CHAPTER 16

The Transuranium Elements

Contents

16.1. Early "transuranium" elements

After the discovery of the neutron by Chadwick in 1932, the group led by Fermi in Rome began bombarding different elements with neutrons to study the radioactivity induced through (n,γ) reactions. The decay characteristics of the radioactivity in neutron-irradiated uranium was interpreted to indicate that some of the products were probably transuranium elements. Similar conclusions were reached by other research groups; for example in 1937 Meitner, Hahn and Strassman in Berlin proposed the following reaction/decay series (omitting mass numbers):

$$_{92}\text{U} + \text{n} \longrightarrow {}_{92}\text{U} \xrightarrow[10\text{ s}]{\beta} {}_{93}\text{EkaRe} \xrightarrow[2.2\text{ m}]{\beta} {}_{94}\text{EkaOs} \xrightarrow[59\text{ m}]{\beta} \text{etc}$$

However, many anomalies existed in the chemical properties of these "transuranium elements" as pointed out by Ida Noddack, Irene Curie, Savitch and others.

In 1939 Hahn and Strassman conducted a series of extremely careful chemical investigations which showed that these "transuranium elements" were in fact isotopes of elements in the middle of the Periodic Table, such as Sr, La, Ba etc. The explanation of this unexpected observation was provided by Meitner and Frisch, who postulated that the uranium atoms were caused to split by thermal neutrons into two approximately equal fragments (as Noddack had proposed several years earlier).

Further investigation showed that it was the isotope ^{235}U which had undergone fission, and that large amounts of energy and about 2.5 neutrons were released in the process. It occurred to a number of scientists that, if at least one of these neutrons could be captured by other uranium atoms to cause further fission, a chain reaction should be the consequence. This led to the development of nuclear energy and nuclear weapons, as described in Chapter 19.

To the present time 23 transuranium elements have been synthesized; the isotopes known are summarized in Figure 16.1; except elements above 114, which are still uncertain.

16.2. Production of transuranic elements

16.2.1. *Neptunium, element 93*

Early in 1940 McMillan and Abelson in the United States synthesized and identified a new element with atomic number 93 to which they gave the name neptunium. The reaction used in the synthesis was

$$^{238}_{92}\mathrm{U}\ (n,\gamma)\ ^{239}_{92}\mathrm{U} \xrightarrow[23\ \mathrm{min}]{\beta^-} {}^{239}_{93}\mathrm{Np} \xrightarrow[2.3\ \mathrm{d}]{\beta^-} \tag{16.1}$$

(cf. Fig. 16.1). The experimental recoil technique for separating the fission and neutron capture products from the target material is described in §15.6.1. Chemical experiments showed that the product had a 2.3 d half-life and could be reduced by SO_2 to a lower valency state (presumably +4), which could be precipitated as a fluoride (carrier: LaF_3); this distinguished the element from uranium. In its oxidized state (using BrO_3^- as oxidant) it showed the same chemistry as hexavalent uranium. Because no fission product is expected to have this behavior, the assumption that the element with the 2.3 d half-life was a transuranic element was verified.

The longest lived isotope is ^{237}Np with $t_{1/2}$ 2.14×10^6 y. It is produced in nuclear reactors (Ch. 19) through the reactions

$$^{238}\mathrm{U}\ (n,2n)\ ^{237}\mathrm{U} \xrightarrow[6.75\ \mathrm{d}]{\beta^-} {}^{237}\mathrm{Np} \quad (\approx 70\%) \tag{16.2a}$$

$$^{235}\mathrm{U}\ (n,\gamma)\ ^{236}\mathrm{U}\ (n,\gamma)\ ^{237}\mathrm{U} \xrightarrow[6.75\ \mathrm{d}]{\beta^-} {}^{237}\mathrm{Np} \quad (\approx 30\%) \tag{16.2b}$$

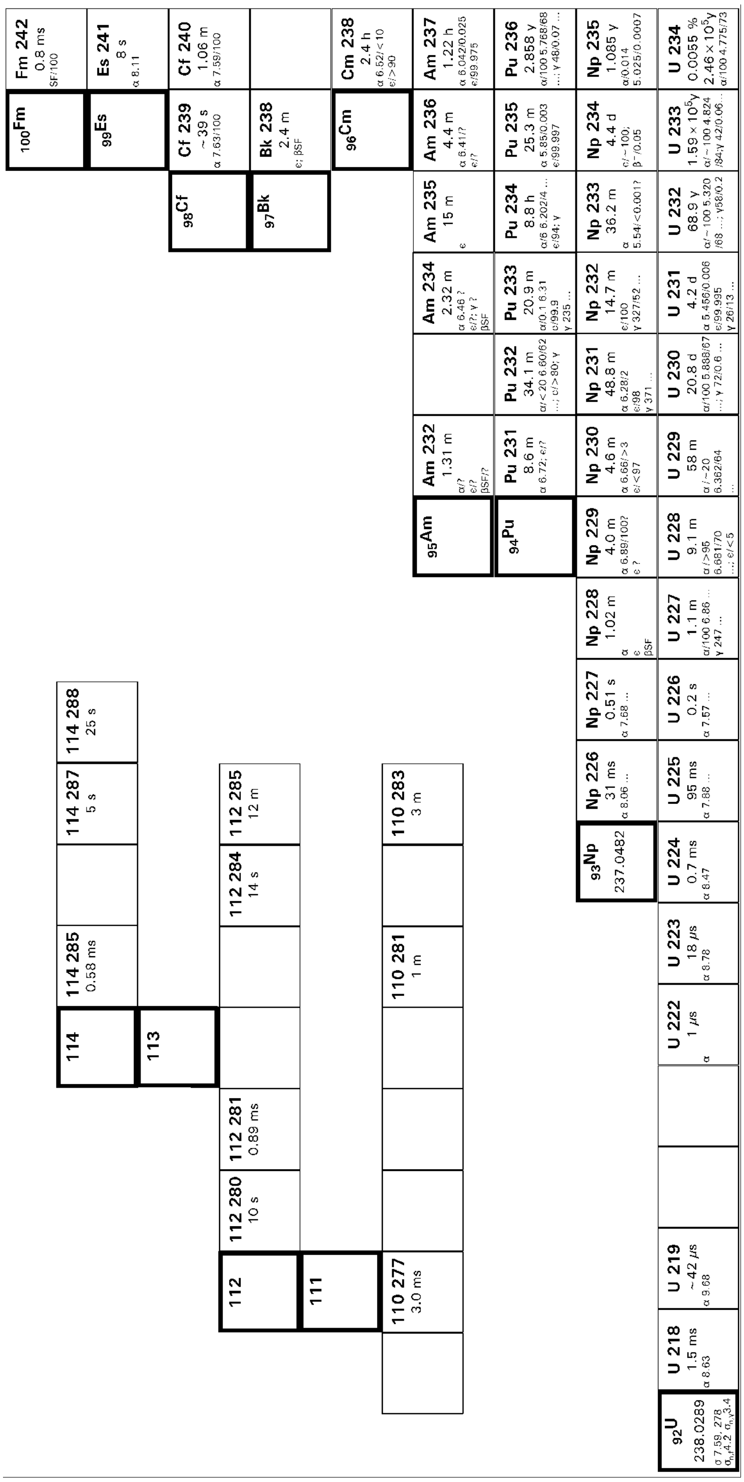

FIG. 16.1. Isotope chart of uranium and transuranium elements.

