

																1	2										
																H	He										
3	4											5	6	7	8	9	10										
Li	Be											B	C	N	O	F	Ne										
11	12											13	14	15	16	17	18										
Na	Mg											Al	Si	P	S	Cl	Ar										
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36										
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr										
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54										
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe										
55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72										
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn										
87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104										
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uun	Uub																

105	106	107	108	109	110	111	112
Th	Pa	U	Np	Pu	Am	Cm	Bk
113	114	115	116	117	118	119	120
Tl	Pb	Bi	Po	At	Rn	Uue	Uuq

31

The Actinide and Transactinide Elements ($Z = 90 - 103$ and $104 - 112$)

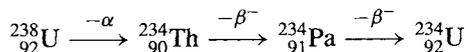
31.1 Introduction

The “actinides” (“actinons” or “actinoids”) are the fourteen elements from thorium to lawrencium inclusive, which follow actinium in the periodic table. They are analogous to the lanthanides and result from the filling of the 5f orbitals, as the lanthanides result from the filling of the 4f. The position of actinium, like that of lanthanum, is somewhat equivocal and, although not itself an actinide, it is often included with them for comparative purposes.

Prior to 1940 only the naturally occurring actinides (thorium, protactinium and uranium) were known; the remainder have been produced artificially since then. The “transactinides” are still being synthesized and so far the nine elements with atomic numbers 104–112 have been reliably established. Indeed, the 20 manmade transuranium elements together with technetium and promethium now constitute one-fifth of all the known chemical elements.

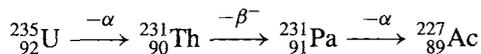
In 1789 M. H. Klaproth examined pitchblende, thought at the time to be a mixed oxide ore of zinc, iron and tungsten, and showed that it contained a new element which he named *uranium* after the recently discovered planet, Uranus. Then in 1828 J. J. Berzelius obtained an oxide, from a Norwegian ore now known as “thorite”; he named this *thoria* after the Scandinavian god of war and, by reduction of its tetrachloride with potassium, isolated the metal *thorium*. The same method was subsequently used in 1841 by B. Peligot to effect the first preparation of metallic uranium.

The much rarer element, protactinium, was not found until 1913 when K. Fajans and O. Göhring identified ^{234}Pa as an unstable member of the ^{238}U decay series:



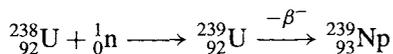
They named it brevium because of its short half-life (6.70 h). The more stable isotope ^{231}Pa

($t_{\frac{1}{2}}$ 32 760 y) was identified 3 years later by O. Hahn and L. Meitner and independently by F. Soddy and J. A. Cranston as a product of ^{235}U decay:



As the parent of actinium in this series it was named protoactinium, shortened in 1949 to *protactinium*. Because of its low natural abundance its chemistry was obscure until 1960 when A. G. Maddock and co-workers at the UK Atomic Energy Authority worked up about 130 g from 60 tons of sludge which had accumulated during the extraction of uranium from UO_2 ores. It is from this sample, distributed to numerous laboratories throughout the world, that the bulk of our knowledge of the element's chemistry was gleaned.

In the early years of this century the periodic table ended with element 92 but, with J. Chadwick's discovery of the neutron in 1932 and the realization that neutron-capture by a heavy atom is frequently followed by β^- emission yielding the next higher element, the synthesis of new elements became an exciting possibility. E. Fermi and others were quick to attempt the synthesis of element 93 by neutron bombardment of ^{238}U , but it gradually became evident that the main result of the process was not the production of element 93 but nuclear fission, which produces lighter elements. However, in 1940, E. M. McMillan and P. H. Abelson in Berkeley, California, were able to identify, along with the fission products, a short-lived isotope of element 93 ($t_{\frac{1}{2}}$ 2.355 days):[†]



As it was the next element after uranium in the now extended periodic table it was named *neptunium* after Neptune, which is the next planet beyond Uranus.

[†] $^{239}_{93}\text{Np}$ itself also decays by β^- emission to produce element 94 but this was not appreciated until after that element (plutonium) had been prepared from $^{238}_{93}\text{Np}$.

The remaining actinide elements were prepared⁽¹⁻⁴⁾ by various "bombardment" techniques fairly regularly over the next 25 years (Table 31.1) though, for reasons of national security, publication of the results was sometimes delayed. The dominant figure in this field has been G. T. Seaborg, of the University of California, Berkeley, in early recognition of which, he and E. M. McMillan were awarded the 1951 Nobel Prize for Chemistry.

The isolation and characterization of these elements, particularly the heavier ones, has posed enormous problems. Individual elements are not produced cleanly in isolation, but must be separated from other actinides as well as from lanthanides produced simultaneously by fission. In addition, all the actinides are radioactive, their stability decreasing with increasing atomic number, and this has two serious consequences. Firstly, it is necessary to employ elaborate radiation shielding and so, in many cases, operations must be carried out by remote control. Secondly, the heavier elements are produced only in the minutest amounts. Thus mendelevium was first prepared in almost unbelievably small yields of the order of 1 to 3 atoms per experiment! Paradoxically, however, the intense radioactivity also facilitated the detection of these minute amounts: first by the development and utilization of radioactive decay systematics, which enabled the detailed properties of the expected radiation to be predicted, and secondly, by using the radioactive decay itself to detect and count the individual atoms synthesized. Accordingly, the separations were effected by ion-exchange techniques, and the elements

¹ G. T. SEABORG (ed.), *Transuranium Elements; Products of Modern Alchemy*, Dowden, Hutchinson & Ross, Stroudsburg, 1978. This reproduces, in their original form, 122 key papers in the story of man-made elements.

² G. T. SEABORG and W. D. LOVELAND, *The Elements Beyond Uranium*, Wiley, New York, 1990, 359 pp.

³ J. J. KATZ, L. R. MORSS and G. T. SEABORG (eds.) *The Chemistry of the Actinide Elements*, Chapman and Hall, London, 1986; Vol. 1, 1004 pp.; Vol 2, 912 pp.

⁴ L. R. MORSS and J. FUGER (eds.), *Transuranium Elements: A Half Century*, Am. Chem. Soc., Washington, 1992, 700 pp.

Table 31.1 The discovery (synthesis) of the artificial actinides

Element	Discoverers	Date	Synthesis	Origin of name
93 Neptunium, Np	E. M. McMillan and P. Abelson	1940	Bombardment of $^{238}_{92}\text{U}$ with ^1_0n	The planet Neptune
94 Plutonium, Pu	G. T. Seaborg, E. M. McMillan, J. W. Kennedy and A. Wahl	1940	Bombardment of $^{238}_{92}\text{U}$ with ^2_1H	The planet Pluto (next planet beyond Neptune)
95 Americium, Am	G. T. Seaborg, R. A. James, L. O. Morgan and A. Ghiorso	1944	Bombardment of $^{239}_{94}\text{Pu}$ with ^1_0n	America (by analogy with Eu, named after Europe)
96 Curium, Cm	G. T. Seaborg, R. A. James and A. Ghiorso	1944	Bombardment of $^{239}_{94}\text{Pu}$ with ^4_2He	P. and M. Curie (by analogy with Gd, named after J. Gadolin)
97 Berkelium, Bk	S. G. Thompson, A. Ghiorso and G. T. Seaborg	1949	Bombardment of $^{241}_{95}\text{Am}$ with ^4_2He	Berkeley (by analogy with Tb, named after the village of Ytterby)
98 Californium, Cf	S. G. Thompson, K. Street, A. Ghiorso and G. T. Seaborg	1950	Bombardment of $^{242}_{96}\text{Cm}$ with ^4_2He	California (location of the laboratory)
99 Einsteinium, Es	Workers at Berkeley, Argonne and Los Alamos (USA)	1952	Found in debris of first thermonuclear explosion	Albert Einstein (relativistic relation between mass and energy)
100 Fermium, Fm	Workers at Berkeley, Argonne and Los Alamos (USA)	1952	Found in debris of first thermonuclear explosion	Enrico Fermi (construction of first self-sustaining nuclear reactor)
101 Mendelevium, Md	A. Ghiorso, B. H. Harvey, G. R. Choppin, S. G. Thompson and G. T. Seaborg	1955	Bombardment of $^{253}_{99}\text{Es}$ with ^4_2He	Dimitri Mendeleev (periodic table of the elements)
102 Nobelium, No ^(a)	Workers at Dubna, USSR ^(b)	1965	Bombardment of $^{243}_{95}\text{Am}$ with $^{15}_7\text{N}$ (or $^{238}_{92}\text{U}$ with $^{22}_{10}\text{Ne}$)	Alfred Nobel (benefactor of science) ^(a)
103 Lawrencium, Lr ^(c)	Workers at Berkeley and at Dubna ^(d)	1961–1971 ^(d)	Bombardment of mixed isotopes of $_{98}\text{Cf}$ with $^{10}_5\text{B}$, $^{11}_5\text{B}$; and of $^{243}_{95}\text{Am}$ with $^{18}_8\text{O}$, etc.	Ernest Lawrence (developer of the cyclotron)

^(a)The first claim for element 102 was in 1957 by an international team working at the Nobel Institute for Physics in Stockholm. Their results could not be confirmed but their suggested name for the element was accepted.

