ACTINIDES AND TRANSACTINIDES

1. Actinides

The actinide elements are a group of chemically similar elements with atomic numbers 89 through 103 and their names, symbols, atomic numbers, and discoverers are given in Table 1 (1–3) (see THORIUM AND THORIUM COMPOUNDS; URANIUM AND URANIUM COMPOUNDS; PLUTONIUM AND PLUTONIUM COMPOUNDS; NUCLEAR REACTORS; and RADIOISOTOPES).

Each of the elements has a number of isotopes (2,4), all radioactive and some of which can be obtained in isotopically pure form. More than 200 in number and mostly synthetic in origin, they are produced by neutron or charged-particle-induced transmutations (2,4). The known radioactive isotopes are distributed among the 15 elements approximately as follows: actinium, 29; thorium, 28; protactinium, 27; uranium, 22; neptunium, 20; plutonium, 18; americium, 14; curium, 15; californium, 20; einsteinium, 16; fermium, 18; berkelium, 12; mendelevium, 16 nobelium, 12; and lawrencium, 10. There is frequently a need for values to be assigned for the atomic weights of the actinide elements. Any precise experimental work would require a value for the isotope or isotopic mixture being used, but where there is a purely formal demand for atomic weights, mass numbers that are chosen on the basis of half-life and availability have customarily been used. A list of these is provided in Table 1.

Thorium and uranium have long been known, and uses dependent on their physical or chemical, not on their nuclear, properties were developed prior to the discovery of nuclear fission. The discoveries of actinium and protactinium were among the results of the early studies of naturally radioactive substances. The first transuranium element, synthetic neptunium, was discovered during an investigation of nuclear fission, and this event rapidly led to the discovery of the next succeeding element, plutonium. The realization that plutonium as ^{239}Pu undergoes fission with slow neutrons and thus could be utilized in a nuclear weapon supplied the impetus for its thorough investigation. This research has provided the background of knowledge and techniques for the production and identification of nine more actinide elements and three transactinide elements by 1974.

Table 1. **The Actinide Elements**

Atomic number	Element	CAS Registry Number	Symbol	Mass number[a]	Discoverers and date of discovery
89	actinium	[7440-34-8]	Ac	227	A. Debierne, 1899
90	thorium	[7440-29-1]	Th	232	J. J. Berzelius, 1828
91	protactinium	[7440-13-3]	Pa	231	O. Hahn and L. Meitner, 1917, and F. Soddy and J. A. Cranston, 1917
92	uranium	[7440-61-1]	U	238	M. H. Klaproth, 1789
93	neptunium	[7439-99-8]	Np	237	E. M. McMillan and P. H. Abelson, 1940
94	plutonium	[7440-07-5]	Pu	242	G. T. Seaborg, E. M. McMillan, J. W. Kennedy, and A. C. Wahl, 1940–1941
95	americium	[7440-35-9]	Am	243	G. T. Seaborg, R. A. James, L. O. Morgan, and A. Ghiorso, 1944–1945
96	curium	[7440-51-9]	Cm	248	G. T. Seaborg, R. A. James, and A. Ghiorso, 1944
97	berkelium	[744-40-6]	Bk	249	S. G. Thompson, A. Ghiorso, and G. T. Seaborg, 1949
98	californium	[7440-71-3]	Cf	249	S. G. Thompson, K. Street, Jr., A. Ghiorso, and G. T. Seaborg, 1950
99	einsteinium	[7429-92-7]	Es	254	A. Ghiorso, S. G. Thompson, G. H. Higgins, G. T. Seaborg, M. H. Studier, P. R. Fields, S. M. Fried, H. Diamond, J. F. Mech, G. L. Pyle, J. R. Huizenga, A. Hirsch, W. M. Manning, C. I. Browne, H. L. Smith, and R. W. Spence, 1952
100	fermium	[7440-72-4]	Fm	257	A. Ghiorso, S. G. Thompson, G. H. Higgins, G. T. Seaborg, M. H. Studier, P. R. Fields, S. M. Fried, H. Diamond, J. F. Mech, G. L. Pyle, J. R. Huizenga, A. Hirsch, W. M. Manning, C. I. Browne, H. L. Smith, and R. W. Spence, 1953
101	mendelevium	[7440-11-1]	Md	258	A. Ghiorso, B. G. Harvey, G. R. Choppin, S. G. Thompson, and G. T. Seaborg, 1955
102	nobelium	[10028-14-5]	No	259	A. Ghiorso, T. Sikkeland, J. R. Walton, and G. T. Seaborg, 1958
103	lawrencium	[22537-19-5]	Lr	262	A. Ghiorso, T. Sikkeland, A. E. Larsh, and R. M. Latimer, 1961

[a] Mass number of longest lived or most available isotope.

After a lapse of nearly seven years, a new production reaction and a new on-line separation technique were used to identify six more actinide elements (107–112) between 1981 and 1996. In 1999, evidence was reported for production and detection of the SuperHeavy Elements (SHEs) 114, 116, and 118. These elements are near the "island of nuclear stability" calculated in the mid-1960s to be at proton number 114 (or possibly 126) and neutron number 184 because of the extra stability resulting from the filling of the spherical shells predicted at those so-called "magic" numbers.

Thorium, uranium, and plutonium are well known for their role as the basic fuels (or sources of fuel) for the release of nuclear energy (5). The importance of the remainder of the actinide group lies at present, for the most part, in the realm of pure research, but a number of practical applications are also known (6). The actinides present a storage-life problem in nuclear waste disposal and consideration is being given to separation methods for their recovery prior to disposal (see WASTE TREATMENT, HAZARDOUS WASTE; NUCLEAR REACTORS, WASTE MANAGEMENT).

1.1. Source. Only the members of the actinide group through Pu have been found to occur in nature (2,3,7,8). Actinium and protactinium are decay products of the naturally occurring uranium isotope ^{235}U, but the concentrations present in uranium minerals are small and the methods involved in obtaining them from the natural source are very difficult and tedious in contrast to the relative ease with which the elements can be synthesized. Thorium and uranium occur widely in the earth's crust in combination with other elements, and, in the case of uranium, in significant concentrations in the oceans. The extraction of these two elements from their ores has been studied intensively and forms the basis of an extensive technology. Neptunium (^{239}Np and ^{237}Np) and plutonium (^{239}Pu) are present in trace amounts in nature, being formed by neutron reactions in uranium ores. Longer-lived ^{244}Pu, possibly from a primordial source, has been found in very small concentration (1 part in 10^{18}) in the rare earth mineral bastnasite [12172-82-6] (8). Mining these elements from these sources is not feasible because the concentrations involved are exceedingly small. Thus, with the exception of uranium and thorium, the actinide elements are synthetic in origin for practical purposes; ie, they are products of nuclear reactions. High neutron fluxes are available in modern nuclear reactors, and the most feasible method for preparing actinium, protactinium, and most of the actinide elements is through the neutron irradiation of elements of high atomic number (3,9).

Actinium can be prepared by the transmutation of radium,

$$^{226}\text{Ra} + n \ \rightarrow {}^{227}\text{Ra} + \gamma; \qquad {}^{227}\text{Ra} \xrightarrow[\text{41.2 min}]{\beta^-} {}^{227}\text{Ac}$$

and gram amounts have been obtained in this way. The actinium is isolated by means of solvent extraction or ion exchange.

Protactinium can be produced in the nuclear reactions

$$^{230}\text{Th} + n \ \rightarrow {}^{231}\text{Th} + \gamma; \qquad {}^{231}\text{Th} \xrightarrow[\text{25.6 h}]{\beta^-} {}^{231}\text{Pa}$$

However, the quantity of ^{231}Pa produced in this manner is much less than the amount (more than 100 g) that has been isolated from the natural source. The methods for the recovery of protactinium include coprecipitation, solvent extraction, ion exchange, and volatility procedures. All of these, however, are rendered difficult by the extreme tendency of protactinium(V) to form polymeric colloidal particles composed of ionic species. These cannot be removed from aqueous media by solvent extraction; losses may occur by adsorption to containers; and protactinium may be adsorbed by any precipitate present.

Kilogram amounts of neptunium (^{237}Np) have been isolated as a by-product of the large-scale synthesis of plutonium in nuclear reactors that utilize ^{235}U and ^{238}U as fuel. The following transmutations occur:

$$^{238}\mathrm{U} + n \;\rightarrow\; {}^{237}\mathrm{U} + 2n; \qquad {}^{237}\mathrm{U} \xrightarrow[6.75\,\mathrm{d}]{\beta^-} {}^{237}\mathrm{Np}$$

and

$$^{235}\mathrm{U} + n \;\rightarrow\; {}^{236}\mathrm{U} + \gamma; \qquad {}^{236}\mathrm{U} + n \;\rightarrow\; {}^{237}\mathrm{U} + \gamma; \qquad {}^{237}\mathrm{U} \xrightarrow{\beta^-} {}^{237}\mathrm{Np}$$

The wastes from uranium and plutonium processing of the reactor fuel usually contain the neptunium. Precipitation, solvent extraction, ion exchange, and volatility procedures (see DIFFUSION SEPARATION METHODS) can be used to isolate and purify the neptunium.

Plutonium as the important isotope ^{239}Pu is prepared in ton quantities in nuclear reactors. It is produced by the following reactions, wherein the excess neutrons produced by the fission of ^{235}U are captured by ^{238}U to yield ^{239}Pu.

$$^{235}\mathrm{U} + n \rightarrow \text{fission products} + 2.5\,n + 200\ \mathrm{MeV}$$

$$^{238}\mathrm{U} + n \rightarrow {}^{230}\mathrm{U} \xrightarrow[23.5\ \mathrm{min}]{\beta^-} {}^{239}\mathrm{Np} \xrightarrow[2.3\,\mathrm{d}]{\beta^-} {}^{239}\mathrm{Pu}$$

The plutonium usually contains isotopes of higher mass number (Fig. 1). A variety of industrial-scale processes have been devised for the recovery and purification of plutonium. These can be divided, in general, into the categories of precipitation, solvent extraction, and ion exchange.

The isotope ^{238}Pu, produced in kilogram quantities by the reactions

$$^{237}\mathrm{Np} + n \;\rightarrow\; {}^{238}\mathrm{Np} \quad \text{and} \quad {}^{238}\mathrm{Np} \xrightarrow[2.1\,\mathrm{d}]{\beta^-} {}^{238}\mathrm{Pu}$$

is an important fuel for isotopically powered energy sources used for terrestrial and extraterrestrial applications.

Kilogram quantities of americium as ^{241}Am can be obtained by the processing of reactor-produced plutonium. Much of this material contains an appreciable proportion of ^{241}Pu, which is the parent of ^{241}Am. Separation of the americium is effected by precipitation, ion exchange, or solvent extraction.

The nuclear reaction sequences of neutron captures and beta decays involved in the preparation of the actinide elements by means of the slow

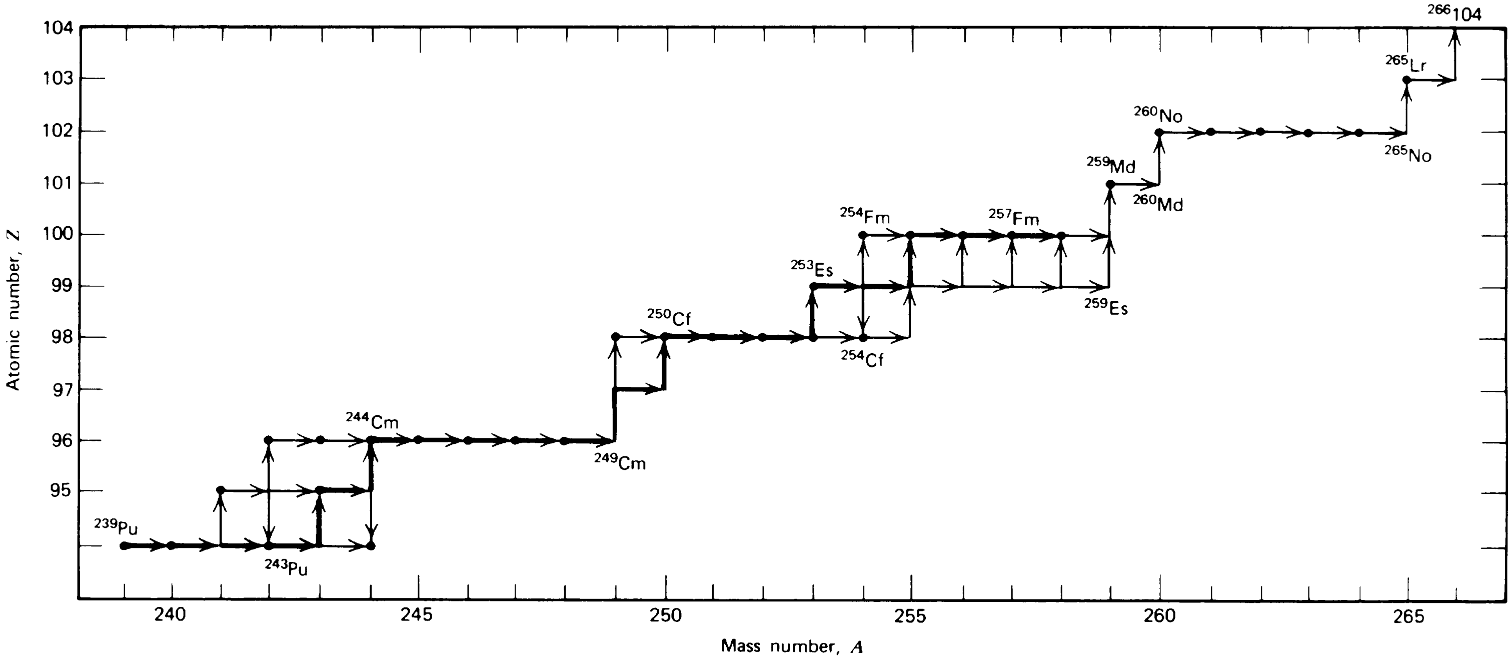


Fig. 1. Nuclear reactions for the production of heavy elements by intensive slow neutron irradiation. The main line of buildup is designated by heavy arrows. The sequence above ^{258}Fm represents predictions.