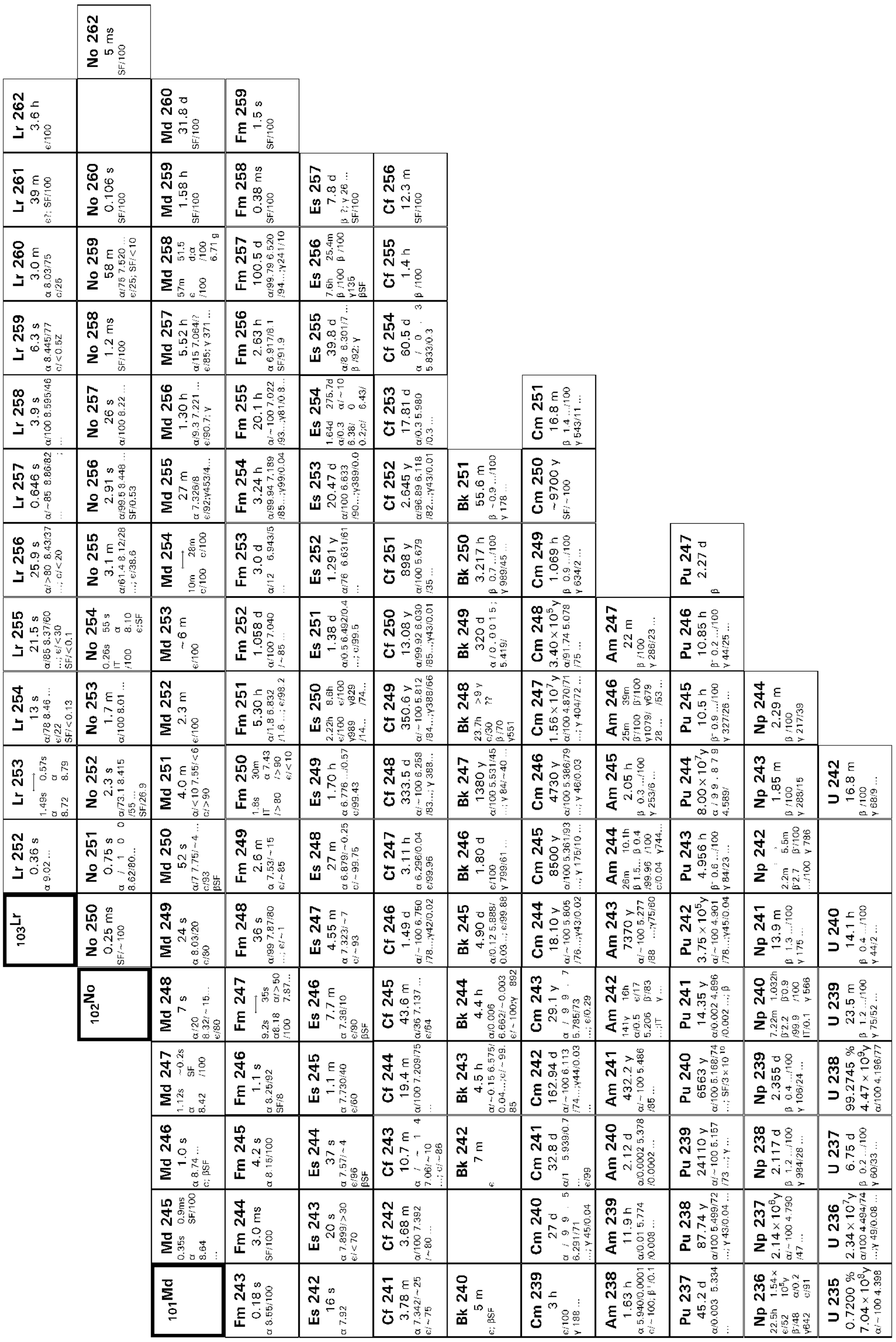

FIG. 16.1. Continued from previous page.

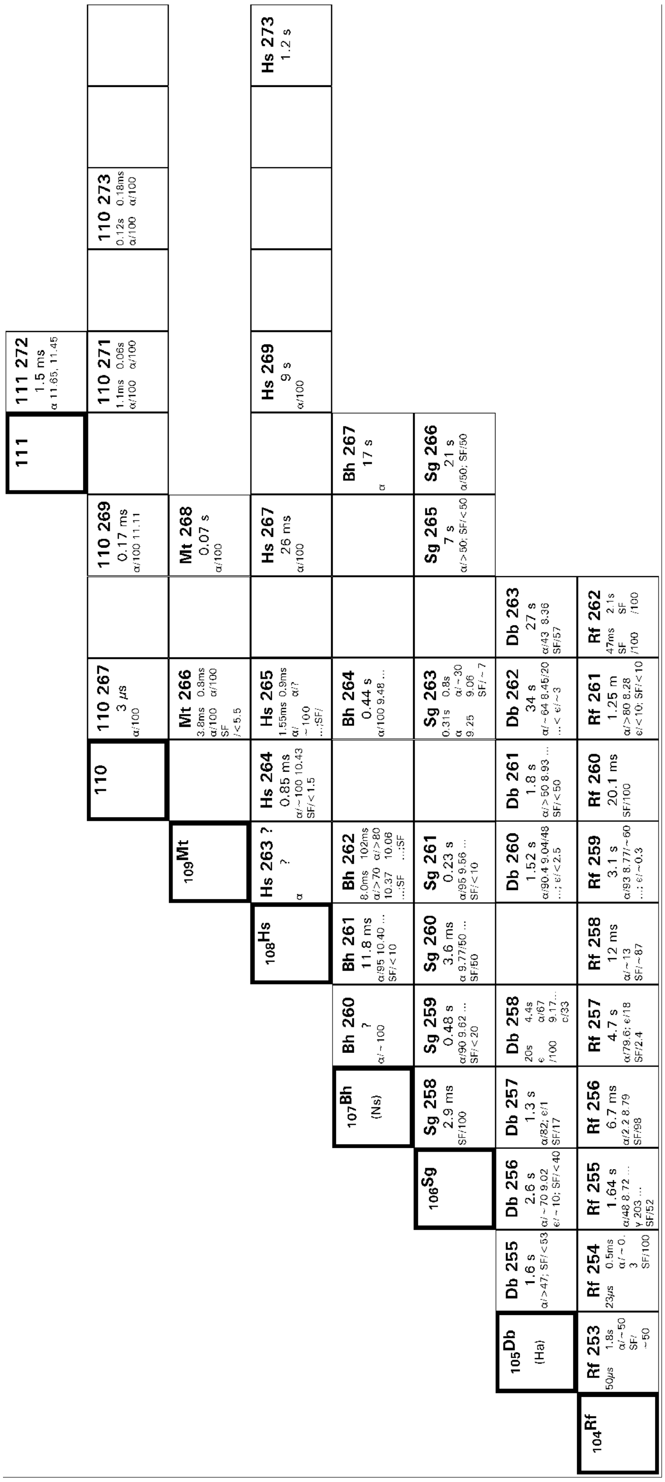

FIG. 16.1. Continued from previous page.

About 0.5 kg ^{237}Np is contained in each ton of spent reactor fuel. By separation processes, similar to those described in Chapter 21, hundreds of kg of Np has been made available for research. So far it has not found any practical use except as target material for production of ^{238}Pu. Though ^{237}Np has too short a half-life to still exist naturally on earth, its optical spectrum has been observed in some stars, from which the star can be deduced to be of relatively young age ($\leq 10^7$ y, cf. next § on ^{244}Pu).

16.2.2. *Plutonium, element 94*

At the end of 1940 an isotope of element 94 (plutonium) was synthesized by Seaborg, McMillan, Kennedy, and Wahl by the bombardment of uranium with deuterons in a cyclotron:

$$^{238}_{92}\text{U (d,2n) } ^{238}_{93}\text{Np} \xrightarrow[2.1\text{ d}]{\beta^-} {}^{238}_{94}\text{Pu} \xrightarrow[88\text{ y}]{\alpha} \qquad (16.3)$$

It was identified as a new element, which was distinctly different from both uranium and neptunium in its redox properties (e.g. the +3 and +4 oxidation states were more stable). A second isotope of element 94, ^{239}Pu, with a half-life of 24 000 y was synthesized very shortly afterwards as an α-radioactive daughter of ^{239}Np.

Experiments with ^{239}Pu confirmed theoretical predictions that it would exhibit high fissibility with both thermal and fast neutrons. This meant that ^{239}Pu in sufficient quantity would also experience an instantaneous nuclear explosion like ^{235}U. If controlled nuclear fission could be accomplished in a nuclear reactor, it would be possible to produce large amounts of plutonium by neutron bombardment of ^{238}U. The ^{239}Pu could be isolated by chemical methods which were expected to be simpler than the isotopic separation required to obtain pure ^{235}U. As a consequence, the production of ^{239}Pu became a major project of the atomic bomb program of the United States during World War II; see further Ch. 19.

Even though plutonium may have been formed in considerable amounts in the cosmic r-process (§17.5.3), the most stable isotope, ^{244}Pu, has a half-life of only 8.3×10^7 y, which prevents it from having survived on earth to our time. However, traces of ^{244}Pu have been discovered in cerium-rich rare earth minerals. If the amount found is extrapolated, considering the enrichment of plutonium in the mineral, one gram of the earth's crust will contain 3×10^{-25} g ^{244}Pu. This would indicate about 10 g of natural plutonium remaining from the genesis of the earth, at which time it existed in parts per million of matter. ^{244}Pu decays by α-emission to ^{240}U ($t_{1/2}$ 14.1 h, β^-).

As discussed in §19.10, ^{239}Pu has been formed in natural uranium reactors at a later stage of the earth's evolution. Many thousands of tons of plutonium has been synthesized in commercial and military reactors; the annual global production rate in nuclear power reactors in the year 2000 was ≈1000 tons/y, contained in the spent fuel elements. The nuclear reactions and chemical separation processes are presented in Chapters 19 and 21. The build-up of heavier elements and isotopes by n-irradiation of ^{239}Pu in nuclear reactors is illustrated in Figures 16.2 and 16.3. The accumulated amount of higher actinides within the European community is many tons for ^{237}Np, ^{238}Pu and ^{241}Am, and hundreds of kg of ^{244}Cm; the amounts in the United States and Russia are of the same magnitude.

