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ACTINIDES AND TRANSACTINIDES

I. Actinides

The actinide elements are a group of chemically similar elements with atomic numbers 89 through 103 (or, more strictly speaking, atomic numbers 90 through 103), and their names, symbols, and atomic numbers are given in Table 1, which also includes information on their discovery. (See also Radioactive elements, natural; Thorium; Uranium; Plutonium; Nuclear reactors; Radioisotopes.)

Each of the elements has a number of isotopes, all radioactive, some of which can be obtained in isotopically pure form. More than 200 in total, most are of synthetic origin, produced by neutron or charged particle induced transmutations. 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, fermium, 15; berkelium, mendelevium, nobelium, 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 which are chosen on the basis of half-life and availbility 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 and 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 identificaiton of nine more actinide elements (and three 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. 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.

Source

Only the first six members of the actinide group have been found to occur in nature. Actinium and protactinium are decay products of the naturally occurring uranium isotope

Table 1. The Actinide Elements

Atomic number	Element	Symbol	Atomic weight[a]	Discoveries and date of discovery
89	actinium	Ac	227	A. Debierne, 1899
90	thorium	Th	232	J. J. Berzelius, 1828
91	protactinium	Pa	231	O. Hahn and L. Meitner, 1917, and F. Soddy and J. A. Cranston, 1917
92	uranium	U	238	M. H. Klaproth, 1789
93	neptunium	Np	237	E. M. McMillan and P. H. Abelson, 1940
94	plutonium	Pu	242	G. T. Seaborg, E. M. McMillan, J. W. Kennedy, and A. C. Wahl, 1940-41
95	americium	Am	243	G. T. Seaborg, R. A. James, L. O. Morgan, and A. Ghiorso, 1944-45
96	curium	Cm	248	G. T. Seaborg, R. A. James, A. Ghiorso, 1944
97	berkelium	Bk	249	S. G. Thompson, A. Ghiorso, and G. T. Seaborg, 1949
98	californium	Cf	249	S. G. Thompson, K. Street, Jr., A. Ghiorso, and G. T. Seaborg, 1950
99	einsteinium	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

Table 1. The Actinide Elements (Con't.)

Atomic number	Element	Symbol	Atomic weight[a]	Discoveries and date of discovery
100	fermium	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	Md	258	A. Ghiorso, B. G. Harvey, G. R. Choppin, S. G. Thompson, and G. T. Seaborg, 1955
102	nobelium	No	259	A. Ghiorso, T. Sikkeland, J. R. Walton, and G. T. Seaborg, 1958
103	lawrencium	Lr	260	A. Ghiorso, T. Sikkeland, A. E. Larsh, and R. M. Latimer, 1961

[a] Mass number of longest lived or more available 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 very 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. 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 can be synthetic in origin for practical purposes, i.e., they are products of nuclear reactions wherein one element is converted into another by means of irradiations with neutrons or bombardments with protons, deuterons, helium ions, or ions heavier than helium ions ("heavy ions"). 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.

The synthesis and chemical isolation of these elements are discussed in this section; more detail on useful individual isotopes is given in the following section Experimental Methods of Investigation.

Actinium can be prepared by the transmutation of radium,

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

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,

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

However, the quantity of ^{231}Pa produced in this manner is much less than the amount (more than 100 grams) 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 ionic species and then colloidal particles. These are not extractable from water by organic solvents; losses may occur by adsorption to containers; and protactinium may be adsorbed and carried on 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 which utilize ^{235}U and ^{238}U as fuel. The following transmutations occur:

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

and

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

The wastes from uranium and plutonium processing of the reactor fuel usually contain the neptunium. Precipitation, solvent extraction, ion exchange, and volatility procedures 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 in ^{238}U to yield ^{239}Pu.

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

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

The plutonium usually contains isotopes of higher mass number (see Figure 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

$$^{237}\mathrm{Np} + n \longrightarrow {}^{238}\mathrm{Np} \qquad {}^{238}\mathrm{Np} \xrightarrow[2.1\ \mathrm{d}]{\beta^-} {}^{238}\mathrm{Pu}$$

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 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 per square centimeter per second 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 one kilogram of ^{239}Pu, about one milligram of ^{252}Cf would be present after five to ten years of continuous irradiation at a neutron flux of 3×10^{14} neutrons per square centimeter per second. 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, ($\sim 10^{15}$ neutrons per square centimeter per second), 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 milligram quantities of berkelium and milligram quantities of einsteinium. The elements 95 to 100 are also produced in increasing quantities as the result of operation of 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. 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 was then subject to considerable delay, pending the production of larger amounts. Solvent extraction is another useful method for purifying and separating actinide elements.

There are many similarities in the chemical properties of the lanthanide elements (see Rare earth metals) and those of the actinide elements, especially where the elements are compared in the same state of oxidation.

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. It can be seen that 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, for example, the anions chloride, nitrate, citrate, lactate, α-hydroxyisobutyrate, and ethylenediaminetetraacetate.

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. 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, 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)orthophosphoric acid, 2-ethylhexyl hydrogen phenylphosphonic acid, and tri-n-butyl phosphate. Excellent anion extracting agents include tertiary amines such as tricapryl amine or trilauryl amine, or quaternary amines such as tricaprylmethyl ammonium chloride (nitrate, thiocyanate). 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. 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 with 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,

$$^{255}\mathrm{U} \xrightarrow{\beta^-} {}^{255}\mathrm{Np} \xrightarrow{\beta^-} {}^{255}\mathrm{Pu} \xrightarrow{\beta^-} \dots {}^{255}\mathrm{Fm}$$

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 which must capture neutrons have half-lives so short as to preclude their presence in the appreciable concentrations that are necessary. Transfermium elements are prepared in charged-particle bombardments. 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 the heaviest actinide elements, mendelevium, nobelium, and lawrencium have been identified and 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), and these isotopes with their half-lives are listed in Table 2. Not all of these are available as individual

Table 2. Actinide Nuclides Suitable for Investigations with Weighable Quantities

Element	Isotope	Half-life
actinium	^{227}Ac	21.8 y
thorium	^{232}Th	1.41×10^{10} y
protactinium	^{231}Pa	3.25×10^{4} y
uranium	^{238}U^{a}	4.47×10^{9} y
neptunium	^{236}Np^{b}	1.29×10^{6} y
	^{237}Np	2.14×10^{6} y
plutonium	^{238}Pu	87.8 y
	^{239}Pu	24,400 y
	^{240}Pu	6540 y
	^{241}Pu	14.9 y
	^{242}Pu	3.87×10^{5} y
	^{244}Pu	8.3×10^{7} y
americium	^{241}Am	433 y
	^{242m}Am	152 y
	^{243}Am	7400 y
curium	^{242}Cm	163.0 d
	^{243}Cm	30 y
	^{244}Cm	18.1 y
	^{245}Cm	8540 y
	^{246}Cm	4800 y
	^{247}Cm	1.6×10^{7} y
	^{248}Cm	3.6×10^{5} y
	^{250}Cm^{c}	1.1×10^{4} y
berkelium	^{247}Bk^{b}	1380 y
	^{249}Bk	314 y
californium	^{249}Cf	350 y
	^{250}Cf	13.1 y
	^{251}Cf	898 y
	^{252}Cf	2.6 y
einsteinium	^{253}Es	20.5 d
	^{254}Es	276 d
	^{255}Es	40 d
fermium	^{257}Fm	100 d

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[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 tracer quantities from charged particle irradiations.

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

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 generally necessary for their manipulation. On a laboratory scale, enclosed containers (gloved boxes) are used to prevent the spread of radioactive substances. In some work, all operations are performed by remote control. Neptunium in the form of the isotope ^{237}Np is relatively safe 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 one of the most dangerous poisons by reason of its intense alpha radioactivity (1.4×10^8 alpha particles per minute per milligram) and of 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 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 since it has a relatively high specific alpha radioactivity, emitting about 7×10^9 alpha particles per minute per milligram. 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. Einsteinium, as 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. Weighable amounts of berkelium, californium, and einsteinium are very difficult to handle because of their intense radioactivity. Spontaneous fission is a mode of decay for ^{252}Cf (half-life, 2.6 y), one microgram of which emits approximately 2×10^{8} neutrons per minute, and the chief mode of decay of ^{254}Cf (half-life, 56 d), one microgram of which emits approximately 8×10^{10} neutrons per minute. Californium produced in the highest flux reactors unfortunately contains ^{252}Cf, and this makes it very difficult to handle. In work with any 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 used when it is available.

Special techniques for experimentation with the actinide elements have been devised because of the potential health hazard to the experimenter and because the amounts of material available are sometimes so very small. In addition, investigations are frequently carried out on the tracer scale, where the substance under examination is present in very low concentration and its radioactivity offers a means for detecting its presence. Such procedures are, of course, applied to work 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 and continue to be used to some extent for these 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, of course, not applicable to some other important fields of investigation, such as crystallography, metallurgy, and spectroscopy.

Microchemical or ultramicrochemical techniques are used extensively in chemical studies of actinide elements. 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 to permit the taking of quantitative measurements with these minute quantities of material; some balances measure magnetic forces due to the paramagnetic nature of the ions. 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 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, however, on the basis of earlier chemical studies of neptunium and plutonium, the similarity between the actinide and the lanthanide elements was recognized. The intensive study of the heaviest elements shows that a series of elements similar to the lanthanide series begins at actinium. Figure 4 shows the position of the actinide and the lanthanide elements in the periodic table. Corresponding pairs of elements show similarities in certain basic properties, notably (*1*) resemblances in spectroscopic and magnetic behavior which arise because of the similarity of electronic configurations for the ions of the homologous elements in the same state of oxidation, and (*2*) correspondences 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 the most stable oxidation state in aqueous solution until americium is reached. The elements uranium through americium have several oxidation states, and there is no analogous example among the lanthanide elements. These differences can be interpreted as resulting from the proximity in the energy of the 7*s*, 6*d*, and 5*f* electronic levels in this region.

Table 3 presents the electronic configuration or the best prediction for the electronic configuration of the actinide elements. Similar information for the lanthanide elements is given for purposes of comparison. As is indicated, fourteen 4*f* electrons are added in the lanthanide series beginning with cerium (atomic number 58) and ending with lutetium (atomic number 71); and in the actinide elements, fourteen 5*f* electons are added beginning formally with thorium and ending with lawrencium (atomic number 103). 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.