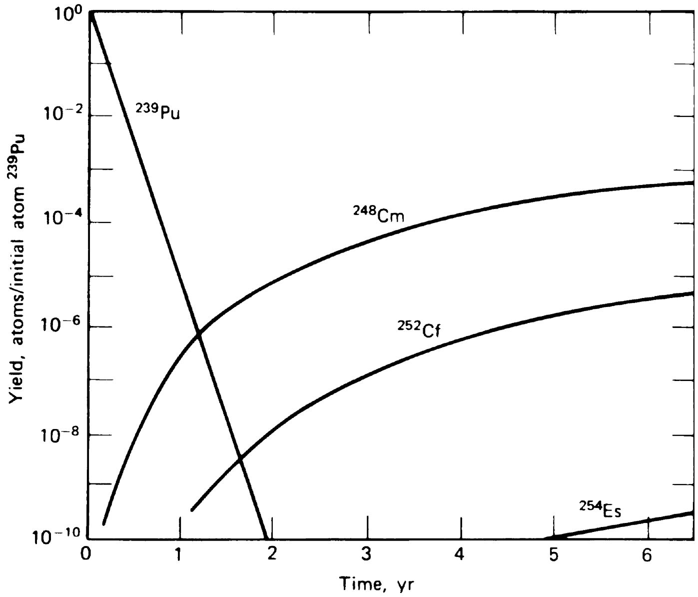


Fig. 2. Production of heavy nuclides by the irradiation of ^{239}Pu at a flux of 3×10^{14} neutrons/(cm$^2 \cdot$ s).

neutron irradiation of ^{239}Pu are indicated in Figure 1. The irradiations can be performed by placing the parent material in the core of a high-neutron-flux reactor where fluxes of neutrons in excess of 10^{14} may be available. Figure 2 gives an indication of the time required for typical preparation of various heavy isotopes from ^{239}Pu as the starting material. For example, beginning with 1 kg of ^{239}Pu, about 1 mg of ^{252}Cf would be present after 5–10 yr of continuous irradiation at a neutron flux 3×10^{14} neutrons/(cm^2·s). Much larger quantities can be produced by irradiating larger quantities of plutonium in production reactors, followed by irradiation of the curium thus produced in higher-neutron-flux reactors, ca 10^{15} neutrons/(cm^2·s), such as those at the Savannah River Plant in South Carolina and the High Flux Isotopes Reactor (HFIR) at the Oak Ridge National Laboratory (ORNL) in Tennessee. Such programs have led to the production of kilogram quantities of curium (^{244}Cm and heavier isotopes), gram quantities of californium, 100-mg quantities of berkelium, and milligram quantities of einsteinium (6,10). The elements 95 to 100 are also produced in increasing quantities by nuclear power reactors.

Ion exchange (qv; see also Chromatography) is an important procedure for the separation and chemical identification of curium and higher elements. This technique is selective and rapid and has been the key to the discovery of the transcurium elements, in that the elution order and approximate peak position for the undiscovered elements were predicted with considerable confidence (9). Thus the first experimental observation of the chemical behavior of a new actinide element has often been its ion-exchange behavior—an observation coincident with its identification. Further exploration of the chemistry of the element often depended on the production of larger amounts by this method.

Solvent extraction is another useful method for separating and purifying actinide elements.

There are many similarities in the chemical properties of the lanthanide elements (see LANTHANIDES) and those of the actinides, especially with elements in the same oxidation state. A striking example of this resemblance is furnished by their ion-exchange behavior. Figure 3 shows the comparative elution data for tripositive actinide and lanthanide ions obtained by the use of the ion-exchange resin Dowex-50 (a copolymer of styrene and divinylbenzene with sulfonic acid groups) and the eluting agent ammonium α-hydroxyisobutyrate [2539-76-6]. In this system, which is used for illustration because of its historical importance,

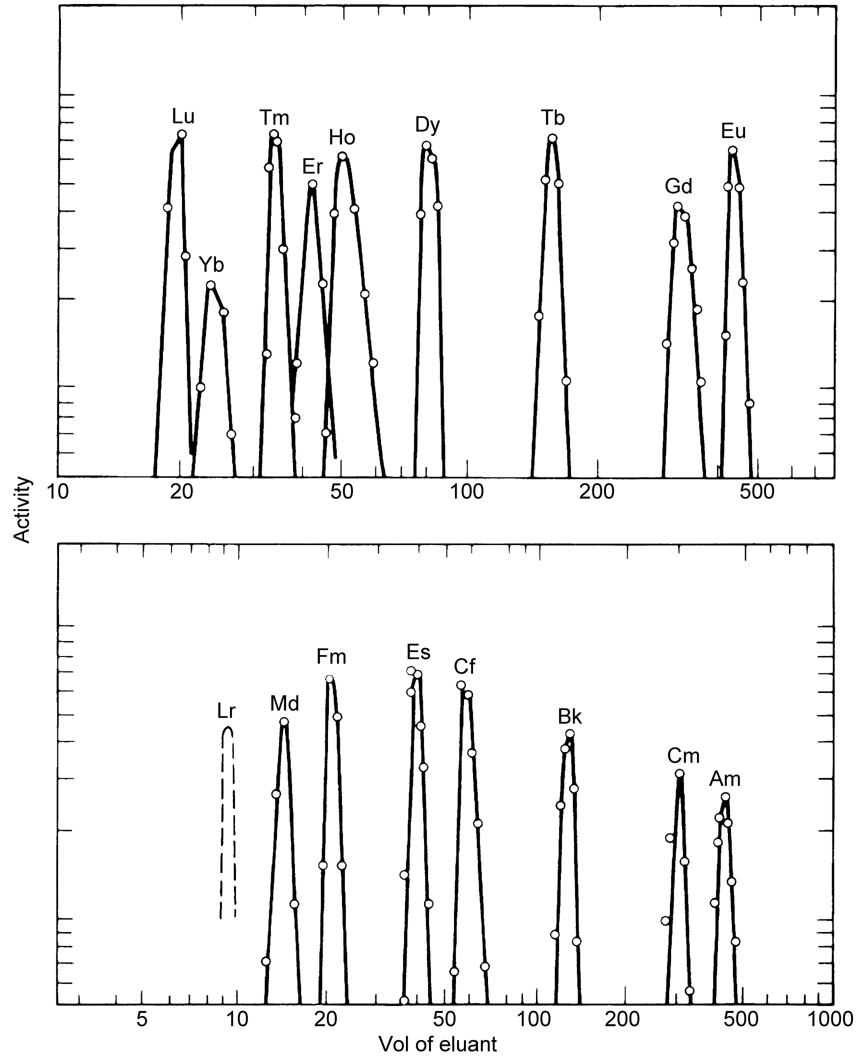


Fig. 3. The elution of tripositive actinide and lanthanide ions. Dowex-50 ion-exchange resin was used with ammonium α-hydroxyisobutyrate as the eluant. The position predicted for short-lived lawrencium is indicated by a broken line.

the elutions occur in the inverse order of atomic number. The elution sequence depends on a balance between the adherence to the resin and the stability of the complex ion formed with the eluting agent and may be correlated with the variation of ionic radius with atomic number.

Actinide ions of the III, IV, and VI oxidation states can be adsorbed by cation-exchange resins and, in general, can be desorbed by elution with chloride, nitrate, citrate, lactate, α-hydroxyisobutyrate, ethylenediaminetetraacetate, and other anions (11,12).

Ion-exchange separations can also be made by the use of a polymer with exchangeable anions; in this case, the lanthanide or actinide elements must be initially present as complex ions (11,12). The anion-exchange resins Dowex-1 (a copolymer of styrene and divinylbenzene with quaternary ammonium groups) and Amberlite IRA-400 (a quaternary ammonium polystyrene) have been used successfully. The order of elution is often the reverse of that from cationic-exchange resins.

Extraction chromatography (see ADSORPTION), in which the organic extractant is adsorbed on the surfaces of a fine, porous powder placed in a column, offers another excellent method for separating the actinide elements from each other. Useful cation extracting agents include bis(2-ethylhexyl)phosphoric acid [298-07-7], mono(2-ethylhexyl)phenylphosphonic acid ester [1518-07-6], and *n*-tributyl phosphate [126-73-8] (12). Excellent anion extracting agents include tertiary amines such as tricapryl amine [1116-76-3] or trilauryl amine [102-87-4], or quaternary amines such as tricaprylmethyl ammonium chloride [5137-55-3] (nitrate, thiocyanate) (12). Satisfactory supporting agents can be found in commercially available diatomaceous earths or silica microspheres.

It is possible to prepare very heavy elements in thermonuclear explosions, owing to the very intense, although brief (order of a microsecond), neutron flux furnished by the explosion (3,13). Einsteinium and fermium were first produced in this way; they were discovered in the fallout materials from the first thermonuclear explosion (the “Mike” shot) staged in the Pacific in November 1952. It is possible that elements having atomic numbers greater than 100 would have been found had the debris been examined very soon after the explosion. The preparative process involved is multiple neutron capture in the uranium in the device, which is followed by a sequence of beta decays. For example, the synthesis of ^{255}FM in the Mike explosion was via the production of ^{255}U from ^{238}U, followed by a long chain of short-lived beta decays,

$$^{255}\text{U} \xrightarrow{-\beta^-} {}^{255}\text{Np} \xrightarrow{-\beta^-} {}^{255}\text{Pu} \xrightarrow{-\beta^-} \cdots \longrightarrow {}^{255}\text{Fm}$$

all of which occur after the neutron reactions are completed.

The process of neutron irradiation in high-flux reactors cannot be used to prepare the elements beyond fermium (^{257}Fm), except at extremely high neutron fluxes, because some of the intermediate isotopes that must capture neutrons have very short half-lives that preclude the necessary concentrations. Transfermium elements are prepared in charged-particle bombardments (2,3). Such syntheses are characterized by the limited availability of target materials of high atomic number, the small reaction yields, and the difficulties intrinsic in the isolation of very short-lived substances. Nonchemical separations of short-lived isotopes from the target materials are carried out during bombardments. Numerous isotopes of mendelevium, nobelium, and lawrencium (the heaviest actinide elements) are produced by bombardment with heavy ions. Despite the fact that these are usually produced on a "one-atom-at-a-time" basis, the chemical properties of these elements have been studied using the tracer technique. Cyclotrons can be used to accelerate heavy ions; in addition, linear accelerators designed for this express purpose are in operation in several laboratories throughout the world.

Isotopes sufficiently long-lived for work in weighable amounts are obtainable, at least in principle, for all of the actinide elements through fermium (100); these isotopes with their half-lives are listed in Table 2 (4). Not all of

Table 2. **Long-Lived Actinide Nuclides Available in Weighable Amounts**

Element	Isotope	CAS Registry Number	Half-life
actinium-227	^{227}Ac	[14952-40-0]	21.8 yr
thorium-232	^{232}Th	[7440-29-1]	1.41×10^{10} yr
protactinium-231	^{231}Pa	[14331-85-2]	3.25×10^{4} yr
uranium-238	^{238}U[a]	[24678-82-8]	4.47×10^{9} yr
neptunium-236	^{236}Np[b]	[15770-36-4]	1.55×10^{5} yr
neptunium-237	^{237}Np	[13994-20-2]	2.14×10^{6} yr
plutonium-238	^{238}Pu	[13981-16-3]	87.8 yr
plutonium-239	^{239}Pu	[15117-48-3]	24,150 yr
plutonium-240	^{240}Pu	[14119-33-6]	6,540 yr
plutonium-241	^{241}Pu	[14119-32-5]	14.9 yr
plutonium-242	^{242}Pu	[13982-10-0]	3.87×10^{5} yr
plutonium-244	^{244}Pu	[14119-34-7]	8.3×10^{7} yr
americium-241	^{241}Am	[14596-10-2]	433 yr
americium-242	^{242}Am	[13981-54-9]	152 yr
americium-243	^{243}Am	[14993-75-0]	7,400 yr
curium-242	^{242}Cm	[15510-73-3]	163.0 d
curium-243	^{243}Cm	[15757-87-6]	30 yr
curium-244	^{244}Cm	[13981-15-2]	18.1 yr
curium-245	^{245}Cm	[15621-76-8]	8,540 yr
curium-246	^{246}Cm	[15757-90-1]	4,800 yr
curium-247	^{247}Cm	[15758-32-4]	1.6×10^{7} yr
curium-248	^{248}Cm	[15758-33-5]	3.6×10^{5} yr
curium-250	^{250}Cm[c]	[15743-88-6]	1.1×10^{4} yr
berkelium-247	^{247}Bkb	[15752-38-2]	1,380 yr
berkelium-249	^{249}Bk	[14900-25-5]	320 d
californium-249	^{249}Cf	[15237-97-5]	350 yr
californium-250	^{250}Cf	[13982-11-1]	13.1 yr
californium-251	^{251}Cf	[15765-19-2]	898 yr
californium-252	^{252}Cf	[13981-17-4]	2.6 yr
einsteinium-253	^{253}Es	[15840-02-5]	20.5 d
einsteinium-254	^{254}Es	[15840-03-6]	276 d
einsteinium-255	^{255}Es	[15840-04-7]	40 d
fermium-257	^{257}Fm	[15750-26-2]	100 d

[a] Natural mixture (^{238}U, 99.3%; ^{235}U, 0.72%; and ^{234}U, 0.006%). Half-life given is for the major constituent ^{238}U.

[b] Available so far only in trace quantities from charged particle irradiations.

[c] Available only in very small amounts from neutron irradiations in thermonuclear explosions.

these are available as individual isotopes. It appears that it will always be necessary to study the elements above fermium by means of the tracer technique (except for some very special experiments) because only isotopes with short half-lives are known.