^(b)A full assessment of this work and that done at Berkeley and elsewhere has been carried out by the Transfermium Working Group, a neutral international group appointed jointly by IUPAC and IUPAP in 1987⁽⁵⁾.

^(c)Formerly Lw; the present symbol was recommended by IUPAC in 1965.

^(d)The Transfermium Working Group concluded that "In the complicated situation presented by element 103, with several papers of varying degrees of completeness and conviction, none conclusive, and referring to several isotopes, it is impossible to say other than that full confidence was built up over a decade with credit attaching to work in both Berkeley and Dubna". The detailed analysis of the many relevant publications is given in ref. 5.

⁵R. C. BARBER, N. N. GREENWOOD, A. Z. HRYNKIEWICZ, Y. P. JEANNIN, M. LEFORT, M. SAKAI, I. ULEHLA, A. H. WAPSTRA and D. H. WILKINSON, Discovery of the Transfermium Elements, *Prog. Particle Nucl. Phys.* **29**, 453–530 (1992). Also published, with comments in *Pure Appl. Chem.* **63**, 879–86 (1991) and **65**, 1757–814, 1815–24 (1993).

identified by chemical tracer methods and by their characteristic nuclear decay properties. In view of the quantities involved, especially of californium and later elements, it is clear that this would not have been feasible without accurate predictions of the chemical properties also. It was Seaborg's realization in 1944 that these elements should be regarded as a second f series akin to the lanthanides that made this possible. (Thorium, protactinium and uranium had previously been regarded as transition elements belonging to groups 4, 5 and 6, respectively.)

Elements beyond 103 are expected to be 6d elements forming a fourth transition series, and attempts to synthesize them have continued during the past thirty years. All 10 (including, of course, actinium) are now known and are discussed in the section on transactinide elements on p. 1280. The work has required the dedicated commitment of extensive national facilities and has been carried out at the Lawrence-Berkeley Laboratories, the Joint Institute for Nuclear Research at Dubna, and the Heavy-Ion Research Centre (GSI) at Darmstadt, Germany.

Superheavy elements

Since the radioactive half-lives of the known transuranium elements and their resistance to spontaneous fission decrease with increase in atomic number, the outlook for the synthesis of further elements might appear increasingly bleak. However, theoretical calculations of nuclear stabilities, based on the concept of closed nucleon shells (p. 13) suggest the existence of an "island of stability" around $Z = 114$ and $N = 184$.⁽⁶⁾ Attention has therefore been directed towards the synthesis of element 114 (a congener of Pb in Group 14 and adjacent "superheavy" elements, by bombardment of heavy nuclides with a wide range of heavy ions, but so far without success.

Searches have been made for naturally occurring superheavies ($Z = 112-15$) in ores of Hg,

Tl, Pb and Bi, on the assumption that they would follow their homologues in their geochemical evolution and could be recognized by the radiation damage caused over geological time by their very energetic decay. Early claims to have detected such superheavies in natural ores have been convincingly discounted.⁽⁷⁾ More recent uncorroborated claims to success have been made but, even if confirmed, the concentrations found in the samples examined, are exceedingly small⁽⁸⁾ (less than 1 in 10^{13}).

31.2 The Actinide Elements^(2,3,9-12)

31.2.1 Terrestrial abundance and distribution

Every known isotope of the actinide elements is radioactive and the half-lives are such that only ^{232}Th , ^{235}U , ^{238}U and possibly ^{244}Pu could have survived since the formation of the solar system. In addition, continuing processes produce equilibrium traces of some isotopes of which the most prominent is ^{234}U ($t_{1/2}$ 2.45×10^5 y,

⁷ F. BOSH, A. ELGORESY, W. KRÄTSCHMER, B. MARTIN, B. POVH, R. NOBILING, K. TRAXEL and D. SCHWALM, *Z. Physik A* **280**, 39-44 (1977); see also C. J. SPARKS, S. RAMAN, H. L. TAKEL, R. V. GENTRY and M. O. KRAUSE, *Phys. Rev. Letters* **38**, 205-8 (1977), for retraction of their earlier claim to have detected naturally occurring primordial superheavy elements.

⁸ See, for instance, E. L. FIREMAN, B. H. KETELLE and R. W. STOUGHTON, *J. Inorg. Nucl. Chem.* **41**, 613-5 (1979).

⁹ *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th edn., Interscience, New York; for Actinides see Vol. 1, 1991, pp. 412-45; for Thorium see Vol. 24, 1997, pp. 68-88; for Uranium see Vol. 24, 1997, pp. 638-94; for Plutonium see Vol. 19, 1996, pp. 407-43.

¹⁰ A. HARPER, Chap 17, pp. 435-56 in D. THOMPSON (ed.), *Insights into Speciality Inorganic Chemicals*, RSC, Cambridge, 1995.

¹¹ S. COTTON, *Lanthanides and Actinides*, Macmillan, Basingstoke, 1991, 192 pp.

¹² L. MANES (ed.) *Structure and Bonding*, Vol. 59/60, *Actinides - Chemistry and Physical Properties*, Springer, Berlin, 1985, 305 pp.

⁶ B. FRICKE, *Struct. Bonding*, (Berlin), **21**, 89-144 (1975).

comprising 0.0054% of naturally occurring U isotopes). ^{231}Pa (and therefore ^{227}Ac) is formed as a product of the decay of ^{235}U , while ^{237}Np and ^{239}Pu are produced by the reactions of neutrons with, respectively, ^{235}U and ^{238}U . Traces of Pa, Np and Pu are consequently found, but only Th and U occur naturally to any useful extent. Indeed, these two elements are far from

rare: thorium comprises 8.1 ppm of the earth's crust, and is almost as abundant as boron, whilst uranium at 2.3 ppm is rather more abundant than tin. The radioactive decay schemes of the naturally occurring long-lived isotopes of ^{232}Th , ^{235}U and ^{238}U , together with the artificially generated series based on ^{241}Pu , are summarized in Fig 31.1.

