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Actinides and Transactinides

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April 1991

ACTINIDES AND TRANSACTINIDES

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 RADIOACTIVITY, NATURAL; 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 and thorium, 25 each; protactinium, 20; uranium, neptunium, plutonium, americium, curium, californium, einsteinium, and fermium, 15 each; berkelium, mendelevium, nobelium, and lawrencium, 10 each. 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 six transactinide elements).

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 HAZARDOUS WASTE TREATMENT; NUCLEAR REACTORS, WASTE MANAGEMENT).

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

Table 1. The Actinide Elements

Atomic number	Element	CAS Registry Number	Symbol	Atomic weight ^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	260	A. Ghiorso, T. Sikkeland, A. E. Larsh, and R. M. Latimer, 1961

^aMass number of longest lived or most available isotope.

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 exceptions 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,

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

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:

and

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 .

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

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 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} neutrons/(cm²·s) 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 of 3×10^{14} neutrons/(cm²·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/(cm²·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

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/($\text{cm}^2\cdot\text{s}$).

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, 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

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.

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,

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. Trans-fermium 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 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.

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

Table 2. Long-Lived Actinide Nuclides Suitable for Investigation

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 Bk ^b	[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

^aNatural mixture (²³⁸U, 99.3%; ²³⁵U, 0.72%; and ²³⁴U, 0.006%). Half-life given is for the major constituent ²³⁸U.

^bAvailable so far only in trace quantities from charged particle irradiations.

^cAvailable only in very small amounts from neutron irradiations in thermonuclear explosions.

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 ²³⁷Np is relatively convenient to work with in chemical investigations. Because of the existence of large quantities of the fissionable isotope ²³⁹Pu, 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 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

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 Ha	106	107	108	109	(110)	(111)	(112)	(113)	(114)	(115)	(116)	(117)	(118)
(119)	(120)	(121)	(154)	(155)	(156)	(157)	(158)	(159)	(160)	(161)	(162)	(163)	(164)	(165)	(166)	(167)	(168)

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
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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
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Superactinides	(122)	(123)	(124)	(125)	(126)											(153)
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Fig. 4. Futuristic periodic table showing predicted locations of a large number of transuranium elements (atomic numbers in parentheses).

become 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 $7s$, $6d$, and $5f$ 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 $4f$ electrons are added in the lanthanide series, beginning with cerium and ending with lutetium; in the actinide elements, fourteen $5f$ 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

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

Atomic number	Element	CAS Registry Number	Electronic configuration ^a
57	lanthanum	[7439-91-0]	$5d6s^2$
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		$6d7s^2$
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		$(5f^{14}6d7s^2 \text{ or } 5f^{14}7s^27p)$

^aBeyond xenon.

^bBeyond radon. The configurations enclosed in parentheses are predicted.

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				

states do not exist in aqueous solution. The wide variety of colors exhibited by 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

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).

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 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

and AmO₂⁺ are very complicated and have been studied extensively. In the case of plutonium, the situation is especially complex: four oxidation states 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 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 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

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 $\pm$ 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 $\pm$ 2	418 (100)	3900	α	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 $\beta = 101.8^\circ$	1.0963	19.86, 21
				β	122–207	BC monoclinic	0.9284	1.0463 $\beta = 92.13^\circ$	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 $\pm$ 30			α	below 900	hexagonal	0.339		1.101	15.1, 25
				β		FC cubic	0.575			8.70, 25
einsteinium	860 $\pm$ 30			α	below 860	hexagonal				
				β		FC cubic	0.575			8.84

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 $5d$ 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 $5f$ electrons in the lighter actinides are not as localized as the $4f$ electrons in the lanthanides and, with energies close to those of the $6d$ and $7s$ electrons, participate actively in bonding. The participation in bonding by $5f$ electrons is apparently more prominent in the early actinides than in the heavier actinides, where a localized behavior becomes evident. The behavior of the $5f$ 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^+ ions form the insoluble crystalline salt $\text{NaMO}_2(\text{O}_2\text{CCH}_3)_3$. The hydroxides of all four ionic types are insoluble; in the case of the MO_2^+ ions, compounds of the type exemplified by sodium diuranate ($\text{Na}_2\text{U}_2\text{O}_7$) can be precipitated from alkaline solution. The NpO_5^{3-} and PuO_4^{2-} 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.

