement, FmF_3 was reduced with ZrC_2 in an atomic-beam apparatus to produce a beam of neutral Fm atoms. Three magnetic resonances were detected and the best value for g_j was calculated. To obtain the level term, it was necessary to extrapolate the mixing due to intermediate coupling in the electron spin-orbit interactions (j-j and L-S). These extrapolations were made from lower actinides and supplemented by Hartree-Fock calculations for free atoms. From similar calculations, the next higher level is predicted to be $^5G_7$ starting about 20,000 cm^{-1} above the ground state and having the configuration $5f^{11}6d7s^2$. However, the $f^{12}sp$ and $f^{11}s^2p$ configurations are very close in energy(5) to the $f^{11}ds^2$ so that it is impossible to unambiguously estimate the next level above the ground state.

The electron binding energies of Fm have been measured for the K, L_{1-3}, N_{1-5}, $N_{6,7}$, O_{1-3}, $O_{4,5}$, and $P_{2,3}$ shells(62,63). These were determined to an accuracy of 10 eV by conversion-electron spectroscopy in the beta decay of ^{254m}Es to ^{254}Fm. A surprisingly low binding energy for the $P_{2,3}$ ($6p_{1/2,3/2}$) shell of 24 ± 9 eV was found. Predicted values derived either from extrapolations of those measured in lower actinides or calculated by Hartree-Fock and relativistic local-density methods are about 20 to 60 eV higher in energy. However, relativistic Dirac-Fock calculations with the addition of a Lamb shift correction gave binding energies in excellent agreement with the experimental ones(64). As the authors suggested, a binding energy of 24 eV might provide a possibility for 6p involvement in chemical and spectroscopic interactions.

The properties of Fm metal and of its solid compounds are for the most part unknown because there are insufficient quantities to prepare even microsamples. In the numerous thermochrometographic studies by Zvara and coworkers, the evaporation of Fm and Md tracer from molten La at 1150°C was compared with the behavior of other selected lanthanides and actinides(65). The volatility of Md and Fm was found to be greater than that of Cf, and Cf was about equivalent to Yb and Eu. All were much more volatile than Am and Ce. A later study at this Laboratory by Hübener(12) extended these studies by comparing the adsorption of elemental Cf, Es, Fm, and Md in the gaseous state on the Ti surface of a thermochromatographic column. Since they had established that for the s and f elements there was a correspondence between the metallic valence and the deposition temperature, their

purpose was to characterize the metallic state properties of the heavy actinides which are available only in trace amounts. On the basis of virtually equal deposition temperatures, Hübener concluded that Cf, Es, Fm, and Md were divalent metals, although Cf condensed at a slightly higher temperature than the other actinides. Ytterbium behaved the same as the Es, Fm, and Md, but Eu and Sm condensed at a temperature 300°C higher. The evaporation rates of Cf and Fm from molten U have also been found to be equal(66) which again shows that if Cf is to be considered a divalent metal, then so should Fm metal.

The separation methods for Fm are the same as those used for separating other trivalent lanthanides and actinides. Additional methods for separating trivalent actinides from lanthanides are given in the Separation and Purification section on einsteinium. For separating the adjacent elements, Es and Md, a high-resolution chromatographic method is necessary. Either ion exchange, using strongly acidic resins(67), or extraction chromatography employing alkylphosphoric acids(68) is strongly preferred. A complexing agent (α-hydroxyisobutyric acid) is required to selectively elute the actinides from cation-exchange resins. The separation factors, defined as the ratio of the distribution coefficients of two metal ions, are small for both cation exchange and extraction chromatography. These factors range from 1.7 to 2.04 for Es-Fm separations using a Dowex-50 cation exchanger (67) or extraction chromatography with HCl as the eluant and bis(2-ethylhexyl)phosphoric acid diluted with heptane as the extractant(69). The FmMd separation factors obtained by these two methods were 1.4 and 4.0, respectively(67,69).

The solution chemistry of Fm deals largely with the highly-stable tripositive oxidation state, although the dipositive state is also known. Formation constants for citrate complexes(70) and the first hydrolysis constant have been accurately determined for Fm^{3+}(71,72). Since the formation and hydrolysis constants for Am, Cm, Cf, and Es were measured simultaneously with those for Fm, the complex strengths of many of the trivalent actinides can be compared(72). All constants were determined at an ionic strength of $\mu = 0.1$ in a perchlorate medium by measuring the partitioning of the radioactive tracers between a thenoyltrifluoroacetonate-benzene phase and the aqueous phase. The results for Fm may be expressed as follows:

$$Fm^{3+} + H_2O \rightleftharpoons FmOH^{2+} + H^+; \qquad \log K = -3.80 \pm 0.2$$

$$Fm^{3+} + 2H_3Cit \rightleftharpoons Fm(HCit_2)^{2-} + 5H^+; \qquad \log \beta_1 = 11.17$$

$$Fm^{3+} + 2H_3Cit \rightleftharpoons FmCit_2^{3-} + 6H^+; \qquad \log \beta_1 = 12.40$$

Compared to the other actinide ions investigated, Fm formed stronger complexes with citrate and hydroxyl ions because of its smaller ionic radius. The smaller radius is a direct consequence of the increased nuclear charge with partial shielding of the outermost 6p electrons by the inner f electrons.

The reduction of Fm^{3+} to Fm^{2+} was first reported in 1972 by N. B. Mikheev and coworkers (73). The reduction was accomplished with Mg metal in the presence of Sm^{3+} which was coreduced in an aqueous-ethanol solution. Identification of the divalent state of Fm was established by determining the extent of its cocrystallization with $SmCl_2$ and this was compared to the amount of tracer Sr^{2+} also carried with $SmCl_2$. A milder reductant, Eu^{2+}, failed to reduce Fm^{3+}, which placed the standard reduction potential of Fm^{3+} between Eu^{2+} and Sm^{2+} or -0.43 to -1.55 V relative to the standard $Pt,H_2|H^+$ elec-

trode. Later work(74) by these scientists narrowed the range to between -0.64 and -1.15 V and, most recently, they were able to estimate the potential was the same as the $Yb^{3+} \rightarrow Yb^{2+}$ couple within 0.02 V, or -1.15 V(75,-76). This was accomplished by measuring the ratio of Fm(III) to Fm(II) by cocrystallization of Fm(II) with $SrCl_2$ while changing the ratio of Yb(II)/Yb(III) in each experiment. The difference between the standard potentials of Fm and Yb is then easily determined from the Nernst equation. The reduction of Fm to a divalent ion with $SmCl_2$ has also been observed recently by Hulet et al.(77).