1.2. Experimental Methods of Investigation. All of the actinide elements are radioactive and, except for thorium and uranium, special equipment and shielded facilities are usually necessary for their manipulation (9,14,15). On a laboratory scale, enclosed containers (gloved boxes) are generally used for safe handling of these substances. In some work, all operations are performed by remote control. Neptunium in the form of the long-lived isotope ^{237}Np is relatively convenient to work with in chemical investigations. Because of the existence of large quantities of the fissionable isotope ^{239}Pu, the physiological toxicity of plutonium deserves emphasis. In this form plutonium is a dangerous poison by reason of its intense alpha radioactivity [1.4×10^8 alpha particles/(mg · min)] and its physiological behavior. Ingested plutonium may be transferred to the bone and, over a period of time, give rise to neoplasms.

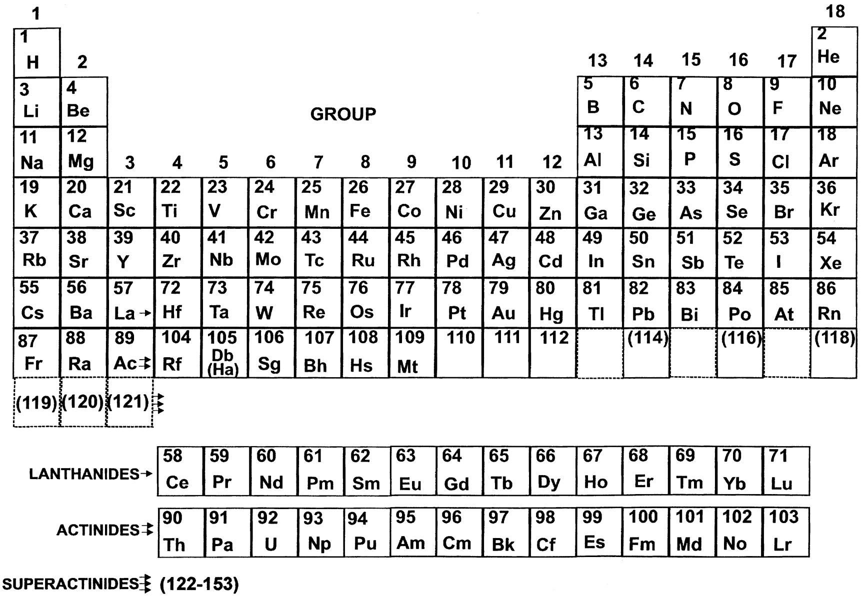
The study of the chemical behavior of concentrated preparations of short-lived isotopes is complicated by the rapid production of hydrogen peroxide in aqueous solutions and the destruction of crystal lattices in solid compounds. These effects are brought about by heavy recoils of high energy alpha particles released in the decay process.

Most chemical investigations with plutonium to date have been performed with ^{239}Pu, but the isotopes ^{242}Pu and ^{244}Pu (produced by intensive neutron irradiation of plutonium) are more suitable for such work because of their longer half-lives and consequently lower specific activities. Much work on the chemical properties of americium has been carried out with ^{241}Am, which is also difficult to handle because of its relatively high specific alpha radioactivity, about 7×10^9 alpha particles/(mg · min). The isotope ^{243}Am has a specific alpha activity about twenty times less than ^{241}Am and is thus a more attractive isotope for chemical investigations. Much of the earlier work with curium used the isotopes ^{242}Cm and ^{244}Cm, but the heavier isotopes offer greater advantages because of their longer half-lives. The isotope ^{248}Cm, which can be obtained in relatively high isotopic purity as the alpha-particle decay daughter of ^{252}Cf, is the most practical for chemical studies. Berkelium (as ^{249}Bk) and californium (as a mixture of the isotopes ^{249}Cf, ^{250}Cf, ^{251}Cf, and ^{252}Cf) are available as the result of intensive neutron irradiation of lighter elements. The best isotope for the study of californium is ^{249}Cf, which can be isolated in pure form through its beta-particle-emitting parent, ^{249}Bk. The isotope ^{253}Es (half-life, 20 d), also a product from such intensive neutron irradiation, is used to study the chemical properties of einsteinium. The isotope ^{254}Es (half-life, 276 d) is more useful for work with macroscopic quantities but is produced in much smaller amounts than ^{253}Es. Weighable amounts of berkelium, californium, and einsteinium are difficult to handle because of their intense radioactivity. Spontaneous fission is a mode of decay for ^{252}Cf (half-life, 2.6 yr), 1 μg of which emits approximately 2×10^8 neutrons/min, and the chief mode of decay of ^{254}Cf (half-life, 56 d), 1 μg of which emits approximately 8×10^{10} neutrons/min. Californium produced in the highest-flux reactors unfortunately contains ^{252}Cf, which makes it very difficult to handle. In work with more than a few micrograms of ^{252}Cf it is necessary to do all manipulations by remote control, which is exceedingly cumbersome on such a small scale; therefore, ^{249}Cf is generally used.

Special techniques for experimentation with the actinide elements other than Th and U have been devised because of the potential health hazard to the experimenter and the small amounts available (15). In addition, investigations are frequently carried out with the substance present in very low concentration as a radioactive tracer. Such procedures continue to be used to some extent with the heaviest actinide elements, where only a few score atoms may be available; they were used in the earliest work for all the transuranium elements. Tracer studies offer a method for obtaining knowledge of oxidation states, formation of complex ions, and the solubility of various compounds. These techniques are not applicable to crystallography, metallurgy, and spectroscopic studies.

Microchemical or ultramicrochemical techniques are used extensively in chemical studies of actinide elements (16). If extremely small volumes are used, microgram or lesser quantities of material can give relatively high concentrations in solution. Balances of sufficient sensitivity have been developed for quantitative measurements with these minute quantities of material. Since the amounts of material involved are too small to be seen with the unaided eye, the actual chemical work is usually done on the mechanical stage of a microscope, where all of the essential apparatus is in view. Compounds prepared on such a small scale are often identified by x-ray crystallographic methods.

Position in the Periodic Table and Electronic Structure. Prior to 1944 the location of the heaviest elements in the periodic table had been a matter of



GROUP

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La →	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac ‡	104 Rf	105 Db (Ha)	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112		(114)		(116)		(118)
(119)	(120)	(121) ⹋															

LANTHANIDES →	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
ACTINIDES ‡	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

SUPERACTINIDES ⹋ (122-153)

Fig. 4. Futuristic periodic table showing elements known as of early 2000. Predicted locations of undiscovered transuranium elements are shown in parentheses. Elements 114, 116, and 118 have been reported in 1999 but are not yet confirmed.

question, and the elements thorium, protactinium, and uranium were commonly placed immediately below the elements hafnium, tantalum, and tungsten. In 1944, on the basis of earlier chemical studies of neptunium and plutonium, the similarity between the actinide and the lanthanide elements was recognized (1, 7,14). The intensive study of the heaviest elements shows a series of elements similar to the lanthanide series, beginning with actinium (Fig. 4). Corresponding pairs of elements show resemblances in spectroscopic and magnetic behavior that arise because of the similarity of electronic configurations for the ions of the homologous elements in the same state of oxidation, and in crystallographic properties, owing to the near matching of ionic radii for ions of the same charge. The two series are not, however, entirely comparable. A difference lies in the oxidation states. The tripositive state characteristic of lanthanide elements does not appear in aqueous solutions of thorium and protactinium and does not become

Table 3. **Electronic Configurations for Gaseous Atoms of Lanthanide and Actinide Elements**

Atomic number	Element	CAS Registry Number4	Electronic configuration
57	lanthanum	[7439-91-0]	$5d6s^2$[a]
58	cerium	[7440-45-1]	$4f5d6s^2$
59	praseodymium	[7440-10-0]	$4f^36s^2$
60	neodymium	[7440-00-8]	$4f^46s^2$
61	promethium	[7440-12-2]	$4f^56s^2$
62	samarium	[7440-19-9]	$4f^66s^2$
63	europium	[7440-53-1]	$4f^76s^2$
64	gadolinium	[7440-54-2]	$4f^75d6s^2$
65	terbium	[7440-27-9]	$4f^96s^2$
66	dysprosium	[7429-91-6]	$4f^{10}6s^2$
67	holmium	[7440-60-0]	$4f^{11}6s^2$
68	erbium	[7440-52-0]	$4f^{12}6s^2$
69	thulium	[7440-30-4]	$4f^{13}6s^2$
70	ytterbium	[7440-64-4]	$4f^{14}6s^2$
71	lutetium	[7439-94-3]	$4f^{14}5d6s^2$
89	actinium		$6d7s^2$[b]
90	thorium		$6d^27s^2$
91	protactinium		$5f^26d7s^2$
92	uranium		$5f^36d7s^2$
93	neptunium		$5f^46d7s^2$
94	plutonium		$5f^67s^2$
95	americium		$5f^77s^2$
96	curium		$5f^76d7s^2$
97	berkelium		$5f^97s^2$
98	californium		$5f^{10}7s^2$
99	einsteinium		$5f^{11}7s^2$
100	fermium		$5f^{12}7s^2$
101	mendelevium		($5f^{13}7s^2$)
102	nobelium		($5f^{14}7s^2$)
103	lawrencium		($5f^{14}6d7s^2$ or $5f^{14}7s^27p$)

[a] Beyond xenon.

[b] Beyond radon. The configurations enclosed in parentheses are predicted.

the most stable oxidation state in aqueous solution until americium is reached. The elements uranium through americium have several oxidation states, unlike the lanthanides. These differences can be interpreted as resulting from the proximity in the energies of the 7*s*, 6*d*, and 5*f* electronic levels.

Table 3 presents the actual or predicted electronic configurations of the actinide elements (2,14). Similar information for the lanthanide elements is given for purposes of comparison (14). As indicated, fourteen 4*f* electrons are added in the lanthanide series, beginning with cerium and ending with lutetium; in the actinide elements, fourteen 5*f* electrons are added, beginning, formally, with thorium and ending with lawrencium. In the cases of actinium, thorium, uranium, americium, berkelium, californium, and einsteinium the configurations were determined from an analysis of spectroscopic data obtained in connection with the measurement of the emission lines from neutral and charged gaseous atoms. The knowledge of the electronic structures for protactinium, neptunium, plutonium, curium, and fermium results from atomic beam experiments (15).

Measurements of paramagnetic susceptibility, paramagnetic resonance, light absorption, fluorescence, and crystal structure, in addition to a consideration of chemical and other properties, have provided a great deal of information about the electronic configurations of the aqueous actinide ions and of actinide compounds. In general, all of the electrons beyond the radon core in the actinide compounds and in aqueous actinide ions are in the 5*f* shell. There are exceptions, such as U_2U_3, and subnormal compounds, such as Th_2S_3, where 6*d* electrons are present.

1.3. Properties. The close chemical resemblance among many of the actinide elements permits their chemistry to be described for the most part in a correlative way (13,14,17,18).

Oxidation States. The oxidation states of the actinide elements are summarized in Table 4 (12–14). The most stable states are designated by bold face type and those which are very unstable are indicated by parentheses. These latter states do not exist in aqueous solutions and have been produced only in solid compounds. The IV state of curium is limited to CmO_2 and CmF_4 (solids) and a complex ion stable in highly concentrated cesium fluoride solution, whereas the IV state of californium is limited to CfO_2 and CfF_4 (solids), and double salts such as $7NaF{\cdot}6CfF_4$ (solid). In the second half of the series the II state first appears in the form of solid compounds at californium and becomes successively more stable in proceeding to nobelium. The II state is observed in aqueous solution for mendelevium (and presumably for fermium) and is the most stable state for nobelium. Americium(II), observed only in solid compounds, and berkelium(IV) show the stability of the half-filled 5*f* configuration ($5f^7$) and nobelium(II) shows the stability of the full 5*f* configuration ($5f^{14}$). The greater tendency toward the II state in the actinides, as compared to the lanthanides, is a result of the increasing binding of the 5*f* (and 6*d*) electrons upon approaching the end of the actinide series.

The actinide elements exhibit uniformity in ionic types. In acidic aqueous solution, there are four types of cations, and these and their colors are listed in Table 5 (12–14,17). The open spaces indicate that the corresponding oxidation states do not exist in aqueous solution. The wide variety of colors exhibited by

Table 4. **The Oxidation States of the Actinide Elements**

Atomic number and element														
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr
						(2)			(2)	(2)	2	2	**2**	
3	(3)	(3)	3	3	3	**3**	**3**	**3**	**3**	**3**	**3**	**3**	3	**3**
	4	4	4	4	**4**	4	4	4	(4)					
		5	5	**5**	5	5								
			6	6	6	6								
				7	(7)									

Table 5. **Ion Types and Colors for Actinide Ions**

Element	M^{3+}	M^{4+}	MO_2^+	MO_2^{2+}	MO_5^{3-}
actinium	colorless				
thorium		colorless			
protactinium		colorless	colorless		
uranium	red	green	color unknown	yellow	
neptunium	blue to purple	yellow-green	green	pink to red	dark green
plutonium	blue to violet	tan to orange-brown	rose	yellow to pink-orange	dark green
americium	pink or yellow	color unknown	yellow	rum-colored	
curium	pale green	color unknown			
berkelium	green	yellow			
californium	green	yellow			
einsteinium	colorless				

actinide ions is characteristic of transition series of elements. In general, protactinium(V) polymerizes and precipitates readily in aqueous solution, and it seems unlikely that ionic forms are present in such solutions.

Corresponding ionic types are similar in chemical behavior, although the oxidation–reduction relationships and therefore the relative stabilities differ from element to element. The ions MO_2^+ and MO_2^{2+} are stable with respect to their binding of oxygen atoms and remain unchanged through a great variety of chemical treatment. They behave as single entities with properties intermediate to singly or doubly charged ions and ions of similar size but of higher charge. The VII oxidation states found for neptunium and plutonium are probably in the form of ions of the type MO_5^{3-} in alkaline aqueous solution; in acid solution these elements in the VII oxidation state readily oxidize water.