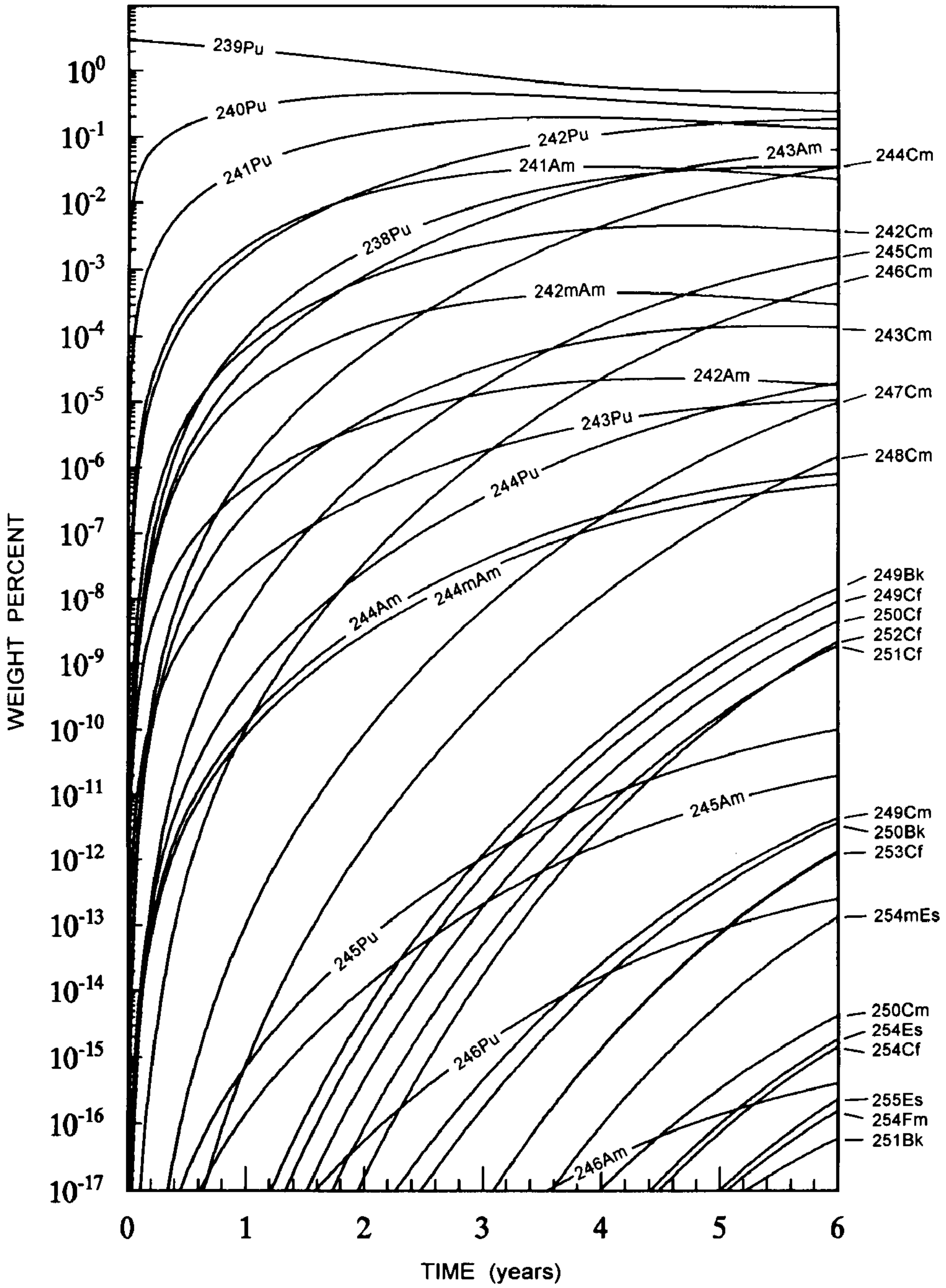

FIG. 16.2. Production of higher actinide isotopes by irradiation of mixed oxide fuel (3% ^{239}Pu, rest depleted U) at constant power in a boiling water reactor.

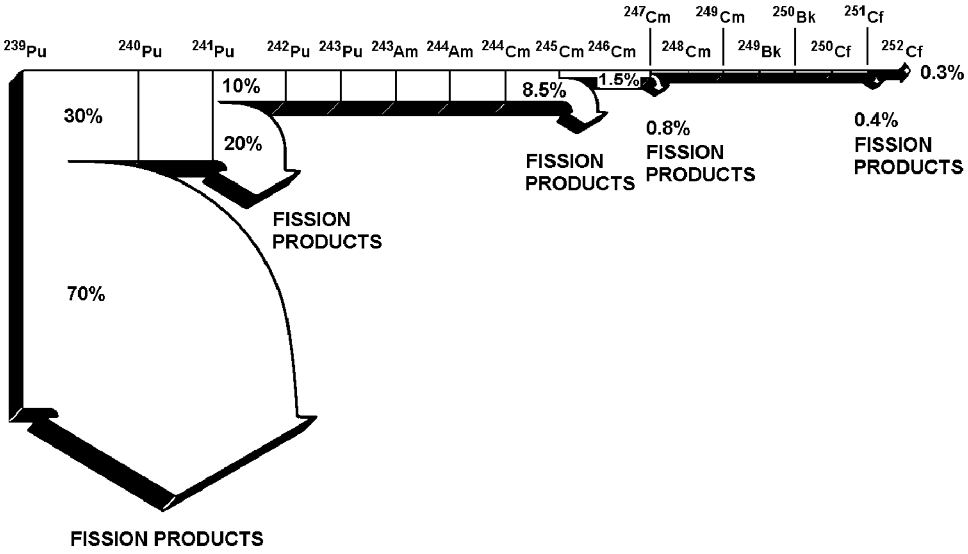

FIG. 16.3. The major paths in transuranium element production in a thermal nuclear reactor; fission and n-capture compete for available nuclei (From Seaborg).

16.2.3. *Americium and curium, elements 95 and 96*

Successive neutron capture in ^{239}Pu (as occurs in nuclear reactors) produces isotopes of plutonium which undergo β^--decay, forming transplutonium elements with atomic numbers 95 (americium) and 96 (curium) (Fig. 16.2). The reaction sequence is

$$
\begin{array}{lll}
{}^{239}_{94}\text{Pu}\ (n,\gamma)\ {}^{240}_{94}\text{Pu}\ (n,\gamma)\ {}^{241}_{94}\text{Pu} & & \\
\qquad\qquad\qquad\qquad\quad \downarrow \beta^-\ 14.4\ \text{y} & & \\
\qquad\qquad\qquad\qquad\quad {}^{241}_{95}\text{Am}\ (n,\gamma)\ {}^{242}_{95}\text{Am} & & \\
\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \beta^-\ 16.01\ \text{h} & & \\
\qquad\qquad\qquad\qquad\qquad\qquad\qquad {}^{242}_{96}\text{Cm} & &
\end{array}
\tag{16.4}
$$

Am and Cm were discovered by Seaborg and co-workers in the USA in 1944-45 in irradiation of plutonium with neutrons in a nuclear reactor according to (16.4) and by irradiation of plutonium with α-particles in a cyclotron according to

$$
{}^{239}_{94}\text{Pu}\ (\alpha,n)\ {}^{242}_{96}\text{Cm}\ \underset{163\ \text{d}}{\overset{\alpha}{\rightarrow}}
\tag{16.5}
$$

All of the isotopes so far described have half-lives of sufficient length for ordinary chemistry although the small amounts made special laboratory techniques necessary (§9.2).

^{241}Am and ^{242}Cm also decay through spontaneous fission. The longest lived isotopes of these elements are ^{243}Am, $t_{½}$ 7370 y, and ^{247}Cm, $t_{½}$ 1.56×10^7 y, decaying by α-emission to ^{239}Np and ^{243}Pu (β^-, $t_{½}$ 5.0 h), respectively; see Fig. 16.1. Both are produced in nuclear power reactors, Figs. 16.2 and 16.3. The much higher stability of the heavier nuclide ^{247}Cm (compared to ^{243}Am) can be explained by its lower Q_α (5.352 as compared to 5.638 MeV) and by the proximity to the next magic neutron number, 152.

16.2.4. *Berkelium and californium, elements 97 and 98*

By 1949 Seaborg's group had synthesized a few milligrams of $^{241}_{95}$Am from reactor bombardment of plutonium. This material was used as the target in a cyclotron bombardment. Immediately following irradiation, the target was dissolved and the products separated by passage through a column of ion exchange resin using an eluting solution of ammonium citrate (§9.2.6). An α-emitting species with a half-life of 4.5 h was identified as the isotope of element 97 of mass number 243; the name berkelium was proposed.

Later the same technique was used with a target of a few micrograms of ^{242}Cm and the first isotopes of californium (Z = 98) were discovered.

$$^{241}_{95}\mathrm{Am}\ (\alpha,2n)\ ^{243}_{97}\mathrm{Bk}\ \xrightarrow[4.5\ \mathrm{h}]{\mathrm{EC}} \qquad (16.6)$$

$$^{242}_{96}\mathrm{Cm}\ (\alpha,n)\ ^{245}_{98}\mathrm{Cf}\ \xrightarrow[44\ \mathrm{min}]{\alpha} \qquad (16.7)$$

The last four actinides (Am, Cm, Bk, and Cf) have +3 as their most stable valency state in solution, just as the rare earth elements, and their chemistry is very similar to that of the lanthanides. This similarity in solution has been commonly used for identification of a particular actinide; Figure 16.7 shows elution curves for lanthanides and actinides from a cation exchange column.

The longest lived isotopes of these elements are ^{247}Bk, $t_{½}$ 1380 y, and ^{251}Cf, $t_{½}$ 898 y, decaying by α-emission to ^{243}Am and ^{247}Cm, respectively.

16.2.5. *Einsteinium and fermium, elements 99 and 100*

In 1952 the United States set off the first test thermonuclear explosion (code name "Mike") at the Eniwetok Island in the Pacific. The early analysis of debris from Mike showed that a heavy isotope of plutonium, ^{244}Pu, had been made by multi-neutron capture in ^{238}U which had been part of the device. More extensive chemical purification of some of the radioactive coral from the test site proved that isotopes of elements 99 (einsteinium) and 100 (fermium) had been made in the explosion. The neutron flux during the very brief burning time of Mike had been so intense that it resulted in capture by ^{238}U nuclei of as

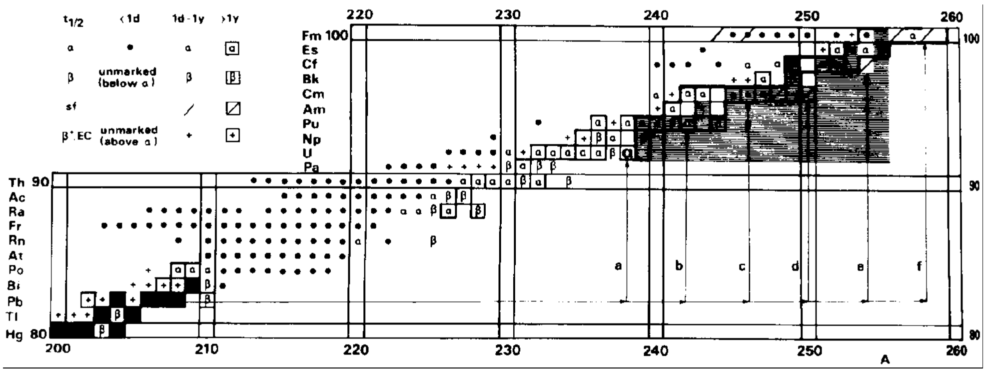

FIG. 16.4. The build-up of heavy actinides through rapid multiple n-capture in lead (arrows) and in uranium (shaded area).

many as 17 neutrons; see Fig. 16.4. This multi-neutron capture ended as the device blew apart and was followed by a sequence of β^--decays.