In further work related to the divalent state, the electrode potential for the reduction of Fm^{2+} to Fm^0 has been measured by Samhoun and David (78). Over a period of years, they developed and refined a radiopolarographic technique for determining half-wave potentials at a dropping-Hg cathode. In addition to Fm, they have measured either the III → 0 or II → 0 potential for all transplutonium actinides except No and Lr(53,78,79). The polarograph for Fm is shown in Fig. 6. The electrochemical reaction taking place at a reversible electrode can be deduced from the slope of the polarographic wave. Specifically, the number of electrons exchanged at the electrode, based on the Nernst equation, is obtained from this slope. From their analysis of the polarograms, there were three electrons involved in the electro-chemical reduction of the trivalent ions of the elements Am through Es and only two electrons for the reduction of Fm. This implies that Fm^{3+} was first reduced to Fm^{2+} before being further reduced to metal. The III→II

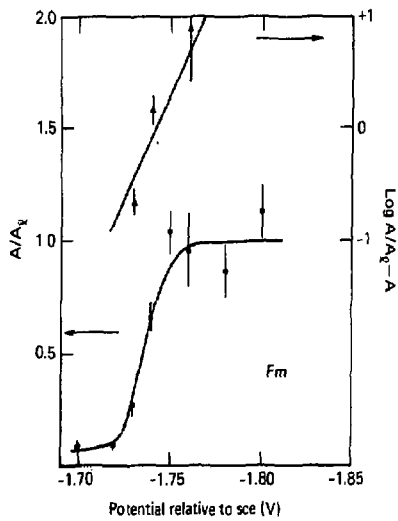

Fig. 6. Distribution of Fm as a function of applied voltage between mercury in a dropping Hg cathode and 0.1 M tetramethyl ammonium perchlorate at pH = 2.4. The slope of the logarithmically-transformed line indicates two electrons were exchanged in the electrolysis reaction (Ref. 79).

reduction step is not detected by this radiopolarographic technique because both the III and II ions are in the solution phase, whereas the measured parameter is the distribution of the tracer between the aqueous and Hg phase. The half-wave potentials measured by this method include the amalgamation potential of the metal-mercury reaction. The potential for the overall process for Fm, i.e.

$$Fm^{2+} + 2e^- = Fm(Hg),$$

was found to be -1.474 V with reference to the standard hydrogen electrode. The amalgamation potential was estimated to be 0.90 V by using the metallic radius as a correlating parameter and interpolating within a series of divalent elements with known amalgamation potentials(52). This correlation is shown in Fig. 7. The standard electrode potential is then given as -2.37 V for the $Fm^{2+} + 2e^- = Fm^0$ reaction. The authors' estimated 5 mV accuracy for the measured half-wave potential seems reasonable, but there is a much larger uncertainty in the estimated amalgamation potential.

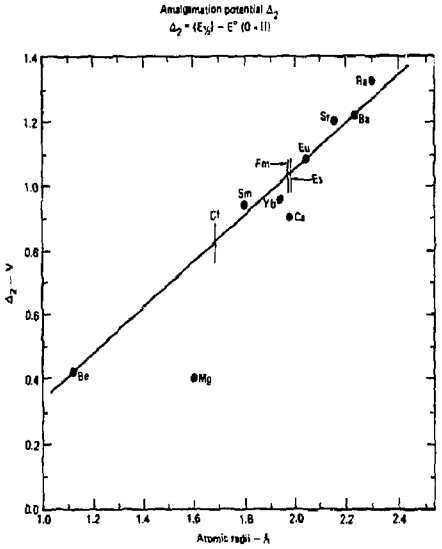

Fig. 7. Amalgamation potentials, Δ_2, derived from experimental data are plotted as a function of the atomic (metallic) radii. The amalgamation potential for Fm is obtained by using an estimated radius. Partially redrawn from Ref. (52).

MENDELEVIUM

The isotope ^{256}Md is nearly always employed for chemical studies of this element. Besides having a convenient half-life of 77 min, this nuclide can be made with millibarn cross sections by a number of nuclear reactions between light and heavy ions with actinide target nuclei. We have found that

the bombardment of fractions of a microgram of ^{254}Es with intense alpha-particle beams will produce ~10^6 atoms of ^{256}Md in one to two hours of irradiation time. The ^{256}Md is most easily detected through spontaneous fission arising from the ingrowth of its electron-capture daughter, ^{256}Fm. A difficulty with using spontaneous-fission counting to determine the Md content of samples is that the growth and decay of fission radioactivity in each sample must be followed with time in order to resolve the amounts of Md and Fm initially present. However, alpha-particles of a distinctive energy coming from a 10% alpha-decay branch can also be used to identify ^{256}Md in a mixture of actinide tracers.

The volatility of mendelevium metal has been compared with that of other actinide metals(12,65); these results were described in the fermium section. Because of the high volatility found, mendelevium was believed to be a divalent metal.

There are no experimental verifications of the electronic structure of Md, but this has been calculated by several methods to be $5f^{13}7s^2$ in which the ground state level is $^2F_{7/2}$(5).

The separation of Md from the other actinides can be accomplished either by reduction of Md^{3+} to the divalent state(80) or by chromatographic separations with Md remaining in the tripositive state. Historically, Md^{3+} has been separated in columns of cation-exchange resin by elution with α-hydroxyisobutyric acid solutions(67). This method is still widely used even though extraction chromatography requires less effort and attention to technique. Horwitz and coworkers(69) developed a highly-efficient and rapid separation of Md^{3+} by employing HNO_3 elutions from columns of silica powder powder saturated with an organic extractant, bis(2-ethylhexyl)phosphoric acid. The separation of Md from Es and Fm could be completed in under 20 minutes and had the advantage of providing final solutions of Md free of complexing agents that might be an interference in subsequent experiments.