Measurements of paramagnetic susceptibility, paramagnetic resonance, light absorption, 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_2S_3)

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

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

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

[b] Beyond xenon.

and subnormal compounds (such as Th_2S_3) where 6*d* electrons are present.

Properties

The close chemical resemblance between the actinide elements permits their chemistry to be described for the most part in a correlative way.

Oxidation States. The oxidation states of the actinide elements are summarized in Table 4. The most stable states are underlined, 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 (solid) and CmF_4 (solid) and a complex ion stable in highly concentrated cesium fluoride solution, while the IV state of californium is limited to CfO_2 (solid) and CfF_4 (solid), and double salts such as $7NaF \cdot 6CfF_4$ (solid). In the second half of the series the II state first manifests itself 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 are manifestations of the stability of the half-filled 5*f* configuration ($5f^7$) and nobelium II is a manifestation of the stability of the full 5*f* configuration ($5f^{14}$). Similarly Md I results from the stability of the $5f^{14}$ configuration.

Table 4. The Oxidation States of the Actinide Elements

Atomic number 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
Oxidation states													1		
							(2)			(2)	(2)	2	2	$\underline{2}$	
	$\underline{3}$	(3)	(3)	3	3	3	$\underline{3}$	$\underline{3}$	$\underline{3}$	$\underline{3}$	$\underline{3}$	$\underline{3}$	$\underline{3}$	3	$\underline{3}$
		$\underline{4}$	4	4	4	$\underline{4}$	4	4	4	(4)					
			$\underline{5}$	5	$\underline{5}$	5	5								
				$\underline{6}$	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	(reddish purple)	yellow to pink-orange	dark green
americium	pink	color unknown	yellow	rum-colored	
curium	colorless	color unknown			
berkelium	green	yellow			
californium	green				

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. The open spaces indicate that the corresponding oxidation states do not exist in aqueous solution. The color of plutonium V has not been observed but is deduced from the absorption spectrum of its aqueous solution. Protactinium V usually exists in aqueous solution as a highly polymerized colloid, and it seems unlikely that PaO_2^+ is present in such solutions. The wide variety of colors exhibited by actinide ions is characteristic of transition series of elements.

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 state is found for neptunium and plutonium, 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 oxdize water.

The reduction potentials for the actinide elements are shown on the following pages. These are "formal potentials," defined as the measured potentials corrected to unit concentration of the substances entering into the reactions, on the basis of the hydrogen-ion-hydrogen couple taken as zero volts, and with no corrections 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.

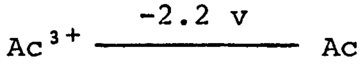
The M^{4+}—M^{3+} and MO_2^{2+}—MO_2^{+} couples are readily reversible, and reactions are rapid with other one-electron reducing or oxidizing agents that involve no bond changes. The rate varies with reagents that normally react by two-electron or bondbreaking changes. The MO_2^{+}—M^{3+}, MO_2^{2+}—M^{3+},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

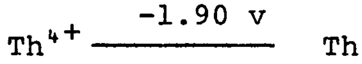
Table 6 presents a summary of the oxidation-reduction characteristics of actinide ions. The disproportionation reactions of UO_2^{+}, Pu^{4+}, PuO_2^{+}, and AmO_2^{+} are very complicated and have been studied extensively. In the case of plutonium, the situation is especially complex: Four oxidation states of plutonium, (III, IV, V, and VI) can exist together in aqueous solution in equilibrium with each other at appreciable concentrations.

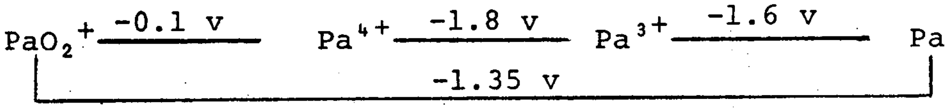
Table 6. Stability of Actinide Ions in Aqueous Solution

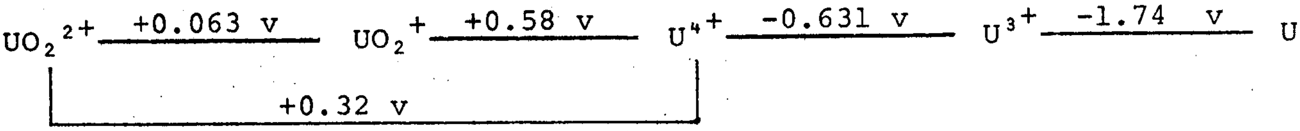
Ion	Stability
Md^{+}	stable to water, but readily oxidized
Md^{2+}	stable to water, but readily oxidized
No^{2+}	stable
Ac^{3+}	stable
U^{3+}	aqueous solutions evolve hydrogen on standing
Np^{3+}	stable to water, but readily oxidized by air to Np^{4+}
Pu^{3+}	stable to water and air, but easily oxidized 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+} and Md^{+}
No^{3+}	easily reduced to No^{2+}
Lr^{3+}	stable
Th^{4+}	stable
Pa^{4+}	stable to water but readily oxidized
Pa V	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 ion
Cm^{4+}	known in solution only as complex fluoride ion
Bk^{4+}	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 it 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

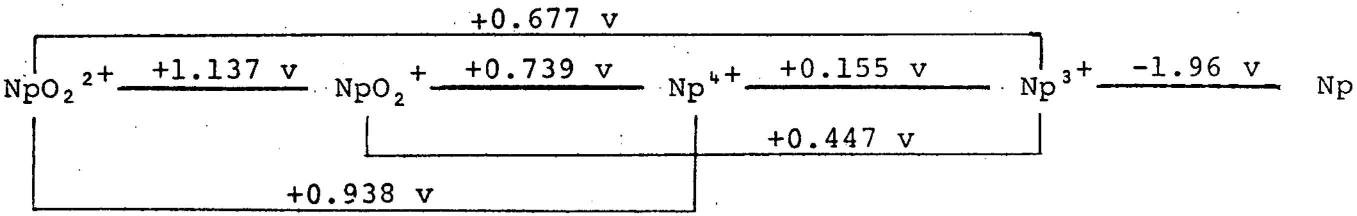
Acidic Aqueous Solution

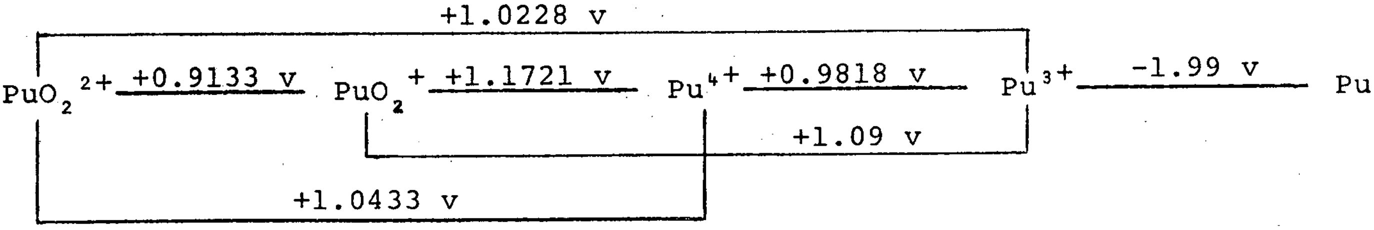


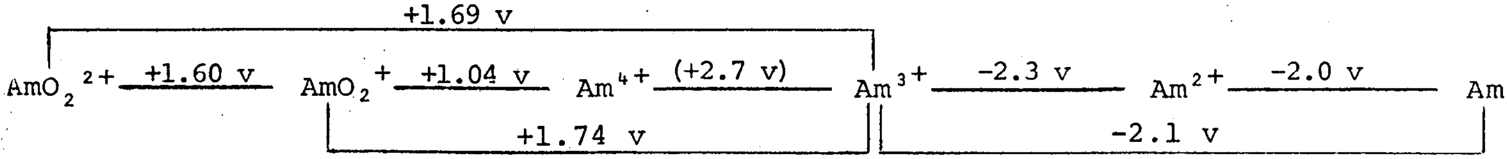












Acidic Aqueous Solution

$$Cm^{4+} \xrightarrow{+2.9\ v} Cm^{3+} \xrightarrow{-2.07\ v} Cm$$

$$Bk^{4+} \xrightarrow{+1.6\ v} Bk^{3+} \xrightarrow{-1.97\ v} Bk$$

$$\underbrace{Cf^{3+} \xrightarrow{-1.6\ v} Cf^{2+} \xrightarrow{-2.2\ v} Cf}_{-2.0\ v}$$

$$\underbrace{Es^{3+} \xrightarrow{-1.3\ v} Es^{2+} \xrightarrow{-2.3\ v} Es}_{-2.0\ v}$$

$$\underbrace{Fm^{3+} \xrightarrow{-1.0\ v} Fm^{2+} \xrightarrow{-2.5\ v} Fm}_{-2.0\ v}$$

$$\underbrace{Md^{3+} \xrightarrow{-0.2\ v} Md^{2+} \xrightarrow{-2.3\ v} Md}_{-1.6\ v}$$

$$\underbrace{No^{3+} \xrightarrow{1.4\ v} No^{2+} \xrightarrow{-2.5\ v} No}_{-1.2\ v}$$

$$Lr^{3+} \xrightarrow{(-2.0\ v)} Lr$$

Alkaline Aqueous Solution

$$\begin{tikzcd}
Th(OH)_4 \arrow[r, dash, "-2.48\ v"] & Th
\end{tikzcd}$$

$$\begin{tikzcd}
UO_2(OH)_2 \arrow[r, dash, "-0.62\ v"] & U(OH)_4 \arrow[r, dash, "-2.14\ v"] & U(OH)_3 \arrow[r, dash, "-2.17\ v"] & U
\end{tikzcd}$$

$$\begin{tikzcd}
NpO_5^{3-} \arrow[r, dash, "+0.6\ v"] & NpO_2(OH)_2 \arrow[r, dash, "+0.48\ v"] \arrow[rr, dash, bend right, "(+0.43\ v)"'] & NpO_2OH \arrow[r, dash, "+0.39\ v"] & Np(OH)_4 \arrow[r, dash, "-1.76\ v"] & Np(OH)_3 \arrow[r, dash, "-2.25\ v"] & Np
\end{tikzcd}$$

$$\begin{tikzcd}
PuO_5^{3-} \arrow[r, dash, "+0.9\ v"] & PuO_2(OH)_3{}^-_{aq} \arrow[r, dash, "+0.26\ v"] \arrow[rr, dash, bend right, "\sim+0.5\ v"'] & PuO_2(OH)_{aq} \arrow[r, dash, "+0.76\ v"] & Pu(OH)_4\,yH_2O \arrow[r, dash, "-0.95\ v"] & Pu(OH)_3\,xH_2O \arrow[r, dash, "(-2.42\ v)"] & Pu
\end{tikzcd}$$

$$\begin{tikzcd}
AmO_2(OH)_2 \arrow[r, dash, "(+1.1\ v)"] \arrow[rr, dash, bend right, "(+0.9\ v)"'] & AmO_2OH \arrow[r, dash, "(0.7\ v)"] & Am(OH)_4 \arrow[r, "+0.4\ to\ +0.5\ v"] & Am(OH)_3 \arrow[r, dash, "-2.71\ v"] & Am
\end{tikzcd}$$

Hydrolysis and Complex Ion Formation. Hydrolysis and complex ion formation are closely related phenomena and will thus be discussed together.