Within a year, element 99 was again synthesized by cyclotron bombardment of uranium with nitrogen

$$^{238}U + {}^{14}N^{6+} \rightarrow {}_{99}Es \qquad (16.8)$$

Several months later, Fm was isolated as a product of reactor irradiation. In this case the neutron capture occurs over a long time and β-decay processes compete with neutron capture depending on the $t_{1/2}$ (β^-) and the neutron flux. The reaction sequences are shown as the shaded area in Figure 16.4. Symbolically, for example the sequence $^{239}Pu + 3n$, β^-, $+8n$, $2\beta^-$, $+4n$, β^-, $+n$, β^-, $+n$ produces $^{254}_{100}Fm$. See also Figures 16.2 and 16.3 for the production of various nuclides in the sequence as a function of time for a reactor with a predominantly thermal neutron flux.

16.2.6. *Mendelevium, nobelium and lawrencium, elements 101 – 103*

By 1955 reactor transmutation of ^{239}Pu had produced 10^9 atoms of ^{253}Es. These atoms were deposited on gold and bombarded with helium ions to make the element 101 by the reaction

$$^{253}_{99}Es + {}^{4}_{2}He \rightarrow {}^{256}_{101}Md + {}^{1}_{0}n \qquad (16.9)$$

A new technique was used that allowed the atoms of ^{256}Md to recoil from the very thin target onto a "catcher" foil. Thirteen atoms of ^{256}Md ($t_{1/2}$ 1.3 h) were made in 9 h of irradiation and isolated by rapid elution from a column of cation exchange resin using a solution of α-hydroxy isobutyric acid. The elution showed 5 atoms of element 101 (identified by the spontaneous fission of the daughter $^{256}_{100}Fm$) and 8 atoms of the Fm daughter (Fig. 16.7; eqn. (16.10)). The recoil – ion exchange technique used in identification of element 101 by Choppin, Seaborg, Harvey and Ghiorso has been successfully applied in the discovery of other heavier elements.

$$ {}^{256}_{101}\mathrm{Md} \xrightarrow[1.3\mathrm{h}]{\mathrm{EC}} {}^{256}_{100}\mathrm{Fm} \xrightarrow[2.6\ \mathrm{h}]{\mathrm{sf}} \tag{16.10} $$

So far we have described two methods of production of heavy elements: n-irradiation followed by β^--decay, and accelerator induced reactions according to relations 16.5 - 16.9. Multiple n-capture has its limitation in the successively decreasing yields, while α-reactions usually yields product nuclides further away from the bottom of the Z-versus-N stability valley (cf. e.g. Fig. 3.1, 16.1 and 16.5) resulting in shorter half-lives. Heavier isotopes (i.e. isotopes with larger mass numbers, that is more neutron rich) of the product element are expected to be more stable (i.e have longer half-lives). However, by irradiating the heavy target atom by "heavy ions" like ${}^{54}_{24}\mathrm{Cr}$ three advantages can be achieved in one reaction: the charge of the compound nucleus is increased several steps, while at the same time more neutrons ("glue") are added, and, if the reaction energy is negative, giving a less exited compound nucleus, hopefully leading to a much heavier and more stable product. This method is used for the production of the heaviest transuranium elements today.

In 1957 Russian scientists at the Joint Institute for Nuclear Research (JINR) at Dubna (now Flerov Laboratory for Nuclear Reactions, FLNR) claimed to have synthesized element 102 by irradiating ${}^{241}\mathrm{Pu}$ with ${}^{16}\mathrm{O}$ ions, using nuclear emulsions for α-energy determination.

$$ {}^{241}_{94}\mathrm{Pu} + {}^{16}_{8}\mathrm{O} \rightarrow {}^{252}_{102}\mathrm{No} + 5\,{}^{1}_{0}\mathrm{n} \tag{16.11} $$

They assigned an 8.8 ± 0.5 MeV α-decay with a half-life of 2 – 40 s, to element 102. However, their results have been contested by scientists at the Lawrence Berkeley Laboratory (LBL) in California, who produced and identified element 102 in 1958 by use of a double-recoil technique[1]. The reaction scheme was

$$\begin{tikzcd} {}^{246}_{96}\mathrm{Cm} + {}^{12}_{6}\mathrm{C} \arrow[r, "\text{1 st recoil}"] & {}^{254}_{102}\mathrm{No} + 4\,{}^{1}_{0}\mathrm{n} \arrow[d, "\alpha"', "\text{2nd recoil}"] \\ & {}^{250}_{100}\mathrm{Fm} \end{tikzcd} \qquad (16.12)$$

Lawrencium, element 103, was synthesized at Berkeley in 1961 by the reactions

$$ {}^{250,1,2}_{98}\mathrm{Cf} + {}^{10,11}_{5}\mathrm{B} \rightarrow {}^{258}_{103}\mathrm{Lr} + (2\text{-}5)\,{}^{1}_{0}\mathrm{n} \tag{16.13} $$

using a system where the recoiling products were caught on a moving band, which rapidly transported them to an array of energy sensitive solid state detectors (cf. Fig. 15.3). The

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[1] The name *nobelium* was selected to honor the Swedish industrialist Alfred Nobel, who donated his fortune to be used as prizes to those who have contributed most to progress in the fields of science, the humanities and peace.

half-life of the product (later determined as ~ 4s) was too short to allow any chemistry. It was the first actinide to be identified through purely instrumental methods.

16.2.7. *The transactinide elements, Z ≥ 104*

The very short half-lives and the small amounts of product did not allow chemical identification of the transactinide elements in the initial experiments. Identification by nuclear properties is less conclusive as it usually depends on correlation with predicted energies and half-lives obtained by extrapolation of systematic trends. The controversies resulting from the uncertainties inherent in this approach have been a feature of the history of the transactinide elements, just as they were for nobelium and lawrencium. In fact, it is still uncertain which claims represent the actual discovery for some of these elements, the Russian group at Dubna or the American group at Berkeley. Both groups undoubtedly have produced isotopes of elements 104 - 106. Partially the disagreements are due to the different techniques used. At Dubna irradiations have often been made with heavier ions (^{50}Ti, ^{51}V, etc) than at Berkeley. The Russian group used one-atom-at-a-time separations with thermochromatography (cf. §15.7.3) and solid track detectors (§8.1.2), while the American group used fast ion exchange separations and energy sensitive solid state detectors (§8.4). At Dubna identification has usually been made by measuring non-specific spontaneous fission events, while the group at Berkeley used α-decay half-lives and α-energies characteristic of known members of the decay chains; the claims of discovery of elements 104 and 105 by the Berkeley group in 1969 seem presently more convincing than the more uncertain Dubna results. In the Berkeley technique, the decay chain of the new isotope was followed until a longlived generic product was reached, whose identity (mass, element and half-life) had been unequivocally established in earlier experiments. At both laboratories nuclear reactions in which four neutrons are evaporated from the compound nucleus, have been used for the first synthesis of elements 104 - 105, e.g.

$$^{249}\mathrm{Cf} + {}^{12}\mathrm{C} \rightarrow {}^{257}104 + 4\mathrm{n} \qquad (16.14)$$

and

$$^{249}\mathrm{Cf} + {}^{15}\mathrm{N} \rightarrow {}^{260}105 + 4\mathrm{n} \qquad (16.15)$$

This type of reaction was used at Berkeley also for production of element 106, while the Dubna group utilized a reaction involving a lighter target element and a heavier projectile:

$$^{207,208}\mathrm{Pb} + {}^{54}\mathrm{Cr} \rightarrow {}^{259,260}106 + 2\mathrm{n} \qquad (16.16)$$

In all cases the product radioactivity was isolated by recoil techniques.

In the early eighties this type of reaction was successfully used by a group at Gesellschaft für Schwerionenforschung (GSI), Darmstadt, to synthesize the elements 107, 108 and 109 (element 108 was simultaneously synthesized at GSI and Dubna). The nuclear reactions were:

$$^{209}\mathrm{Bi} + {}^{54}\mathrm{Cr} \rightarrow {}^{262}107 + \mathrm{n} \qquad (16.17)$$

$$^{208}\mathrm{Pb} + {}^{58}\mathrm{Fe} \rightarrow {}^{265}108 + \mathrm{n} \qquad (16.18)$$

$$^{209}\mathrm{Bi} + {}^{58}\mathrm{Fe} \rightarrow {}^{266}109 + \mathrm{n} \qquad (16.19)$$

At Darmstadt these elements were identified using the velocity filter SHIP, which provides an in-flight separation of the heavy-ion nuclear reaction fragments. The products were then identified by α-spectroscopic measurements of the new elements and of their decay products. The production rates are extremely low in this type of experiments. So far only 38 atoms of element 107, 3 atoms of element 108 and 3 atoms of element 109 have been observed. Attempts to synthesize heavier elements via the same type of reaction continue at Darmstadt, Dubna and Berkeley.