When the divalent state of Md was first discovered, extraction chromatography was used to prove that the behavior of Md^{2+} was dissimilar to that of Es^{3+} and Fm^{3+}(80). The extractant, bis(2-ethylhexyl)phosphoric acid (HDEHP), has a much lower affinity for divalent ions than it does for the tri- and tetravalent ones. Thus, the extraction of Md^{2+} is much poorer than the extraction of the neighboring tripositive actinides as indicated by the results shown in Table 6. This became the basis for a separation method in which tracer Md in 0.1 M HCl is reduced by fresh Jones Reductor in the upper half of an extraction column containing HDEHP absorbed on a fluorocarbon powder in the lower half. Mendelevium, in the dipositive state, is rapidly eluted with 0.1 M HCl whereas the other actinides are retained by the extractant. The separation is quickly performed, but the Md contains small amounts of Zn^{2+} from the Jones Reductor and also Eu^{2+}, which was added prior to the elution to prevent reoxidation of Md^{2+} by the extractant.

TABLE 6. Comparison of the Extraction Behavior of tracer Einsteinium, Fermium, and Mendelevium after Treatment with Various Reducing Agents. The Column-Elution Method of Extraction Chromatography Was Used with the Extractant HDEHP Adsorbed on a Column Bed of a Fluoroplastic Powder Ref. 80

Conditions for Reduction	Standard Potential of Reducing Agent (volts)	% Non-Extracted By HDEHP Column	
		Md	Es-Fm
Zn(Hg) amalgam in upper half of extraction column	-0.763	77	0.10
0.01 M Eu^{2+}, 0.1 M HCl, ~2-3 min, 80°C; Zn(Hg) amalgam in upper half of extraction column	-0.43	75	0.10
0.6 M Cr^{2+}, 0.1 M HCl, ~2 min, 25°C; extraction column prewashed with 0.6 M Cr^{2+} in 0.1 M HCl	-0.41	99	0.56

The solution chemistry of the trivalent oxidation state has not been investigated beyond its behavior in the separation procedures described above. All observations indicate that Md^{3+} is a "normal" actinide with an ionic radius slightly less than that of Fm. As might be expected, attempts to oxidize Md^{3+} with sodium bismuthate failed to show any evidence for Md^{4+}(80).

The divalent oxidation state was the first found for any member of the actinide series(80,81) and, therefore, stirred a strong theoretical and experimental effort to establish the reasons for the unexpected stability of this state in Md and, subsequently, in the adjacent actinides. We shall summarize the interpretations for divalency in the heaviest actinides in a later section of this review, but in this section, only the known properties of Md^{2+} will be presented.

In the earliest experiments with Md^{2+}, rough measurements were made of the reduction potential for the half-reaction

$$Md^{3+} + e^- = Md^{2+}.$$

The first measurement gave a reduction potential of -0.2 V with respect to the standard hydrogen electrode(80). This value was obtained from determining the equilibrium concentration of each metal ion in the reaction

$$V^{2+} + Md^{3+} \rightleftharpoons V^{3+} + Md^{2+}$$

and then calculating the equilibrium constant. After entering the equilibrium constant into the Nernst equation, it was found that V^{3+} was a better

reducing agent than Md^{2+} by about 0.07 V. In other experiments, Mály observed the complete reduction of Md^{3+} with V^{2+} but the reduction was incomplete when Ti^{3+} was used(81). From these observations, he concluded the standard reduction potential of Md^{3+} was close to -0.1 volt. The standard potentials obtained by both groups are in reasonable agreement and, most importantly, they conclusively show that the stability of Md^{2+} is greater than any lanthanide(II) ion. This finding was surprising since divalency in the lanthanides is mainly associated with the special stability given by the half-filled and fully-filled f-electron shell. Divalent Md ions are at least one electron short of the stable $5f^{14}$ configuration.

Additional experiments, which may not be clearly relevant to the divalent oxidation state, include the reduction of Md^{3+} to Md(Hg) by sodium amalgams and by electrolysis(82). Both the extraction experiments with Na amalgams and the electrolysis at a Hg cathode indicated a large enrichment of Md in the Hg phase relative to that of Np, Pu, Am, Cm, and Cf. The percentages of Es and Fm in the sodium amalgam were not greatly different from the percentage of Md. But a clear enrichment of Md was obtained in the electrolysis experiments because the initial rate of amalgamation was much larger for Md than for Es and Fm.

Recently, new electrochemical experiments were carried out with Md in which controlled-potential electrolysis was used to study the reduction of Md^{3+} to the metallic state in a Hg amalgam(79,93). Half-wave potentials were measured by radiocoulometry and radiopolarography in the presence of noncomplexing and weak and strong complexing agents. The radiopolarogram obtained for Md in a noncomplexing medium is presented in Fig. 8. The half-wave potential for Fm was remeasured at the same time as that of Md because of its presence as a decay product of ^{256}Md. The results showed that the reduction potential of Md was about 10 mV more negative than Fm and that no significant difference was observed upon changing the medium from ClO_4^- to Cl^-. In citrate solutions, a shift of 90 mV was obtained for Md which is about the same shift seen with Fm and Ba ions in a citrate medium. The slope of the logarithmically transformed wave was 30 mV for Md and Fm and, for the reasons noted in the section on Fm, this slope corresponds to a two-electron exchange at the electrode. These results demonstrate that the electrochemical behavior of Md is very similar to that of Fm and can be summarized in the equation

$$Md^{2+} + 2e^- = Md(Hg); \qquad E^o = -1.50 \text{ V}.$$

If a 0.90 V amalgamation potential is assumed, then a standard reduction potential of -2.40 V is obtained.

In addition to the di- and trivalent ions of Md, a stable monovalent ion was reported by Mikheev et al. in 1972(84). This oxidation state was indicated in the cocrystallization of Md with CsCl and RbCl after the coreduction of Md^{3+} and Sm^{3+} with Mg in an ethanol-7 M HCl solution. Mendelevium was also found enriched in Rb_2PtCl_6 precipitates, a specific carrier for the larger ions of the alkali metals. These results were explained by a stabilization of the monovalent ion due to completing the f shell which would give the $5f^{14}$ electronic configuration.