The reduction potentials for the actinide elements are shown in Figure 5 (12–14,17,20). These are formal potentials, defined as the measured potentials corrected to unit concentration of the substances entering into the reactions; they are based on the hydrogen-ion–hydrogen couple taken as zero volts; no corrections are made for activity coefficients. The measured potentials were established by cell, equilibrium, and heat of reaction determinations. The potentials for acid solution were generally measured in 1 *M* perchloric acid and for alkaline solution in 1 *M* sodium hydroxide. Estimated values are given in parentheses.

The $M^{4+} \rightleftharpoons M^{3+}$ and $MO_2^{2+} \rightleftharpoons MO_2^+$ couples are readily reversible, and reactions are rapid with other one-electron reducing or oxidizing agents that involve no bond changes. The rate varies with reagents that normally react by two-electron or bond-breaking changes. The $MO_2^+ \rightleftharpoons M^{3+}$, $MO_2^{2+} \rightleftharpoons M^{3+}$, $MO_2^+ \rightleftharpoons M^{4+}$, and $MO_2^{2+} \rightleftharpoons M^{4+}$ couples are not reversible, presumably because of slowness introduced in the making and breaking of oxygen bonds.

Table 6 presents a summary of the oxidation–reduction characteristics of actinide ions (12–14,17,20). The disproportionation reactions of UO_2^+, Pu^{4+}, PuO_2^+, and AmO_2^+ are very complicated and have been studied extensively. In the case of plutonium, the situation is especially complex: four oxidation states

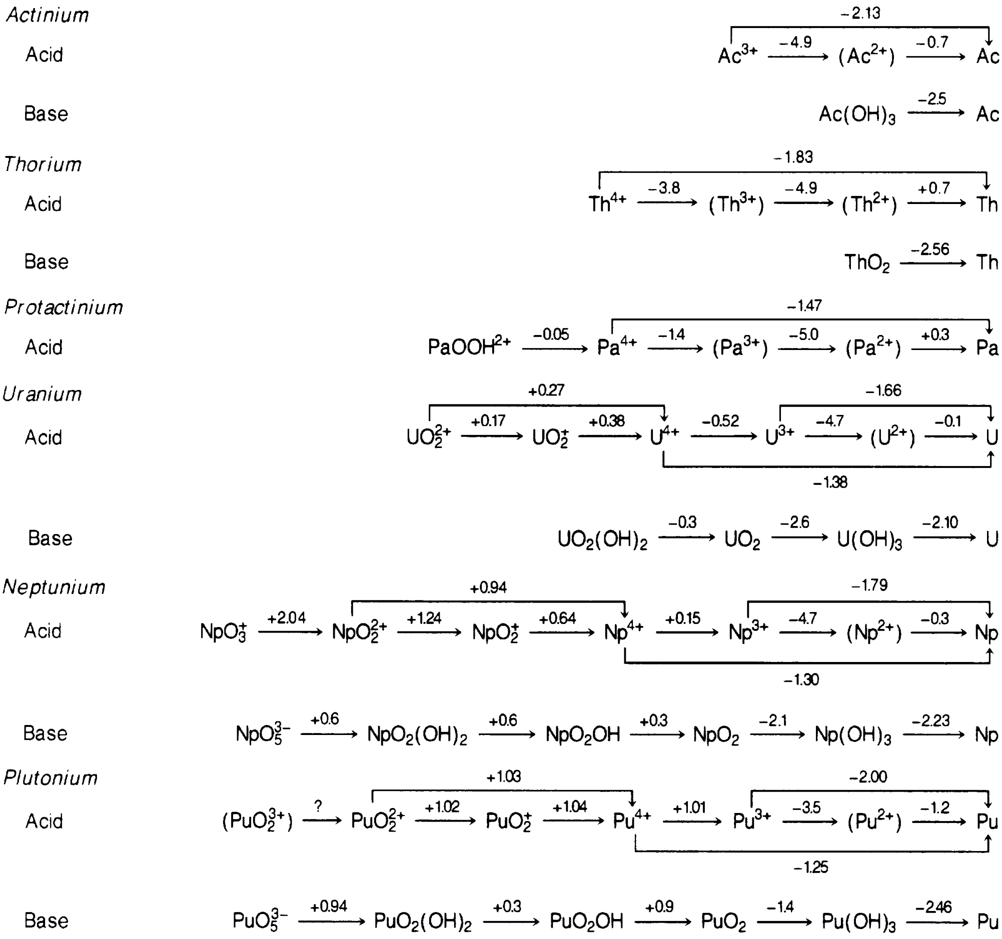


Fig. 5. Standard (or formal) reduction potentials of actinium and the actinide ions in acidic (pH 0) and basic (pH 14) aqueous solutions (values are in volts vs standard hydrogen electrode) (19).

of plutonium [(III), (IV), (V), and (VI)] can exist together in aqueous solution in equilibrium with each other at appreciable concentrations.

Hydrolysis and Complex Ion Formation. Hydrolysis and complex ion formation are closely related phenomena (13,14).

Of the actinide ions, the small, highly charged M^{4+} ions exhibit the greatest degree of hydrolysis and complex ion formation. For example, the ion Pu^{4+} hydrolyzes extensively and also forms very strong anion complexes. The hydrolysis of Pu^{4+} is of special interest in that polymers that exist as positive colloids can be produced; their molecular weight and particle size depend on the method of preparation. Polymeric plutonium with a molecular weight as high as 10^{10} has been reported.

The degree of hydrolysis or complex ion formation decreases in the order $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+}$. Presumably the relatively high tendency toward

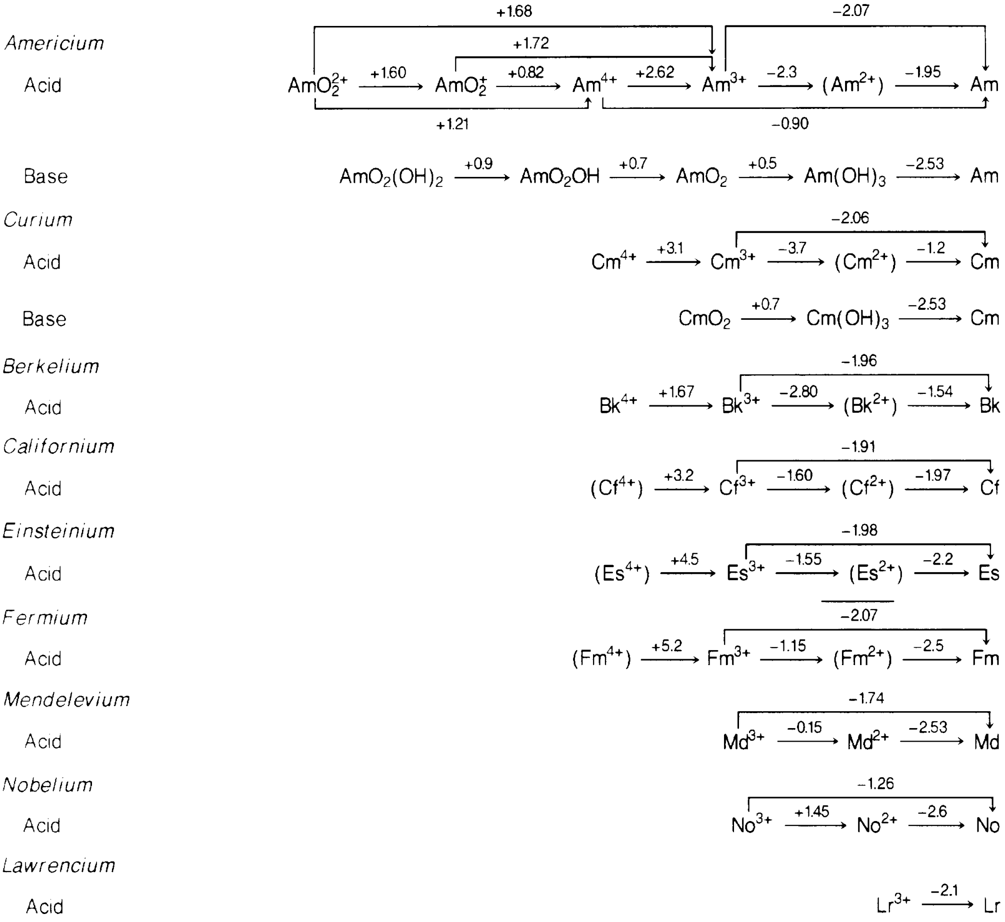


Fig. 5 (*Continued*)

hydrolysis and complex ion formation of MO_2^{2+} ions is related to the high concentration of charge on the metal atom. On the basis of increasing charge and decreasing ionic size, it could be expected that the degree of hydrolysis for each ionic type would increase with increasing atomic number. For the ions M^{4+} and M^{3+}, beginning at about uranium, such a regularity of hydrolytic behavior is observed, but for the remaining two ions, MO_2^{+} and MO_2^{2+}, the degree of hydrolysis decreases with increasing atomic number, thus indicating more complicated factors than simple size and charge.

The extensive hydrolysis of protactinium in its V oxidation state makes the chemical investigation of protactinium extremely difficult. Ions of protactinium(V) must be held in solution as complexes, eg, with fluoride ion, to prevent hydrolysis.

The tendency toward complex ion formation of the actinide ions is determined largely by the factors of ionic size and charge. Although there is variation

Table 6. **Stability of Actinide Ions in Aqueous Solution**

Ion	Stability
Md^{2+}	stable to water, but readily oxidized
No^{2+}	stable
Ac^{3+}	stable
U^{3+}	aqueous solutions evolve hydrogen on standing
Np^{3+}	stable to water, but readily oxidized by air to Np^{4+}
Pu^{3+}	stable to water and air, but easily oxidized to Pu^{4+}; oxidizes slightly under the action of its own alpha radiation (in form of ^{239}Pu)
Am^{3+}	stable; difficult to oxidize
Cm^{3+}	stable
Bk^{3+}	stable; can be oxidized to Bk^{4+}
Cf^{3+}	stable
Es^{3+}	stable
Fm^{3+}	stable
Md^{3+}	stable, but rather easily reduced to Md^{2+}
No^{3+}	easily reduced to No^{2+}
Lr^{3+}	stable
Th^{4+}	stable
Pa^{4+}	stable to water, but readily oxidized
Pa^{5+}	stable; hydrolyzes readily
U^{4+}	stable to water, but slowly oxidized by air to UO_2^{2+}
Np^{4+}	stable to water, but slowly oxidized by air to NpO_2^+
Pu^{4+}	stable in concentrated acid, eg, 6 M HNO_3, but disproportionates to Pu^{3+} and PuO_2^{2+} at lower acidities
Am^{4+}	known in solution only as complex fluoride and carbonate ions
Cm^{4+}	known in solution only as complex fluoride ion
Bk^{4+}	marginally stable; easily reduced to Bk^{3+}
UO_2^+	disproportionates to U^{4+} and UO_2^{2+}; most stable at pH 2–4
NpO_2^+	stable; disproportionates only at high acidities
PuO_2^+	always tends to disproportionate to Pu^{4+} and PuO_2^{2+} (ultimate products); most stable at very low acidities
AmO_2^+	disproportionates in strong acid to Am^{3+} and AmO_2^{2+}; reduces fairly rapidly under the action of its own alpha radiation at low acidities (in form of ^{241}Am)
UO_2^{2+}	stable; difficult to reduce
NpO_2^{2+}	stable; easy to reduce
PuO_2^{2+}	stable; easy to reduce; reduces slowly under the action of its own alpha radiation (in form of ^{239}Pu)
AmO_2^{2+}	easy to reduce; reduces fairly rapidly under the action of its own alpha radiation (in form of ^{241}Am)
NpO_5^{3-}	observed only in alkaline solution
PuO_5^{3-}	observed only in alkaline solution; oxidizes water

within each of the ionic types, the order of complexing power of different anions is, in general, fluoride > nitrate > chloride > perchlorate for mononegative anions and carbonate > oxalate > sulfate for dinegative anions. The actinide ions form somewhat stronger complex ions than homologous lanthanide ions.

Actinide ions form complex ions with a large number of organic substances (12). Their extractability by these substances varies from element to element and depends markedly on oxidation state. A number of important separation procedures are based on this property. Solvents that behave in this way are tributyl phosphate, diethyl ether [60-29-7], ketones such as diisopropyl ketone [565-80-5] or methyl isobutyl ketone [108-10-1], and several glycol ether type solvents such as diethyl Cellosolve [629-14-1] (ethylene glycol diethyl ether) or dibutyl Carbitol [112-73-2] (diethylene glycol dibutyl ether).

A number of organic compounds, eg, acetylacetone [123-54-6] and cupferron [135-20-6], form compounds with aqueous actinide ions (IV state for reagents mentioned) that can be extracted from aqueous solution by organic solvents (12). The chelate complexes are especially noteworthy and, among these, the ones formed with diketones, such as 3-(2-thiophenoyl)-1,1,1-trifluoroacetone [326-91-0] ($C_4H_3SCOCH_2COCF_3$), are of importance in separation procedures for plutonium.

Metallic State. The actinide metals, like the lanthanide metals, are highly electropositive (13,14,17). They can be prepared by the electrolysis of molten salts or by the reduction of a halide with an electropositive metal, such as calcium or barium. Their physical properties are summarized in Table 7 (13,14, 17,21). Metallic protactinium, uranium, neptunium, and plutonium have complex structures that have no counterparts among the lanthanide metals. Plutonium metal has very unusual metallurgical properties. It is known to exist in six allotropic modifications between room temperature and its melting point. One of the most interesting features of plutonium metal is the contraction undergone by the δ and δ' phases with increasing temperature. Also noteworthy is the fact that for no phase do both the coefficient of thermal expansion and the temperature coefficient of resistivity have the conventional sign. The resistance decreases if the phase expands on heating. Americium is the first actinide to show resemblance in crystal structure to the lanthanide metals.