For element 104 the names Kurchatovium (Ku) and Rutherfordium (Rf) were proposed by the groups at Dubna and Berkeley, respectively, thereby emphasizing their claim to the discoveries. The International Union on Pure and Applied Chemistry (IUPAC) has now decided on the following names: element 104 Rutherfordium (Rf), element 105 Dubnium (Db), element 106 Seaborgium (Sg), element 107 Bohrium (Bh), element 108 Hassium[1] (Hs), and element 109 Meitnerium (Mt). In the Periodic Table and nuclide charts we have thus used $_{104}\mathrm{Rf}$, $_{105}\mathrm{Db}$, $_{106}\mathrm{Sg}$, $_{107}\mathrm{Bh}$, $_{108}\mathrm{Hs}$ and $_{109}\mathrm{Mt}$. So far no names have been suggested for the newly discovered elements 110, 111, 112, 114, 116 and 118.

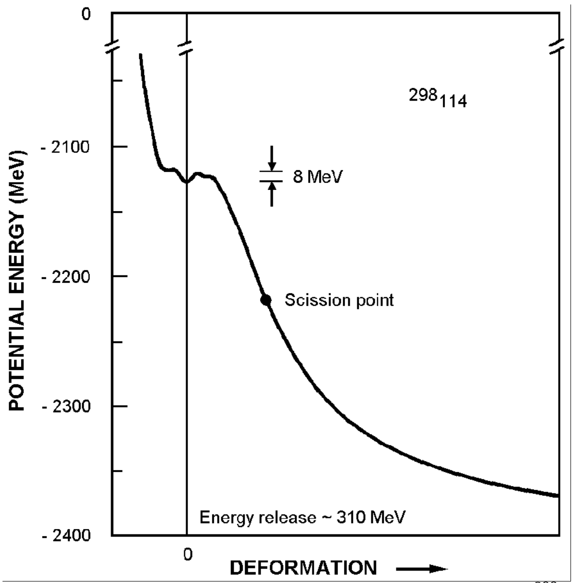

FIG. 16.5. Dependence of potential energy on deformation for a nucleus like $^{298}114$. (From R. Nix.)

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[1] After the latin Hassia, the county of Darmstadt.

The controversies regarding the discovery claims of the heaviest elements were the result of the very short half-lives of these elements. Both the half-lives of α-decay (Fig. 11.13) and of spontaneous fission (Fig. 14.13) generally decrease as Z increases.

Some years ago it was generally assumed that the next proton magic number after $Z = 82$ would be $Z = 126$ since this was the neutron pattern. However, more careful theoretical study indicates that the proton shell closure occurs probably for $Z = 112$. The most probable neutron magic number is $N = 184$, although some calculations indicate $N = 162$ as a possibility. These calculations are sensitive to the exact nature and shape of the nuclear potential, so the proton magic number may be slightly smaller or larger than 112 while the same is true for the neutron number of 184. Nevertheless, the superheavy nucleus $^{296}112$ seems to be the best bet for maximum stability in this region.

Figure 16.5 shows the variation in nuclear deformation calculated for the fission barrier of $^{298}114$. Of particular interest are the small local fluctuations at small deformation. The minimum of 8 MeV at zero deformation constrains the nucleus to a spherical shape. Spontaneous fission is a very slow process in this situation since it involves tunneling through the 8 MeV barrier. These local fluctuations in the potential energy curve in Figure 16.5 result from adding corrections for shell effects to a liquid drop model. The resistance to deformation associated with closed shell nuclei produces much longer half-lives to spontaneous fission than would be expected from calculations based on a standard liquid drop model.

The predictions that the half-lives of some superheavy elements may be very long have led to searches for evidence of their existence in nature. Several reports of tentative evidence for such elements have appeared but subsequent experimentation has explained the observations as based on known elements with only a few exceptions. Attempts to synthesize superheavy elements with sufficient number of neutrons by bombardment of targets with heavy ions have so far not been successful. However, the increase in half-life with increasing N in the heaviest elements is seen in Figure 16.1

16.3. Actinide properties

16.3.1. *The actinide series*

As early as 1923 N. Bohr suggested that there might exist a group of 15 elements at the end of the Periodic Table that would be analogous in their properties to the 15 lanthanide ("rare earth") elements. This idea, combined with the increasing stability of the +3 oxidation state for the transuranium elements as the atomic number increases from $Z = 93$ to 96, led Seaborg to the conclusion that these new elements constituted a second rare earth series whose initial member was actinium. As the atomic number increases from 90, electrons are added in the 5f subshell similar to the occupation of the 4f subshell in the lanthanides, see Table 16.1. This series would be terminated with element 103 since this would correspond to the addition of 14 electrons for a completed 5f subshell.

Seaborg's actinide hypothesis was initially a subject of considerable objection since the trivalent oxidation state, unlike in the lanthanide family, was not the most stable in aqueous solution for the elements between $Z = 90$ and 94. In aqueous solution the most stable

Table 16.1. *Electronic configuration, radii (in picometers, pm), and oxidation states in (acid, non-complexing) aqueous solution.*

Atomic number	Element	Metallic radius (pm)	Atomic (g)‡ config.	Effective ionic radius‡		Oxidation† states
				M^{3+}	M^{4+}	
89	Ac	188	$5f^0 6d 7s^2$	111.9		**3**
90	Th	180	$5f^0 6d^2 7s^2$	(108)	97.2	(3) **4**
91	Pa	163	$5f^2 6d 7s^2$	(105)	93.5	(3) 4 **5**
92	U	156	$5f^3 6d 7s^2$	104.1	91.8	3 4 5 **6**
93	Np	155	$5f^4 6d 7s^2$	101.7	90.3	3 4 **5** 6 (7)
94	Pu	160	$5f^6 7s^2$	99.7	88.7	3 **4** 5 6 (7)
95	Am	174	$5f^7 7s^2$	98.2	87.8	**3** 4 5 6
96	Cm	175	$5f^7 6d 7s^2$	97.0	87.1	**3** 4
97	Bk		$5f^9 7s^2$	94.9	86.0	**3** 4
98	Cf		$5f^{10} 7s^2$	93.4	85.1	(2) **3**
99	Es		$5f^{11} 7s^2$	92.5		(2) **3**
100	Fm		$5f^{12} 7s^2$			(2) **3**
101	Md		$(5f^{13} 72^2)$	89.6		2 **3**
102	No		$(5f^{14} 7s^2)$			**2** 3
103	Lr		$(5f^{14} 6d 7s^2)$	88.2		**3**

† The most stable oxidation state in (acid, non-complexing) aqueous solution is given in fat, most unstable (or only found in the solid state) within parenthesis.

‡ Electronic configuration and ionic radii (coordination number 8) according to Katz, Seaborg and Morss and to Seaborg and Loveland.

oxidation states are +4 for thorium, +5 for protactinium, +6 for uranium, +5 for neptunium, and +4 for plutonium, see Table 16.1, right column. Only for the elements beginning with americium is the +3 the most stable state in solution. Seaborg, however, had correctly identified Ac as the precursor (analogous to La) and Cm as the midpoint element (analogous to Gd). Recent investigations have shown that mendelevium and nobelium have a divalent state in solution (which probably is the most stable for nobelium). This corresponds to the divalent state observed for ytterbium in the lanthanide elements. For $Z = 90$ to $Z = 94$ the 5f and 6d orbitals are very close in energy and the electronic occupation is variable.

The recognition of the similarity in chemical properties between the actinide and lanthanide elements was an important contributing factor in the synthesis and isolation of the transcurium elements. Most of the chemical identification was carried out by eluting the elements from columns of cation exchange resin. The pattern of the elution behavior from the resin bed of the lanthanide elements made it possible to predict with good accuracy the expected elution position for a new actinide element (Fig. 16.7). This technique constituted the most definitive chemical evidence in the discovery experiments for the elements from atomic numbers 97 through 101. More recently these conclusions have been confirmed by spectroscopy.

The electronic ground state of $_{89}$Ac contains four filled inner electronic shells (the main quantum numbers 1, 2, 3 and 4, designated K, L, M and N, and containing 2, 8, 18 and 32 electrons, respectively);see Ch. 11. The subsequent outer 5th, 6th and 7th shells