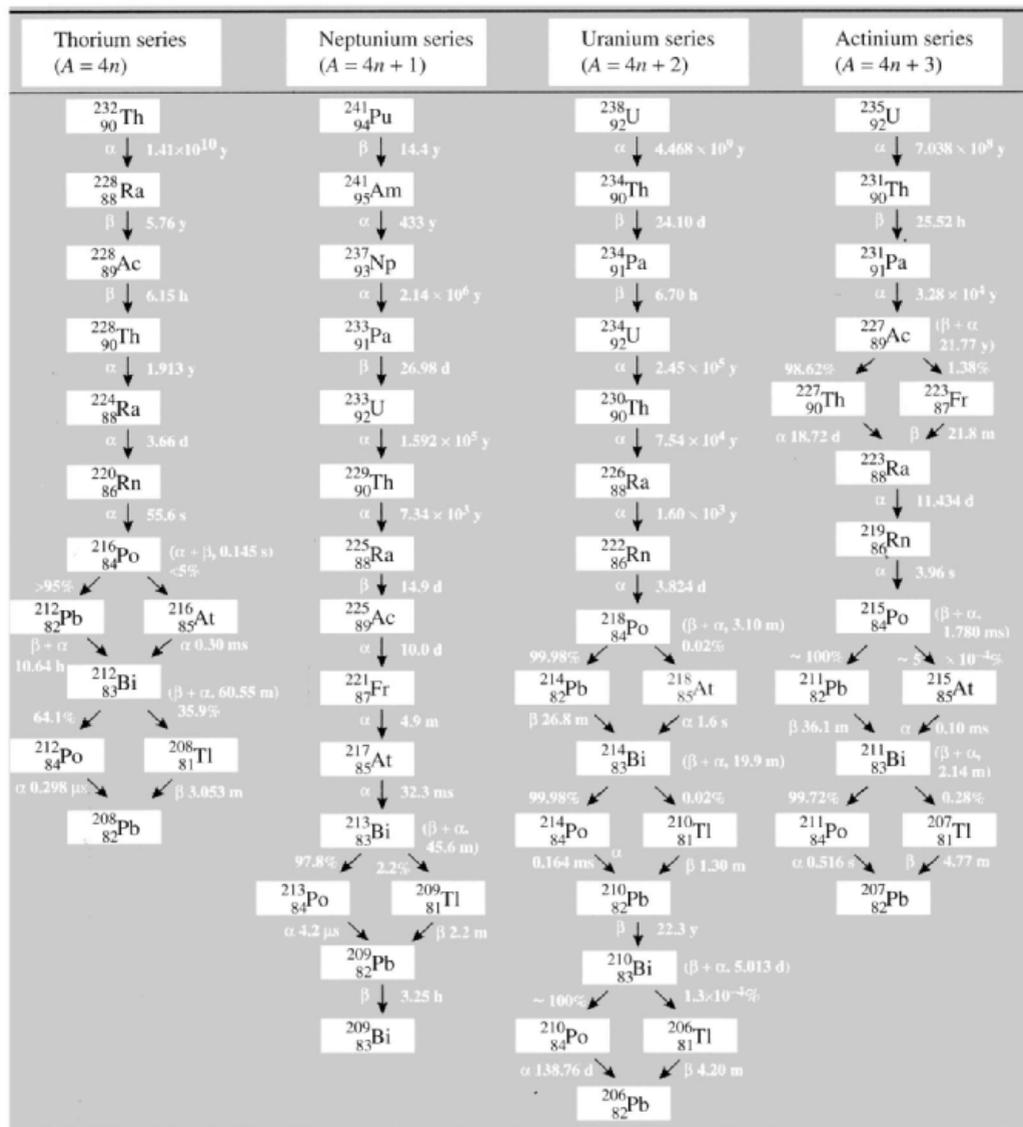


Figure 31.1 The radioactive decay series.

Thorium is widely but rather sparsely distributed and its only commercial sources are monazite sands (see p. 1229) and the mineral conglomerates of Ontario. The former are found in India, South Africa, Brazil, Australia and Malaysia, and in exceptional cases may contain up to 20% ThO₂ but more usually contain less than 10%. In the Canadian ores the thorium is present as uranothorite, a mixed Th,U silicate, which is accompanied by pitchblende. Even though present as only 0.4% ThO₂, the recovery of Th, as a co-product of the recovery of uranium, is viable.

Uranium, too, is widely distributed and, since it probably crystallized late in the formation of igneous rocks, tends to be scattered in the faults of older rocks. Some concentration by leaching and subsequent re-precipitation has produced a large number of oxide minerals of which the most important are pitchblende or uraninite, U₃O₈, and carnotite, K₂(UO₂)₂(VO₄)₂·3H₂O. However, even these are usually dispersed so that typical ores contain only about 0.1% U, and many of the more readily exploited deposits are nearing exhaustion. The principal sources are Canada, Africa and countries of the former USSR.

The transuranium elements must all be prepared artificially. In the case of plutonium about 1200 tonnes have so far been produced worldwide, about three-quarters of it in civilian reactors.

31.2.2 Preparation and uses of the actinide elements^(2,9)

The separation of basic precipitates of hydrous ThO₂ from the lanthanides in monazite sands has been outlined in Fig. 30.1 (p. 1230). These precipitates may then be dissolved in nitric acid and the thorium extracted into tributyl phosphate, (BuⁿO)₃PO, diluted with kerosene. In the case of Canadian production, the uranium ores are leached with sulfuric acid and the anionic sulfato complex of U preferentially absorbed onto an anion exchange resin. The Th is separated from Fe, Al and other metals in the liquor by solvent extraction.

Metallic thorium can be obtained by reduction of ThO₂ with Ca or by reduction of ThCl₄ with Ca or Mg under an atmosphere of Ar (like Ti, finely divided Th is extremely reactive when hot).

The uses of Th are at present limited and only a few hundred tonnes are produced annually, about half of this still being devoted to the production of gas mantles (p. 1228). In view of its availability as a by-product of lanthanide and uranium production, output could be increased easily if it were to be used on a large scale as a nuclear fuel (see below).

Uranium production depends in detail on the nature of the ore involved but, after crushing and concentrating by conventional physical means, the ore is usually roasted and leached with sulfuric acid in the presence of an oxidizing agent such as MnO₂ or NaClO₃ to ensure conversion of all uranium to UO₂²⁺. In a typical process the uranium is concentrated as a sulfato complex on an anion exchange resin from which it is eluted with strong HNO₃ and further purified by solvent extraction into tributyl phosphate (TBP) in either kerosene or hexane. The uranium is then stripped from the organic phase to give an aqueous sulfate solution from which so-called "yellow cake" is precipitated* by addition of ammonia. This is converted to UO₃ by heating at 300°C, and then to UO₂ by reducing in H₂ at 700°C. Conversion to the metal is generally effected by reduction of UF₄ with Mg at 700°C.

Apart from its long-standing though small-scale use for colouring glass and ceramics, uranium's only significant use is as a nuclear fuel. The extent of this use depends on environmental and political considerations. In 1994 world production after nearly a decade of decline was 31 000 tonnes, 30% of which came from Canada and 23% each from the former Soviet Union and African countries (Niger, Namibia, the Republic of South Africa and Gabon). This, however, represented only half the reactor requirements. The rest came from recycling and stockpiles

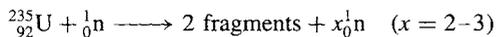
* Yellow cake is a complicated mixture of salts and oxides, the composition of which approximates to (NH₄)₂U₂O₇ but is dependent on the method by which it is produced (see p. 276 of ref. 2).

(which were expected to be exhausted within 4 or 5 years).

Nuclear reactors and atomic energy^(13–15)

In the process of nuclear fission a large nucleus splits into two highly energetic smaller nuclei and a number of neutrons; if there are sufficient neutrons and they have the correct energy, they can induce fission of further nuclei, so creating a self-propagating chain reaction. The kinetic energy of the main fragments is rapidly converted to heat as they collide with neighbouring atoms, the amount being of the order of 10^6 times that produced by chemically burning the same mass of combustible material such as coal.

In practical terms, the only naturally occurring fissile nucleus is $^{235}_{92}\text{U}$ (0.72% abundant):



The so-called “fast” neutrons which this fission produces have energies of about 2 MeV ($190 \times 10^6 \text{ kJ mol}^{-1}$) and are not very effective in producing fission of further $^{235}_{92}\text{U}$ nuclei. Better in this respect are “slow” or “thermal” neutrons whose energies are of the order of 0.025 eV (2.4 kJ mol^{-1}), i.e. equivalent to the thermal energy available at ambient temperatures. In order to produce and sustain a chain reaction in uranium it is therefore necessary to counter the inefficiency of fast neutrons by either (a) increasing the proportion of $^{235}_{92}\text{U}$ (i.e. fuel enrichment) or (b) slowing down (i.e. moderating) the fast neutrons. In addition, there must be sufficient uranium to prevent excessive loss of neutrons from the surface (i.e. a “critical mass” must be exceeded). If the reaction is not to run out of control, an adjustable neutron absorber is also required to ensure that the rate

of production of neutrons is balanced by the rate of their absorption.

The first manmade self-sustaining nuclear fission chain reaction was achieved on 2 December 1942 in a disused squash court at the University of Chicago by a team which included E. Fermi. This was before nuclear-fuel enrichment had been developed: alternate sections of natural-abundance UO_2 and graphite moderator were piled on top of each other (hence, nuclear reactors were originally known as “atomic piles”) and the reaction was controlled by strips of cadmium which could be inserted or withdrawn as necessary. In this crude structure, 6 tonnes of uranium metal, 50 tonnes of uranium oxide and nearly 400 tonnes of graphite were required to achieve criticality. The dramatic success of Fermi’s team in achieving a self-sustaining nuclear reaction invited the speculation as to whether such a phenomenon could occur naturally.⁽¹⁶⁾ In one of the most spectacular pieces of scientific detection work ever conducted, it has now unambiguously been established that such natural chain reactions have indeed occurred in the geological past when conditions were far more favourable than at present (see Panel).