With respect to chemical reactivity, the actinide metals resemble the lanthanide metals more than metals of the 5*d* elements such as tantalum, tungsten, rhenium, osmium, and iridium. A wide range of intermetallic compounds has been observed and characterized, including compounds or alloys with members of groups IB, IIA, IIIA, IVA, VIII, VA, and the VIB chalcogenides (13,17). The 5*f* electrons in the lighter actinides are not as localized as the 4*f* electrons in the lanthanides and, with energies close to those of the 6*d* and 7*s* electrons, participate actively in bonding. The participation in bonding by 5*f* electrons is apparently more prominent in the early actinides than in the heavier actinides, where a localized behavior becomes evident. The behavior of the 5*f* electrons makes the actinide metals and their metallic compounds different in their behavior than the transition and lanthanide metals and their compounds.

Solid Compounds. The tripositive actinide ions resemble tripositive lanthanide ions in their precipitation reactions (13,14,17,20,22). Tetrapositive actinide ions are similar in this respect to Ce^{4+}. Thus the fluorides and oxalates are insoluble in acid solution, and the nitrates, sulfates, perchlorates, and sulfides are all soluble. The tetrapositive actinide ions form insoluble iodates and various substituted arsenates even in rather strongly acid solution. The MO_2^+ actinide ions can be precipitated as the potassium salt from strong carbonate solutions. In solutions containing a high concentration of sodium and acetate ions, the actinide MO_2^{2+} ions form the insoluble crystalline salt $NaMO_2(O_2CCH_3)_3$. The hydroxides of all four ionic types are insoluble; in the case of the MO_2^{2+} ions, compounds of the type exemplified by sodium diuranate

Table 7. **Properties of Actinide Metals**

Element	Melting point, °C	Heat of vaporization, ΔH_v, kJ/mol (kcal/mol)	Boiling point, °C	Crystal structure						
				Phase	Range of stability, °C	Symmetry	Lattice parameters, nm			Density, g/mL, at T, °C
							a_0	b_0	c_0	
actinium	1100 ± 50	293 (70)				FC cubic	0.5311			10.07, 25
thorium	1750	564 (130)	3850	α	RT–1360	FC cubic	0.5086			11.724, 25
				β	1360–1750	BC cubic	0.411			
protactinium	1575			α	RT–1170	tetragonal	0.3929		0.3241	15.37, 25
				β	1170–1575	BC cubic	0.381			
uranium	1132	446.4 (106.7)	3818	α	RT–668	orthorhombic	0.2854	0.5869	0.4956	18.97, 25
				β	668–774	tetragonal	1.0759		0.5656	18.11, 720
				γ	774–1132	BC cubic	0.3525			18.06, 805
neptunium	637 ± 2	418 (100)	3900	α	$\mathrm{RT} - 280 \pm 5$	orthorhombic	0.4721	0.4888	0.4887	20.45, 25
				β	$280 \pm 5 - 577 \pm 5$	tetragonal	0.4895		0.3386	19.36, 313
				γ	$577 \pm 5 - 637 \pm 2$	BC cubic	0.3518			18.04, 600
plutonium	646	333.5 (79.7)	3235	α	RT–122	monoclinic	0.6183	0.4822 $\beta = 101.8°$	1.0963	19.86, 21
				β	122–207	BC monoclinic	0.9284	1.0463 $\beta = 92.13°$	0.7859	17.70, 190
				γ	207–315	orthorhombic	0.3159	0.5768	1.0162	17.13, 235
				δ	315–457	FC cubic	0.4637			15.92, 320
				δ′	457–479	tetragonal	0.3326		0.4463	16.01, 460
				ε	479–640	BC cubic	0.3636			16.48, 490
americium	1173	230 (55)	2011	α	RT–658	hexagonal	0.3468		1.1241	13.67, 20
				β	793–1004	FC cubic	0.4894			13.65, 20
				γ	1050–1173					
curium	1345	386 (92.2)	3110	α	below 1277	hexagonal	0.3496		1.1331	13.51, 25
				β	1277–1345	FC cubic	0.5039			12.9, 25
berkelium	1050			α	below 930	hexagonal	0.3416		1.1069	14.78, 25
				β	930–986	FC cubic	0.4997			13.25, 25
californium	900 ± 30			α	below 900	hexagonal	0.339		1.101	15.1, 25
				β		FC cubic	0.575			8.70, 25
einsteinium	860 ± 30			α	below 860	hexagonal				
				β		FC cubic	0.575			8.84

($Na_2U_2O_7$) can be precipitated from alkaline solution. The NpO_5^{3-} and PuO_5^{3-} anions, which seem to exist in alkaline solution, form insoluble compounds with several di- and tripositive cations. Peroxide solutions react with actinide ions, particularly M^{4+} ions, to form complex peroxy compounds in solution, and such compounds can be precipitated even from moderately acid solutions. Inorganic anions, eg, sulfate, nitrate, and chloride, are often incorporated in the solid peroxy compounds.

Thousands of compounds of the actinide elements have been prepared, and the properties of some of the important binary compounds are summarized in Table 8 (13,17,18,22). The binary compounds with carbon, boron, nitrogen, silicon, and sulfur are not included; these are of interest, however, because of their stability at high temperatures. A large number of ternary compounds, including numerous oxyhalides, and more complicated compounds have been synthesized and characterized. These include many intermediate (nonstoichiometric) oxides, and besides the nitrates, sulfates, peroxides, and carbonates, compounds such as phosphates, arsenates, cyanides, cyanates, thiocyanates, selenocyanates, sulfites, selenates, selenites, tellurates, tellurites, selenides, and tellurides.

Hundreds of actinide organic derivatives, including organometallic compounds, are known (12,19,23). A number of interesting actinide organometallic compounds of the π-bonded type have been synthesized and characterized. The triscyclopentadienyl compounds, although more covalent than the analogous lanthanide compounds, are highly ionic and include UCp_3, $NpCp_3$, $PuCp_3$, $AmCp_3$, $CmCp_3$, $BkCp_3$, and $CfCp_3$ ($Cp = C_5H_5$); each, except the uranium compound, is relatively stable and appreciably volatile but is sensitive to air (23). The tetrakiscyclopentadienyl complexes ($ThCp_4$, $PaCp_4$, UCp_4, and $NpCp_4$) are, like the Cp_3 complexes, soluble in organic solvents and moderately air-sensitive but not appreciably volatile. A number of triscyclopentadienyl actinide halides, of the general formula MCp_3X (M = Th, U, Np), are known, and these are soluble in a range of organic solvents, are more stable to heat than the tetrakis complexes, and are moderately air-sensitive. The pentamethylcyclopentadienides of thorium and uranium also exist. Of special interest are the cyclooctatetraene [629-20-1] (COT) complexes, including the bis compounds $Th(COT)_2$, $Pa(COT)_2$, $U(COT)_4$, $Np(COT)_4$, and $Pu(COT)_4$, and substituted derivatives of these (23). Characterized by monoclinic symmetry with a π-bonding sandwich structure involving 5*f* electron orbitals, the prototype compound involving uranium is known as uranocene, in view of the analogy to ferrocene. The compounds are air-sensitive, are only sparingly soluble in organic solvents, and can be sublimed in vacuum. A few are very stable to air. The actinides also form tetraallyl complexes, $M(C_3H_5)_4$, but these are stable only at low temperatures. Many organoactinide complexes with ς and π ligands of the type ($Cp_3M—R$($R =$ alkyl, aryl, or alkynyl) are known, as well as a number of borohydride compounds. Additional solid organoactinide complexes include alkoxides, dialkylamides, chelates such as β-diketones and β-ketoesters, β-hydroxyquinolines, *N*-nitroso-*N*-phenylhydroxylamines (cupferron type), tropolones, *N,N*-dialkyldithiocarbamates, and phthalocyanines; many of these are useful for separation schemes.

Crystal Structure and Ionic Radii. Crystal structure data have provided the basis for the ionic radii (coordination number = CN = 6), which are

Table 8. **Properties and Crystal Structure Data for Important Actinide Binary Compounds**

Compound	Color	Melting point, °C	Symmetry	Space group or structure type	Lattice parameters				Density, g/mL
					a_0, nm	b_0, nm	c_0, nm	Angle, deg	
AcH_2	black		cubic	fluorite ($\mathrm{F}m3m$)	0.5670				8.35
ThH_2	black		tetragonal	$\mathrm{F}4/mmm$	0.5735		0.4971		9.50
Th_4H_{15}	black		cubic	$\mathrm{I}4\bar{3}d$	0.911				8.25
α-PaH_3	gray		cubic	$\mathrm{P}m3n$	0.4150				10.87
β-PaH_3	black		cubic	β-W	0.6648				10.58
α-UH_3	?		cubic	$\mathrm{P}m3n$	0.4160				11.12
β-UH_3	black		cubic	β-W ($\mathrm{P}m3n$)	0.6645				10.92
NpH_2	black		cubic	fluorite	0.5343				10.41
NpH_3	black		trigonal	$\mathrm{P}\bar{3}c1$	0.651		0.672		9.64
PuH_2	black		cubic	fluorite	0.5359				10.40
PuH_3	black		trigonal	$\mathrm{P}\bar{3}c1$	0.655		0.676		9.61
AmH_2	black		cubic	fluorite	0.5348				10.64
AmH_3	black		trigonal	$\mathrm{P}\bar{3}c1$	0.653		0.675		9.76
CmH_2	black		cubic	fluorite	0.5322				10.84
CmH_3	black		trigonal	$\mathrm{P}\bar{3}c1$	0.6528		0.6732		10.06
BkH_2	black		cubic	fluorite	0.5248				11.57
BkH_3	black		trigonal	$\mathrm{P}\bar{3}c1$	0.6454		0.6663		10.44
Ac_2O_3	white		hexagonal	La_2O_3 ($\mathrm{P}\bar{3}m1$)	0.407		0.629		9.19
Pu_2O_3	?		cubic	$\mathrm{I}a3$ (Mn_2O_3)	1.103				10.20
Pu_2O_3	black	2085	hexagonal	La_2O_3	0.3841		0.5958		11.47
Am_2O_3	tan		hexagonal	La_2O_3	0.3817		0.5971		11.77
Am_2O_3	reddish brown		cubic	$\mathrm{I}a3$	1.103				10.57
Cm_2O_3	white to faint tan	2260	hexagonal	La_2O_3	0.3792		0.5985		12.17
Cm_2O_3			monoclinic	$\mathrm{C}2/m$ (Sm_2O_3)	1.4282	0.3641	0.8883	$\beta = 100.29$	11.90
Cm_2O_3	white		cubic	$\mathrm{I}a3$	1.1002				10.80
Bk_2O_3	light green		hexagonal	La_2O_3	0.3754		0.5958		12.47
Bk_2O_3	yellow-green		monoclinic	$\mathrm{C}2/m$	1.4197	0.3606	0.8846	$\beta = 100.23$	12.20
Bk_2O_3	yellowish brown		cubic	$\mathrm{I}a3$	1.0887				11.66
Cf_2O_3	pale green		hexagonal	La_2O_3	0.372		0.596		12.69
Cf_2O_3	lime green		monoclinic	$\mathrm{C}2/m$	1.4121	0.3592	0.8809	$\beta = 100.34$	12.37

Cf_2O_3	pale green		cubic	I*a*3	1.083				11.39
Es_2O_3	white		hexagonal	La_2O_3	0.37		0.60		12.7
Es_2O_3	white		monoclinic	C2/*m*	1.41	0.359	0.880	$\beta = 100$	12.4
Es_2O_3	white		cubic	I*a*3	1.0766				11.79
ThO_2	white	ca 3050	cubic	fluorite	0.5597				10.00
PaO_2	black		cubic	fluorite	0.5509				10.45
UO_2	brown to black	2875	cubic	fluorite	0.5471				10.95
NpO_2	apple green		cubic	fluorite	0.5425				11.14
PuO_2	yellow-green to brown	2400	cubic	fluorite	0.53960				11.46
AmO_2	black		cubic	fluorite	0.5374				11.68
CmO_2	black		cubic	fluorite	0.5358				11.92
BkO_2	yellowish-brown		cubic	fluorite	0.5332				12.31
CfO_2	black		cubic	fluorite	0.5310				12.46
Pa_2O_5	white		cubic	fluorite-related	0.5446 or 0.5492				11.14
Np_2O_5	dark brown		monoclinic	$P2_1/c$	0.4183	0.6584	0.4086	$\beta = 90.32$	8.18
α-U_3O_8	black-green	1150 (dec)	orthorhombic	C2*mm*	0.6716	1.1960	0.4147		8.39
β-U_3O_8	black-green		orthorhombic	C*mcm*	0.7069	1.1445	0.8303		8.32
γ-UO_3	orange	650 (dec)	orthorhombic	F*ddd*	0.981	1.993	0.971		7.80
$AmCl_2$	black		orthorhombic	P*bnm* ($PbCl_2$)	0.8963	0.7573	0.4532		6.78
$CfCl_2$	red-amber		?						
$AmBr_2$	black		tetragonal	$SrBr_2$ (P4/*n*)	1.1592		0.7121		7.00
$CfBr_2$	amber		tetragonal	$SrBr_2$	1.1500		0.7109		7.22
ThI_2	gold		hexagonal	$P6_3/mmc$	0.397		3.175		7.45
AmI_2	black	ca 700	monoclinic	EuI_2 ($P2_1/c$)	0.7677	0.8311	0.7925	$\beta = 98.46$	6.60
CfI_2	violet		hexagonal	CdI_2 ($P\bar{3}m1$)	0.456		0.699		6.63
CfI_2	violet		rhombohedral	$CdCl_2$ ($R\bar{3}m$)	0.743			$\alpha = 36$	6.58
AcF_3	white		trigonal	LaF_3 ($P\bar{3}c1$)	0.741		0.753		7.88
UF_3	black	>1140 (dec)	trigonal	LaF_3	0.718		0.7348		8.95
NpF_3	purple		trigonal	LaF_3	0.7129		0.7288		9.12
PuF_3	purple	1425	trigonal	LaF_3	0.7092		0.7254		9.33
AmF_3	pink	1393	trigonal	LaF_3	0.7044		0.7225		9.53
CmF_3	white	1406	trigonal	LaF_3	0.7014		0.7194		9.85
BkF_3	yellow-green		orthorhombic	YF_3 (P*nma*)	0.670	0.709	0.441		9.70
BkF_3	yellow-green		trigonal	LaF_3	0.697		0.714		10.15