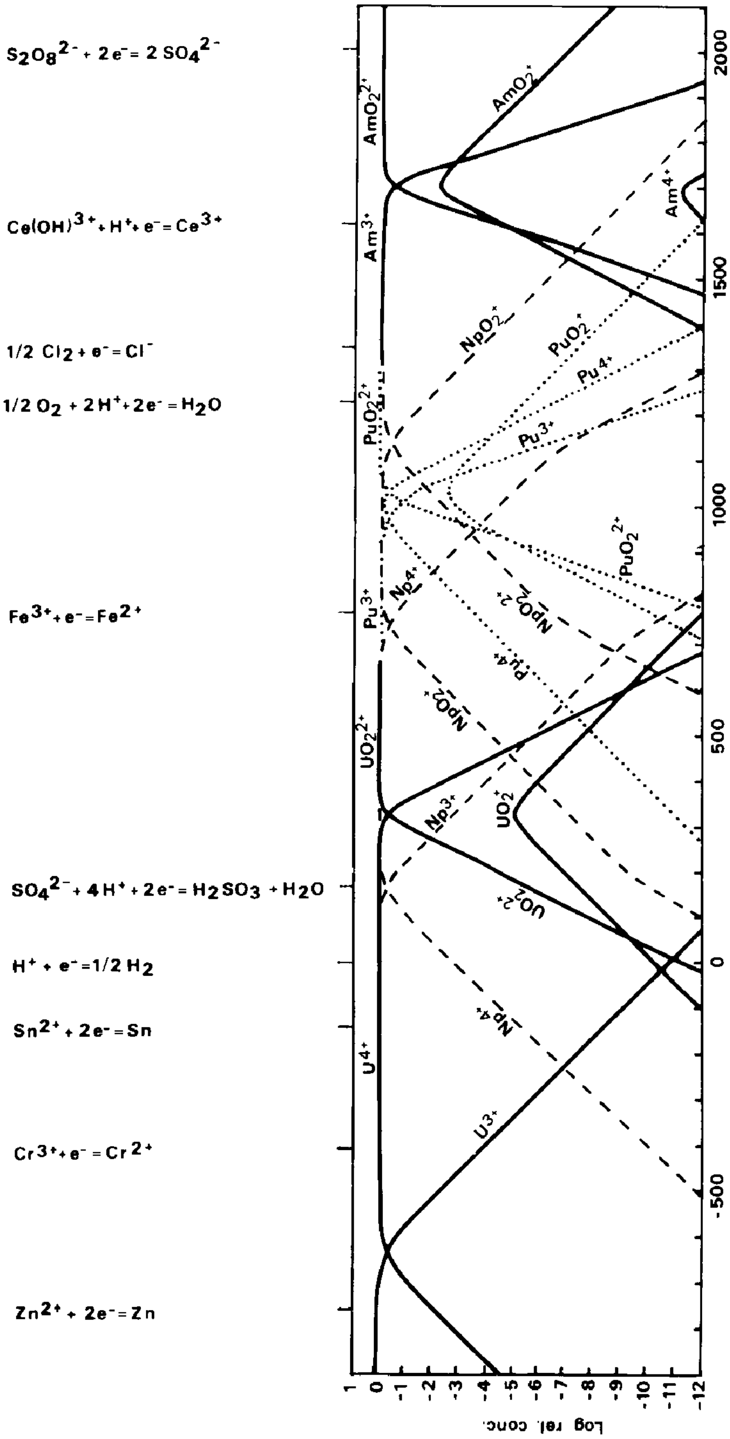

FIG. 16.6. Redox diagrams for U, Np, Pu, and Am in 1 M $HClO_4$ at 25°C. Each actinide is assumed to be in equilibrium in its own solution at the indicated redox potential.

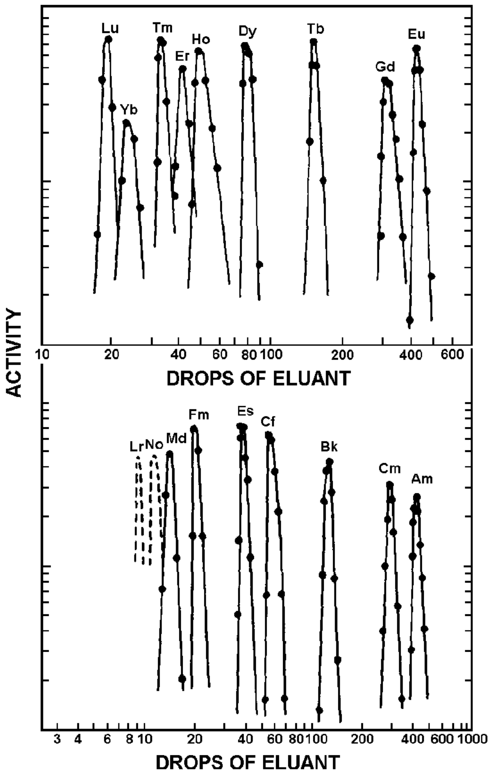

FIG. 16.7. Elution curves for 3+ lanthanide and actinide ions from Dowex-50 ion exchange resin with ammonium-α-hydroxy isobutyrate eluant. (From Katz and Seaborg.)

(designated "O", "P" and "Q", respectively) are partly empty. In the symbolism used to designate the electronic structure of an atom, the filled shells are usually omitted, as they do not contribute to the chemical properties (and interactions) of the atom. The symbolism $5s^2p^6d^{10}f^06s^2p^6d^17s^2$ for $_{89}$Ac indicates that in the 5th shell the subshells s, p, d and f contain 2, 6, 10 and 0 electrons, respectively; the 6th subshell contains 2 s-electrons, 6 p-electrons and 1 d-electrons; the outermost 7th shell contains 2 s-electrons. Remembering that the s-, p-, d- and f-subshells can accommodate 2, 6, 10 and 14 electrons respectively, these four outer shells are partly empty. Also leaving out the filled sub-shells, the electronic structure for Ac can be written $5f^06d^17s^2$; though the 2 7s-electrons could have been left out we keep them for specific purpose. The construction of the electronic configuration for gaseous atomic actinide atoms in Table 16.1 then becomes obvious. These electronic structures have been determined spectroscopically.

From Table 16.1 it is obvious that there can be interaction between the 5f, 6d and 7s orbitals, as a consequence of their very similar binding energies. As these partly empty outer orbitals are the ones which may take part in the chemical bondings we can expect the actinides to show a highly variable chemistry.

The main feature of the electronic structure, when going from $_{89}$Ac to $_{103}$Lr is the successive filling of the 5f subshell. This leads to a slight contraction of the atomic and ionic radii with increasing atomic number (the *actinide contraction*), as seen from several columns. However, there are irregularities, which are attributed to the extra stability of the half-filled 5f subshell (at 7 electrons), leading to more labile 6d-electrons.

We shall now see what effect these electron configurations have on the redox and complex chemistry of the actinides.

16.3.2. *Actinide oxidation states*

The electrons in the 6d and 7s subshells are more loosely bound than the electrons in the filled subshells, and, in general, also than the 5f electrons. In these outer shells the binding energies are in the range of a few eV, i.e. the same order of magnitude as is common in chemical bonding. Thus, from Table 16.1, it is understandable that Ac easily looses its $6d7s^2$ electrons to form Ac^{3+}, and Th its $6d^27s^2$ electrons to form Th^{4+}. For the subsequent elements, from Pa to Am, the situation is more complicated. There are reasons to suppose that the spatial characteristics of the f-subshell orbitals may change abruptly at certain atomic numbers; that is, the f-shell electrons may be shielded more strongly in some elements than in others where the f-orbitals extend close to the surface of the electronic cloud (where chemical interaction occurs), and where the 5f-electrons are in closer contact with the d- and s-shell electrons. There can be little doubt that the 5f-electrons are present in all of the actinide elements after Pa.

The chemical properties of the actinide elements have been intensely studied for the elements available in at least microgram quantities (Z 90 - 99) but much less so for the heaviest members of the family (Z 100 - 103). Table 16.1 lists the valency states. In Figure 16.6 redox diagrams are given for the most important actinides; for comparison, standard potentials are included for some useful redox reagents. Any particular actinide can be obtained in a desired valence state by the use of proper oxidizing or reducing agents (Table 16.2).

The pentavalent state of the actinides (except for Pa and Np) is less stable than the other states and normally undergoes disproportionation in acid solutions. Plutonium is particularly interesting in the variety of oxidation states that can coexist in aqueous solutions (Fig. 16.6, at 1000 mV). For example, a plutonium solution in 0.5 M HCl of 3×10^{-4} M Pu concentration at 25°C, which is initially 50% Pu(IV) and 50% Pu(VI), will equilibrate within a few days via disproportionation reactions to an equilibrium system that is 75% Pu(VI), 20% Pu(IV), and few percent each of Pu(V) and Pu(III), in the absence of complexing anions.

The reactions are:

$$2PuO_2^{+} + 4H^{+} \rightleftarrows Pu^{4+} + PuO_2^{2+} + 2H_2O \tag{16.20}$$

and

$$PuO_2^{+} + Pu^{4+} \rightleftarrows PuO_2^{2+} + Pu^{3+} \tag{16.21}$$

TABLE 16.2. *Preparation methods and stability of actinide ions in aqueous solutions*

Ion	Stability and method of preparation
U^{3+}	Slow oxidation by water, rapid oxidation by air, to U^{4+}. Prepared by electrolytic reduction (Hg cathode).
Np^{3+}	Stable to water, rapid oxidation by air to Np^{4+}. Prepared by electrolytic reduction (Hg cathode).
Pu^{3+}	Stable to water and air. Oxidizes by action of its own α-radiation to Pu^{4+}. Prepared by reduction by SO_2, Zn, U^{4+} or H_2(g) with Pt catalyst.
Md^{3+}	Stable. Can be reduced to Md^{2+}.
No^{3+}	Unstable, reduces to No^{2+}.
Th^{4+}	Stable.
Pa^{4+}	Stable to water. Rapid oxidation by air to Pa(V). Prepared by electrolytic reduction (Hg cathode) and by the action of Zn(Hg), Cr^{2+} or Ti^{3+} in HCl.
U^{4+}	Stable to water. Slow oxidation by air to UO_2^{2+}. Oxidation in nitrate media catalyzed by UV light. Prepared by oxidation of U^{3+} by air, by electrolytic reduction of UO_2^{2+} (Hg cathode) and by reduction of UO_2^{2+} by Zn or H_2(g) with Ni catalyst.
Np^{4+}	Stable to water. Slow oxidation by air to NpO_2^{+}. Prepared by oxidation of Np^{3+} by air or reduction of higher oxidation states by Fe^{2+}, SO_2, I^- or H_2(g) with Pt catalyst.
Pu^{4+}	Stable in concentrated acids, e.g. 6 M HNO_3. Disproportionates to Pu^{3+} and PuO_2^{+} at lower acidities. Prepared by oxidation of Pu^{3+} by BrO_3^-, Ce^{4+}, $Cr_2O_7^{2-}$, HIO_3 or MnO_4^- in acid solution or by reduction of higher oxidation states by HNO_2, NH_3OH^+, I^-, 3 M HI, 3M HNO_3, Fe^{2+}, $C_2O_4^{2-}$ or HCOOH in acid solution.
Am^{4+}	Not stable in water.
Bk^{4+}	Stable to water. Slow reduction to Bk^{3+}. Prepared by oxidation of Bk^{3+} by $Cr_2O_7^{2-}$ or BrO_3^-.
PaO^{3+} or PaO_2^{+}	Stable. Difficult to reduce.
UO_2^{+}	Disproportionates to U^{4+} and UO_2^{2+}. Most stable at pH 2.5. Prepared by electrolytic reduction of UO_2^{2+} (Hg cathode) and by reduction of UO_2^{2+} by Zn(Hg) or H_2(g). pH around 2.5 used.
NpO_2^{+}	Stable. Disproportionates only at high acidities. Prepared by oxidation of lower oxidation states by Cl_2 or ClO_4^- and by reduction of higher oxidation states by NH_2NH_2, NH_2OH, HNO_2, H_2O_2/HNO_3, Sn^{2+} or SO_2.
PuO_2^{+}	Disproportionates to Pu^{4+} and PuO_2^{2+}. Most stable at low acidities. Prepared by reduction of PuO_2^{2+} by I^- or SO_2 at pH 2.
UO_2^{2+}	Stable. Difficult to reduce.
NpO_2^{2+}	Stable. Easy to reduce. Prepared from lower oxidation states by oxidation by Ce^{4+}, MnO_4^-, Ag^{2+}, Cl_2 or BrO_3^-.
PuO_2^{2+}	Stable. Fairly easy to reduce. Reduces slowly under the action of its own α-radiation. Prepared by oxidation of lower oxidation states by BiO_3^-, HOCl or Ag^{2+}.
AmO_2^{2+}	Stable. Reduces fairly rapidly under action of its own α-radiation. Prepared by electrolytic oxidation (Pt anode) in 5 M H_3PO_4, by $S_2O_8^{2-}$ in presence of Ag^+ or by Ag^{2+} in K_2CO_3 solution.