In response to the totally negative findings from others' studies(77,83), Mikheev and his colleagues(85) carried out new cocrystallizations of Md with NaCl and KCl after reducing with Eu^{2+} or Yb^{2+}. The NaCl or KCl salts were forced to crystallize by heavily salting the nearly neutral H_2O-

ethanol solutions, containing tracer Md, with 4 M LiCl. Because anomalous mixed crystals were not formed, they again claimed the cocrystallization of Md with NaCl or KCl demonstrated the presence of Md^+.

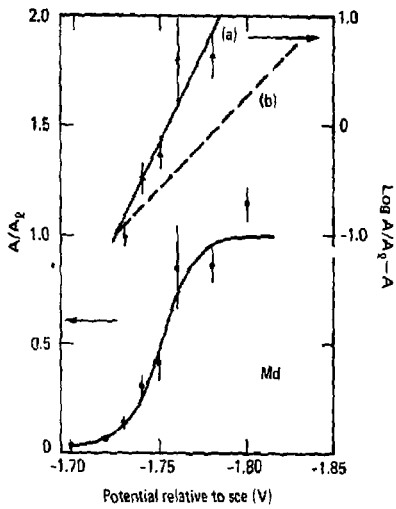

Fig. 8. Distribution of Md as a function of applied voltage between mercury in a dropping Hg cathode and 0.1 M tetramethyl ammonium perchlorate at ph = 2.4. The slope of the logarithmically-transformed line indicates the number of electrons exchanged in the electrolysis reaction. The slope of line (a) is 30 mV, and (b) is 60 mV, which corresponds to a one-electron reduction (Ref. 79).

The RbCl cocrystallizations and Rb_2PtCl_6 coprecipitations of Ref. 84 were recently repeated and an extensive series of new experiments were performed in which attempts were made to prepare Md^+ by reduction with $SmCl_2$ in an ethanolic or fused KCl medium(77). After the reductions, the coprecipitation behavior of Md was compared with the behavior of tracer amounts of Es, Fm, Eu, Sr, Y, and Cs, also present in the same solution. A large number of experiments showed that Md consistently followed the behavior of Fm^{2+}, Eu^{2+}, and Sr^{2+} rather than the behavior of Cs^+. The most telling experiment was the precipitation of Rb_2PtCl_6 after reduction of Md^{3+} with Sm^{2+}. The distribution of the tracer elements between the precipitate and an 85% ethanol solution is given in the form of a ratio in Table 7. These results clearly demonstrate that Md did not coprecipitate with Rb_2PtCl_6, whereas virtually all of the Cs did so. The overall conclusion of this work was that Md cannot be reduced to a monovalent ion with Sm^{2+} and, therefore, the earlier claim for Md^+ was unsubstantiated.

TABLE 7 Distribution of Tracer Elements After Reduction with Sm^{2+} and Coprecipitation with Rb_2PtCl_2 in 85% Ethanol (Ref. 77)

Distribution ratio for						
Fm	Md	Eu	Sr	Y	Es	Cs
0.004	0.005	0.006	0.012	0.017	0.033	110

This same conclusion was reached also by Samhoun et al.(83) and David and coworkers(79) on the basis of their electrochemical investigations of Md, which we described earlier. If the potential for the reaction $Md^+ + e^- = Md$ was more positive than -1.5 V, it would have been observed in the electrochemical reductions. Furthermore, the logarithmic slope of the Md reduction waves could not be fitted to a slope of 60 mV expected for a one-electron change. And lastly, the shifts in potential caused by complexing Md with either citrate or chloride ions were consistent with it being a divalent ion and not with it being either a cesium-like or silver-like ion.

Because of the large number and variety of negative results, the weight of evidence is heavily against Md^+, but the attempts to produce a monovalent state have the positive effect of setting limits on its stability. From the limits obtained, we can then make an estimate of the stability of the $5f^{14}$ configuration relative to the $5f^{13}7s$. Presumably, the $f^{13}s$ configuration lies lower in energy than the f^{14} because there is no obvious stabilization of a monovalent state due to a possible closing of the 5f shell. The divalent ion is then at least 1.3 V more stable than the monovalent ion.

NOBELIUM

The principle isotope of nobelium produced for investigations of its chemical properties is 3.1-min ^{255}No. In the earliest studies(86), this nuclide was synthesized by irradiating ^{244}Pu with 97-MeV ^{16}O ions, but larger yields were later obtained in bombardments of ^{249}Cf targets with 73-MeV ^{12}C ions(87). From the latter nuclear reaction, about 1200 atoms of ^{255}No were collected every ten minutes. Of these 1200 atoms, only 3 to 20% were detected after the chemical experiments because of losses by radioactive decay, losses in the experiments, and a 30% geometry for counting alpha particles emitted in the decay of this isotope. To obtain results that were were statistically significant, the experiments were repeated until the required accuracy was attained.

Future work with No may require techniques or procedures of greater complexity than the one-step chemical methods used in past studies. The author believes that ^{259}No, because of its 1-h half-life, would permit these more extensive investigations of No chemistry. Approximately 700 atoms can be made in a two-hour irradiation of ^{248}Cm with 96-MeV ^{18}O ions. In combination with the long half-life, this number of atoms is sufficient to permit a broader range of experiments to be performed.

A central feature in the chemistry of No is the dominance of the divalent oxidation state(86). In this respect, No is unique within the lanthanide and actinide series, since none of the other twenty-seven members possess a

highly-stable divalent ion. The electronic configuration of the neutral atom obtained from relativistic Hartree-Fock calculations is $5f^{14}7s^2$(5). Clearly, the special stability of No^{2+} must arise from the difficulty in ionizing an f valence electron from the completed 5f shell. Thus, pairing of the last electron to close the shell results in the f electron levels taking a rather abrupt drop in energy below the Fermi surface.

The separation of No from other actinide elements is based entirely on the dissimilar behavior of No^{2+} in comparison with the tripositive actinide ions. Without the addition of strong oxidants, No will be present as No^{2+} in acidic solutions and will have the general chemical properties of Group IIA elements in the Periodic Table. We have found that the extraction chromatographic method described in the section on Md provides an effective separation from all other actinides and lanthanides. In contrast to Md, reducing agents are unnecessary in separating No by this extraction chemistry.