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 especial interest in that polymers which exist as positive colloids can be produced; their molecular weight and particle size depend on the preparative method. 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 the operation of more complicated factors than simple size and charge.

The extensive hydrolysis of protactinium in its V oxidation state is noteworthy because it is a trait which makes the chemical investigation of protactinium extremely difficult. Simple ions of protactinium V do not exist in aqueous solution, and, to prevent hydrolysis, the ion must be held in solution by a complexing agent as, for example, fluoride ion.

The tendency toward complex ion formation of the actinide ions is determined largely by the factors of ionic size and charge. Although there is some variation within each of the ionic types, the order of complexing power of different anions is, in general, in the order 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. Their extractability into 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 which react in this way are tributyl phosphate, diethyl ether, ketones such as diisopropyl ketone or methyl isobutyl ketone, and several glycol ether-type solvents such as diethyl Cellosolve (ethylene glycol ether) or dibutyl Carbitol (diethylene glycol dibutyl ether).

A number of organic compounds, for example, acetylacetone and cupferron, form compounds with aqueous actinide ions (IV state for reagents mentioned) that can be extracted from aqueous solution into immiscible organic solvents. The chelate complexes are especially noteworthy and, among these, the ones formed with diketones, such as 2-thenoyltrifluoroacetone ($C_4H_3SCOCH_2COCF_3$), are of importance in separation procedures for plutonium.

Metallic State. The actinide metals, like the lanthanide metals, are highly electropositive. 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. Metallic protactinium, uranium, neptunium, and plutonium have complex structures which 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 delta and delta-prime 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

Table 7. Properties of Actinide Metals

Element	Melting point, °C	Heat of vaporization and boiling point, keal/mole, °C	Crystal Structure						Density g/cm^3 at °C
			Phase	Range of stability, °C	Symmetry	Lattice parameters, A a_0	b_0	c_0	
actinium	1100 ± 50	(70)			FC cubic	5.311			10.07, 25°
thorium	1750	(130) (3850)	α	RT to 1400	FC cubic	5.086			11.724, 25°
			β	1400 to 1750	BC cubic	4.11			
protactinium	1575		α	RT to 1170	tetragonal	3.929		3.241	15.37, 25°
			β	1170 to 1575	BC cubic	3.81			
uranium	1132	(106.7) (3818)	α	RT to 668	orthorhombic	2.854	5.869	4.956	18.97, 25°
			β	668 to 774	tetragonal	10.759		5.656	18.11, 720°
			γ	774 to 1132	BC cubic	3.525			18.06, 805°
neptunium	637 ± 2	(100) (3900)	α	RT to 280 ± 5	orthorhombic	4.721	4.888	6.661	20.45, 25°
			β	280 ± 5 to 577 ± 5	tetragonal	4.895		3.386	19.36, 313°
			γ	577 ± 5 to 637 ± 2	BC cubic	3.518			18.04, 600°
plutonium	639.5	(79.7) (3235)	α	RT to 115	monoclinic	6.183	4.822 β=101.8°	10.963	19.86, 21°
			β	115 to 185	BC monoclinic	9.284	10.463 β= 92.13°	7.859	17.70, 190°
			γ	185 to 310	orthorhombic	3.159	5.768	10.162	17.13, 235°
			δ	310 to 452	FC cubic	4.637			15.92, 320°
			δ′	452 to 480	tetragonal	3.326		4.463	16.01, 460°
			ε	480 to 639.5	BC cubic	3.636			16.48, 490°
americium	1176	(55) (2011)	α	RT to 1079	hexagonal	3.468		11.241	13.67, 20°
			β	1079 to 1176	FC cubic	4.894			13.65, 20°

Table 7. Properties of Actinide Metals (Con't.)

Element	Melting point, °C	Heat of vaporization and boiling point, keal/mole, °C	Crystal structure						Density g/cm^3 at °C
			Phase	Range of stability, °C	Symmetry	Lattice parameters, A			
						a_0	b_0	c_0	
curium	1340 ± 40	(92.2) (3110)	α		hexagonal	3.496		11.331	13.51, 25°
			β	<1340	FC cubic	5.039			12.66, 25°
berkelium	986 ± 25		α		hexagonal	3.416		11.069	14.78, 25°
			β	<986	FC cubic	4.997			13.25, 25°
californium	900 ± 30		α		hexagonal	3.39		11.01	15.1, 25°
			β		FC cubic	4.94			13.7, 25°
			γ		FC cubic	5.75			8.70, 25°
einsteinium	860 ± 30				FC cubic	5.75			

NOTE: Estimates and uncertian quantities in parentheses.

compounds has been observed and characterized. These include compounds or alloys with members of group IB (Cu, Ag, Au), IIB (Be, Mg, Zn, Cd, Hg), IIIB (Al, Ga, In, Tl), IVB (Ge, Sn, Pb), VIII (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt), VB-pnictides (P, As, Sb), and VIB-chalcogenides (Se, Te). The 5f electrons in the actinides are not as well localized as the 4f electrons in the lanthanides and have energies close to those of the 6d and 7s electrons, leading to the strong participation of 5f electrons in binding. Such itinerant 5f electrons are apparently more prominent in the early actinides and in the heavier actinides a localized behavior becomes evident. It can be said that the behavior of the 5f electrons makes the actinide metals and their metallic compounds different in their behavior than the transition and rare earth metals and their compounds.

Solid Compounds. The tripositive actinide ions resemble tripositive lanthanide ions in their precipitation reactions. 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 $NaMO_2(CH_3COO)_3$. 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 ($Na_2U_2O_7$) can be precipitated from alkaline solution. The NpO_5^{3-} and PuO_5^{3-} anions, which exist in alkaline solution, form insoluble compounds with several di- and tri-positive 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, e.g., sulfate, nitrate, or 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 ones are summarized in Table 8. 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, sulphates, peroxides, and carbonates, compounds such as phosphates, arsenates, cyanides, cyanates, thiocyanates, selenocyanates, sulphites, selenates, selenites, tellurates, tellurites, selenides, tellurides.

Hundreds of actinide organic derivatives, including organometallic compounds, are known. A number of interesting actinide organometallic compounds of the π-bonded type have been synthesized and characterized. The triscyclopentadienyl

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

Compound	Color	Melting point, °C	Crystal structure					Density, g/cm^3
			Symmetry	Space group or structure type	Lattice parameters, A			
					a_0	b_0	c_0	
AcH_2	black		cubic	fluorite (*Fm*3*m*)	5.670			8.35
ThH_2	black		tetragonal	*F*4/*mmm*	5.735		4.971	9.50
Th_4H_{15}	black		cubic	$I\bar{4}3d$	9.11			8.25
PaH_3	black		cubic	βW	6.648			
β-UH_3	black		cubic	βW	6.645			10.91
NpH_3	black		hexagonal	$P6_3/mmc$	3.77		6.72	9.64
PuH_2	black		cubic	fluorite	5.359			10.40
PuH_3	black		hexagonal	$P6_3/mmc$	3.78		6.76	9.61
AmH_2	black		cubic	fluorite	5.35			10.6
AmH_3	black		hexagonal	$P6_3/mmc$	3.77		6.75	9.76
CmH_2	black		cubic	fluorite	5.344			10.7
BkH_2	black		cubic	fluorite	5.226			
Ac_2O_3	white		hexagonal	La_2O_3 ($P\bar{3}ml$)	4.07		6.29	9.19
Pu_2O_3	black		hexagonal	La_2O_3	3.841		5.958	11.47

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

			Crystal structure					
				Space group or structure type	Lattice parameters, A			
Compound	Color	Melting point, °C	Symmetry		a_0	b_0	c_0	Density, g/cm^3
Am_2O_3	tan		hexagonal	La_2O_3	3.805		6.96	11.77
Am_2O_3	reddish-brown		cubic	Mn_2O_3 ($Ia3$)	11.03			10.57
Cm_2O_3	white		monoclinic	Sm_2O_3 ($C2/m$)	14.28	3.65 β=100.3°	8.90	11.91
Bk_2O_3	yellow green		monoclinic	$C2/m$	14.197	3.606 β=100.23°	8.846	12.20
Bk_2O_3	yellowish-brown		cubic	$Ia3$	10.880			11.66
Cf_2O_3	pale green		hexagonal	La_2O_3	3.72		5.96	12.69
Cf_2O_3	lime green		monoclinic	$C2/m$	14.121	3.592 β=100.34°	8.809	12.37
Cf_2O_3	pale green		cubic	$Ia3$	10.838			11.39
Es_2O_3	white		cubic	$Ia3$	10.766			11.79
ThO_2	white	~3050	cubic	fluorite	5.597			10.00
PaO_2	black		cubic	fluorite	5.509			10.45
UO_2	brown to black	2875	cubic	fluorite	5.471			10.95