If a chain reaction is to provide useful energy, the heat it generates must be extracted by means of a suitable coolant and converted, usually by steam turbines, into electrical energy. The high temperatures and the intense radioactivity generated within a reactor pose severe, and initially totally new, constraints on the design. The choices of fuel and its immediate container (cladding), of the moderator, coolant and controller involve problems in nuclear physics, chemistry, metallurgy and engineering. Nevertheless, the first commercial power station (as opposed to experimental reactors or those whose function was to produce plutonium for bomb manufacture) was commissioned in 1956 at Calder Hall in Cumberland, UK. Since then a variety of different types has been developed in several countries, as summarized in Fig. 31.2. At

¹³ S. GLASSTONE and A. SESONSKE, *Nuclear Reactor Engineering*, 4th edn., Chapman and Hall, New York, 1994, 852 pp.

¹⁴ R. L. MURRAY, *Nuclear Energy*, 4th edn., Pergamon, Oxford, 1993, 437 pp.

¹⁵ Kirk–Othmer *Encyclopedia of Chemical Technology*, Vol. 17, 4th edn., 1996, pp. 369–465, Interscience, New York.

¹⁶ P. K. KURODA, *Nature* **187**, 36–8 (1960).

Natural Nuclear Reactors — The Oklo Phenomenon¹⁷⁾

Natural uranium consists almost entirely of the α emitters ^{235}U and ^{238}U . As ^{235}U decays more than six times faster than ^{238}U (Fig. 31.1) the proportion of ^{235}U is very slowly but inexorably decreasing with time. Prior to 1972, all analyses of naturally occurring uranium had shown this proportion to be notably constant at $0.7202 \pm 0.0006\%$.[†] In that year, however, workers at the French Atomic Energy laboratories in Pierrelatte performing routine mass spectrometric analyses recorded a value of 0.7171%. The difference was small but significant.

Contamination with commercially depleted U was immediately assumed, but it was gradually realized that the depletion was characteristic of the ore, which came from a mine at Oklo in Gabon, near the west coast ($1^{\circ} 25'S$, $13^{\circ} 10'W$). An intensive examination of the mine was quickly mounted and it was found that the depletion was not uniform but was greatest near those areas where the total U content was highest. The record depletion was an astonishingly low 0.296% ^{235}U from an area where the total U content of the ore rose to around 60%. Incredible as it may appear in view of the diverse and exacting requirements for the construction of a manmade nuclear reactor, the only satisfactory explanation is that the Oklo mine is the site of a spent, prehistoric, natural nuclear reactor. There are now known to have been 14 such reactors in the Franceville basin at Oklo, all of which have been mined, plus a further one some 30 km to the southeast at Bangombé, which it is hoped to preserve essentially undisturbed.

The Oklo ore bed consists of sedimentary rocks believed to have been laid down about 1.8×10^9 y ago. U^{IV} minerals in the igneous rocks, formed in the early history of the earth when the atmosphere was a reducing one, were converted to soluble U^{VI} salts by the atmosphere which had since become oxidizing. These were then re-precipitated as U^{IV} by bacterial reduction in the silt of a river delta and gradually buried under other sedimentary deposits. During this process the underlying granite rocks were tilted, the ores which contained about 0.5% U were fractured, and water percolating through the fissures created rich pockets of ore which in places consisted of almost pure UO_2 . At that time the ^{235}U content of the uranium was about 3%, which is the value to which the fuel used in most modern water-moderated reactors is now artificially enriched.

Under these circumstances the critical mass could be attained and a nuclear chain reaction initiated, with water as the necessary moderator. The 15% water of hydration contained in the clays associated with the ore would be ideal for this purpose. As the reaction proceeded, the consequent rise in temperature would have driven off water, so producing "undermoderation" and slowing the reaction, thereby avoiding a "run away" reaction. As a result, a particular reactor may have operated in a steady manner or perhaps in a slowly pulsating manner, as water was alternately driven off (causing loss of criticality and cooling) and re-absorbed (recovering criticality and again heating).

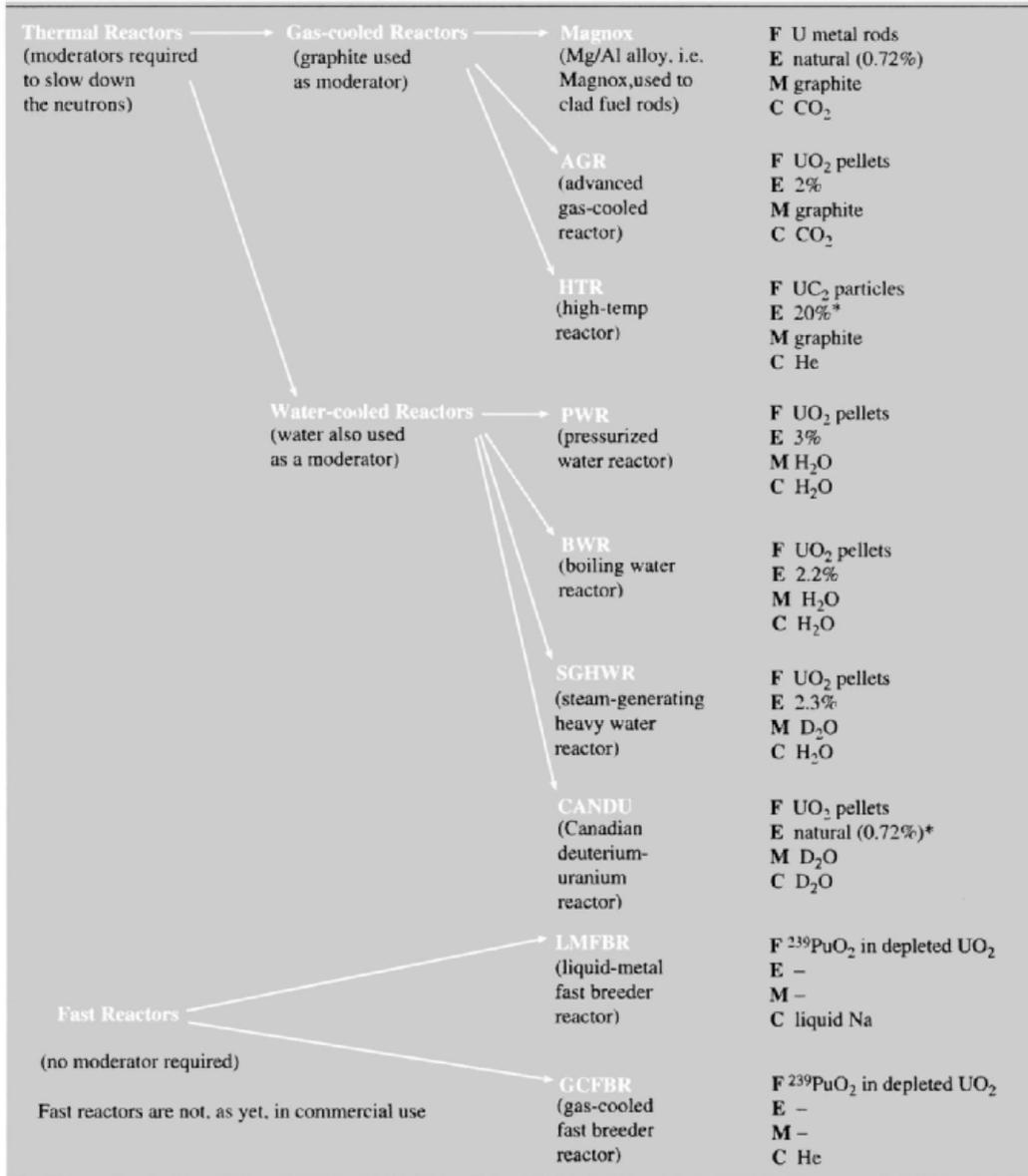
Further control of the reactions must have been effected by neutron-absorbing "poisons", such as lithium and boron, which are nearly always present in clays. That these are present in the Oklo clays in comparatively low concentrations is one of the factors which allowed the reactions to take place. As the nuclear fuel in the original, rich pockets was being used up, the poisons in the surrounding ore would be simultaneously "burned out" by escaping neutrons. Thus ore of only slightly poorer quality, which was initially prevented only by the poisons from being critical, would gradually become so and the chain reaction would be propagated further through the ore bed. It is thought that these reactors operated for about $(0.2 - 1) \times 10^6$ y with output in the region of 10–100 kW, consuming altogether 4–6 tonnes of ^{235}U from a total deposit of the order of 400 000 tonnes of uranium. Subsequent preservation of the fossil reactors is a result of continued burial which protected the uranium from redissolution.