Table 8 (*Continued*)

Compound	Color	Melting point, °C	Symmetry	Space group or structure type	Lattice parameters				Density, g/mL
					a_0, nm	b_0, nm	c_0, nm	Angle, deg	
CfF_3	light green		orthorhombic	YF_3	0.6653	0.7039	0.4393		9.88
CfF_3	light green		trigonal	LaF_3	0.6945		0.7101		10.28
$AcCl_3$	white		hexagonal	UCl_3 ($P6_3/m$)	0.762		0.455		4.81
UCl_3	green	835	hexagonal	$P6_3/m$	0.7443		0.4321		5.50
$NpCl_3$	green	ca 800	hexagonal	UCl_3	0.7413		0.4282		5.60
$PuCl_3$	emerald green	760	hexagonal	UCl_3	0.7394		0.4243		5.71
$AmCl_3$	pink or yellow	715	hexagonal	UCl_3	0.7382		0.4214		5.87
$CmCl_3$	white	695	hexagonal	UCl_3	0.7374		0.4185		5.95
$BkCl_3$	green	603	hexagonal	UCl_3	0.7382		0.4127		6.02
α-$CfCl_3$	green	545	orthorhombic	$TbCl_3$ ($Cmcm$)	0.3859	1.1748	0.8561		6.07
β-$CfCl_3$	green		hexagonal	UCl_3	0.7379		0.4090		6.12
$EsCl_3$	white to orange		hexagonal	UCl_3	0.740		0.407		6.20
$AcBr_3$	white		hexagonal	UBr_3 ($P6_3/m$)	0.806		0.468		5.85
UBr_3	red	730	hexagonal	$P6_3/m$	0.7936		0.4438		6.55
$NpBr_3$	green		hexagonal	UBr_3	0.7916		0.4390		6.65
$NpBr_3$	green		orthorhombic	$TbCl_3$ ($Cmcm$)	0.4109	1.2618	0.9153		6.67
$PuBr_3$	green	681	orthorhombic	$TbCl_3$	0.4097	1.2617	0.9147		6.72
$AmBr_3$	white to pale yellow		orthorhombic	$TbCl_3$	0.4064	1.2661	0.9144		6.85
$CmBr_3$	pale yellow-green	625 ± 5	orthorhombic	$TbCl_3$	0.4041	1.2700	0.9135		6.85
$BkBr_3$	light green		monoclinic	$AlCl_3$ ($C2/m$)	0.723	1.253	0.683	$\beta = 110.6$	5.604
$BkBr_3$	light green		orthorhombic	$TbCl_3$	0.403	1.271	0.912		6.95
$BkBr_3$	yellow green		rhombohedral	$FeCl_3$ ($R\overline{3}$)	0.766			$\alpha = 56.6$	5.54
$CfBr_3$	green		monoclinic	$AlCl_3$	0.7214	1.2423	0.6825	$\beta = 110.7$	5.673
$CfBr_3$	green		rhombohedral	$FeCl_3$	0.758			$\alpha = 56.2$	5.77
$EsBr_3$	straw		monoclinic	$AlCl_3$	0.727	1.259	0.681	$\beta = 110.8$	5.62
PaI_3	black		orthorhombic	$TbCl_3$ ($Cmcm$)	0.433	1.40	1.002		6.69
UI_3	black		orthorhombic	$TbCl_3$	0.4328	1.3996	0.9984		6.76
NpI_3	brown		orthorhombic	$TbCl_3$	0.430	1.403	0.995		6.82
PuI_3	green		orthorhombic	$TbCl_3$	0.4326	1.3962	0.9974		6.92
AmI_3	pale yellow	ca 950	hexagonal	BiI_3 ($R\overline{3}$)	0.742		2.055		6.35

AmI_3	yellow		orthorhombic	$PuBr_3$	0.428	1.394	0.9974		6.95
CmI_3	white		hexagonal	BiI_3	0.744		2.040		6.40
BkI_3	yellow		hexagonal	BiI_3	0.7584		02.087		6.02
CfI_3	red-orange		hexagonal	BiI_3	0.7587		2.081		6.05
EsI_3	amber to light yellow		hexagonal	BiI_3	0.753		2.084		6.18
ThF_4	white	1068	monoclinic	UF_4 (C2/*c*)	1.300	1.099	0.860	$\beta = 126.4$	6.20
PaF_4	reddish-brown		monoclinic	UF_4	1.288	1.088	0.849	$\beta = 126.4$	6.38
UF_4	green	960	monoclinic	C2/*c*	1.2803	1.0792	0.8372	$\beta = 126.3$	6.73
NpF_4	green		monoclinic	UF_4	1.268	1.066	0.834	$\beta = 126.3$	6.86
PuF_4	brown	1037	monoclinic	UF_4	1.260	1.057	0.828	$\beta = 126.3$	7.05
AmF_4	tan		monoclinic	UF_4	1.256	1.058	0.825	$\beta = 125.9$	7.23
CmF_4	light gray-green		monoclinic	UF_4	1.250	1.049	0.818	$\beta = 126.1$	7.36
BkF_4	pale yellow-green		monoclinic	UF_4	1.2396	1.0466	0.8118	$\beta = 126.3$	7.55
CfF_4	light green		monoclinic	UF_4	1.2327	1.0402	0.8113	$\beta = 126.4$	7.57
α-$ThCl_4$	white		orthorhombic		1.118	0.593	0.909		4.12
β-$ThCl_4$	white	770	tetragonal	UCl_4 ($I4_1/amd$)	0.8473		0.7468		4.60
$PaCl_4$	greenish-yellow		tetragonal	UCl_4	0.8377		0.7481		4.72
UCl_4	green	590	tetragonal	$I4_1/amd$	0.8296		0.7481		4.89
$NpCl_4$	red-brown	518	tetragonal	UCl_4	0.8266		0.7475		4.96
α-$ThBr_4$	white		tetragonal	$I4_1/a$	0.6737		1.3601		5.94
β-$ThBr_4$	white		tetragonal	UCl_4	0.8931		0.7963		5.77
$PaBr_4$	orange-red		tetragonal	UCl_4	0.8824		0.7957		5.90
UBr_4	brown	519	monoclinic	2/*c*-/-	1.092	0.869	0.705	$\beta = 93.15$	
$NpBr_4$	dark red	464	monoclinic	2/*c*-/-	1.089	0.874	0.705	$\beta = 94.19$	
ThI_4	yellow	556	monoclinic	$P2_1/n$	1.3216	0.8068	0.7766	$\beta = 98.68$	6.00
PaI_4	black								
UI_4	black								
PaF_5	white		tetragonal	$I\bar{4}2d$	1.153		0.519		
α-UF_5	grayish white		tetragonal	$I4/m$	0.6512		0.4463		5.81
β-UF_5	pale yellow		tetragonal	$I\bar{4}2d$	1.1456		0.5196		6.47
NpF_5			tetragonal	$I4/m$	0.653		0.445		
$PaCl_5$	yellow	306	monoclinic	C2/*c*	0.800	1.142	0.843	$\beta = 106.4$	
α-UCl_5	brown		monoclinic	$P2_1/n$	0.799	1.069	0.848	$\beta = 91.5$	3.81

Table 8 (*Continued*)

Compound	Color	Melting point, °C	Symmetry	Space group or structure type	Lattice parameters				Density, g/mL
					a_0, nm	b_0, nm	c_0, nm	Angle, deg	
β-UCl_5	red-brown		triclinic	$P\overline{1}$	0.707	0.965	0.635	$\alpha = 89.10$ $\beta = 117.36$ $\gamma = 108.54$	
α-$PaBr_5$			monoclinic	$P2_1/c$	1.264	1.282	0.992	$\beta = 108$	
β-$PaBr_5$	orange-brown		monoclinic	$P2_1/n$	0.9385	1.2205	0.895	$\beta = 91.1$	
UBr_5	brown		monoclinic	$P2_1/n$					
PaI_5	black		orthorhombic		0.698	0.2160	2.130		
UF_6	white	64.02[a]	orthorhombic	$Pnma$	0.9900	0.8962	0.5207		5.060
NpF_6	orange	55	orthorhombic	$Pnma$	0.9909	0.8997	0.5202		5.026
PuF_6	reddish-brown	52	orthorhombic	$Pnma$	0.995	0.902	0.526		4.86
UCl_6	dark green	178	hexagonal	$P\overline{3}m1$	1.09		0.603		3.62

[a] At 151.6 kPa, to convert kPa to atm, divide by 101.3.

Table 9. **Ionic Radii of Actinide and Lanthanide Elements**

No. of 4*f* or 5*f* electrons	Lanthanide series				Actinide series			
	Element	Radius, nm	Element	Radius, nm	Element	Radius, nm	Element	Radius, nm
0	La^{3+}	0.1032			Ac^{3+}	0.112	Th^{4+}	0.094
1	Ce^{3+}	0.101	Ce^{4+}	0.087	(Th^{3+})	(0.108)	Pa^{4+}	0.090
2	Pr^{3+}	0.099	Pr^{4+}	0.085	(Pa^{3+})	0.104	U^{4+}	0.089
3	Nd^{3+}	0.0983			U^{3+}	0.1025	Np^{4+}	0.087
4	Pm^{3+}	0.097			Np^{3+}	0.101	Pu^{4+}	0.086
5	Sm^{3+}	0.0958			Pu^{3+}	0.100	Am^{4+}	0.085
6	Eu^{3+}	0.0947			Am^{3+}	0.0980	Cm^{4+}	0.084
7	Gd^{3+}	0.0938			Cm^{3+}	0.0970	Bk^{4+}	0.083
8	Tb^{3+}	0.0923	Tb^{4+}	0.076	Bk^{3+}	0.0960	Cf^{4+}	0.0821
9	Dy^{3+}	0.0912			Cf^{3+}	0.0950	Es^{4+}	0.081
10	Ho^{3+}	0.0901			Es^{3+}	0.0940		
11	Er^{3+}	0.0890						
12	Tm^{3+}	0.0880			Fm^{3+}	0.0924[a]		
13	Yb^{3+}	0.0868			Md^{3+}	0.0896[a]		
14	Lu^{3+}	0.0861			Lr^{3+}	0.0881[a]		

[a] These ionic radii were obtained by determining the elution position of these ions from cation exchange columns with alpha-hydroxyisobutyrate relative to those of Ho^{3+}, Er^{3+}, and Tm^{3+}. The ionic radius of Er^{3+} was taken from crystallographic data to be 0.0881. (D. H. Templeton and C. H. Dauben, J. Am. Chem. Soc. **76**, 5237 (1954).

summarized in Table 9 (13,14,17). For both M^{3+} and M^{4+} ions there is an actinide contraction, analogous to the lanthanide contraction, with increasing positive charge on the nucleus.

As a consequence of the ionic character of most actinide compounds and of the similarity of the ionic radii for a given oxidation state, analogous compounds are generally isostructural. In some cases, eg, UBr_3, $NpBr_3$, $PuBr_3$, and $AmBr_3$, there is a change in structural type with increasing atomic number, which is consistent with the contraction in ionic radius. The stability of the MO_2 structure (fluorite type) is especially noteworthy, as is shown by the existence of such compounds as PaO_2, AmO_2, CmO_2, and CfO_2 despite the instability of the IV oxidation state of these elements in solution. The actinide contraction and the isostructural nature of the compounds constitute some of the best evidence for the transition character of this group of elements.

Absorption and Fluorescence Spectra. The absorption spectra of actinide and lanthanide ions in aqueous solution and in crystalline form contain narrow bands in the visible, near-ultraviolet, and near-infrared regions of the spectrum (13,14,17,24). Much evidence indicates that these bands arise from electronic transitions within the 4*f* and 5*f* shells in which the $4f^n$ and $5f^n$ configurations are preserved in the upper and lower states for a particular ion. In general, the absorption bands of the actinide ions are some ten times more intense than those of the lanthanide ions. Fluorescence, for example, is observed in the trichlorides of uranium, neptunium, americium, and curium, diluted with lanthanum chloride (15).

1.4. Practical Applications. The practical use of three actinide nuclides, ^{239}Pu, ^{235}U, and ^{233}U, as nuclear fuel is well known (5,9). When a neutron of any energy strikes the nucleus of one of these nuclides, each of which is capable of undergoing fission with thermal (essentially zero-energy) neutrons, the fission reaction can occur in a self-sustaining manner. A controlled self-perpetuating chain reaction using such a nuclear fuel can be maintained in such a manner that the heat energy can be extracted or converted by conventional means to electrical energy. The complete utilization of nonfissionable ^{238}U (through conversion to fissionable ^{239}Pu) and nonfissionable ^{232}Th (through conversion to fissionable ^{233}U) can be accomplished by breeder reactors.