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

Compound	Color	Melting point, °C	Crystal structure					Density, g/cm^3
			Symmetry	Space group or structure type	Lattice parameters, A			
					a_0	b_0	c_0	
NpO_2	apple-green		cubic	fluorite	5.433			11.14
PuO_2	yellow-green to brown	2400	cubic	fluorite	5.3960			11.46
AmO_2	black		cubic	fluorite	5.374			11.68
CmO_2	black		cubic	fluorite	5.358			11.92
BkO_2	yellowish-brown		cubic	fluorite	5.332			12.31
CfO_2	black		cubic	fluorite	5.310			12.46
Pa_2O_5	white		cubic	fluorite?	5.446			
α-U_3O_8	black-green		orthorhombic	*C2mm*	6.716	11.960	4.169	8.35
β-U_3O_8	black-green		orthorhombic	*Cmcm*	7.069	11.445	8.303	8.32
γ-UO_3	orange		orthorhombic	Fddd	9.81	19.93	9.71	7.75
AcF_3	white		hexagonal	LaF_3 ($P\bar{3}c1$)	7.41		7.55	7.88
UF_3	black	>1140(dec)	hexagonal	LaF_3	7.18		7.348	8.95

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

			Crystal structure					
				Space group or structure type	Lattice parameters, A			
Compound	Color	Melting point, °C	Symmetry		a_0	b_0	c_0	Density, g/cm^3
NpF_3	purple		hexagonal	LaF_3	7.129		7.288	9.12
PuF_3	purple	1425	hexagonal	LaF_3	7.092		7.254	9.33
AmF_3	pink	1393	hexagonal	LaF_3	7.044		7.225	9.53
CmF_3	white		hexagonal	LaF_3	6.999		7.179	
α-BkF_3	yellow-green		orthorhombic	YF_3(*Pnma*)	6.70	7.09	4.41	9.70
β-BkF_3	yellow-green		hexagonal	LaF_3	6.97		7.14	10.15
α-CfF_3	light green		orthorhombic	YF_3	6.653	7.039	4.393	9.88
β-CfF_3	light green		trigonal	LaF_3	6.945		7.101	10.28
$AcCl_3$	white		hexagonal	UCl_3	7.62		4.55	4.81
UCl_3	green	835	hexagonal	$P6_3/m$	7.443		4.321	5.50
$NpCl_3$	green	~800	hexagonal	UCl_3	7.413		4.282	5.60
$PuCl_3$	emerald-green	760	hexagonal	UCl_3	7.394		4.243	5.71
$AmCl_3$	pink		hexagonal	UCl_3	7.382		4.214	5.87

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

			Crystal structure					
				Space group or structure type	Lattice parameters, A			
Compound	Color	Melting point, °C	Symmetry		a_0	b_0	c_0	Density, g/cm^3
$CmCl_3$	white		hexagonal	UCl_3	7.374		4.185	5.81
$BkCl_3$	green		hexagonal	UCl_3	7.382		4.127	5.8
α-$CfCl_3$	green		orthorhombic	$TbCl_3$(Cmcm)	3.869	11.748	8.561	6.07
β-$CfCl_3$	green		hexagonal	UCl_3	7.379		4.090	6.12
$EsCl_3$	white to orange		hexagonal	UCl_3	7.40		4.07	
$AcBr_3$	white		hexagonal	UBr_3	8.06		4.68	5.85
UBr_3	red	730	hexagonal	$P6_3/m$	7.936		4.438	6.55
α-$NpBr_3$	green		hexagonal	UBr_3	7.916		4.390	6.65
β-$NpBr_3$	green		orthorhombic	$TbCl_3$	4.109	12.618	9.153	6.67
$PuBr_3$	green	681	orthorhombic	$TbCl_3$	4.097	12.617	9.147	6.72
$AmBr_3$	white		orthorhombic	$TbCl_3$	4.064	12.661	9.144	6.85
$CmBr_3$	pale yellow green	625 ± 5	orthorhombic	$TbCl_3$	4.041	12.700	9.135	6.85
α-$BkBr_3$	light green		orthorhombic	$AlCl_3$($C2/m$)	7.23	12.53 β=110.6°	6.83	5.604

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

			Crystal structure					
					Lattice parameters, A			
Compound	Color	Melting point, °C	Symmetry	Space group or structure type	a_0	b_0	c_0	Density, g/cm^3
β-BkBr$_3$	light green		rhombohedral	TbCl$_3$	4.03	12.76	9.12	6.95
γ-BkBr$_3$	yellow green		monoclinic	FeCl$_3$($R\bar{3}$)	7.66	α=56.6°		
α-CfBr$_3$	green		monoclinic	AlCl$_3$	7.214	12.423 β=110.7	6.825	5.673
β-CfBr$_3$	green		rhombohedral	FeCl$_3$	7.58	α=56.2°		
CfBr$_2$	amber		tetragonal	SrBr$_2$($P4/n$)	11.500		7.109	7.22
EsBr$_3$	straw		monoclinic	AlCl$_3$	7.27	12.59 β=110.8°	6.81	
β-ThI$_2$	gold		hexagonal	$P6_3/mmc$	3.97		31.75	
PaI$_3$	black		orthorhombic	TbCl$_3$	4.33	14.00	10.02	6.69
UI$_3$	black		orthorhombic	TbCl$_3$	4.328	13.996	9.984	6.76
NpI$_3$	purple		orthorhombic	TbCl$_3$	4.326	13.980	9.982	6.82
PuI$_3$	green		orthorhombic	TbCl$_3$	4.326	13.962	9.974	6.92
AmI$_3$	yellow	~950	hexagonal	BiI$_3$($R\bar{3}$)	7.42		20.55	

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

Compound	Color	Melting point, °C	Crystal structure: Symmetry	Space group or structure type	Lattice parameters, A: a_0	b_0	c_0	Density, g/cm^3
AmI_2	black	~700	monoclinic	EuI_2	7.677	8.311 β=98.5°	7.925	
CmI_3	white		hexagonal	BiI_3	7.44		20.40	5.51
BkI_3	yellow		hexagonal	BiI_3	7.50		20.40	
CfI_3	red orange		hexagonal	BiI_3	7.55		20.80	
CfI_2	violet		hexagonal	CdI_2				
CfI_2	violet		rhombohedral	$CdCl_2$	7.38	α=36°		
EsI_3	red							
ThF_4	white	1068	monoclinic	UF_4	13.00	10.99 β=126.4°	8.60	6.20
PaF_4	reddish-brown		monoclinic	UF_4	12.88	10.88 β=126.4°	8.49	6.38
UF_4	green	960	monoclinic	$C2/c$	12.76	10.57 β=126.3°	8.40	6.73

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

			Crystal structure					
					Lattice parameters, A			
Compound	Color	Melting point, °C	Symmetry	Space group or structure type	a_0	b_0	c_0	Density, g/cm^3
NpF_4	green		monoclinic	UF_4	12.68	10.66 β=126.3°	8.34	6.86
PuF_4	brown	1037	monoclinic	UF_4	12.60	10.57 β=126.3°	8.28	7.05
AmF_4	tan		monoclinic	UF_4	12.54	10.52 β=126.2°	8.20	7.23
CmF_4	light gray-green		monoclinic	UF_4	12.50	10.49 β=126.1°	8.18	7.36
BkF_4	pale yellow		monoclinic	UF_4	12.47	10.48 β=126.1°	8.13	7.55
CfF_4	green		monoclinic	UF_4	12.425	10.468 β=126.02°	8.126	7.57
$ThCl_4$	white	770	tetragonal	UCl_4	8.491		7.483	4.60
$PaCl_4$	greenish-yellow		tetragonal	UCl_4	8.377		7.481	4.72
UCl_4	green	590	tetragonal	$I4_1/amd$	8.296		7.481	4.89
$NpCl_4$	red-brown	518	tetragonal	UCl_4	8.25		7.457	4.96
β-$ThBr_4$	white		tetragonal	UCl_4	8.931		7.963	5.77

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

			Crystal structure					
				Space group or structure type	Lattice parameters, A			
Compound	Color	Melting point, °C	Symmetry		a_0	b_0	c_0	Density, g/cm^3
$PaBr_4$	brown		tetragonal	UCl_4	8.824		7.957	5.90
UBr_4	brown	519	monoclinic	$2/c$-/-	10.92	8.69 β=93.15°	7.05	
$NpBr_4$	dark red	464	monoclinic	$2/c$-/-	10.89	8.74 β=94.19°	7.05	
ThI_4	yellow	556	monoclinic	$P2_1/n$	13.216	8.068 β=98.68°	7.66	6.00
PaI_4	black							
UI_4	black							
PaF_5	white		tetragonal	$I\bar{4}2d$	11.53		5.19	
α-UF_5	grayish-white		tetragonal	$I4/m$	6.512		4.463	5.81
β-UF_5	pale yellow		tetragonal	$I\bar{4}2d$	11.456		5.195	6.47
$PaCl_5$	yellow	306	monoclinic	$C2/c$	7.97	11.35 β=106.4°	8.36	
UCl_5	brown		monoclinic	$P2_1/n$	7.99	10.69 β=91.5°	8.48	

Table 8. Properties and Crystal Structure Data for Some Important Actindie Binary Compounds

			Crystal structure					
					Lattice parameters, A			
Compound	Color	Melting point, °C	Symmetry	Space group or structure type	a_0	b_0	c_0	Density, g/cm^3
β-$PaBr_5$	red		monoclinic	$P2_1/n$	8.385	11.205 β=91.1°	8.950	
UBr_5	brown		monoclinic	$P2_1/n$				
PaI_5	black		orthorhombic		7.22	21.20	6.85	
UF_6	white	64.02/1137 mm	orthorhombic	*Pnma*	9.900	8.962	5.207	5.060
NpF_6	orange	55	orthorhombic	*Pnma*	9.909	8.997	5.202	5.026
PuF_6	reddish-brown	54	orthorhombic	*Pnma*	9.912	8.942	5.206	5.081
UCl_6	dark-green	178	hexagonal	$P\bar{3}m1$	10.90		6.03	3.62

compounds, although more covalent than the analogous lanthanide compounds, are highly ionic and include $ThCp_3$; UCp_3, $NpCp_3$, $PuCp_3$, $AmCp_3$, $CmCp_3$, $BkCp_3$, and $CfCp_3$ (where Cp = C_5H_5); apart from the uranium compound they are relatively stable and appreciably volatile but are sensitive to air. The tetrakiscyclopentadienyl complexes--$ThCp_4$, $PaCp_4$, UCp_4, $NpCp_4$--are, like the Cp_3 complexes, soluble in organic solvents, but are not appreciably volatile and are moderately air sensitive. 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. Of special interest are the cyclooctatetraene (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. 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; some are remarkably 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), tropolones, N,N-dialkyldithiocarbamates, phthalocyanines; many of these are useful in solvents for use in separation schemes.