Confirmation of this explanation is unequivocally provided by the presence in the reactor zones of at least half of the more than 30 fission products of uranium. Although soluble salts, such as those of the alkali and alkaline earth metals, have been leached out, lanthanide and platinum metals remain along with traces of trapped krypton and xenon. Most decisively, the observed distribution of the various isotopes of these elements is that of fission products as opposed to the distribution normally found terrestrially. The reasons for the retention of these elements on this particular site is clearly germane to the problem of the long-term storage of nuclear wastes, and is therefore the subject of continuing study.

The circumstances which led to the Oklo phenomenon may well have occurred in other, as yet unidentified, places, but in view of the intervening natural depletion of ^{235}U , the possibility of a natural chain reaction being initiated at the present time or in the future may be discounted.

¹⁷*Le Phenomene d'Oklo*, Proceedings of a Symposium on the Oklo Phenomenon, International Atomic Energy Agency, Vienna, Proceedings Series, 1975. *Natural Fission Reactions*, IAEA, Vienna, Panel Proceedings Series STI/PUB/475, 1978, 754 pp. R. WEST, Natural nuclear reactors. *J. Chem. Ed.* **53**, 336–40 (1976).

[†]If, as is believed (p. 13), the earth was formed about 4.6×10^9 y ago it follows that the proportion of ^{235}U at that time must have been about 25%.



* HTR and CANDU could also possibly use ²³²Th-²³³U fuel

Figure 31.2 Various types of nuclear reactor currently in use or being developed (F fuel; E enrichment, expressed as %²³⁵U present; M moderator; C coolant).

the present time (1996) some 30 countries are operating nuclear power stations to supply energy.

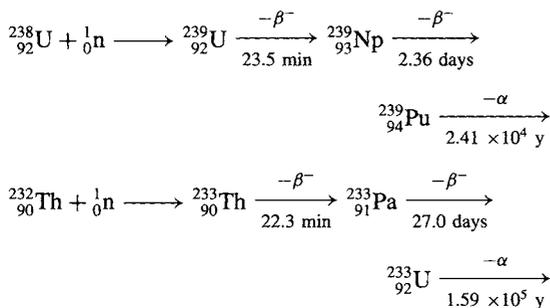
Fuels. Although the concentration of ²³⁵U in natural uranium is sufficient to sustain a chain reaction, its effective dilution by the fuel

cladding and other materials used to construct the reactor make fuel enrichment advantageous. Indeed, if ordinary (light) water is used as moderator or coolant, a concentration of 2–3% ²³⁵U is necessary to compensate for the inevitable

absorption of neutrons by the protons of the water. Enrichment also has the advantage of reducing the critical size of the reactor but this must be balanced against its enormous cost.

Early reactors used uranium in metallic form but this has been superseded by UO_2 which is chemically less reactive and has a higher melting point. UC_2 is also sometimes used but is reactive towards O_2 .

In addition to ${}^{235}_{92}\text{U}$, which occurs naturally, two other fissile nuclei are available artificially. These are ${}^{239}_{94}\text{Pu}$ and ${}^{233}_{92}\text{U}$ which are obtained from ${}^{238}_{92}\text{U}$ and ${}^{232}_{90}\text{Th}$ respectively:



${}^{239}\text{Pu}$ is therefore produced to some extent in all currently operating reactors because they contain ${}^{238}\text{U}$, and this contributes to the reactor efficiency. More significantly, it offers the possibility of generating more fissile material than is consumed in producing it. Such "breeding" of ${}^{239}\text{Pu}$ is not possible in thermal reactors because the net yield of neutrons from the fission of ${}^{235}\text{U}$ is inadequate. But, if the moderator is dispensed with and the chain reaction sustained by using enriched fuel, then there are sufficient fast neutrons to "breed" new fissile material. Fast-breeder reactors are not yet in commercial use but prototypes are operating in France, the UK and Japan and use a core of PuO_2 in "depleted" UO_2 (i.e. ${}^{238}\text{UO}_2$) surrounded by a blanket of more depleted UO_2 in which the ${}^{239}\text{Pu}$ is generated. By making use of the ${}^{238}\text{U}$ as well as the ${}^{235}\text{U}$, such reactors can extract 50–60 times more energy from natural uranium, so using more efficiently the reserves of easily accessible ores. Sadly there are possible dangers associated with a "plutonium economy" which

have led to well-publicized objections, and future developments will be determined by social and political as well as by economic considerations.

The net yield of thermal neutrons from the fission of ${}^{233}\text{U}$ is higher than from that of ${}^{235}\text{U}$ and, furthermore, ${}^{232}\text{Th}$ is a more effective neutron absorber than ${}^{238}\text{U}$. As a result, the breeding of ${}^{233}\text{U}$ is feasible even in thermal reactors. Unfortunately the use of the ${}^{232}\text{Th}/{}^{233}\text{U}$ cycle has been inhibited by reprocessing problems caused by the very high energy γ -radiation of some of the daughter products.

Fuel enrichment. All practicable enrichment processes require the uranium to be in the form of a gas. UF_6 , which readily sublimates (p. 1269), is universally used and, because fluorine occurs in nature only as a single isotope, the compound has the advantage that separation depends solely on the isotopes of uranium. The first, and until recently the only, large-scale enrichment process was by gaseous diffusion which was originally developed in the "Manhattan Project" to produce nearly pure ${}^{235}\text{U}$ for the first atomic bomb (exploded at Alamogordo, New Mexico, 5.30 a.m., 16 July 1945). UF_6 is forced to diffuse through a porous membrane and becomes very slightly enriched in the lighter isotope. This operation is repeated thousands of times by pumping, in a kind of cascade process in which at each stage the lighter fraction is passed forward and the heavier fraction backwards. Unfortunately gaseous diffusion plants are large, very demanding in terms of membrane technology, and extremely expensive in energy: alternatives have therefore actively been sought.⁽¹⁸⁾ So far the only viable alternative is the gas centrifuge process currently operating in the UK, The Netherlands, Germany, Japan and Russia. In a cylindrical centrifuge ${}^{238}\text{UF}_6$ concentrates towards the walls and ${}^{235}\text{UF}_6$ towards the centre. In practice the radial concentration gradient is transformed into an axial gradient by injecting the UF_6 so as to set up an axial counter current so that both the enriched and depleted materials can be drawn off from

¹⁸ C. WHITEHEAD, *Chem. Brit.* **26**, 1161–4 (1990).

peripheral positions where the pressure is higher. The centrifuges rotate at about 1000 revolutions per second and are arranged in a cascade system.

A promising alternative is provided by "Laser isotope separation". Because the ionization energies of ^{235}U and ^{238}U differ slightly, it is possible to ionize the former selectively by irradiating U vapour with laser beams precisely tuned to the appropriate wavelength. The ions can then be collected at a negative electrode.

Cladding. The Magnox reactors get their name from the magnesium-aluminium alloy used to clad the fuel elements, and stainless steels are used in other gas-cooled reactors. In water reactors zirconium alloys are the favoured cladding materials.

Moderators. Neutrons are most effectively slowed by collisions with nuclei of about the same mass. Thus the best moderators are those light atoms which do not capture neutrons. These are ^2H , ^4He , ^9Be and ^{12}C . Of these He, being a gas, is insufficiently dense and Be is expensive and toxic, so the common moderators are highly purified graphite or the more expensive heavy water. In spite of its neutron-absorbing properties, which as mentioned above must be offset by using enriched fuel, ordinary water is also used because of its cheapness and excellent neutron-moderating ability.

Coolants. Because they must be mobile, coolants are either gases or liquids. CO_2 and He are appropriate gases and are used in conjunction with graphite moderators. The usual liquids are heavy and light water, with water also as moderator. In order to keep the water in the liquid phase it must be pressurized (PWR), otherwise it boils in the reactor core (BWR, etc.) in which case the coolant is actually steam. In the case of breeder reactors the higher temperatures of their more compact cores pose severe cooling problems and liquid Na (or Na/K alloy) is favoured, although highly compressed He is another possibility.

Control rods. These are usually made of boron steel or boron carbide (p. 149), but other good neutron absorbers which can be used are Cd and Hf.

Nuclear fuel reprocessing^(3,10)

Many of the fission products formed in a nuclear reactor are themselves strong neutron absorbers (i.e. "poisons") and so will stop the chain reaction before all the ^{235}U (and ^{239}Pu which has also been formed) has been consumed. If this wastage is to be avoided the irradiated fuel elements must be removed periodically and the fission products separated from the remaining uranium and the plutonium. Such reprocessing is of course inherent in the operation of fast-breeder reactors, but whether or not it is used for thermal reactors depends on economic and political factors. Reprocessing is currently undertaken in the UK, France and Russia but is not considered to be economic in the USA.