In addition, three other actinide nuclides (^{238}Pu, ^{241}Am, and ^{252}Cf) have other practical applications (6). One gram of ^{238}Pu produces approximately 0.56 W of thermal power, primarily from alpha-particle decay, and this property has been used in space exploration to provide energy for small thermoelectric power units (see THERMOELECTRIC ENERGY CONVERSION). The most noteworthy example of this latter type of application is a radioisotopic thermoelectric generator left on the moon. It produced 73 W of electrical power to operate the scientific experiments of the Apollo lunar exploration, and was fueled with 2.6 kg of the plutonium isotope in the form of plutonium dioxide, PuO_2. Similar generators powered the instrumentation for other Apollo missions, the Viking Mars lander, and the Pioneer and Voyager probes to Jupiter, Saturn, Uranus, Neptune, and beyond. Americium-241 has a predominant gamma-ray energy of 60 keV and a long half-life of 433 yr for decay by the emission of alpha particles, which makes it particularly useful for a wide range of industrial gaging applications, the diagnosis of thyroid disorders, and for smoke detectors. When mixed with beryllium it generates neutrons at the rate of 1.0 × 10^7 neutrons/(s·g) ^{241}Am. The mixture is designated ^{241}Am–Be, and a large number of such sources are in worldwide daily use in oil-well logging operations to find how much oil a well is producing in a given time span. Californium-252 is an intense neutron source: 1 g emits 2.4 × 10^{12} neutrons/s. This isotope is being tested for applications in neutron activation analysis, startup sources for nuclear reactors, neutron radiography, portable sources for field use in mineral prospecting and oil-well logging, and in airport neutron-activation detectors for nitrogenous materials (ie, explosives). Both ^{238}Pu and ^{252}Cf are being studied for possible medical applications: the former as a heat source for use in heart pacemakers and heart pumps and the latter as a neutron source for irradiation of certain tumors for which gamma-ray treatment is relatively ineffective.

2. Transactinides and Superheavy Elements

The elements beyond the actinides in the Periodic Table can be termed the transactinides. These begin with the element having atomic number 104 and extend, in principle, indefinitely. Nine such elements were definitely known by 1996. They were synthesized in bombardments of heavy targets with heavy-ion projectiles. In 1999, evidence was reported for the SHEs 114, 116, and 118, and 18 new isotopes of seaborgium (106) and heavier elements; these results have not yet been confirmed.

As indicated in Figure 4, the early transactinide elements find their place back in the main body of the Periodic Table as members of the new 6*d* transition series. The discoverers of the currently known transactinide elements, names and symbols approved by IUPAC in August 1997, and dates of discovery are listed in Table 10.

Fully relativistic calculations have indicated that the electronic configurations of the transactinide elements will be different than those based on simple extrapolation from their lighter homologues in the same group in the periodic table. There may be changes in the valence electron configurations, differences in ionic radii, complexing ability, and other chemical properties. Studies of the chemical properties (25) of elements 104 (rutherfordium) through 106 (seaborgium) in both aqueous and gas phase have now been conducted and confirm that these elements in general resemble the lighter members of groups 4 through 6 of the Periodic Table and should be placed under them in the Periodic Table as the heaviest members of those groups. In agreement with relativistic calculations, reversals in trends in properties in going down groups 4 and 5 have been observed. The behavior of the transactinides cannot be simply extrapolated from their lighter homologues, and in some cases they behave more like actinides of the same oxidation state.

Chemical studies are extremely difficult because the longest-lived isotopes of the transactinides are a minute or less as shown in Fig. 6 and the production rates for their synthesis are extremely small. The first chemical studies of bohrium (element 107) were conducted in 1999 using a longer-lived isotope, 17-s ^{267}Bh, discovered in early 1999. Studies of the volatility of its oxychloride based on detection of the decay of only four atoms showed that it was similar

Table 10. **The Transactinide Elements**

Atomic number	Element	Symbol	Mass number[a]	Discoverers and date of discovery
104	rutherfordium	Rf	261	A. Ghiorso, M. Nurmia, J. Harris, K. Eskola, and P. Eskola, 1969
105	(hahnium) dubnium	(Ha) Db[b]	262	A. Ghiorso, M. Nurmia, K. Eskola, J. Harris, and P. Eskola, 1970
106	seaborgium [54038-81-2]	Sg	266	A. Ghiorso, J. M. Nitschke, J. R. Alonso, C. T. Alonso, M. Nurmia, G. T. Seaborg, E. K. Hulet, and R. W. Lougheed, 1974
107	bohrium	Bh	267	G. Münzenberg, S. Hofmann, F. P. Hessberger, W. Reisdorf, K. H. Schmidt, J. H. R. Schneider, W. F. W. Schneider, P. Armbruster, C. C. Sahm, and B. Thuma, 1981
108	hassium	Hs	269	G. Münzenberg, P. Armbruster, H. Folger, F. P. Hessberger, S. Hofmann, J. Keller, K. Poppensieker, W. Reisdorf, K. H. Schmidt, H. J. Schött, M. E. Leino, and R. Hingmann, 1984
109	meitnerium	Mt	268	G. Münzenberg, P. Armbruster, F. P. Hessberger, S. Hofmann, K. Poppensieker, F. P. Hessberger, S. Hofmann, K. Poppensieker, W. Reisdorf, J. H. R. Schneider, K. H. Schmidt, C. C. Sahm, and D. Vermeulen, 1982

[a] Mass number of longest lived isotopes.

[b] The name dubnium (Db) has been approved by IUPAC, but the name hahnium (Ha) is commonly used in the US.

Note: 109 elements are listed here. In addition, discovery of elements 110–112 has been reported. Discovery of element 110 has been reported by three different groups between 1994–1996, but since they have reported different isotopes, none can be considered confirmation of the others. A Ghiorso *et al.*(1) at the Lawrence Berkeley National Laboratory (LBNL) in Berkeley, California reported evidence for element 110 with mass number 267; S. Hofmann *et al.*(2) at the Gesellschaft für Schwerionenforschung (GSI) at Darmstadt, Germany reported element 110 with mass numbers 269 and 271; Yu. Lazarev *et al.*(3) at the Flerov Laboratory for Nuclear Reactions, Dubna, Russia reported element 110 with mass 273. The group of S. Hofmann has the more convincing data for their discovery of 110, but the half-lives and cross sections of all appear reasonable. In 1995–1996 Hofmann et al.(4,5) also reported discovery of elements 111 and 112 at GSI with mass numbers of 272 and 277, respectively. These elements have not yet been named. In August 1999, scientists at LBNL published evidence for three new superheavy elements(6): 118 with mass number 293, 116 with mass number 289, and 114 with mass number 285. In July 1999, a multinational group(7) working at Dubna, Russia published their evidence for observation of element 114 with mass number 287. A Dubna/Lawrence Livermore National Laboratory group(8) published evidence in Occtober 1999 for element 114 with mass number 289 and later reported(9) observation of element 114 with mass number 288. As of March 2000, none of these reports has been confirmed by another group.

(1) A. Ghiorso *et al.*, *Nucl. Phys.* **A583**, 861 (1994); *Phys. Rev. C* **51**, R2293 (1995).
(2) S. Hofmann *et al.*, *Z. Phys.* **A350**, 277 (1995).
(3) Yu. A. Lazarev *et al.*, *Phys. Rev. C* **54**, 620 (1996).
(4) S. Hofmann *et al.*, *Z. Phys.* **A350**, 281 (1995).
(5) S. Hofmann *et al.*, *Z. Phys.* **A354**, 229 (1996).
(6) V. Ninov *et al.*, *Phys. Rev. Lett.* **83** 1104 (1999).
(7) V. Ninov *et al.*, *Phys. Rev. Lett.* **83** 1104 (1999).
(8) Yu. Ts. Oganessian *et al.*, *Phys. Rev. Lett.* **83**, 3154 (1999).
(9) R. W. Lougheed *et al.*, 219th National ACS meeting, San Francisco, California, March 2000.

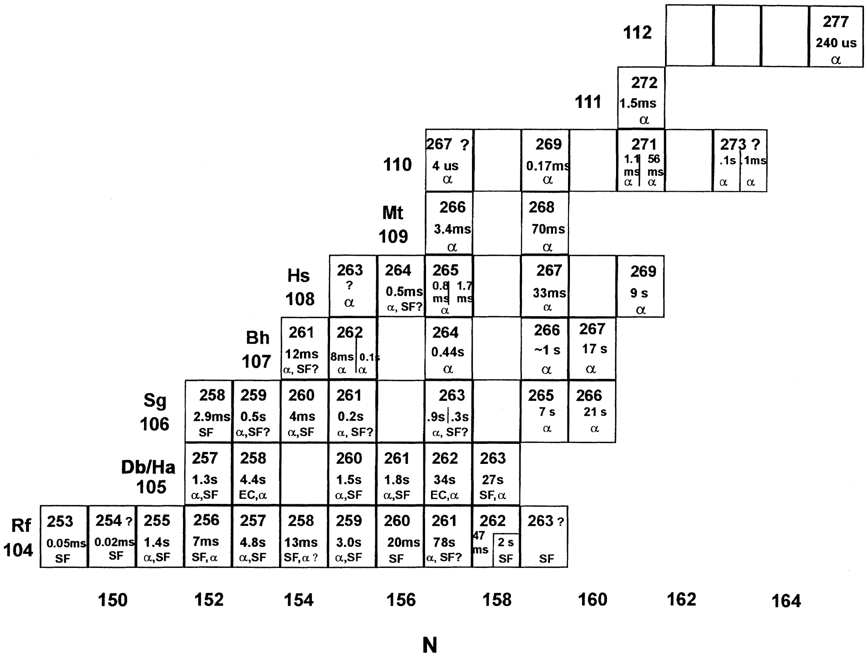


Fig. 6. All known isotopes of rutherfordium (element 104) through element 112 as of 1998.

to those of the lighter group 7 elements, technetium and rhenium, and different from the actinides. studies of hassium (element 108) probably will be possible in the near future using the known 9-s ^{269}Hs. It is expected that isotopes of meitnerium (109) can exist with half-lives long enought to permit studies of its chemical properties, and recent calculations suggest that ^{292}110 will decay by alpha emission with a half-life of about 50 yr. However, the number of atoms that can be produced for study is decreasing rapidly as we go to heavier and heavier elements. New synthesis reactions and improvements in production rates and in the efficiency and speed of chemical separations will be required in order to extend chemical studies to heavier elements.

Studies of the chemical properties of the heaviest elements are challenging for theorists as well as for experimentalists and fully relativistic calculations must be performed. Modern high-speed computers have made possible the calculation of electronic structures and the deviations that might be expected due to relativistic effects (13,26,27). Elements 104 through 112 are predicted to be members of a 6*d* transition series as shown in Figure 4, making them generally homologous in chemical properties with the elements hafnium through mercury as discussed earlier. The 7*p* shell is filled in elements 113–118 and they are expected to be similar to the elements thallium ($Z = 81$) through radon ($Z = 86$), although some calculations have suggested that elements 112 and 114 as well as 118 (eka-Rn) might be volatile, relatively inert gases, rather than similar to lead and mercury. If there is an island of stability at element 126, this element and its neightbors should have chemical properties similar to those of the actinide and lanthanide elements (26).

The 8*s* subshell should fill at elements 119 and 120, thus making these an alkali and alkaline earth metal, respectively. Next, the calculations point to the filling, after the addition of a 7*d* electron at element 121 of the inner 5*g* and 6*f* subshells, 32 places in all, which have been called the superactinide elements and which terminates at element 153. This is followed by the filling of the 7*d* subshell (elements 154 through 162) and 8*p* subshell (elements 163 through 168).

Actually, more careful calculations have indicated that the picture is not this simple, and that other electrons (8*p* and 7*d*) in addition to those identified in the above discussion enter prominently as early as element 121, and other anomalies may enter as early as element 103, thus further complicating the picture. These perturbations, caused by spin-orbit splitting, become especially significant beyond the superactinide series, and lead to predictions of chemical properties that are not consistent, element by element, with those suggested by Figure 4.

It should be pointed out that although these atomic calculations give some general guideance for experimental research, they do not predict the behavior of molecular species under actual experimental conditions. This even more difficult and complex theoretical problem has been addressed recently (28). systematic theoretical studies of heavy element compounds using relativistic quantum-chemical calculations are combined with fundamental physicochemical considerations to make detailed predictions relevant to both gas-phase volatility studies and partitioning studies between aqueous and organic phases.

On the basis of simple extrapolation of known half-lives, it would appear that the half-lives of the elements beyond element 112 would become ever shorter as the atomic number increases, even for the isotopes with the longest half-life for each element. This would make future prospects for the existence of heavier transuranium elements appear extremely unlikely, but new theoretical calculations and experimental observations have changed this outlook and led to optimism concerning the prospects for the synthesis and identification of elements beyond the observed upper limit of the periodic table, elements that have come to be referred to as SuperHeavy Elements.

The existence of superheavy elements was predicted as early as 1955. Theoretical calculations in the mid 1960s, based on filled shells (magic numbers) and other nuclear stability considerations, led to extrapolations to the far transuranium region (2,26,27). These suggestged the existence of closed nucleon shells at proton numbers (atomic numbers) 114 and 126 and neutron number 184 that helped stabilize the nucleus against decay by spontaneous fission, the main cause of instability of the heaviest elements. Table 11 shows the known closed proton and neutron shells and the predicted closed nuclear shells (in parantheses) that were originally predicted might be important in stabilizing the superheavy elements. Included by way of analogy are the long-known closed electron shells observed in the buildup of the electronic structure of atoms. These correspond to the noble gases, and the extra stability of these closed shells is reflected in the relatively small chemical reactivity of these elements. The predicted closed electron shells (in parentheses) occur at $Z = 118$ and 168.

Searches for long-lived superheavy elements in nature were initiated in the late 1960s sparked by the early predictions of half-lives as long as a billion years. If the half-life of a superheavy nucleus should happen to be as long as a few times

Table 11. **Closed Proton (*Z*) and Neutron (*N*) Shells with Closed Electron (Noble Gas) Shells for Comparison**[a]

Z	N	e^-
2(He)	2(^{4}He)	2(He)
8(O)	8(^{16}O)	10(Ne)
20(Ca)	20(^{40}Ca)	18(Ar)
28(Ni)	28(^{56}Ni)	36(Kr)
50(Sn)	50(^{88}Sr)	54(Xe)
82(Pb)	82(^{140}Ce)	86(Rn)
	126(^{208}Pb)	
(114)	(184)	(118)
(126)		
		(168)

[a] Predicted shells shown in parentheses.