Although Pu(V) readily disproportionates at concentrations $\geq 10^{-8}$ M in acidic solutions, it is the state observed in more basic natural and ocean waters, partly due to the stability of the bicarbonate complex, cf. Ch. 22.

TABLE 16.3. *Characteristic reactions of actinide ions of different valency states with some important anions.†*

Reagent	Conditions	Precipitated ions	Not precipitated
OH^-	pH ≥ 5	M^{3+}, M^{4+}, MO_2^+, MO_2^{2+}	
F^-	4 M H^+	M^{3+}, M^{4+}	MO_2^+, MO_2^{2+}
IO_3^-	0.1 M H^+	M^{4+} (M^{3+} may oxidize)	MO_2^+, MO_2^{2+}
PO_4^{3-}	0.1 M H^+	M^{4+} (Ac^{3+} partly)	M^{3+} (Pu^{3+} and higher An)
CO_3^{2-}	pH > 10	M^{3+}, M^{4+} (as hydroxide)	MO_2^{2+} (anionic complex)
CH_3COO^-	0.1 M H^+	MO_2^{2+}	M^{3+}, M^{4+}, MO_2^+
$C_2O_4^{2-}$	1 M H^+	M^{3+}, M^{4+}	MO_2^+, MO_2^{2+}

† Cl^-, NO_3^-, and SO_4^{2-} do not precipitate actinide ions. An = actinide.

16.3.3. *Actinide complexes*

Since the differences in energy of the electronic levels are similar to chemical bond energies, the most stable oxidation states of the actinides may change from one chemical compound to another, and the solution chemistry will be sensitive to the ligands present.Thus complex formation becomes an important feature of the actinide chemistry (cf. §9.4.3).

The chemical properties are different for the different valency states (Table 16.3), while in the same valency state the actinides closely resemble each other. These properties have

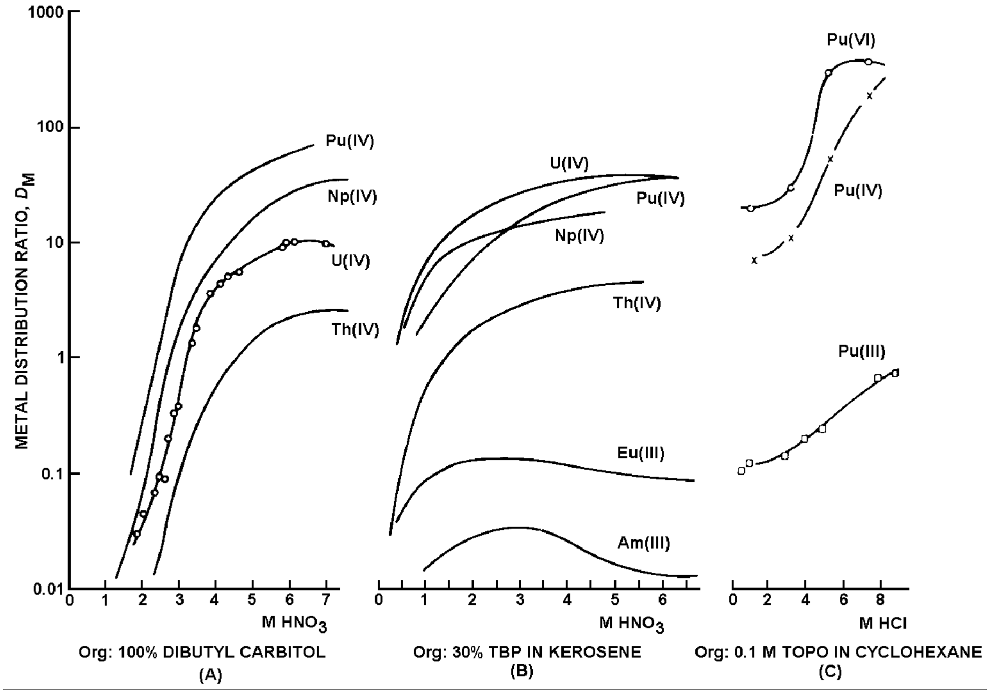

FIG. 16.8. Extraction of actinide complexes into various solvents. (From Ahrland, Liljenzin and Rydberg.)

been extensively exploited for the separation and isolation of the individual elements in pure form; see Ch. 21.

The compounds formed are normally quite ionic. The ionic radii of the actinide elements of the different valency states decrease with increasing atomic number (the actinide contraction, Table 16.1). Consequently the charge density of the actinide ions increases with increasing atomic number and, therefore, the probability of formation of complexes and of hydrolysis increases with atomic number. This is illustrated in Figure 16.7, where the heavier actinides are eluted before the lighter ones because the α-hydroxy-isobutyrate eluant forms stronger complexes as the cation radius decreases.

The pattern of stabilities of complexes in the tetravalent states and hexavalent states is the same and follows the order of decreasing ionic radius, Table 16.1.

$$Th^{4+} < U^{4+} < Np^{4+} < Pu^{4+} \qquad (16.22)$$

$$UO_2^{2+} < NpO_2^{2+} < PuO_2^{2+} \qquad (16.23)$$

This also explains the extraction behavior (cf. §9.4.3) for the M^{4+} (actinide) ions in Figure 16.8, where Pu^{4+} is better extracted than Th^{4+}; the Figure shows the extraction of some actinide ions from HCl or HNO_3 solutions by the different reagents. In the case of tributyl phosphate ,TBP, dissolved in kerosene, the extracted M(VI), M(IV) and M(III) species are $MO_2(NO_3)_2(TBP)_2$, $M(NO_3)_4(TBP)_2$, and $M(NO_3)_3(TBP)_3$, respectively.

For the same element, the stability of the complexes varies with the oxidation state in the series

$$M^{4+} \geq MO_2^{2+} > M^{3+} \geq MO_2^{+} \qquad (16.24)$$

The reversal between M^{3+} and MO_2^{2+} reflects that the hexavalent metal atom in the linear $[OMO]^{2+}$ is only partially shielded by the two oxygen atoms; thus the metal ion MO_2^{2+} has a higher charge density than M^{3+} (i.e. about 3.2 ± 0.1). Similarly in MO_2^{+}, the effective charge is ca. 2.2 ± 0.1. This gives a reasonable explanation of the extraction pattern of Figure 16.8, though other factors (molar volume of the complex etc.) also contributes. Of importance in reprocessing (§21.6.3) are the low distribution ratios ($D_M \leq 0.01$) of fission products like Cs, Sr, Ru and Zr in the systems in Figure 16.8 (A) and (B).

The extraction of trivalent actinides in general follows the sequence

$$Ac^{3+} < Am^{3+} < Cm^{3+} \text{ etc} \qquad (16.25)$$

(for example, Cm^{3+} is extracted easier, i.e. at a lower pH, than Am^{3+}, etc.), as the ionic radii decrease in that order.

The chemistry involved in the isolation and purification of the actinide elements from irradiated reactor fuel elements is further discussed in Chapter 21. Actinide chemistry in the ecosphere is discussed in §22.6.

16.3.4. *The solid state*

The actinide metals can be produced by heating the tri- or tetra-fluoride with metallic alkaline earth or alkali elements:

$$PuF_4 + 2Ca \rightarrow Pu + 2CaF_2 \qquad (16.26)$$

The metals exhibit several allotropic modifications: 3 for uranium and 6 for plutonium between room temperature and the melting point (1130°C for U and 640°C for Pu) (Fig. 16.9). The density of the actinide metals at room temperature shows an unusual variation: Th 11 800; Pa 15 400; U 19 100; Np 20 500; Pu 19 900; Am 13 700; Cm 13 500; Bk 14 800 kg m^{-3}.

All the metals are very electropositive and attacked by water vapor with production of hydrogen. They are slowly oxidized in air and at higher temperatures; in the form of small chips, they are pyrophoric. The oxides, nitrides, and halides are produced most easily by heating the metals in the appropriate elemental gas. The fluorides are among the most important solid actinide compounds since they are the starting material for the production of the metals. The volatile hexafluoride of uranium is used in isotopic enrichment (Ch. 2). The preparation and properties of U and Th is described in §§5.4 – 5.5. Actinide chemistry is also discussed in §§21.5 and 22.6.