As has been mentioned, the standard techniques used in inorganic chemistry, modified in the direction of microchemical methods because of the small amounts of material available or the radioactivity of the material, are used to prepare actinide compounds. Table 9 presents an indication of the methods employed in the synthesis of some common species of actinide compounds.

Crystal Structure and Ionic Radii. Crystal structure data have provided the basis for the ionic radii (coordination number = CN = 6) which are summarized in Table 10. It can be noted that 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 (for example, UBr_3--$NpBr_3$--$PuBr_3$--$AmBr_3$) there is a change in structural type with increasing atomic number, which is consistent with the contraction in ionic radius that takes place. The stability of the MO_2 structure (fluorite type) is especially noteworthy as it leads to the existence of such

Table 9. Synthetic Methods for Preparation of Some Actinide Compounds

Compound	Preparative method	Comments
hydrides	H_2 on metals	decomposition of hydride by heating produces finely divided metal which is useful starting point for the preparation of many other compounds
oxides	O_2 on metals or decomposition of an oxygen-containing compound, such as a hydroxide, nitrate, or oxalate	for elements with multiple oxidation states, many phases with variable composition can occur
fluorides	for the lower fluorides, HF on oxides; for higher fluorides, additional use of F_2 or ClF_3	
chlorides	Cl_2 on metal or hydride; hydrochlorination of oxides with HCl, CCl_4, $COCl_2$, S_2Cl_2 $BrCl_3$ or other powerful chlorinating agents (a lower form, such as UCl_3, may require the use of H_2 as a reducing agent)	
bromides	Br_2 on metal or hydrobromination of oxides	
iodides	I_2 on metal or HI on metal or a lighter halide	

Table 10. Ionic Radii of Actinide and Lanthanide Elements

No. of 4*f* or 5*f* electrons	Lanthanide series				Actinide series			
	Element	Radius, A	Element	Radius, A	Element	Radius, A	Element	Radius, A
0	La^{3+}	1.061			Ac^{3+}	1.119	Th^{4+}	0.972
1	Ce^{3+}	1.034	Ce^{4+}	0.92	(Th^{3+})	(1.08)	Pa^{4+}	0.935
2	Pr^{3+}	1.013	Pr^{4+}	0.90	(Pa^{3+})	(1.05)	U^{4+}	0.918
3	Nd^{3+}	0.995			U^{3+}	1.041	Np^{4+}	0.903
4	Pm^{3+}	(0.979)			Np^{3+}	1.017	Pu^{4+}	0.887
5	Sm^{3+}	0.964			Pu^{3+}	0.997	Am^{4+}	0.878
6	Eu^{3+}	0.950			Am^{3+}	0.982	Cm^{4+}	0.871
7	Gd^{3+}	0.938			Cm^{3+}	0.970	Bk^{4+}	0.860
8	Tb^{3+}	0.923	Tb^{4+}	0.84	Bk^{3+}	0.949	Cf^{4+}	0.851
9	Dy^{3+}	0.908			Cf^{3+}	0.934		
10	Ho^{3+}	0.984			Es^{3+}	0.925		
11	Er^{3+}	0.881						
12	Tm^{3+}	0.869						
13	Yb^{3+}	0.858						
14	Lu^{3+}	0.848						

compounds as PaO_2, AmO_2, CmO_2, and CfO_2 despite the instability of IV oxidation state of these elements in solution. The actinide contraction and the isotructural 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 crystals contain narrow bands in the visible, near-ultraviolet, and near-infrared regions of the spectrum. Much evidence indicates that these bands arise from electronic transitions within the $4f$ and $5f$ 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 is generally observed in actinide compounds under the proper conditions for excitation. For example, it is observed in the trichlorides of uranium, neptunium, americium, and curium, diluted with lanthanum chloride, through the action of ultraviolet radiation.

Practical Applications

The practical use of three actinide nuclides (plutonium-239, uranium-235 and uranium-233) as nuclear fuel is well known. 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 a manner that the energy in the form of heat can be extracted and used either as heat or converted by conventional means to electrical energy. The complete utilization of non-fissionable uranium-238 (through conversion to fissionable plutonium-239) and non-fissionable thorium-232 (through conversion to fissionable uranium-233) can be accomplished through the development of breeder reactors.

In addition, three other actinide nuclides (plutonium-238, americium-241, and californium-252) have demonstrated substantial practical applications. One gram of plutonium-238 produces approximately 0.56 watt 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. The most noteworthy example of this latter type of application is a radioisotopic thermoelectric generator left on the moon. It produced 73 watts of electrical power to operate the scientific experiments of the Apollo lunar exploration, and was fueled with 2.6 kilograms (5.7 pounds) of the plutonium isotope in the form of plutonium dioxide, PuO_2. A similar generator powers the instrumentation for Viking on Mars. Americium-241 has a predominant gamma-ray (energy 60 KeV) and a long half-life (433 years) for decay by the emission of alpha particles, which make it particularly useful for a wide range of industrial gauging applications and the diagnosis of thyroid disorders. When mixed with beryllium it generates neutrons at the rate of 1.0 × 10^7 neutrons per second per gram of americium-241. The mixture is designated ^{241}Am-Be and a large number of such sources are in worldwide daily use in oil-well logging operations; i.e., to find how much oil a well is producing in a given time span. Californium-252 is an intense neutron source: one gram emits 2.4 × 10^{12} neutrons per second. This isotope is being tested for applications in neutron activation analysis, neutron radiography, and portable sources for field use in mineral prospecting and oil-well logging. Both plutonium-238 and californium-252 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 certian tumors for which gamma-ray treatment is relatively ineffective.

Encyclopedia of Chemical Technology

ACTINIDES AND TRANSACTINIDES

II. Transactinides

The elements beyond the actinides in the periodic table can be termed the "transactinides." These begin with the element with atomic number 104 and extend, in principle, indefinitely. Although only three such elements, numbers 104, 105 and 106, are definitely known at the time of this writing (1976), there are good prospects for the discovery of a number of additional elements. Such elements may be synthesized and identified in the region just beyond number 106, or may be synthesized and identified, or even found in nature, in the region of much 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 up in the main body of the periodic table. The discoverers of the known (1976) transactinide elements, suggested names and symbols, and dates of discovery are listed in Table 11. 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 as a consequence of the traditional privilege of discoverers to do so; in the case of element 106 neither group has suggested a name for the element in order to avoid another duplication.

Table 11. The Transactinide Elements

Atomic Number	Element	Symbol	Atomic Weight [a]	Discoverers and date of discovery
104	rutherfordium (U.S.A.)	Rf	261	A. Ghiorso, M. Nurmia, J. Harris, K. Eskola and P. Eskola, 1969
104	kurchatovium (U.S.S.R.)	Ku		G. N. Flerov, Yu. Ts. Oganesyan, 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 (U.S.A.)	Ha	262	A. Ghiorso, M. Nurmia, K. Eskola, J. Harris and P. Eskola, 1970
105	nielsbohrium (U.S.S.R.)	Ns		G. N. Flerov, Yu. Ts. Oganesyan, Yu. V. Lobanov, Yu. A. Lazarev, and S. P. Tretiakova, 1970
106			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. Oganesyan, Yu. P. Tretiakov, A. S. Iljinov, A. G. Demin, A. A. Pleve, S. P. Tretoalpva, V. M. Plotko, M. P. Ivanov, N. A. Danilov, Yu. S. Korotkin and G. N. Flerov, 1974

[a] Mass number of longest-lived isotopes.

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. No meaningful chemical studies have been made for element 105, and no chemical studies have been made for element 106. Such studies are very difficult because the longest lived isotope of 104 ($^{261}104$) has a half-life of only about one minute, of 105 ($^{262}105$) a half-life of about 40 seconds, and of 106 ($^{263}106$) a half-life of about one second.

On the basis of the simplest projections, it is expected that the half-lives of the elements beyond element 106 will become shorter and 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 5 in which the half-lives of the longest-lived isotopes (for alpha and spontaneous fission decay) of transuranium elements on a logarithmic scale are plotted against the increasing atomic number. Thus, if this rate of decrease could be extrapolated to ever-increasing atomic numbers, we would expect half-lives of the order of 10^{-10} second for the longest-lived isotope of element 110, and 10^{-20} second for element 115, and so forth, with decay by spontaneous fission becoming of dominating importance beginning with element 106. This would present somewhat dismal future prospects for heavier transuranium elements, but fortunately other factors have entered the picture in recent years. These have led to an increased optimism concerning the prospects for the synthesis and identification, or the discovery in nature, of elements well beyond the observed upper limit of the periodic table--elements that have come to be referred to as "superheavy" elements.

Complicated theoretical calculation, based on filled shell (magic number) and other nuclear stability considerations, have led to extrapolations to the far transuranium region. These suggest the existence of closed nucleon shells at $Z = 114$ and $N = 184$ 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 $N = 126$, and some calculations suggest a closed shell at $N = 228$. Although $Z = 164$ and $N = 318$ may represent additional hypothetical points of stability, they correspond to a much more extensive extrapolation and any predictions are therefore much more uncertain.

Table 12 illustrates the known closed proton (Z) and neutron (N) shells and the predicted closed nuclear shells (shown in parentheses) that might be important in stabilizing the superheavy elements. The indicated shells at $Z = 164$ and $N = 318$ are included for completeness, although there

Table 12. Closed Proton (*Z*) and Neutron (*N*) Shells with Closed Electron (Noble Gas) Shells for Comparison. (Predicted shells shown in parentheses.)

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)	- - - - -	(118)
(126)	(184)	
	(228)	(168)
(164)	(318)	

appears to be little hope of ever observing these on earth; it is, of course, conceivable that nuclei containing such extremely large numbers of protons or neutrons may someday be observed by identification of their characteristic radiation emanating from stars. 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 relative chemical nonreactivity 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 the single long-lived specimen but to be merely the center of a rather large "island of stability" in a "sea of spontaneous fission." In Figure 6 nuclear stability is depicted in a scheme that shows regions of known or predicted stability as land masses in a sea of instability representing forms of decay. The grid lines 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 mountain; a predicted doubly magic but less stable region at 114 protons and 184 neutrons by a hill at the island of stability. The ridges depict areas of enhanced stability due to a single magic number. The submerged ridges show isotopes that are unstable but more stable than nearby ones because of increased stability afforded by closed shells of nucleons in the nucleus.