Irradiated nuclear fuel is one of the most complicated high-temperature systems found in modern industry, and it has the further disadvantage of being intensely radioactive so that it must be handled exclusively by remote control. The composition of the irradiated nuclear fuel depends on the particular reactor in question, but in general it consists of uranium, plutonium, neptunium, americium and various isotopes of over 30 fission-product elements. The distribution of fission products is such as to produce high concentrations of elements with mass numbers in the regions 90–100 (second transition series) and 130–145 (^{54}Xe , ^{55}Cs , ^{56}Ba and lanthanides). The more noble metals, such as ^{44}Ru , ^{45}Rh and ^{46}Pd , tend to form alloy pellets while class-a metals such as ^{38}Sr , ^{56}Ba , ^{40}Zr , ^{41}Nb and the lanthanides are present in complex oxide phases.

The first step is to immerse the fuel elements in large "cooling ponds" of water for a hundred days or so, during which time the short-lived, intensely radioactive species such as $^{131}_{53}\text{I}$ ($t_{1/2} = 8.04$ days) lose most of their activity and the generation of heat subsides.

Then the fuel elements are dissolved in 7M HNO_3 to give a solution containing U^{VI} and Pu^{IV} which, in the widely used plutonium-uranium-reduction, or Purex process, are extracted into 20% tributyl phosphate (TBP) in kerosene leaving most of the fission products

(FP) in the aqueous phase. Subsequent separation of U and Pu depends on their differing redox properties (Fig. 31.3). The separations are far from perfect (see p. 1097), and recycling or secondary purification by ion-exchange techniques is required to achieve the necessary overall separations.

This reprocessing requires the handling of kilogram quantities of Pu and must be adapted to

avoid a chain reaction (i.e. a criticality accident). The critical mass for an isolated sphere of Pu is about 10 kg, but in saturated aqueous solutions may be little more than 500 g. (Because of the large amounts of “inert” ^{238}U present, U does not pose this problem.)

The solution of waste products is concentrated and stored in double-walled, stainless steel tanks shielded by a metre or more of concrete.

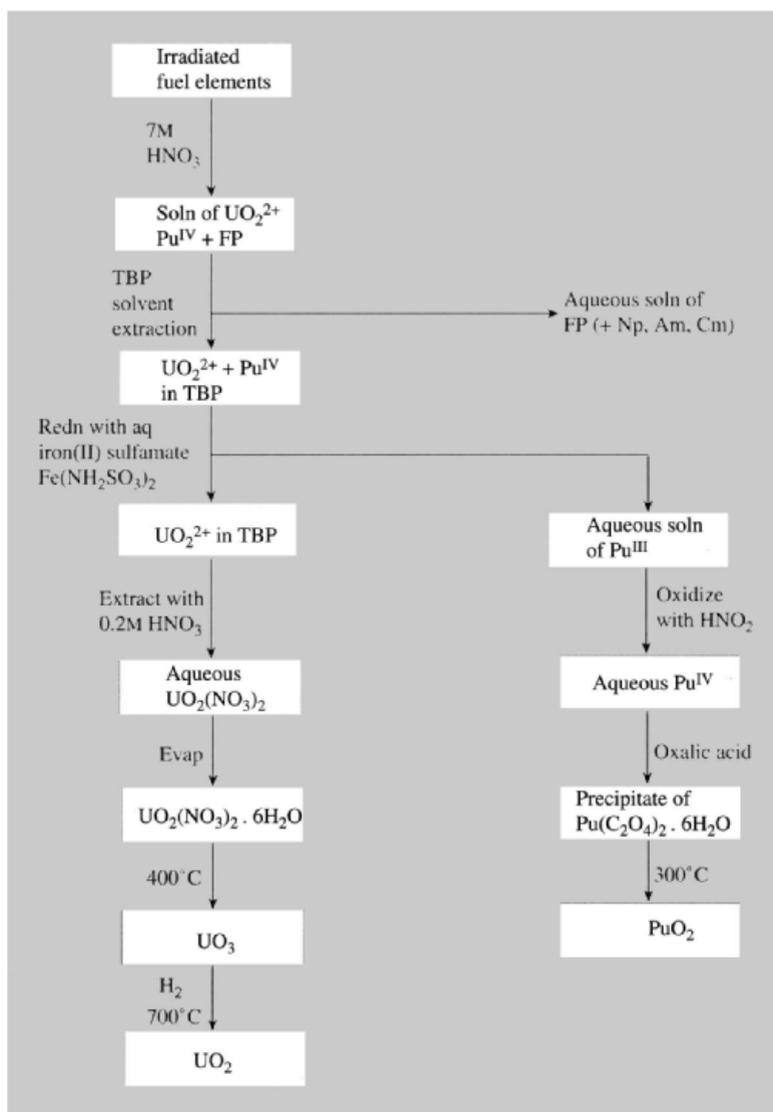


Figure 31.3 Flow diagram for the reprocessing of nuclear fuel [FP = fission products; TBP = $(\text{Bu}^n\text{O})_3\text{PO}$].

Vitrification processes are being developed in several countries in which the dried waste is calcined and heated with ground glass "frit" to produce a borosilicate glass which can be stored or disposed of more permanently if there is agreement on suitable sites.

$^{237}_{93}\text{Np}$, $^{241}_{95}\text{Am}$ and $^{243}_{95}\text{Am}$ can be extracted from reactor wastes and are available in kg quantities. Prolonged neutron irradiation of $^{239}_{94}\text{Pu}$ is used at the Oak Ridge laboratories in Tennessee to produce: $^{244}_{96}\text{Cm}$ on a 100-g scale; $^{242}_{96}\text{Cm}$, $^{249}_{97}\text{Bk}$, $^{252}_{98}\text{Cf}$ and $^{253}_{99}\text{Es}$ all on a mg scale; and $^{257}_{100}\text{Fm}$ on a μg scale. For trace amounts of these mixtures, dissolution in nitric acid, absorption of the +3 ions on to a cation exchange resin and elution with ammonium α -hydroxyisobutyrate provides an efficient separation of the elements from each other and from accompanying lanthanides, etc. The separation of macro amounts of these elements, however, is not feasible by this method because of radiolytic damage to the resin caused by their intense radioactivity. Much quicker solvent extraction processes similar to those used for reprocessing nuclear fuels are therefore used.

Because the sequence of neutron captures inevitably leads to $^{258}_{100}\text{Fm}$ which has a fission half-life of only a few seconds, the remaining three actinides, ^{101}Md , ^{102}No and ^{103}Lr , can only be prepared by bombardment of heavy nuclei with the light atoms ^4_2He to $^{20}_{10}\text{Ne}$. This raises the mass number in multiple units and allows the $^{258}_{100}\text{Fm}$ barrier to be avoided; even so, yields are minute and are measured in terms of the number of individual atoms produced.

Apart from $^{239}_{94}\text{Pu}$, which is a nuclear fuel and explosive, the transuranium elements have in the past been produced mainly for research purposes. A number of specialized applications, however, have led to more widespread uses. $^{238}_{94}\text{Pu}$ (produced by neutron bombardment of $^{237}_{93}\text{Np}$ to form $^{238}_{93}\text{Np}$ which decays by β -emission to $^{238}_{94}\text{Pu}$) is a compact heat source (0.56 W g^{-1} as it decays by α -emission) which, in conjunction with PbTe thermoelectric elements, for instance, provides a stable and totally reliable source of electricity with no moving parts. It has been

used in the form of PuO_2 in kg quantities in the American Apollo and Galileo spacecraft. Since its α -emission is harmless and is not accompanied by γ -radiation it is also used in heart pacemakers ($\sim 160\text{ mg }^{238}_{94}\text{Pu}$) where it lasts about 5 times longer than conventional batteries before requiring replacements. $^{241}_{95}\text{Am}$ is also widely used as an ionization source in smoke detectors and thickness gauges.