The solution chemistry of No was explored shortly after the discovery of divalent Md(86). Subsequent studies include an estimation of the III→II reduction potential(88), aqueous complexing with carboxylate ions(89), and a determination of No^{2+} extraction and ion-exchange behavior in comparison with the alkaline earths(87). The first studies(86) indicated that the normal state of No in aqueous solution was that of a divalent ion. Nobelium was coprecipitated with $BaSO_4$ but not with LaF_3. After oxidation with Ce^{4+}, a large fraction of the No coprecipitated with LaF_3. This behavior is consistent with a change in oxidation state from (II) to (III). An elution position of No relative to tracer quantities of Es, Y, Sr, Ba, and Ra (Fig. 9) showed that No did not elute before Es as would be expected of a tripositive actinide ion.

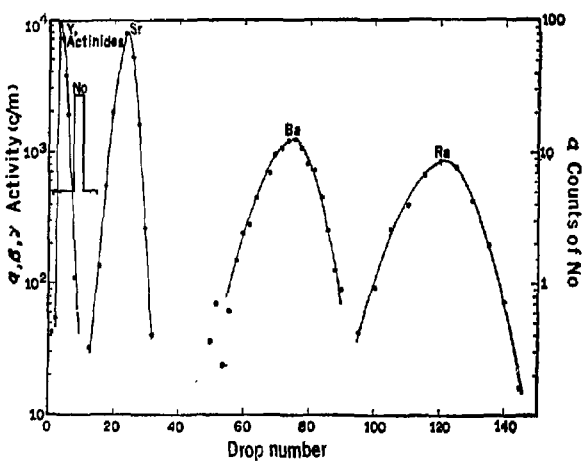

Fig. 9. Elution of nobelium from a heated (80°C) Dowex 50-x12 cation-exchange column with 1.9 M ammonium α-hydroxyisobutyrate (pH 4.8). (Reprinted with the permission of Science (Ref. 86): Copyright 1968 by the American Association for the Advancement of Science)

The standard reduction potential of the No^{3+}/No^{2+} couple in aqueous solution was estimated by Silva and coworkers(88) from the extractibility of No after treatment with a variety of oxidants. The distinction between No^{2+} and No^{3+} was made on the basis of the affinity of the extractant, bis(2-ethylhexyl) phosphoric acid, for highly-charged cations. In 0.1 M acid, mono- and di-positive ions are poorly extracted, whereas the tri- and tetrapositive ions are strongly absorbed in the extractant. In comparison with the behavior of the tracer ions of Ra, Tl, Ce, Cm, and Cf (see Fig. 10) it was shown that No was not fully extracted until H_5IO_6 (standard potential = 1.6 V) was used as an oxidant. Chromate and $HBrO_3$ partially oxidized No^{2+} to No^{3+}. From these observations, a potential of 1.4 to 1.5 V was estimated for the couple.

The extraction behavior of No^{2+} in a tri-n-octylamine-HCl system was compared with that of divalent Hg, Cd, Cu, Co, and Ba(87). This experiment provided a test of the chloride complex strength of No^{2+} because the amine anion-exchanger will only extract anionic species. It was found that Ba^{2+} and No^{2+} were not extractable over a range of 0.2 to 10 M HCl, while the other divalent ions of Hg, Cd, Cu, and Co were strongly extracted. This implies non-complexing of No in the chloride medium which is a characteristic of the alkaline earths.

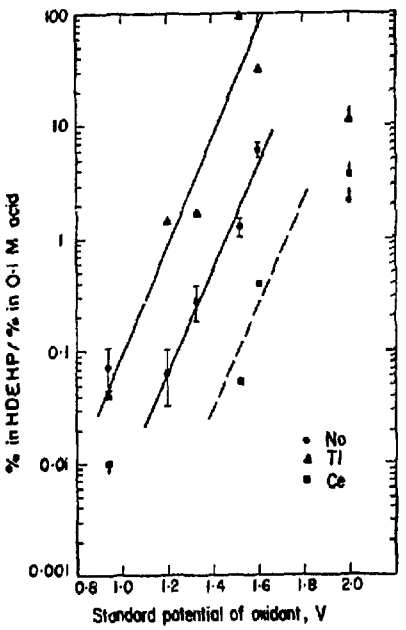

Fig. 10. Ratio of the percent of nobelium, thallium, and cerium extracted into the organic phase (HDEHP) to the percent left in the ~0.1M acid phase versus the standard potential of the oxidant used. Reprinted with the permission of Pergamon Press (Ref. 88).

The elution position of No^{2+} from a cation-exchange resin with 4 M HCl eluant was compared with the elution positions of Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, and Ra^{2+}(87). The No^{2+} ions eluted at exactly the Ca^{2+} position. Similar column elution experiments, using bis(2-ethylhexyl)phosphoric acid (HDEHP) adsorbed on an inert support material and 0.025 M HCl as the eluting acid, showed No^{2+} eluting between Ca^{2+} and Sr^{2+}. These elution curves are illustrated in Fig. 11. With the same extractant, the distribution coefficient for No^{2+} was measured as a function of hydrogen-ion concentration. From the mass-action expression for the ion exchange, a slope of +2 was obtained from the line describing the log of the distribution coefficients vs. pH. The extraction of No^{2+} is second power with respect to the H^+ concentration, thus indicating a charge state of two for No because of the cation-exchange mechanism for extraction in this system.

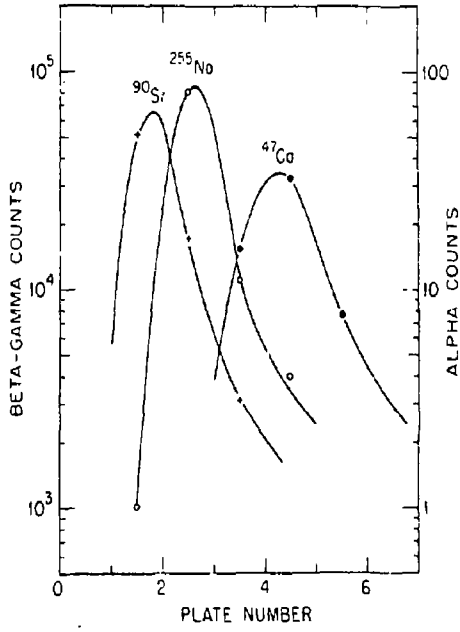

Fig. 11. Elution of No^{2+}, Ca^{2+}, and Sr^{2+} with 0.025 M HCl from a column of bis(2-ethylhexyl)phosphoric acid on an inert support. Reprinted with the permission of Inorganic Chemistry (Ref. 87).