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. The calculations show that elements 104 through 112 are formed by filling the 6*d* electron subshell, which makes them, as expected, homologous in chemical properties with the elements hafnium (no. 72) through mercury (no. 80). Elements 113 through 118 result from the filling of the 7*p* subshell and are expected to be similar to the elements thallium (no. 81) through radon (no. 86). Thus these calculations are consistent with the Periodic Table shown in Figure 4 and are better illustrated in the Periodic Table shown in Figure 7, which shows the filling of the electron subshells extending beyond element 118.

The calculations indicate 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 the author has termed 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. The calculations indicate that other electrons (8*p* and 7*d*) in addition to those identified in the above discussion enter the picture as early as element 121 (or even element 104), thus further complicating the picture. These perturbations, caused by spin-orbit splitting, became especially significant beyond the superactinide series, and lead to predictions of chemical properties that are not consistent, element by element, with those suggested by Figures 4 and 7. This, of course, is a region 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 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, while element 112 should be eka-mercury, element 110 should be eka-platinum, etc. If there is island of stability at element 126, this element and its neighbors should have chemical properties like those of the actinide and lanthanide elements.

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 (1976) been unsuccessful. 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 of knowing 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 which are not understood and which might present serious or fatal impediments to the production of superheavy nuclei; for example, 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 be as long as a few times 100 million years, this would be long enough to allow the isotope to survive and still be present on earth (as in the case of uranium-235, which has a half-life of 700 million years), 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, direct or indirect, of the superheavy elements in nature associated with the island of stability centered around element 114 has not been conclusive enough to give a clear-cut answer. 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--for example, much less than one part in a million million 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 is some evidence that volatile element 115 (or 114 or 113) may have been present in a rare chromium mineral found in the Allende meteroite which fell in Mexico in 1969; the evidence for such an extinct superheavy element is the observation of a unique composition of xenon isotopes that might have been formed from decay by spontaneous fission with a half-life of some 10^7-10^9 years. 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; elements as heavy as uranium have apparently been found in cosmic rays emanating from such stars.

III. Bibliography

1. C. Keller, The Chemistry of the Transuranium Elements, Verlag Chemie GmbH, 1971.
   Comprehensive review of the chemistry, including some nuclear chemistry, of the actinide elements beyond uranium.

2. J. C. Bailor, Jr., J. Emeleus, Ronald Nyholm and A. F. Trotman-Dickenson, Editors, Comprehensive Inorganic Chemistry, vol. 5, Actinides, Pergamon Press, Oxford, New York, 1973.
   Good review of the solid and solution chemistry of the actinides.

3. W. Muller and R. Lindner, Editors, Transplutonium 1975, 4th International Transplutonium Element Symposium, Proceedings of the Symposium at Baden Baden September 13-17, 1975, North Holland Publishing Co., Amsterdam, Oxford, American Elsevier Publishing Co. Inc., New York.
   Compilation of recent excellent papers on chemistry of actinides and transactinides.

4. J. J. Katz and G. T. Seaborg, The Chemistry of the Actinide Elements, Methuen & Co., Ltd., London, and Wiley & Sons, Inc., New York, 1957.
   Early comprehensive review of the chemistry of the actinide elements, with extensive references.

5. G. T. Seaborg, The Transuranium Elements, Yale University Press, New Haven, 1958.
   Early survey of the chemical and nuclear properties and the history of the transuranium elements.

6. G. T. Seaborg, J. J. Katz, and W. M. Manning, eds., The Transuranium Elements: Research Papers, National Nuclear Energy Series, Div. IV, 14B, McGraw-Hill Book Co., New York, 1949.

7. G. T. Seaborg and J. J. Katz, eds., The Actinide Elements, National Nuclear Energy Series, Div. IV, 14A, McGraw-Hill Book Co., New York, 1954.
   Early comprehensive description of chemical and nuclear properties of the actinide elements.

8. Proceedings of the First United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955, United Nations, New York, 1955. Proceedings of the Second

United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, United Nations, Geneva, 1958. Proceedings of the Third United Nations International Conference on the Peaceful Uses of Atomic Energy, New York, 1964, United Nations, Geneva, 1964. Proceedings of the Fourth United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1971, United Nations, Geneva, 1971.

Early and current information relating to all phases of nuclear energy.

9. Series on Radiochemistry, National Academy of Sciences. Reports available from Office of Technical Services, Department of Commerce, Washington 25, D. C.
    - P. C. Stevenson and W. E. Nervik, Actinium (with scandium, yttrium, rare earths), NAS-NS-3020.
    - E. Hyde, Thorium, NAS-NS-3004.
    - H. W. Kirby, Protactinium, NAS-NS-3016.
    - J. E. Gindler, Uranium, NAS-NS-3050.
    - R. K. Sjoblom, Neptunium,NAS-NS-3060.
    - G. H. Coleman and R. W. Hoff, Plutonium, NAS-NS-3058.
    - R. A. Penneman and R. K. Keenan, Americium and Curium, NAS-NS-3006.
    - G. H. Higgins, The Transcurium Elements, NAS-NS-3031.

10. G. T. Seaborg, Elements Beyond 100, Present Status and Future Prospects 18, 53 (1968)

    Discussion of predicted chemical properties of Transactinide Elements, including those of the Superactinide Elements.

11. C. M. Lederer, J. M. Hollander and I. Perlman, Table of Isotopes, Sixth Edition, John Wiley & Sons, Inc., New York, London, Sydney, 1967.

    Complete listing of known isotopes and their radioactive decay characteristics.

12. G. Hermann, Superheavy Elements, International Review of Science, Inorganic Chemistry, Series Two, vol. 8, Radiochemistry. Edited by A. G. Maddock, University of Cambridge, Butterworths, London, University Park Press, Baltimore, 1975.

13. E. Anders, H. Huguchi, J. Gros, H. Takahashi and J. W. Morgan, Extinct Superheavy Element in Allende Meteorite, Science 190, 1262 (1975).

    Evidence for extinct element 115 (or 114, 113) in rare chromium mineral found in Allende meteorite.

IV. Abstract

Distributed among the 15 radioactive actinide elements (atomic numbers 89-103, actinium, thorium, protactinium, uranium, neptunium, plutonium, americium, curium, berkelium, californium, einsteinium, fermium, mendelevium, nobelium, lawrencium) are more than 200 isotopes, some present in nature, most synthesized by nuclear reactions. For the elements through fermium (100) there are isotopes sufficiently long-lived for work with weighable amounts. For the actinide elements nuclear synthesis and chemical isolation, experimental methods of investigation, position in periodic table, electronic structure, oxidation states, ionic types and ionic colors in aqueous solution, reduction potentials, stability of ions in aqueous solution, hydrolysis of ions and complex ion formation, the metallic state, solid binary (and some ternary) compounds, organic derivatives and organometallic compounds, crystal structures, methods for preparation of compounds, ionic radii, absorption and fluorescence spectra, and practical applications are described.

The transactinide elements include all the elements beyond the actinide elements, including those already known and those yet to be synthesized or discovered in nature. Three such elements are known (atomic numbers 104-106, rutherfordium or kurchatovium, hahnium or nielsbohrium and element 106). Nuclear stability considerations suggest

that it may be possible to synthesize "superheavy elements" with long half-lives situated in an "island of stability" (centered around atomic number 114). For the transactinide elements methods of synthesis and identification, position in the periodic table, chemical properties, electronic structure including that of the "superactinide" elements (numbers 121-153), and possible presence in nature are discussed.

FIGURE CAPTIONS

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 per square centimeter per second.

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 broken line.

Fig. 4. Modern Periodic Table Showing Predicted Locations of Transuranium Elements (Atomic numbers in parentheses)

Fig. 5. Longest lived isotopes of transuranium elements

Fig. 6. Allegorical Representation of Island of Stability (Magic Island)

Fig. 7. Futuristic Periodic Table Showing Predicted Locations of a Large Number of Transuranium Elements (Atomic numbers in parentheses)