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			Angle, deg	Density, g/mL
					a_0 , nm	b_0 , nm	c_0 , nm		
AcH ₂	black		cubic	fluorite ($Fm\bar{3}m$)	0.5670				8.35
ThH ₂	black		tetragonal	$F4/mmm$	0.5735		0.4971		9.50
Th ₄ H ₁₅	black		cubic	$I43d$	0.911				8.25
α -PaH ₃	gray		cubic	$Pm\bar{3}n$	0.4150				10.87
β -PaH ₃	black		cubic	β -W	0.6648				10.58
α -UH ₃	?		cubic	$Pm\bar{3}n$	0.4160				11.12
β -UH ₃	black		cubic	β -W ($Pm\bar{3}n$)	0.6645				10.92
NpH ₂	black		cubic	fluorite	0.5343				10.41
NpH ₃	black		trigonal	$P\bar{3}c1$	0.651		0.672		9.64
PuH ₂	black		cubic	fluorite	0.5359				10.40
PuH ₃	black		trigonal	$P\bar{3}c1$	0.655		0.676		9.61
AmH ₂	black		cubic	fluorite	0.5348				10.64
AmH ₃	black		trigonal	$P\bar{3}c1$	0.653		0.675		9.76
CmH ₂	black		cubic	fluorite	0.5322				10.84
CmH ₃	black		trigonal	$P\bar{3}c1$	0.6528		0.6732		10.06
BkH ₂	black		cubic	fluorite	0.5248				11.57
BkH ₃	black		trigonal	$P\bar{3}c1$	0.6454		0.6663		10.44
Ac ₂ O ₃	white		hexagonal	La ₂ O ₃ ($P\bar{3}m1$)	0.407		0.629		9.19
Pu ₂ O ₃	?		cubic	Ia ₃ (Mn ₂ O ₃)	1.103				10.20
Pu ₂ O ₃	black	2085	hexagonal	La ₂ O ₃	0.3841		0.5958		11.47
Am ₂ O ₃	tan		hexagonal	La ₂ O ₃	0.3817		0.5971		11.77
Am ₂ O ₃	reddish brown		cubic	Ia ₃	1.103				10.57
Cm ₂ O ₃	white to faint tan	2260	hexagonal	La ₂ O ₃	0.3792		0.5985		12.17
Cm ₂ O ₃			monoclinic	C2/m (Sm ₂ O ₃)	1.4282	0.3641	0.8883	$\beta = 100.29$	11.90
Cm ₂ O ₃	white		cubic	Ia ₃	1.1002				10.80
Bk ₂ O ₃	light green		hexagonal	La ₂ O ₃	0.3754		0.5958		12.47
Bk ₂ O ₃	yellow-green		monoclinic	C2/m	1.4197	0.3606	0.8846	$\beta = 100.23$	12.20
Bk ₂ O ₃	yellowish brown		cubic	Ia ₃	1.0887				11.66
Cf ₂ O ₃	pale green		hexagonal	La ₂ O ₃	0.372		0.596		12.69
Cf ₂ O ₃	lime green		monoclinic	C2/m	1.4121	0.3592	0.8809	$\beta = 100.34$	12.37
Cf ₂ O ₃	pale green		cubic	Ia ₃	1.083				11.39
Es ₂ O ₃	white		hexagonal	La ₂ O ₃	0.37		0.60		12.7
Es ₂ O ₃	white		monoclinic	C2/m	1.41	0.359	0.880	$\beta = 100$	12.4
Es ₂ O ₃	white		cubic	Ia 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 ₂ O ₅	white		cubic	fluorite-related	0.5446 or 0.5492				11.14
Np ₂ O ₅	dark brown		monoclinic	P2 ₁ /c	0.4183	0.6584	0.4086	$\beta = 90.32$	8.18
α -U ₃ O ₈	black-green	1150 (dec)	orthorhombic	C2mm	0.6716	1.1960	0.4147		8.39
β -U ₃ O ₈	black-green		orthorhombic	Cmcm	0.7069	1.1445	0.8303		8.32
γ -UO ₃	orange	650 (dec)	orthorhombic	Fddd	0.981	1.993	0.971		7.80
AmCl ₂	black		orthorhombic	Pbnm (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 (P3m1)	0.456		0.699		6.63
CfI ₂	violet		rhombohedral	CdCl ₂ (R3m)	0.743			$\alpha = 36$	6.58
AcF ₃	white		trigonal	LaF ₃ (P3c1)	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 (Pnma)	0.670	0.709	0.441		9.70
BkF ₃	yellow-green		trigonal	LaF ₃	0.697		0.714		10.15
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