Silva and coworkers(87) noted that other investigators had shown a linear correlation between the log of the distribution coefficients of the alkaline earths and their ionic radii. This appeared to be the case wherever a pure cation-exchange mechanism governed the distributions between phases and, hence, was applicable to distributions obtained with either cation-exchange

resins or extractants. In Fig. 12, log D is plotted as a function of ionic radius for the extraction of various dipositive cations into 0.1 M HDEHP from aqueous solutions. The measured distribution coefficient for No^{2+}, when placed on the correlation line, gave an ionic radius of 0.11 nm. If the distribution coefficients from their ion-exchange elutions were used, the ionic radius of No^{2+} would be the same as that of Ca^{2+} (0.10 nm), since both ions have the same elution position. An ionic radius of 0.11 nm was also obtained by applying Pauling's correction to the radius of the outermost, $6p_{3/2}$ shell, which was calculated from a relativistic radial wave function (Hartree-Fock-Slater). The calculated ionic radius is in agreement with the radii derived from their solvent-extraction and ion-exchange results. A radius of 0.11 nm for No^{2+} can be compared with 0.103 nm found for Yb^{2+}(90), the lanthanide homolog of No. Insertion of the No^{2+} ionic radius into an empirical form of the Born equation gave a single-ion heat of hydration of -1490 kJ $mole^{-1}$.

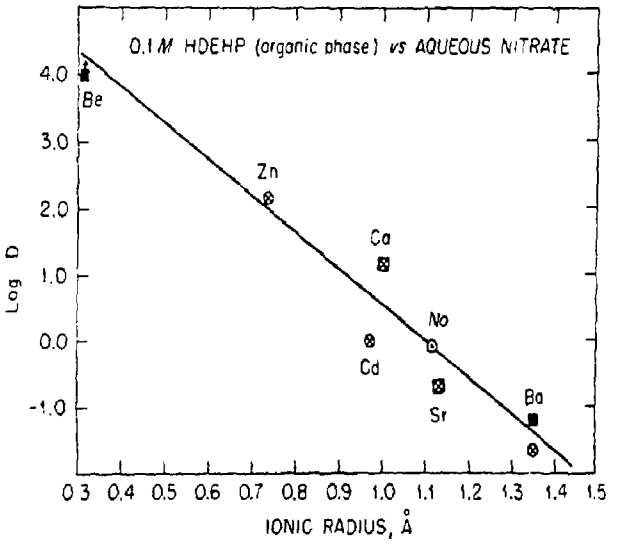

Fig. 12. Log D vs. ionic radius for typical divalent cations in the bis(2-ethylhexyl)phosphoric acid-aqueous nitrate system. Reprinted with the permission of Inorganic Chemistry (Ref. 87).

The ability of No^{2+} to form complexes with citrate, oxalate, and acetate ions in an aqueous solution of 0.5 M NH_4NO_3 was investigated by McDowell and coworkers(89). The complex strengths of Ca^{2+} and Sr^{2+} with these carboxylate ions were measured under the same conditions for comparison with the No results. The formation constants they obtained are given in Table 8 and indicate for each anion, the complexing tendency of No^{2+} is between that of Ca^{2+} and Sr^{2+} with Sr^{2+} being slightly more favored.

TABLE 8 Complex Formation Constants for No^{2+}, Ca^{2+}, and Sr^{2+} from Distribution Data (Ref. 89)

System		Formation Constants	
Cation	Ligand	β_1	σ^a
No^{2+}	Cit	151.9	18.5
	Ox	48	5.6
	Ac	- 5	5
Ca^{2+}	Cit	333	11.2
	Ox	88.9	2.1
	Ac	5.5	0.7
Sr^{2+}	Cit	96.7	1.7
	Ox	25.3	0.5
	Ac	0.58	0.12

[a]Standard deviation of fitting of β_1.

The standard potential for the reduction of No^{2+} to No(Hg) was measured by a modified radiopolarographic technique(91). Usually, the half-wave potential is determined by measuring the distribution of an element between the mercury and aqueous phase as a function of applied voltage. The half-life of ^{255}No is too short to allow time for the recovery of No from the Hg phase for assay, therefore Meyer et al. measured the depletion of No in the aqueous phase as a function of a controlled potential. They assumed that equilibrium was reached in 3 minutes of electrolysis and that the electrode reaction was reversible. A sharp drop in No concentration in the aqueous phase occurred between -1.8 and -1.9 V vs. the saturated calomel electrode or -1.6 V vs. the standard hydrogen electrode. Thus, their best estimates are summarized in the following equation.

$$No^{2+} + 2e^- = No(Hg); \qquad E^0 = -1.6 \pm 0.1 \text{ V}$$

If this potential is reduced by about the 0.9 V estimated for the amalgamation potential, then a value of about -2.5 V would be given for the II→0 couple.

LAWRENCIUM

Element 103, lawrencium, is the last member of the actinide series and its chemical nature should be similar to its counterpart in the lanthanide series, Lu. However, confirming experimental information is nearly nonexistent because of the 35-s half-life of ^{256}Lr and the great difficulty in producing a useful quantity for experiments. The bombardment of ^{249}Cf with ^{11}B ions is probably the most favorable nuclear reaction for producing ^{256}Lr. Even so, only about ten atoms have been made in each short irradiation and of these, only one or two were detected after completion of the chemical tests(92).

Lawrencium was expected to have a $5f^{14}6d7s^2$ electronic configuration(93) although Brewer computed a $5f^{14}7s^27p$ configuration(5). Brewer's estimates have now been confirmed by multiconfigurational (relativistic) Dirac-Fock calculations in which the ground state of lawrencium was found to be a $^2P_{1/2}$ or $7s^27p$ electronic configuration(94). This deviation from the $6d7s^2$ configuration expected from extrapolation of the Periodic Table is due entirely to

strong relativistic effects on the outermost $7p_{1/2}$ orbital. The energy difference between the two possible ground states is no more than a few thousand wave numbers.