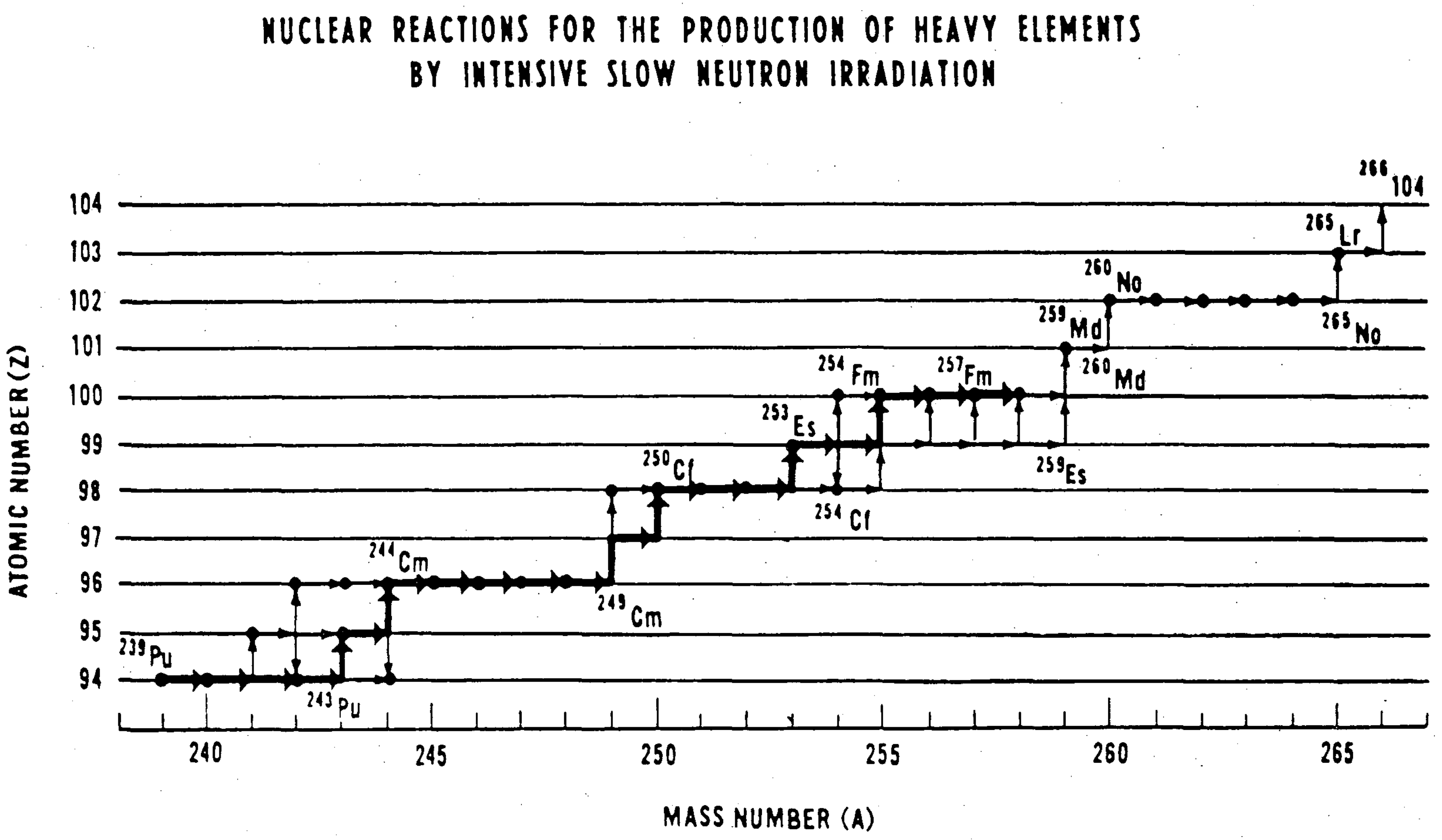


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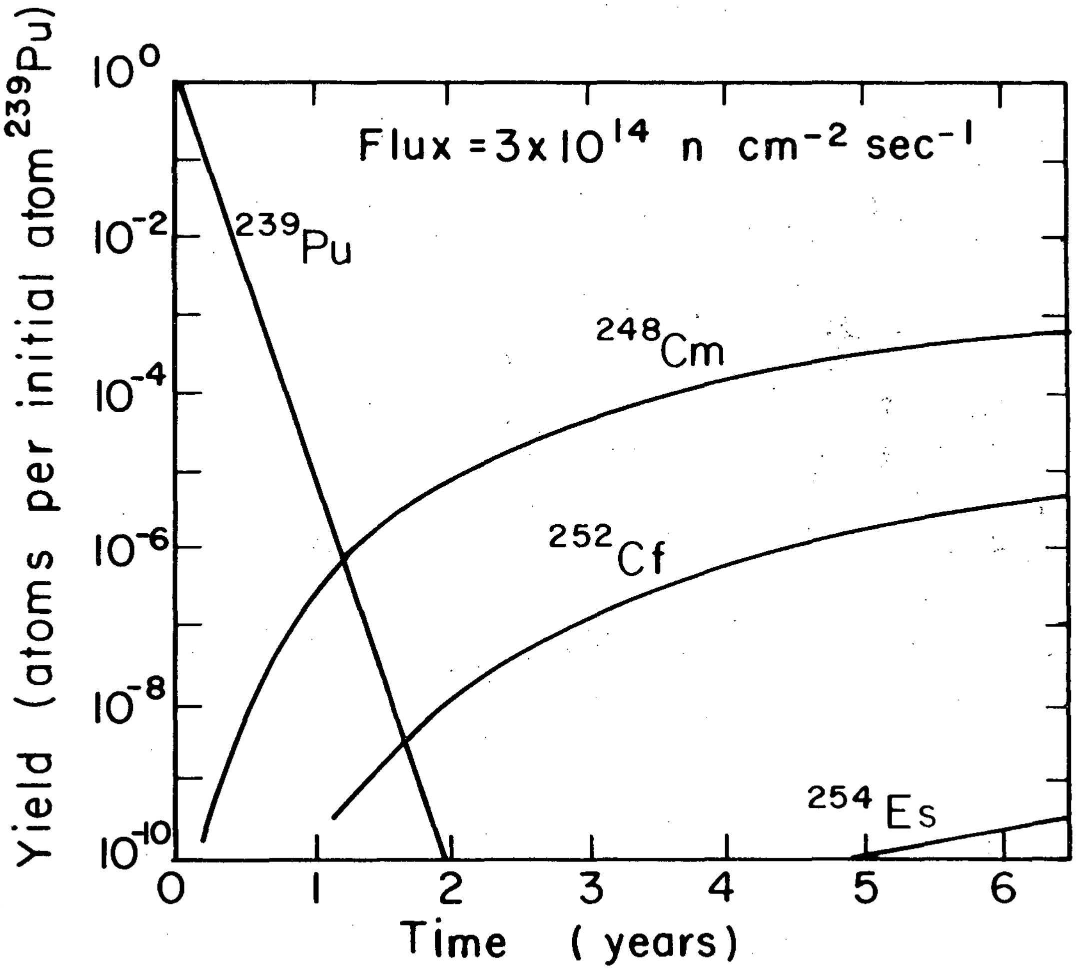
Figure 1.



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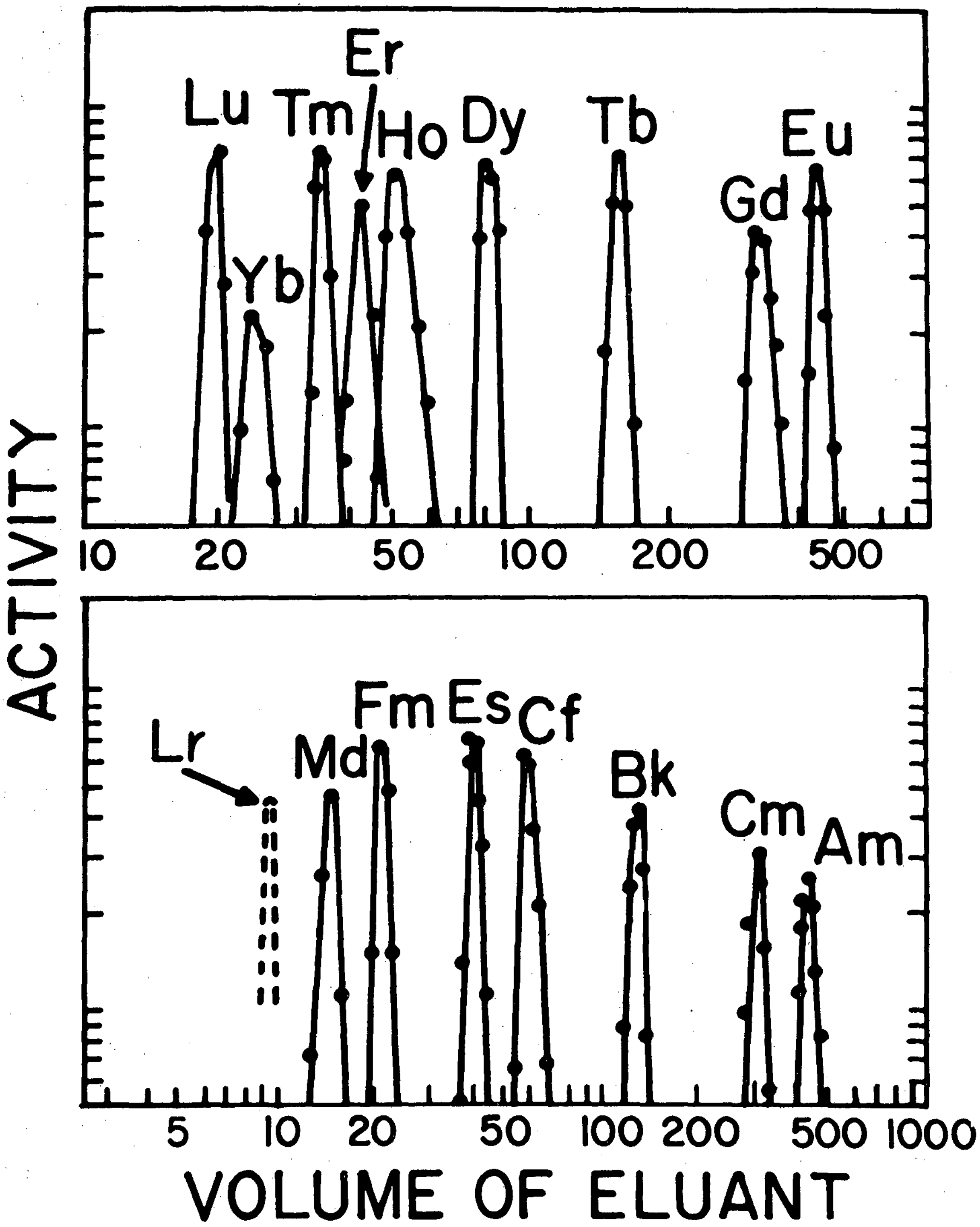

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Figure 3.