10^8yr (now considered to be extremely unlikely), this would be long enough to allow the isotope to survive and still be present on the earth (as in the case of ^{235}U, which has a half-life of 7×10^8 yr), provided that it was initially present as a result of the cosmic nuclear reactions that led to the creation of the solar system. All evidence in nature, direct or indirect, for superheavy elements associated with the island of stability centered around element 114 has been inconclusive. Because of the physical limitations inherent in any experimental technique, it is not possible to say that such superheavy eleemnts do not exist in nature, but only to set limits on the amount that can be present. The results of such searches establish that their concentration is extremely small, eg, much less than one part in 10^{12} parts of ore. Searches have also been made in cosmic rays, meteorites, and moon rocks, with generally negative results except for some indirect evidence of possible previous presence in meteorites during the early history of the meteorite's life. Some evidence was reported for a now extinct superheavy element in the Allende meteorite, which fell in Mexico in 1969. The evidence for such an extinct superheavy element (now considered to be unlikely) was the observation of a unique composition of xenon isotopes that might have been formed from decay by spontaneous fission with a half-life of 10^7–10^9 yr (29). The postulated current synthesis of a broad range of chemical eleemnts, possibly even including superheavy elements, in stars might enhance the prospects for finding even shorter-lived superheavy elements in cosmic rays (30); elements as heavy as uranium have apparently been found in cosmic rays emanating from such stars.

The effects of a rather distinct deformed shell at $N = 152$ were clearly seen as early as 1954 in the alpha-decay energies and half-lives of isotopes of californium, einsteinium, and fermium. In fact, a number of authors have suggested that the entire transuranium region is stabilized by shell effects with an influence that increases markedly with atomic number. Thus the effects of shell substructure lead to an increase in spontaneous fission half-lives of up to about 15 orders of magnitude for the heavy transuranium elements, the heaviest of which would otherwise have half-lives of the order of those for a compound nucleus (10^{14} s or less) and not of milliseconds or longer, as found experimentally. But the influence of the N=152 subshell appeared to be nearly gone by element

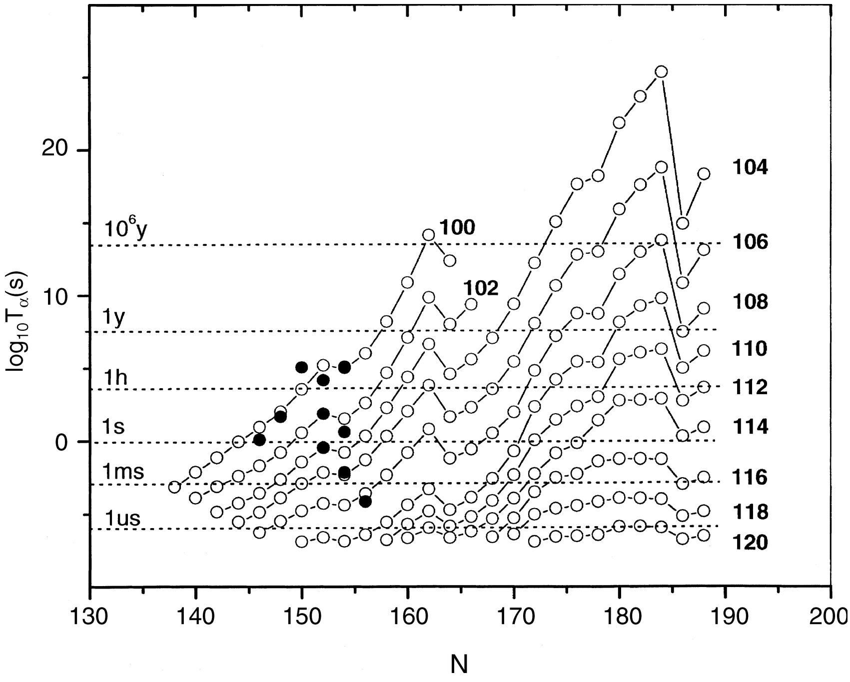


Fig. 7. Theoretical calculation of half-lives for alpha-decay of even-even isotopes of elements 100 through 120 plotted as a function of neutron number. Filled circles represent experimental data (31).

105. However, the recent theoretical calculations of alpha-decay half-lives as a function of neutron number shown in Figure 7 indicate even stronger deformed subshells around $N = 108$ (hassium) that lengthen the half-lives of nuclides in this region. The measurement of the unexpectedly long half-life of 21 s for the isotope of seaborgium with 160 neutrons, the identification of ^{266}Bh and ^{267}Bh with half-lives of ~1 and ~20 s, respectively, and the discovery that the elements bohrium (107) through 112 decay predominantly by alpha emission rather than spontaneous fission provide experimental support for these predictions. Furthermore, the calculations indicate that the half-lives continue to lengthen as neutron number 184 is approached so half-lives of milliseconds or more are predicted for isotopes of elements up through 116. The odd-neutron and odd-proton isotopes are expected to be considerably longer so it is reasonable to expect half-lives of milliseconds or longer for some isotopes of elements up through 120. It is now predicted that new isotopes with measurable half-lives can be produced all along the path to the "island" of nuclear stability at $Z = 114$ and $N = 184$. It is no longer a remote and inaccessible island and may extend as far as element 120!

Attempts at GSI in 1998 failed to produce element 113 using the same techniques as for elements 110–112. However, in 1999 evidence for the long-sought superheavy elements was reported by three other groups. (See footnote to Table 10.) In August, the Heavy Element Nuclear and Radiochemistry Group of the Lawrence Berkeley National Laboratory (LBNL)/University of California, Berkeley reported the observation of three six-member alpha-decay chains from

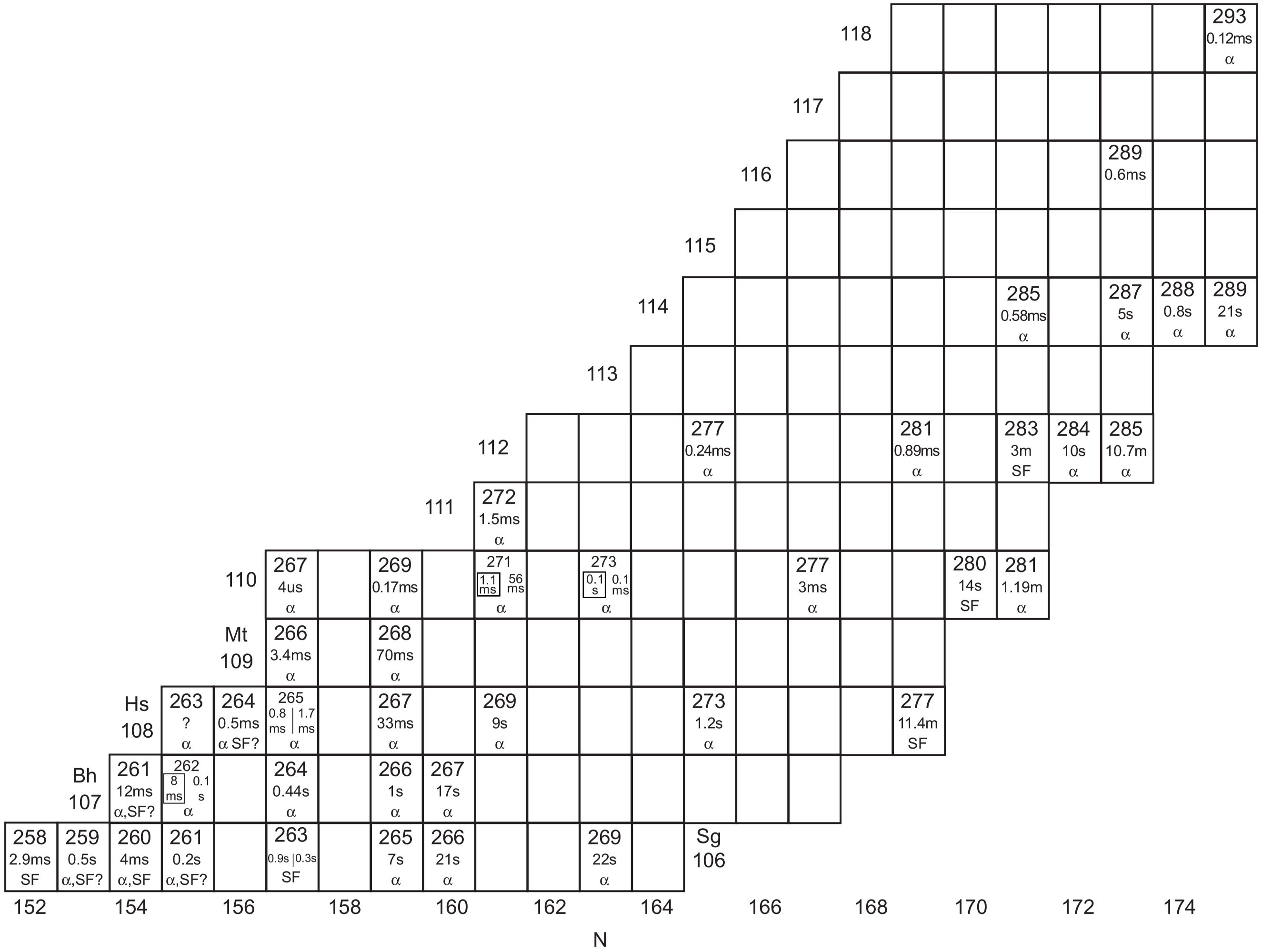


Fig. 8. All isotopes of seaborgium through element 118 reported as of early 2000.

^{293}118 produced in the reaction of ^{208}Pb targets with ^{86}Kr projectiles at the LBNL Cyclotron. The newly completed Berkeley Gas-filled Separator was used to separate and measure these decay chains. The sequence of successive alpha-decays from element 118 also produced the new elements 116 and 114 and new isotopes of 110, hassium, and seaborgium. The alpha-decay energies and half-lives of the all of the 118 decay chain members were in remarkable agreement with recent predictions (31). In july, a multinational group working at the U-400 cyclotron at the Flerov Laboratory for Nuclear Reactions in Dubna, Russia, reported using their vacuum separator to detect and measure two events in which alpha-decay was followed by spontaneous fission decay which they attributed to ^{287}114 produced in the bombardment of ^{242}Pu targets with ^{48}Ca projectiles via emission of three neutrons from the compound nucleus. In October, a Dubna/Lawrence Livermore National Laboratory group reported using the Dubna gas-filled recoil separator to measure a single three-member alpha-decay chain followed by spontaneous fission, which was produced in the bombardment of ^{244}Pu with ^{48}Ca projectiles. They attributed this to single event to ^{289}114 formed via a 3-neutron out reaction. These results were also in agreement with recent prodictions. In subsequent bombardments, they also recently reported observation of a two-member alpha-decay chain followed by spontaneous fission which they attribute to the decay of ^{288}114 produced via a 4-neutron out reaction. None of these reports has yet been confirmed, but they are all included in Figure 8. If all of these and the reported new ^{266,267}Bh isotopes are confirmed, 18 new heavy element isotopes will have been added to the chart of the nuclides, nearly doubling the number known beyond element 105. The prospects for

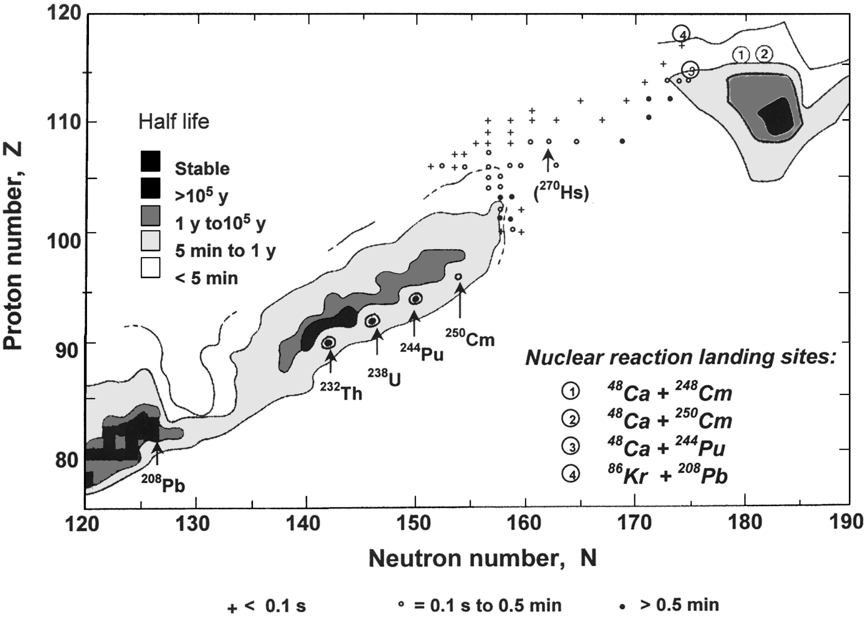


Fig. 9. Plot of heavy element topology from 1978. New heavy element isotopes reported as of 1999 are shown with the following symbols: + <0.1 s; o = 0.1 s to 0.5 min; • >0.5 min.

producing element 119 using similar reactions to those used for 118 appear promising. It is also expected to decay by a long sequence of high-energy alpha particles, which will produce the missing elements 117, 115, and 113.

A topological representation from about 1978 of the heavy element region and the spherical island of superheavy elements around $Z = 114$ and $N = 184$ is shown in Figure 9. The new heavy element isotopes discovered since then have been added. Possible reactions for making element 116 isotopes and their landing sites are shown as 1 and 2. The newly reported landing sites for $^{289}114$ and $^{293}118$ and the nuclear reactions used to make them are shown as 3 and 4. The doubly magic deformed nucleus ^{279}Hs ($Z = 108$, $N = 162$) is shown; it is expected to have a half-life of only about 5 s. Although the spherical doubly magic nucleus $^{298}114$ is now predicted to have a half-life of only about 12 min, the beta-stable nuclide $^{292}110$ is expected to alpha-decay with a half-life of about 50 yr. although it now appears that many long-lived superheavy elements can exist, new imaginative production reactions and techniques for increasing the overall yields and provision for “stockpiling” long-lived products for future studies must be developed in order to explore this exciting new landscape.

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