The ionization of Lr would be expected to stop with the f^{14} core intact because of the enhanced binding energy of possible valence electrons in the filled f shell. The stable valence state of Lr would then be the (III) state. Experiments to confirm this oxidation state of Lr were undertaken by Silva and co-workers(92). They compared the extraction behavior of Lr with several tri- and tetravalent actinides and with Ba^{2+}, Ra^{2+}, and No^{2+}. A chelating extractant, thenoyltrifluoroacetone dissolved in methyl isobutyl ketone, was employed to extract the tracer ions from aqueous solutions that had been buffered with acetate anions. Their results, shown in Fig. 13, demonstrate that Lr is extracted within the same pH range as the trivalent actinides and, therefore, prove that Lr is trivalent.

Further studies of Lr have not been attempted.

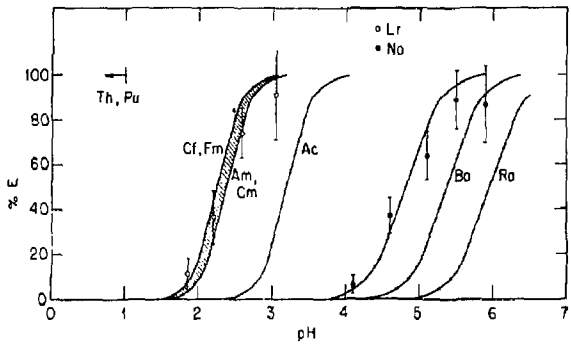

Fig. 13. Percent extracted into the organic phase as a function of the pH of the aqueous phase. Solid lines are a summary of earlier data by the same authors. Reprinted with the permission of Pergamon Press (Ref. 92).

ACTINIDE SUMMARY

The main result ensuing from about 14 years of intensive study of the heavier actinides is the finding of an unexpected stability of the divalent state. Table 9, summarizing the redox properties of these elements, most clearly shows the increasing stability of this state with increasing atomic number. The sinking of the 5f levels with respect to the Fermi level provides the explanation for this behavior. Thus, we see, as is also the case in the light actinides, another major differentiation between the 5f actinide and 4f lanthanide series of elements.

TABLE 9 Reduction Potentials of the Heavier Actinides. Reported as $-E^{\circ}$ vs Standard H^{+} Electrode

Half Reaction	Es	Fm	Md	No	Lr
III→II	1.55	1.15	0.2	-1.4	-
II→ 0	2.20	2.37	2.4	2.5	-
III→ 0	1.98	1.95	1.7	1.18	2.06

TRANSACTINIDES

Four elements are known with atomic numbers greater than that of lawrencium. Because none of the names proposed for these elements have received official acceptance from the International Union of Pure and Applied Chemistry, they are referred to as elements 104, 105, 106, and 107, or E-104, etc. This lack of authorized names is very likely to continue for many more years because of difficulties in resolving conflicting claims for their discovery. A dimension of these conflicts, namely, the certitude of the atomic number assigned to a particular nuclide used in several of the chemical investigations, is not examined in this review.

The chemistry of these elements, as estimated from extrapolation of the Periodic Table and verified by quantum mechanical calculations, should follow that of another d transition series, comparable with the 5d series beginning with Hf. Therefore, the chemical properties of E-104 should be quite similar to those of Hf, and E-105 to those of Ta, and so forth. In aqueous solutions, E-104 would be expected to possess a stable tetravalent state while E-105 would be pentavalent. It is the verification of these predicted chemical properties that has been the main thrust of the experimental work with these elements.

Element 104

The chemistry of E-104 has been investigated in the gas phase as the tetrachloride(95-98) and in aqueous solution as complexes of chloride(99) and α-hydroxyisobutyrate anions(100). It has been very much of an uphill struggle to produce and identify the few atoms used in these experiments and to perform the experiments many times over with very short-lived isotopes. In the thermo-chromatography research carried out at the Joint Institute for Nuclear Research, Dubna, USSR, a 3-s isotope, ^{259}104, was produced by ^{22}Ne bombardment of ^{242}Pu targets. The aqueous chemistry was carried out with 1-min ^{261}104 formed in the reaction of ^{248}Cm with ^{18}O ions. Very few atoms were produced and identified in any of the E-104 chemical investigations.

The goal of the gas-phase experiments was to show the sharp difference in volatility of the higher halides of eka-Hf relative to the volatility of the preceeding Group IIIB series of actinides(95-97). The Group IVB tetrachlorides sublime at temperatures slightly over 300°C, whereas the actinide trichlorides would require temperatures three to four times greater before they became volatile at an atmosphere of pressure. Therefore, the volatility of E-104Cl_4 would be a distinctive measure of whether or not this element was eka-Hf. All such experiments were performed on-line at the Dubna accelerator. Atoms of E-104 recoiling from the target were stopped in a heated

stream of inert carrier gas of N_2 and then chorinated downstream with $TiCl_4$ or mixtures of $SOCl_2$, $NbCl_5$, $ZrCl_4$, and $TiCl_4$. The molecules of E-104Cl_4 passed through a chromatographic column heated to 300-350°C and eventually deposited on mica detectors located inside and along the length of a section of the column held at 280°C. Hundreds of hours of accelerator beam time resulted in the detection of 79 spontaneous fission events, at first attributed to the decay of 0.3-s ^{260}104(97). However, current work supports a half-life of only 20 ms for this isotope(101).

In the last vapour-phase experiments performed by Zvara's group(98), frontal chromatography of the chlorides was used to separate 3-s ^{259}104 and coproduced ^{170,171}Hf from Sc, ^{242}Cm, ^{246}Cf, and ^{242}Pu also swept into the gas stream from the target region. The apparatus employed in this work was essentially unchanged from earlier experiments except that a thermal gradient was maintained beginning with 400°C at the entrance and decreasing to 50°C at the exit of the 70-cm long thermo-chromatographic section. The Hf isotopes and 15 spontaneous-fission events were found deposited in this section of the thermal-gradient column at a position corresponding to a condensation temperature of 220°C. Scandium and various actinide nuclides produced by other nuclear reaction with the target were found 100 to 125 cm upstream in an initial section of a 400°C tube. The volatility of 104Cl_4 clearly corresponded to that of $HfCl_4$ and established E-104 as being eka-Hf.