Table 8 (continued)

Compound	Color	Melting point, °C	Symmetry	Space group or structure type	Lattice parameters			Angle, deg	Density, g/mL
					a_0 , nm	b_0 , nm	c_0 , nm		
PuCl ₃	emerald green	760	hexagonal	UCl ₃	0.7394		0.4245		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 (<i>Cmcm</i>)	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 (<i>P6₃/m</i>)	0.806		0.468		5.85
UBr ₃	red	730	hexagonal	<i>P6₃/m</i>	0.7936		0.4438		6.55
NpBr ₃	green		hexagonal	UBr ₃	0.7916		0.4390		6.65
NpBr ₃	green		orthorhombic	TbCl ₃ (<i>Cmcm</i>)	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 $\pm$ 5	orthorhombic	TbCl ₃	0.4041	1.2700	0.9135		6.85
BkBr ₃	light green		monoclinic	AlCl ₃ (<i>C2/m</i>)	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 (<i>R$\bar{3}$</i>)	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 (<i>Cmcm</i>)	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 (<i>R$\bar{3}$</i>)	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		2.087		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 (<i>C2/c</i>)	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	<i>C2/c</i>	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

435	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	I4 ₂ d	1.153		0.519		
	α -UF ₅	grayish white		tetragonal	I4/m	0.6512		0.4463		5.81
	β -UF ₅	pale yellow		tetragonal	I4 ₂ d	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
	β -UCl ₅	red-brown		triclinic	P1	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	P3m1	1.09		0.603		3.62

^aAt 151.6 kPa, to convert kPa to atm, divide by 101.3.

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 (see ORGANOMETALLICS). 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 ($\text{Cp} = \text{C}_5\text{H}_5$); each, except the uranium compound, is relatively stable and appreciably volatile but is sensitive to air (23). The tetrakis-cyclopentadienyl 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 ($\text{M} = \text{Th}, \text{U}, \text{Np}$), 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 $\text{Th}(\text{COT})_2$, $\text{Pa}(\text{COT})_2$, $\text{U}(\text{COT})_4$, $\text{Np}(\text{COT})_4$, and $\text{Pu}(\text{COT})_4$, and substituted derivatives of these (23). Characterized by monoclinic symmetry with a π -binding sandwich structure involving $5f$ 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, $\text{M}(\text{C}_3\text{H}_5)_4$, but these are stable only at low temperatures. Many organoactinide complexes with σ and π ligands of the type $\text{Cp}_3\text{M}-\text{R}$ ($\text{R} = \text{alkyl}, \text{aryl}, \text{or alkynyl}$) 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 = $\text{CN} = 6$), which are 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 $4f$ and $5f$ shells in which the $4f^n$ and $5f^n$ configura-

Table 9. Ionic Radii of Actinide and Lanthanide Elements

No. of 4f or 5f 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						
13	Yb ³⁺	0.0868						
14	Lu ³⁺	0.0861						

tions 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).

Practical Applications

The practical use of three actinide nuclides, ²³⁹Pu, ²³⁵U, and ²³³U, 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 ²³⁸U (through conversion to fissionable ²³⁹Pu) and nonfissionable ²³²Th (through conversion to fissionable ²³³U) can be accomplished by breeder reactors.

In addition, three other actinide nuclides (²³⁸Pu, ²⁴¹Am, and ²⁵²Cf) have other practical applications (6). One gram of ²³⁸Pu 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 $^{241}\text{Am}-\text{Be}$ 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.

TRANSACTINIDES

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. Although only six such elements, numbers 104–109, were definitely known in 1991, there are good prospects for the discovery of a number of additional elements just beyond number 109 or in the region of larger atomic numbers. They are synthesized by the bombardment of heavy nuclides with heavy ions.