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)

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

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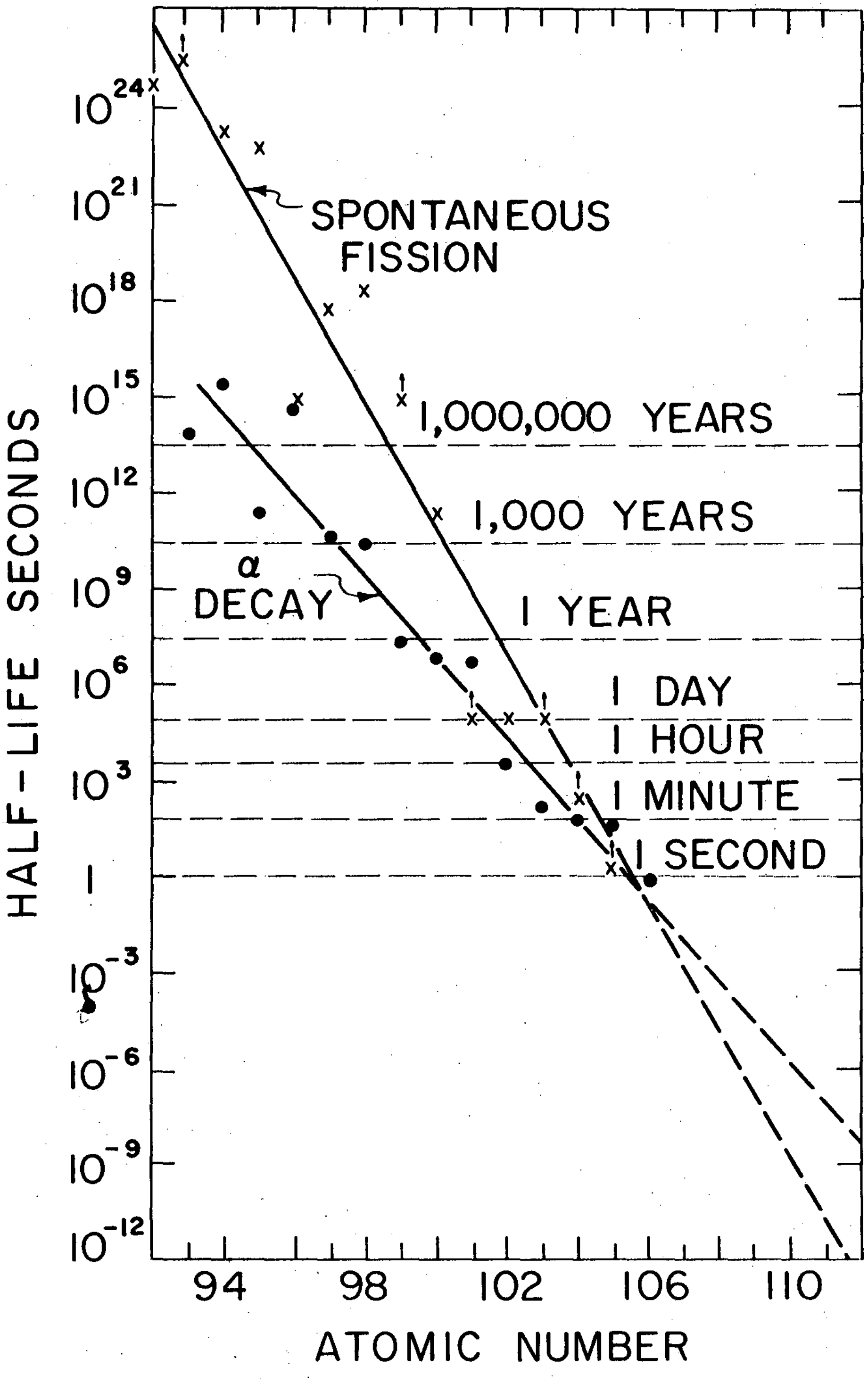
Figure 4.



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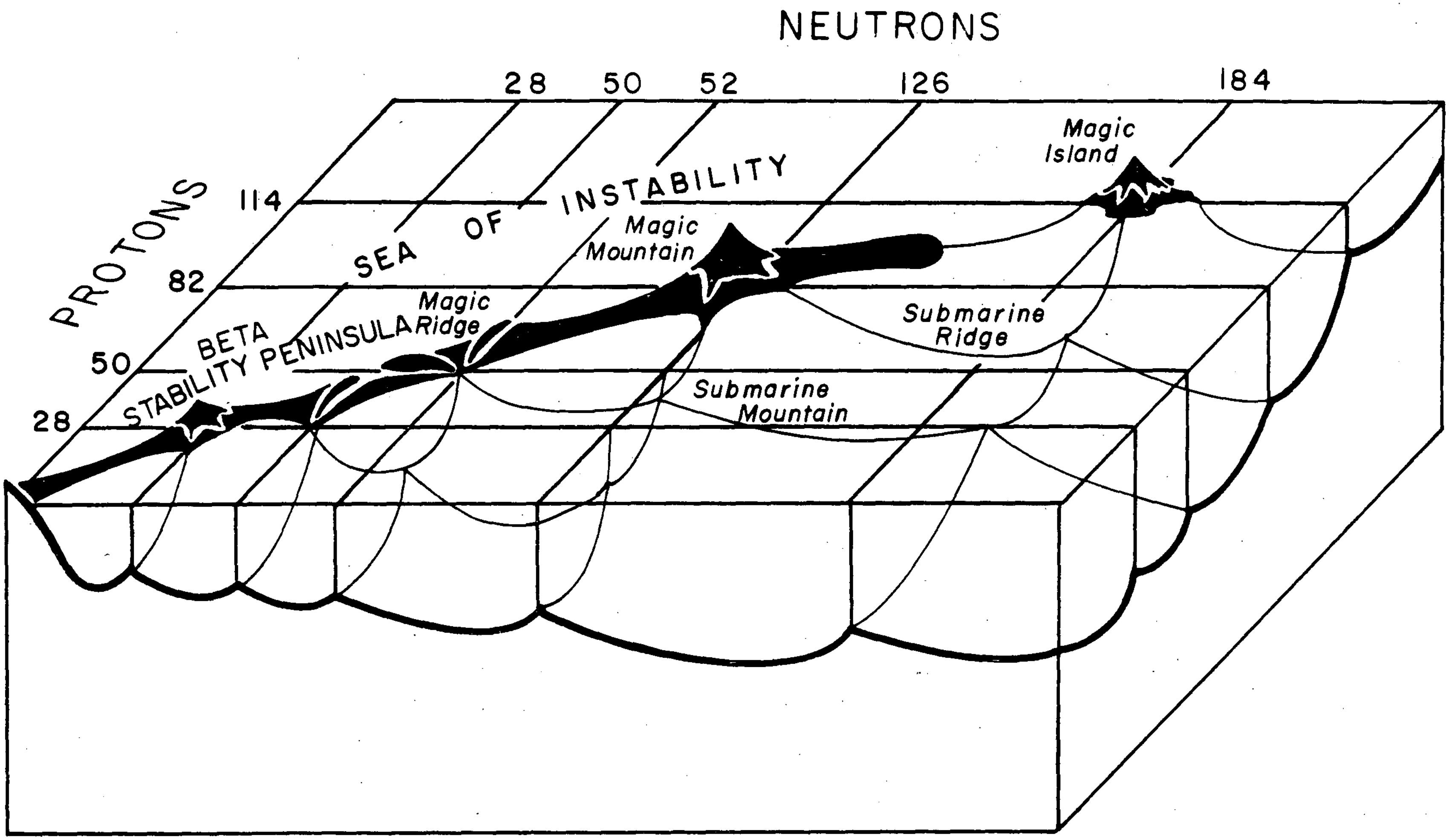

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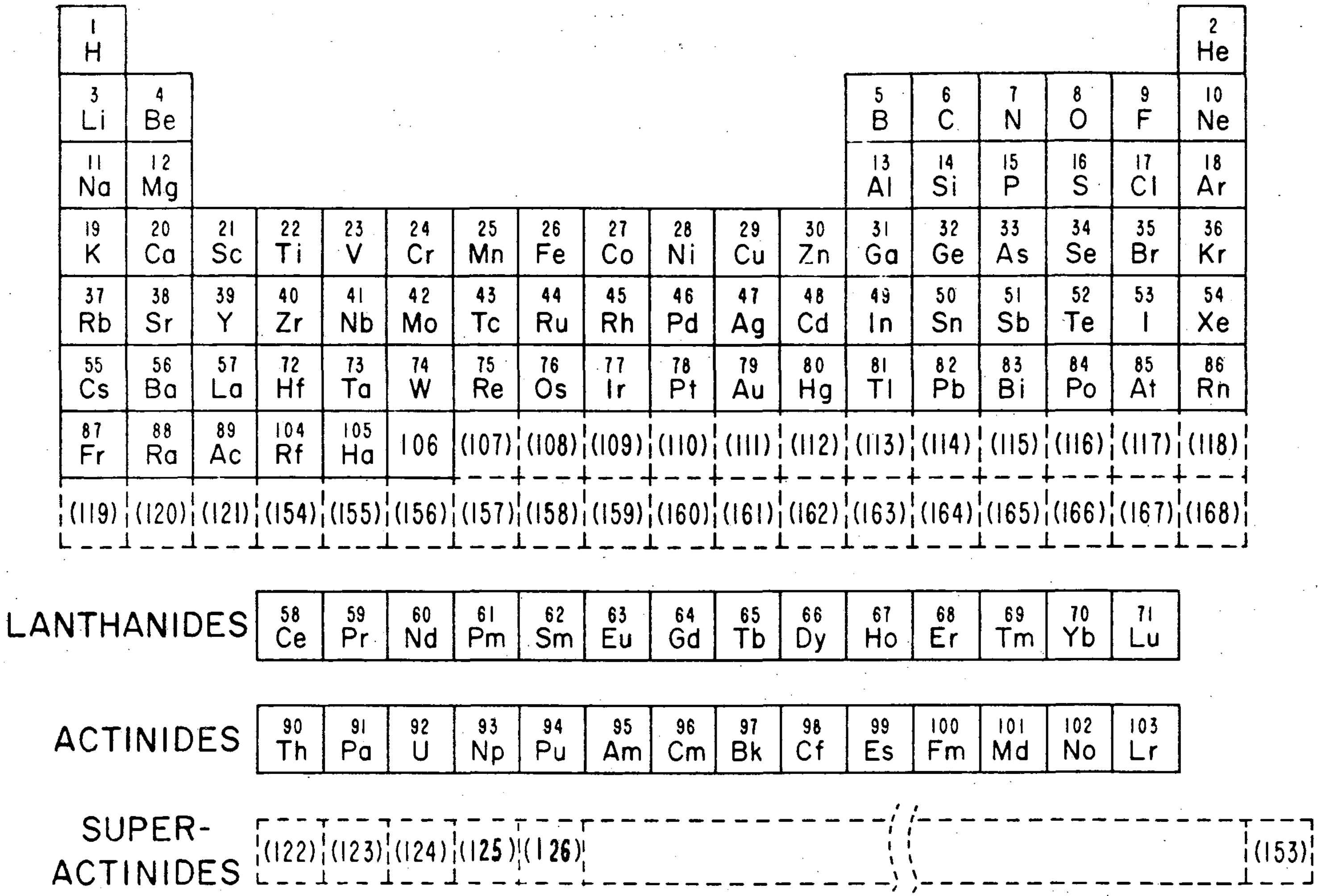

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 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
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

SUPER- ACTINIDES	(122)	(123)	(124)	(125)	(126)	(153)

XBL 751-2036

Figure 7.

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