During several hundred experiments, Silva and coworkers(100) investigated the complexing and cation-exchange behavior of 1-min ^{261}104. Recoil atoms of E-104 were trapped in an NH_4Cl layer sublimed onto Pt discs, dissolved with ammonium α-hydroxyisobutyrate and passed onto a column of heated cation resin. Because of the strong formation of neutral and anionic complexes by the tetravalent IVB elements, one would expect very little adsorption and retention by the cation resin in the column. Indeed, this was the outcome of the many experiments, although the decay of only 17 atoms was observed after elution from the resin column. The elution position was the same as Hf and Zr, which were separately tested. Nobelium and other actinides were retained on the resin until over 100 column-volumes of eluant had passed through the column.

In later experiments which tested the chloride complexation of E-104(99), computer automation was used to perform all chemical manipulations rapidly, to prepare α sources, and to do α spectroscopy. An extraction chromatographic method was chosen to investigate chloride complexing in high concentrations of HCl which thereby avoided the hydrolysis reaction possible at lower acidities. The extraction columns were loaded with 0.25 F trioctylmethylammonium chloride, since anionic-chloride complexes formed in the aqueous phase are strongly extracted by this ammonium compound. Such complexes are formed in 12 M HCl by the Group IVB elements and are extracted, whereas Group IA, IIA, and IIIB elements, including the actinides, form weaker complexes and are not appreciably extracted. Thus, these latter recoil products were eluted with 12 M HCl while Zr, Hf, and E-104 were extracted and subsequently eluted with 6M HCl, in which anionic chloride complexation is less favored. Figure 14 shows the atoms of ^{261}104 observed by α decay in three sequential elution fractions. Only six events were observed in over one hundred experiments; one in fraction (a), two in fraction (b), and three in fraction (c). The percentage of Hf corresponding to these same fractions was 12%, 59%, and 29%. These results showed the chloride complexation of E-104 is considerably stronger than that of the trivalent actinides and is similar to that of Hf.

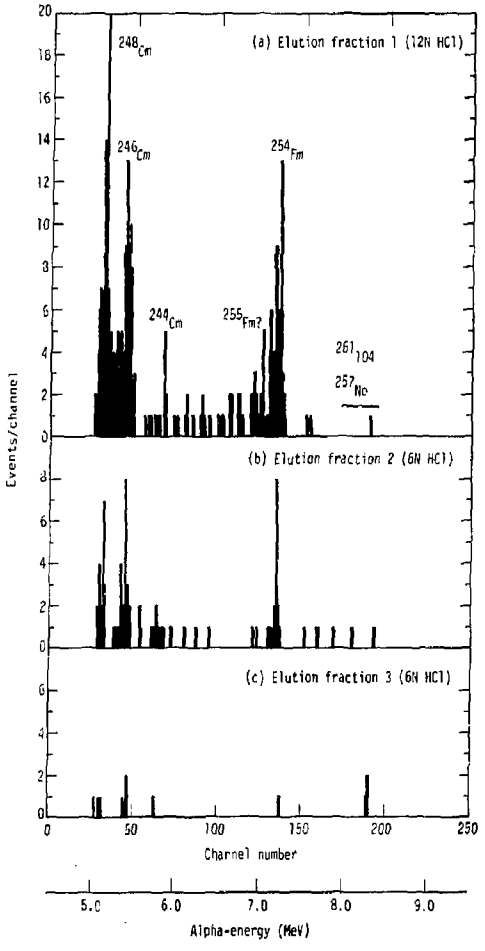

Fig. 14. Alpha spectra showing the decay of a few $^{261}104$ atoms in three, sequential elution fractions from a column containing an anionic extractant (see text). Reprinted with the permission of Pergamon Press (Ref. 99).

Element 105

Our chemical knowledge of the heavy elements ends with E-105 although the nuclear properties are known for several isotopes of elements 106 and 107. Element 105, with a $6d^3$ electronic configuration, is expected to have the general chemical properties of its $5d^3$ homolog, Ta. Zvara et al., using much of the same thermochromatographic techniques employed earlier in their studies of element 104, have extended the method to determining the volatilities of the chloride and bromide compounds of E-105(102,103). The chloride of E-105 was deposited on the walls of the chromatography tube at ~150°C, but because of the short 2-s half-life of ^{261}105, a new distribution 50°C lower in temperature was suggested by the authors. This correction was based on the appreciable decay of the ^{261}105 nuclei during their travel through the tube. The corrected distribution of the 18 observed spontaneous fission events indicated that the chlorides of E-105 are more volatile than Hf and less volatile than Nb, a $4d^3$ homolog of E-105.

The bromides of E-105 were also found to be very volatile as shown by the location of the circles in relation to the thermal gradient in the upper part of Fig. 15. Niobium, which in separate experiments was shown to have the same deposition temperature as Ta, is obviously more volatile than E-105. From this work, the boiling point of E-105Br_5 was estimated to be 430°C. An analysis of the boiling points of pentabromides of the same structure allowed an estimate of ~0.09 nm for the metallic radius, or ~0.02 nm larger than that of Nb and Ta. In sum, all of the experimental observations are consistent with E-105 being a homolog of Nb and Ta.

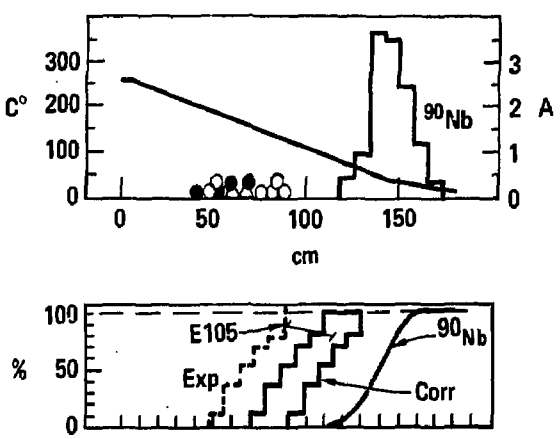

Fig. 15. Upper: Thermal gradient and deposition positions of E-105 (circles) and Nb (histogram) bromides.
Lower: Integral distributions of experimental (dashed lines), and corrected (solid area) of E-105 and of Nb (solid curve) bromides. Redrawn from Ref. 103.

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