As indicated in Figure 4, the early transactinide elements find their place back in the main body of the periodic table. The discoverers of the currently known transactinide elements, suggested names and symbols, and dates of discovery are listed in Table 10 (19). Because there are competing claims for the discovery of these elements, the two groups of discoverers in each case have suggested names for elements 104 and 105. In the case of elements 106–109, names for the elements have not been suggested in order to avoid another duplication.

Study of the chemical properties of element 104 has confirmed that it is indeed homologous to hafnium as demanded by its position in the periodic table (20). Chemical studies have been made for element 105, showing some similarity to tantalum (25); no chemical studies have been made for elements 106–109. Such studies are very difficult because the longest-lived isotope of 104 ($^{261}104$) has a half-life of only about 1 min, of 105 ($^{262}105$) a half-life of about 40 s, of 106 ($^{263}106$) a half-life of about 1 s, and of elements 107–109 half-lives in the range of milliseconds.

On the basis of the simplest projections it is expected that the half-lives of the elements beyond element 109 will become shorter as the atomic number is increased, and this is true even for the isotopes with the longest half-life for each element. This is illustrated by Figure 6, in which the half-lives of the longest-lived

Table 10. The Transactinide Elements

Atomic number	Element	Symbol	Atomic weight ^a	Discoverers and date of discovery
104	rutherfordium [53850-36-5] (U.S.A.)	Rf	261	A. Ghiorso, M. Nurmia, J. Harris, K. Eskola, and P. Eskola, 1969
104	kurchatovium (USSR)	Ku		G. N. Flerov, Yu. Ts. Oganessian, Yu. V. Lobanov, V. I. Kuznetsov, V. A. Druin, V. P. Perelygin, K. A. Gavrihov, S. P. Tretiakova, and V. M. Plotko, 1964
105	hahnium [53850-35-4] (U.S.A.)	Ha	262	A. Ghiorso, M. Nurmia, K. Eskola, J. Harris, and P. Eskola, 1970
105	nielsbohrium (USSR)	Ns		G. N. Flerov, Yu. Ts. Oganessian, Yu. V. Lobanov, Yu. A. Lazarev, and S. P. Tretiakova, 1970
106	[54038-81-2]		263	A. Ghiorso, J. M. Nitschke, J. R. Alonso, C. T. Alonso, M. Nurmia, G. T. Seaborg, E. K. Hulet, and R. W. Lougheed, 1974
106				Yu. Ts. Oganessian, Yu. P. Tretiakov, A. S. Iljinov, A. G. Demin, A. A. Pleve, S. P. Tretiakova, V. M. Plotko, M. P. Ivanov, N. A. Danilov, Yu. S. Korotkin, and G. N. Flerov, 1974
107			262	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
107				Y. T. Oganessian, A. G. Demin, N. A. Danilov, M. P. Ivanov, A. S. Iljinov, N. N. Kolesnikov, B. N. Markov, V. M. Plotko, S. P. Tretiakova, and G. N. Flerov, 1976
108			265	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			264	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

^aMass number of longest lived isotopes.

Fig. 6. Longest-lived isotopes of transuranium elements.

isotopes (for alpha and spontaneous fission decay) of transuranium elements are plotted against the increasing atomic number. Thus, if this rate of decrease could be extrapolated to ever-increasing atomic numbers, it would present somewhat dismal future prospects for heavier transuranium elements, but other factors have entered the picture in recent years. These have led to an 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.

Complicated theoretical calculations, based on filled shell (magic number) and other nuclear stability considerations, have led to extrapolations to the far transuranium region (2,26,27). These suggest the existence of closed nucleon shells at $Z = 114$ (proton number) and $N = 184$ (neutron number) that exhibit great resistance to decay by spontaneous fission, the main cause of instability for the heaviest elements. Earlier considerations had suggested a closed shell at $Z = 126$, by analogy to the known shell at $N = 126$, but this is not now considered to be important.

Table 11 illustrates the known closed proton and neutron shells and the predicted closed nuclear shells (shown in parentheses) that 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 (in parentheses) closed electronic structures occur at $Z = 118$ and $Z = 168$.