31.2.3 Properties of the actinide elements

The dominant feature of the actinides is their nuclear instability, as manifest in their radioactivity (mostly α -decay) and tendency to spontaneous fission; both of these modes of decay become more pronounced (shorter half-lives) with the heavier elements. The radioactivity of Th and U is probably responsible for much of the earth's internal heat, but is of a sufficiently low level to allow their compounds to be handled and transported without major problems. By contrast, the instability of the heavier elements not only imposes most severe handling problems⁽¹⁹⁾ but drastically limits their availability. Thus, for instance, the crystal structures of Cf and Es were determined on only microgram quantities,⁽¹⁾ while the concept of "bulk" properties is not applicable at all to elements such as Md, No and Lr which have never been seen and have only been produced in unweighably small amounts. Even where adequate amounts are available, the constant build-up of decay products and the associated generation of heat may seriously affect the measured properties (see also p. 753). An indication of the difficulties of working with these elements can be gained from the fact that two phases described in 1974 as two forms of Cf metal were subsequently shown, in fact, to be hexagonal $\text{Cf}_2\text{O}_2\text{S}$ and fcc CfS.⁽²⁰⁾

Some of the more important known properties of the actinides are summarized in Table 31.2.

¹⁹ R. A. BULMAN, *Coord. Chem. Revs.* **31**, 221–50 (1980).

²⁰ W. H. ZACHARIASEN, *J. Inorg. Nucl. Chem.* **37**, 1441–2 (1975).

Table 31.2 Some properties of the actinide elements

Property	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
Atomic number	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Number of naturally occurring isotopes	1	—	3	—	—	—	—	—	—	—	—	—	—	—
Most common isotope:														
Mass number	232	231	238	237	239	241	244	249	252	252	257	256	259	262
Half-life ^(a)	1.40×10^{10} y (α)	3.25×10^4 y (α)	4.47×10^9 y (α)	2.14×10^6 y (α)	2.41×10^4 y (α)	433 y (α)	18.1 y (α)	320 d (β^-)	2.64 y (α)	472 d (α)	100.5 d (α)	78 min (β^+/EC)	58 min (α , EC)	3.6 h (α)
Relative nuclidic mass	232.0380	231.0359	238.0289 ^(b)	237.0482	239.0522	241.0568	244.0627	249.0750	252.0816	252.0830	257.0951	256.0941	259.1011	262.110
Electronic configuration, [Rn] plus	$6d^2 7s^2$	$5f^2 6d^1 7s^2$ or $5f^3 6d^2 7s^2$	$5f^3 6d^1 7s^2$	$5f^4 6d^1 7s^2$ or $5f^6 7s^2$	$5f^6 7s^2$	$5f^7 7s^2$	$5f^7 6d^1 7s^2$	$5f^9 7s^2$ or $5f^8 6d^1 7s^2$	$5f^{10} 7s^2$	$5f^{11} 7s^2$	$5f^{12} 7s^2$	$5f^{13} 7s^2$	$5f^{14} 7s^2$	$5f^{14} 6d^1 7s^2$
Metal radius (CN12) ^(c) /pm	179	163	156	155	159	173	174	170	186 ± 2	186 ± 2	—	—	—	—
Ionic radius (CN6)/pm	—	—	—	71	—	—	—	—	—	—	—	—	—	—
VI	—	—	73	72	71	—	—	—	—	—	—	—	—	—
V	—	78	76	75	74	—	—	—	—	—	—	—	—	—
IV	94	90	89	87	86	85	85	83	82.1	—	—	—	—	—
III	—	104	102.5	101	100	97.5	97	96	95	—	—	—	—	—
II	—	—	—	110	—	126 ^(d)	—	—	—	—	—	—	—	—
$E^\circ(\text{MO}_2^{2+}/\text{MO}_2^+)/\text{V}$	—	—	0.17	1.24	1.02	1.60	—	—	—	—	—	—	—	—
$E^\circ(\text{MO}_2^+/\text{M}^{4+})/\text{V}$	—	-0.05	0.38	0.64	1.04	0.82	—	—	—	—	—	—	—	—
$E^\circ(\text{M}^{3+}/\text{M}^{2+})/\text{V}$	-3.8	-1.4	-0.52	0.15	1.01	2.62	3.1	1.67	3.2	4.5	5.2	—	—	—
$E^\circ(\text{M}^{3+}/\text{M})/\text{V}$	-1.83	-1.47	-1.38	-1.30	-1.25	-0.90	—	—	—	—	—	—	—	—
$E^\circ(\text{M}^{2+}/\text{M})/\text{V}$	—	—	-1.66	-1.79	-2.00	-2.07	-2.06	-2.00	-1.91	-1.98	-2.07	-1.74	-1.26	-2.1
MP ^o /C	1750	1572	1135	644	640	1176	1345	1050	900	860	1527	827	827	1627
BP ^o /C	4788	(4722)	3818	(3902)	3228	(2607)	—	—	—	—	—	—	—	—
$\Delta H_{\text{fus}}/\text{kJ mol}^{-1}$	16.11	16.7	12.6	(9.46)	2.80	14.4	—	—	—	—	—	—	—	—
$\Delta H_{\text{vap}}/\text{kJ mol}^{-1}$	513.7	481	417	336	343.5	238.5	—	—	—	—	—	—	—	—
ΔH_f (monatomic gas)/ kJ mol ⁻¹	575	—	482	—	352	—	—	—	—	—	—	—	—	—
Density (25°C)/g cm ^{-3(e)}	11.72	15.37	19.05	20.45	19.86	13.67	13.51	14.78	—	—	—	—	—	—
Electrical resistivity (22°C)/ $\mu\text{ohm cm}$	15.4	19.1	30.8	122	150	71	—	—	—	—	—	—	—	—

^(a)The rate of decay by spontaneous fission increases with atomic number and is an important additional cause of instability in the later actinides (*trans*-Np).^(b)This value refers to the natural mixture of uranium isotopes, i.e. it is the atomic weight. Variations are possible because (i) some geological samples have anomalous isotopic compositions, and (ii) commercially available samples may have been depleted in ²³⁵U. The value for ²³⁸U itself is 238.0508.^(c)For Pa, CN = 10 and for U, Np and Pu the structures are rather irregular so that the coordination number is not a precise concept.^(d)For Am^{II}, radius refers to CN = 8.^(e)Polymorphism is common amongst the actinides and these data refer to the form most stable at room temperature.

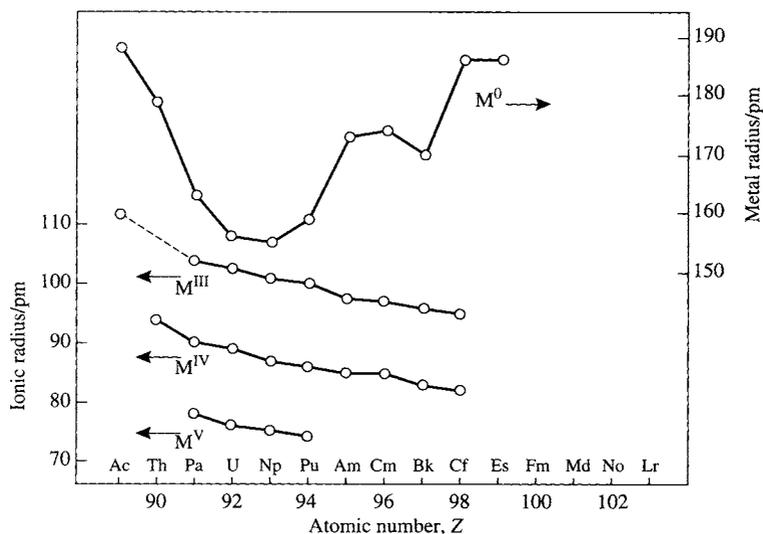


Figure 31.4 Metal and ionic radii of Ac and the actinides.

The metals are silvery in appearance but display a variety of structures. All except Cf have more than one crystalline form (Pu has six) but most of these are based on typically metallic close-packed arrangements. Structural variability is mirrored by irregularities in metal radii (Fig. 31.4) which are far greater than are found in lanthanides and probably arise from a variability in the number of electrons in the metallic bands of the actinide elements. From Ac to U, since the most stable oxidation state increases from +3 to +6, it seems likely that the sharp fall in metal radius is due to an increasing number of electrons being involved in metallic bonding. Neptunium and Pu are much the same as U but thereafter increasing metal radius is presumably a result of fewer electrons being involved in metallic bonding since it roughly parallels the reversion to a lanthanide-like preference for tervalency in the heavier actinides.

By contrast, the ionic radius in a given oxidation state falls steadily and, though the available data are less extensive, it is clear that an “actinide contraction” exists, especially for the +3 state, which is closely similar to the “lanthanide contraction” (see p. 1232).

31.2.4 Chemical reactivity and trends

The actinide metals are electropositive and reactive, apparently becoming increasingly so with atomic number. They tarnish rapidly in air, forming an oxide coating which is protective in the case of Th but less so for the other elements. Because of the self-heating associated with its radioactivity (100 g ^{239}Pu generates ~ 0.2 watts of heat) Pu is best stored in circulating dried air. All are pyrophoric when finely divided.