16.4. Uses of actinides

The use of the actinide elements fall into three categories: (i) for understanding fundamental chemistry and the nature of the periodic system, (ii) as products, in the large scale use of nuclear energy, and (iii) miscellaneous applications, where the particular physical, chemical or nuclear properties are valuable. Only the last aspect is discussed here, the others are treated elsewhere in this book. The availability of transuranium element isotopes suitable for experiments is listed in Table 16.4.

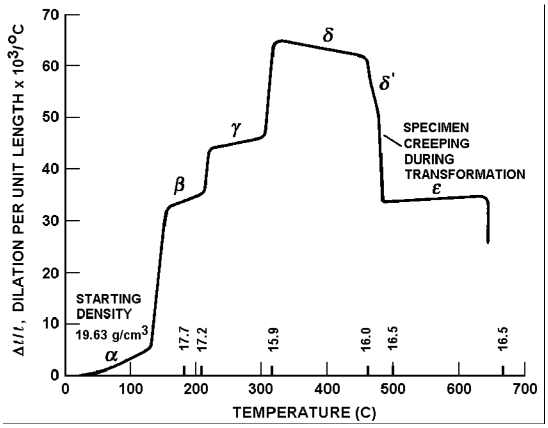

FIG. 16.9. Dilation curve and densities of high purity plutonium. (From Waldron, Garstone, Lee, Mardon, Marples, Poole and Williamson.)

TABLE 16.4. *Availability of Transuranium Element Materials*

Nuclide	$t_{1/2}$	Decay Mode	Specific Amounts† Available	Specific Activity (Bq/g)
^{237}Np	2.14×10^6 y	α, SF(10^{-10}%)	kg	2.61×10^7
^{238}Pu	87.7 y	α, SF(10^{-7}%)	kg	6.33×10^{11}
^{239}Pu	2.41×10^4 y	α, SF(10^{-4}%)	kg	2.30×10^9
^{240}Pu	6.56×10^3 y	α, SF(10^{-6}%)	kg	8.40×10^{10}
^{241}Pu	14.4 y	β, α(10^{-3}%)	1-10 g	3.82×10^{12}
^{242}Pu	3.76×10^5 y	α, SF(10^{-3}%)	100 g	1.46×10^8
^{244}Pu	8.00×10^7 y	α, SF(10^{-1}%)	10 - 100 mg	6.52×10^5
^{241}Am	433 y	α, SF(10^{-10}%)	kg	1.27×10^{11}
^{243}Am	7.38×10^3 y	α, SF(10^{-8}%)	10 - 100 g	7.33×10^9
^{242}Cm	162.9 d	α, SF(10^{-5}%)	100 g	1.23×10^{14}
^{243}Cm	28.5 y	α, ϵ(0.2%)	10 - 100 mg	1.92×10^{12}
^{244}Cm	18.1 y	α, SF(10^{-4}%)	10 - 100 g	3.00×10^{12}
^{248}Cm	3.40×10^5 y	α, SF(8.3%)	10 - 100 mg	1.57×10^8
^{249}Bk	320 d	β, α(10^{-3}%), SF(10^{-8}%)	10-50 mg	6.00×10^{10}
^{249}Cf	350.6 y	α, SF(10^{-7}%)	1 - 10 mg	1.52×10^{11}
^{250}Cf	13.1 y	α, SF(0.08%)	10 mg	4.00×10^{12}
^{252}Cf	2.6 y	α, SF(3.1%)	10 - 1000 mg	2.00×10^{13}
^{254}Cf	60.5 d	SF, α(0.3%)	μg	3.17×10^{14}
^{253}Es	20.4 d	α, SF(10^{-5}%)	1 - 10 mg	9.33×10^{14}
^{254}Es	276 d	α	1 - 5 μg	6.83×10^{13}
^{257}Fm	100.5 d	α, SF(0.2%)	1 pg	1.83×10^{14}

† According to Oak Ridge Nat. Lab., USA.

The spontaneous decay of the transuranium elements by α-decay and/or fission results in energy release. Since very small amounts of some nuclides (e.g. ^{238}Pu, ^{244}Cm, ^{252}Cf) can be sources of appreciable energy, these radionuclides can be used in *small power generators*. This use of actinide elements is discussed in §6.9.3.

^{241}Am emits a 60 keV γ-ray and has been used as a γ-radiation source to measure thickness of metal sheets and of deposited metal coatings, the degree of soil compaction, sediment concentration in flowing streams, and to induce X-ray fluorescence in chemical analysis (§6.8). As an α-particle emitter, ^{241}Am has been mixed with beryllium to make intense neutron sources for oil well logging and for measuring water content in soils and in process streams in industrial plants. It is extensively used for elimination of static electricity and in smoke detectors where its use depends on the ionization of air.

^{252}Cf ($t_{1/2}$ 2.73 y) has found several uses. It decays to 3.1% by spontaneous fission (the main decay mode is through α emission) leading to a neutron emission rate of 2.3×10^{15} n s^{-1} kg^{-1} (average n-energy 2.35 MeV). The n-dose rate is 22 kSv h^{-1} kg^{-1}. ^{252}Cf is the only nuclide that can provide a useful neutron intensity over a sufficiently long half-life to make it a useful neutron source. The low rates of heat emission (38.5 kW/kg), γ-radiation (initially 1.3×10^{16} photons s^{-1} kg^{-1}, yielding an initial dose rate of 1.6 kGy h^{-1} kg^{-1}; γ-ray intensity increases with time due to fission product build-up) and helium evolution (from α decay) allow fabrication of simple, small ^{252}Cf sources that require no external power supply nor any maintenance but that can provide moderately high neutron fluxes. The 1990 production rate of ^{252}Cf from the Oak Ridge facilities (HFIR-TRU) was ~ 500 mg/y. Among the applications of ^{252}Cf we list the following: (a) process control by a variety of on-stream nondestructive analytical techniques; (b) medical diagnosis by activation analysis; (c) production of short-lived radioisotopes at locations where they will be used, thus avoiding decay during transportation from an accelerator or reactor at another site; (d) industrial neutron radiography, which images low density materials - especially hydrogenous materials - better than X-rays; (e) possible medical treatment of tumors with ^{252}Cf sources that can be implanted in the body; (f) petroleum and mineral exploration in which the compactness and portability of ^{252}Cf neutron sources facilitate testing for valuable deposits, particularly in inaccessible places such as deep wells and the sea floor; (g) moisture measurements; (h) hydrology studies to locate sources of water; (i) nuclear safeguards tests, e.g. for criticality control in reactor fuel storage areas and for nuclear materials accountability (detection and recovery of fissionable material; implementation of nuclear agreements).

16.5. Chemistry of the transactinide elements

The study of the chemical properties of the transactinide elements has been hampered by the short half-lives of many of the isotopes (the half-life of the longest known isotopes of the elements 106 and 107 are 21 s and 17 s, respectively, while those of 108 and 109 range from a few seconds down to milliseconds). In addition the production cross sections are very small (0.5 – 0.01 nb) so chemical studies must be done very rapidly on a few atoms at a time. However, these elements offer a fertile area to investigate the possibility of relativistic effects of the electrons which could alter the relative stability of the 7s, 6d and 7p valence electrons. The result would be the existence of the elements in oxidation states other than those predicted from their expected position in the periodic table, see App. I.

Element 104 has an isotope of mass number 261 with 78 s half-life. This isotope has been used to study the chemical properties of element 104 which confirmed its tetravalent nature. Moreover the element 104 resembles Zr(+4) and Hf(+4) more closely than Th(+4), as expected for a transition element.

Chemical studies with the 35 s isotope of element 105 confirmed its similarity to the Group 5 transition elements Nb and Ta, for which +5 is a stable oxidation state, indicating the pentavalent nature of element 105. However, in several properties 105(+5) behaves more similar to Pa(+5) than to Ta(+5), which is not expected from a simple extrapolation of Group 5 properties to $Z = 105$.

Chemical properties of elements with $Z \geq 106$ have so far not been studied in aqueous solutions. However, experiments based on ultra fast chemical separations using OLGA, cf. §15.7, have been made.

16.6. Exercises

16.1. What nuclear reactions would be suitable to make gold?

16.2. What fraction of neptunium is in the +4 state in a 0.1 M $Fe(SO_4)_2$ solution of acidity 1 M H^+, assuming that Np initially is present as Np(V) at a total concentration of 9.4 mM?

16.3. Irradiation of ^{238}U with deuterium yields ^{238}Pu. Will any other plutonium isotope be produced?

16.4. What are the decay products of ^{252}Cf, of ^{253}Cf and of ^{254}Cf?

16.5. ^{244}Pu decays through spontaneous fission with a half-life of 6.6×10^{10} y. Estimate the number of neutrons emitted per fission if the measured n-emission rate is 1890 n s^{-1} g^{-1}.

16.6. Flerov bombarded ^{207}Pb with ^{54}Cr and obtained a product which within 4-10 ms decayed by spontaneous fission. Suggest a product nucleus.

16.7. In Figure 16.8, Eu(III) is more easily extracted than its homolog Am(III). Suggest an explanation.

16.8. A cardiac pacemaker contains 150 mg of ^{238}Pu. What is its heat output? Use data in the isotope chart.

16.9. What electronic configuration would you ascribe to nobelium considering its place in the periodic system and its chemistry?

16.10. Based on the redox diagrams in Figure 16.6, estimate the reduction potentials for the one-electron step in the following series of plutonium species in acid solution: Pu(III), Pu(IV), Pu(V), and Pu(VI).

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