Enhancing the prospects for the actual synthesis and identification of superheavy nuclei is the fact that the calculations show the doubly magic nucleus $^{298}114$ not to be a single long-lived specimen but to be a part of a rather large "island of stability" in a "sea of spontaneous fission" (2,26,27). The grid lines of Figure 7 show "magic" numbers of protons or neutrons giving rise to exceptional stability. The doubly magic region at 82 protons and 126 neutrons is shown by a

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

<i>Z</i>	<i>N</i>	<i>e</i> ⁻
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)

^aPredicted shells shown in parentheses.

Fig. 7. Allegorical representation of island of stability (magic island) (28).

mountain; a predicted doubly magic but less stable region at 114 protons and 184 neutrons is shown by a hill at the island of stability. The ridges depict areas of enhanced stability due to a single magic number. Other calculations suggest that there should be stabilizing, deformed nuclear shells (or subshells) at lower neutron numbers, such as $N = 162$.

The effects of a rather distinct deformed shell at $N = 152$ were clearly seen as early as 1954 in the alpha-decay energies 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. This gives hope for the synthesis and identification of several elements beyond the present heaviest (element 109) and suggest that the peninsula of nuclei with measurable half-lives may extend up to the island of stability at $Z = 114$ and $N = 184$.

Turning to consideration of electronic structure, upon which chemical properties must be based, modern high speed computers have made possible the calculation of such structures (13,26,27). The calculations show that elements 104 through 112 are formed by filling the $6d$ electron subshell, which makes them, as expected, homologous in chemical properties with the elements hafnium ($Z = 72$) through mercury ($Z = 80$). Elements 113 through 118 result from the filling of the $7p$ subshell and are expected to be similar to the elements thallium ($Z = 81$) through radon ($Z = 86$). Thus these calculations are consistent with the periodic table shown in Figure 4, which shows the filling of the electron subshells extending beyond element 118.

The calculations indicate that the $8s$ 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 $7d$ electron at element 121 of the inner $5g$ and $6f$ subshells, 32 places in all, which the author has termed the superactinide elements and which terminates at element 153. This is followed by the filling of the $7d$ subshell (elements 154 through 162) and $8p$ subshell (elements 163 through 168).

Actually, more careful calculations have indicated that the picture is not this simple. The calculations indicate that other electrons ($8p$ and $7d$) 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. The largest deviations occur far beyond the region of expected nuclear stability, the only region where it might be possible to synthesize or find superheavy elements.

Thus it can be seen that elements in and near the island of stability based on element 114 can be predicted to have chemical properties as follows. Element 114 should be a homologue of lead, that is, should be eka-lead, and element 112 should be eka-mercury, element 110 should be eka-platinum, etc (26,27). If there is an island of stability at element 126, this element and its neighbors should have chemical properties like those of the actinide and lanthanide elements (26).

Attempts to synthesize and identify superheavy elements, through bombardments of a wide range of heavy nuclides with a wide range of heavy ions, have so far been unsuccessful (27). Unfortunately, the yield of the desired product nuclei is predicted to be very small because the overwhelming proportion of the nuclear reactions lead to fission and other reactions, rather than to the desired synthesis of superheavy nuclei through amalgamation of the heavy ion projectile and the target nucleus. An inherent difficulty in the synthesis of the superheavy nuclei situated near the center of the island of stability is the simultaneous requirement that there be a sufficient number of neutrons as well as protons in the product nucleus. The desired product nuclei have larger ratios of neutrons to

protons than the constituent projectiles and target nuclei, and hence, somewhat unusual nuclear reactions are required. There is no way to know, prior to the actual experimental attempts, which nuclear reactions will be most effective. There are a number of aspects of the dynamics of the reaction of the heavy incident nuclear projectile with the heavy target nucleus that are not understood and that might present serious or fatal impediments to the production of superheavy nuclei; eg, the coulomb repulsive force exerted on a heavy projectile may be too large relative to the nuclear attractive force to allow the desired amalgamation reaction to occur, and nuclear matter may be too viscous to allow the required ready amalgamation of the incident heavy ion with the heavy target nucleus.

If the half-life of a superheavy nucleus should happen to be as long as a few times 10^8 yr (now considered to be very 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. Every attempt to find evidence in nature, direct or indirect, of the 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 elements do not exist in nature. The results of such searches establish that the concentration, if they are present, 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 former presence in meteorites during the early history of the meteorite's life. There was some evidence found 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 elements, possibly 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.

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