The metals react with most non-metals especially if heated, but resist alkali attack and are less reactive towards acids than might be expected. Concentrated HCl probably reacts most rapidly, but even here insoluble residues remain in the cases of Th (black), Pa (white) and U (black). Those of Th and U have the approximate compositions $\text{HThO}(\text{OH})$ and $\text{UH}(\text{OH})_2$. Concentrated HNO_3 passivates Th, U and Pu, but the addition of F^- ions avoids this and provides the best general method for dissolving these metals.

Reactions with water are complicated and are affected by the presence of oxygen. With boiling water or steam, oxide is formed on the surface of the metal and H_2 is liberated. Since the metals react readily with the latter, hydrides are produced which themselves react rapidly with

Table 31.3 Oxidation states of actinide elements

Oxidation states found only in solids are given in brackets; numbers in **bold** indicate the most stable oxidation states in aqueous solution. Colours refer to aqueous solutions^(a)

Species present in H ₂ O	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
M ^{II}	—	—	—	—	—	(2)	—	—	(2)	(2)	2	2	2	—
M ^{III}	3	(3)	3	3	3	3	3	3						
M ^{IV}	4	4	4	4	4	4	4	4	(4)	—	—	—	—	—
MO ₂ ⁺	c-less	c-less	g	y-g	br	pink	pale y	y	—	—	—	—	—	—
	—	5	5	5	5	5	—	—	—	—	—	—	—	—
MO ₂ ²⁺	—	c-less	unknown	g	purple ^(b)	y	—	—	—	—	—	—	—	—
	—	—	6	6	6	6	—	—	—	—	—	—	—	—
(MO ₅ ³⁻) ^(c)	—	—	y	p	o	br	—	—	—	—	—	—	—	—
	—	—	—	7	7	—	—	—	—	—	—	—	—	—
	—	—	—	g	g	—	—	—	—	—	—	—	—	—

^(a)bl = blue; br = brown; c-less = colourless; gr = green; o = orange; r = red; v = violet; y = yellow.

^(b)Because of disproportionation, PuO₂⁺ is never observed on its own and its colour must therefore be deduced from the spectrum of a mixture involving Pu in several oxidation states.

^(c)This is probably too simple, hydroxo species such as [MO₄(OH)₂]³⁻ being more likely.

water and so facilitate further attack on the metals.

Knowledge of the detailed chemistry of the actinides is concentrated mainly on U and, to a lesser extent, Th and Pu.⁽²¹⁾ Availability and safety are, of course, major problems for the remaining elements, but self-heating and radiolytic damage can be troublesome, the energy evolved in radioactive decay being far greater than that of chemical bonds. Thus in aqueous solutions of concentrations greater than 1 mg cm⁻³ (i.e. 1 g l⁻¹), isotopes with half-lives less than, say, 20 years, will produce sufficient H₂O₂ to produce appreciable oxidation or reduction where the redox behaviour of the element allows this. Fortunately, the nuclear instability which produces these problems also assists in overcoming them: by performing chemical reactions with appropriate, non-radioactive, carrier elements containing only trace amounts of the actinide in question, it is possible to detect the presence of the latter, and hence explore its chemistry because of the extreme sensitivity of radiation detectors. Such “tracer” techniques have

provided remarkably extensive information particularly about the aqueous solution chemistry of the actinides.

Table 31.3 lists the known oxidation states. For the first three elements (Th, Pa and U) the most stable oxidation state is that involving all the valence electrons, but after this the most stable becomes progressively lower until, in the second half of the series, the +3 state becomes dominant. Appropriate quantitative data for elements up to Am are summarized in Fig. 31.5. The highest oxidation state attainable by Th, and the only one occurring in solution, is +4. Data for Pa are difficult to obtain because of its propensity for hydrolysis which results in the formation of colloidal precipitates, except in concentrated acids or in the presence of complexing anions such as F⁻ or C₂O₄²⁻. However, it is clear that +5 is its most stable oxidation state since its reduction to +4 requires rather strong reducing agents such as Zn/H⁺, Cr^{II} or Ti^{III} and the +4 state in solution is rapidly reoxidized to +5 by air. In the case of uranium the shape of the volt-equivalent versus oxidation state curve (pp. 435–8) reflects the ready disproportionation of UO₂⁺ into the more stable U^{IV} and UO₂²⁺; it should also be possible for atmospheric oxygen ($\frac{1}{2}$ O₂ + 2H⁺ +

²¹ G. R. CHOPPIN and B. E. STOUT, *Chem. Brit.*, **27**, 1126–9 (1991).

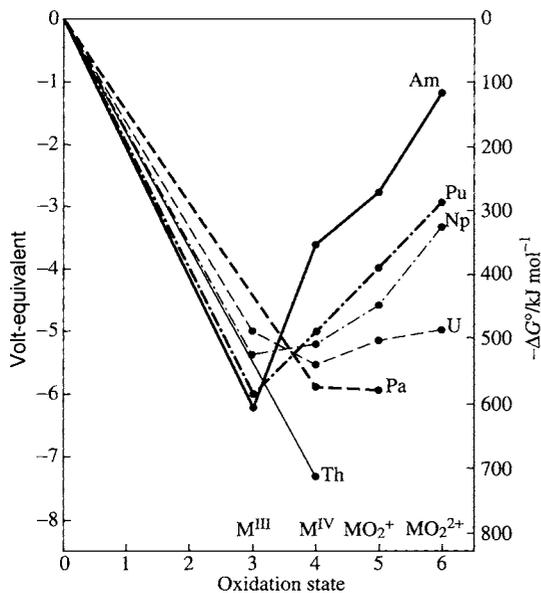


Figure 31.5 Volt-equivalent versus oxidation state for actinide ions.

$2e^- \rightleftharpoons \text{H}_2\text{O}$, $E^\circ = 1.229 \text{ V}$) to oxidize U^{IV} to UO_2^{2+} though in practice this occurs only slowly. For the heavier elements the increasingly steep-sided trough indicates the increasing stability of the +3 state.

The redox behaviour of Th, Pa and U is of the kind expected for d-transition elements which is why, prior to the 1940s, these elements were commonly placed respectively in groups 4, 5 and 6 of the periodic table. Behaviour obviously like that of the lanthanides is not evident until the second half of the series. However, even the early actinides resemble the lanthanides in showing close similarities with each other and gradual variations in properties, providing comparisons are restricted to those properties which do not entail a change in oxidation state. The smooth variation with atomic number found for stability constants, for instance, is like that of the lanthanides rather than the d-transition elements, as is the smooth variation in ionic radii noted in Fig. 31.4. This last factor is responsible for the close similarity in the structures of many actinide and lanthanide compounds especially noticeable in the +3 oxidation state for which

a given actinide ion is only about 4 pm larger than the corresponding Ln^{3+} .

It is evident from the above behaviour that the ionization energies of the early actinides, though not accurately known, must be lower than for the early lanthanides. This is quite reasonable since it is to be expected that, when the 5f orbitals of the actinides are beginning to be occupied, they will penetrate less into the inner core of electrons, and the 5f electrons will therefore be more effectively shielded from the nuclear charge than are the 4f electrons of the corresponding lanthanides (i.e. the relationship between 4f and 5f series may be compared to that between 3d and 4d). Because the outer electrons are less firmly held, they are all available for bonding in the actinide series as far as Np (4th member), but only for Ce (1st member) in the lanthanides, and the onset of the dominance of the +3 state is accordingly delayed in the actinides. That the 5f and 6d orbitals of the early actinides are energetically closer than the 4f and 5d orbitals of the early lanthanides is evidenced by the more extensive occupation of the 6d orbitals in the neutral atoms of the former (compare the outer electron configuration in Tables 31.2 and 30.2). These 5f orbitals also extend spatially further than the 4f and are able to make a covalent contribution to the bonding which is much greater than that in lanthanide compounds. This leads to a more extensive actinide coordination chemistry and to crystal-field effects, especially with ions in oxidation states above +3, much larger than those found for lanthanide complexes. It is also important to remember that relativistic effects on the atomic properties and chemistry of these heavy elements cannot be safely ignored in attempts to explain or predict their behaviour.

Table 31.4 is a list of typical compounds of the actinides and demonstrates the wider range of oxidation states compared to lanthanide compounds. High coordination numbers are still evident, and distortions from the idealized stereochemistries which are quoted are again general. However, no doubt at least partly because the early actinides have received most attention, the widest range of stereochemistries is