CHAPTER TWO

ACTINIUM

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2.1 INTRODUCTION

The actinide series of elements encompasses all the 15 chemical elements that have properties attributable to the presence of low-lying 7p, 6d, and 5f orbitals such that their tripositive ions have electronic configurations $7p^0 6d^0 5f^n$, where $n = 0,1,2,\ldots,14$. According to this definition, actinium, element 89, is the first member of the actinide series of elements, although it has no 5f electrons in its metallic, gaseous, or ionic forms. As such, its position in group 3 (in current IUPAC terminology) or group 3B (commonly used in some American textbooks) of the periodic table is analogous to that of its homolog, lanthanum, in the lanthanide series. This definition, which includes actinium as the first of the actinides (Seaborg, 1994), parallels the accepted inclusion of lanthanum as the first member of the lanthanide series (Moeller, 1963).

The chemistry of actinium closely follows that of lanthanum. There are no qualitative differences between them; the only quantitative differences are those attributable to the difference in their ionic radii (1.12 Å for Ac^{3+} and 1.032 Å for La^{3+} in six-fold coordination) (Shannon, 1976 and Chapter 15, section 7.5, of this book). Because of this similarity, lanthanum is a nearly ideal surrogate for actinium in the development of preparative or analytical procedures. As a carrier for trace amounts of actinium, lanthanum suffers from only one disadvantage: Once mixed, the two elements behave like any pair of adjacent rare earths and can be separated only by ion-exchange chromatography, solvent extraction, or fractional crystallization.

The most important isotope of actinium is ^{227}Ac, a member of the naturally occurring uranium–actinium ($4n + 3$) family of radioelements. Its applications

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are derived from its unique radioactive properties. Although ^{227}Ac itself is essentially ($\geq$98%) a weak β^- emitter, with a moderately long half-life (21.773 years), its decay chain includes five short-lived α emitters. The net effect is one of high specific power and long service life, a combination that makes ^{227}Ac suitable as a heat source in thermoelectric generators on space missions to the outer planets and beyond. Recently ^{225}Ac and ^{228}Ac have found applications (see Section 2.9).

The early actinium literature (up to January 1940) was comprehensively reviewed by the staff of the Gmelin Institute, and an English translation is available (Gmelin, 1942). Later reviews and bibliographies have appeared with the waxing and waning of interest in possible applications of actinium (Clarke, 1954, 1958; Hagemann, 1954; Bagnall, 1957; Katz and Seaborg, 1957; Bouissières, 1960; Stevenson and Nervik, 1961; Salutsky, 1962; Sedlet, 1964; Kirby, 1967; Keller, 1977). The most recent monograph on actinium chemistry is the *Gmelin Handbook* supplement (Gmelin, 1981).

2.1.1 Historical

In 1899, André Debierne, in the laboratory of Pierre and Marie Curie, reported that he had found a new radioactive substance, whose chemistry closely followed that of titanium (Debierne, 1899). Six months later, he said that the titanium fraction was no longer very active, but that the radioactive material he was now recovering exhibited the same chemical behavior as thorium (Debierne, 1900). Debierne claimed the right of discovery and named the new substance actinium (*aktis*, ray). His claim was accepted uncritically at the time, but, in the light of what we now know of the chemical and nuclear properties of actinium, it is clear that his 1899 preparation contained no actinium at all and that his 1900 preparation was a mixture of several radioelements, possibly including actinium as a minor constituent (Kirby, 1971; Adloff, 2000).

In 1902, Friedrich Giesel reported a new 'emanation-producing' substance among the impurities he had separated with radium from pitchblende residues (Giesel, 1902). He correctly established many of its chemical properties, including the important fact that it followed the chemistry of the cerium group of rare earths. By 1903, he had concentrated and purified it to a point where lanthanum was the chief impurity and thorium was spectroscopically undetectable (Giesel, 1903). A year later, he proposed the name, emanium, for what was clearly a new radioelement (Giesel, 1904a).

Giesel's claim was vigorously attacked by Debierne (1904), who now had an emanation-producing substance of his own, which, he insisted, was the same as the substance he had originally named actinium, although the 1900 preparation had titanium- or thorium-like properties (Adloff, 2000). Debierne's claim prevailed, and has been propagated by historians (Ihde, 1964; Partington, 1964; Weeks and Leicester, 1968), largely because of the prestige of the Curies and the support of Rutherford (1904). The latter based his conclusion solely on

the similarity in the decay characteristics of the "emanations" (i.e. ^{219}Rn) and the "active deposits" (^{211}Pb) given off by the samples supplied to him by the two claimants. Although some historical studies (Weeks and Leicester, 1968; Adloff, 2000) give both Debierne and Giesel credit for the discovery, Kirby (1971), Keller (1977), and the second author of this chapter believe that it is more appropriate to give credit for discovery of actinium to Giesel.

The actinium decay chain was sorted out rather quickly. In 1905, Godlewski (1904–5, 1905) and Giesel (1904b, 1905) independently reported the existence of actinium X (also referred to as "emanium X"), now known as ^{223}Ra, and showed it to be the direct source of the actinium emanation and its active deposit. The following year, Hahn (1906a,b) discovered radioactinium (^{227}Th), the immediate descendant of actinium and the parent of actinium X. ^{231}Pa, the parent of actinium, was discovered independently in 1918 by Soddy and Cranston (1918a,b) and by Hahn and Meitner (1918). The primordial origin of the actinium series ($4n + 3$ or uranium–actinium series, Fig. 2.1) was not finally resolved until 1935, when Dempster (1935) detected the uranium isotope of atomic weight 235 by mass spectroscopy.

2.2   NUCLEAR PROPERTIES

Of the 29 known isotopes of actinium (Table 2.1) only three are of particular significance to chemists. Two of these isotopes are the naturally occurring isotopes, ^{227}Ac (Fig. 2.1, $4n + 3$ or uranium–actinium series) and ^{228}Ac (mesothorium II, Fig. 2.2, $4n$ or thorium series). The third is ^{225}Ac, a descendant of reactor-produced ^{233}U (Fig. 2.3, $4n + 1$ or neptunium series).

2.2.1   Actinium–227

The isotope ^{227}Ac, a β^- emitter, is a member of the naturally occurring ^{235}U (AcU) decay series (Fig. 2.1). It is the daughter of ^{231}Pa and the parent of ^{227}Th (RdAc). It is also the parent, by a 1.38% α branch (Kirby, 1970; Monsecour *et al.*, 1974), of ^{223}Fr, which was discovered in 1939 by Perey (1939a,b). The half-life of ^{227}Ac is (21.772 ± 0.003) years (Jordan and Blanke, 1967; Browne, 2001), as determined by calorimetric measurements made over a period of 14 years. The thermal-neutron-capture cross section σ_t and the resonance integral are (762 ± 29) barn and (1017 ± 103) barn, respectively (1 barn = 10^{-28} m^2) (Monsecour and De Regge, 1975).

The β^- radiation of ^{227}Ac is so weak (0.045 MeV maximum) (Beckmann, 1955; Novikova *et al.*, 1960) that the nuclide was once thought to be 'rayless' (Marckwald, 1909; Rutherford, 1911). Even with modern nuclear spectrometers, neither the β^- nor the γ radiation is useful for analytical purposes because of interference from the rapidly growing decay products. On the other hand, ^{227}Ac is readily identified, even in the presence of its decay products,
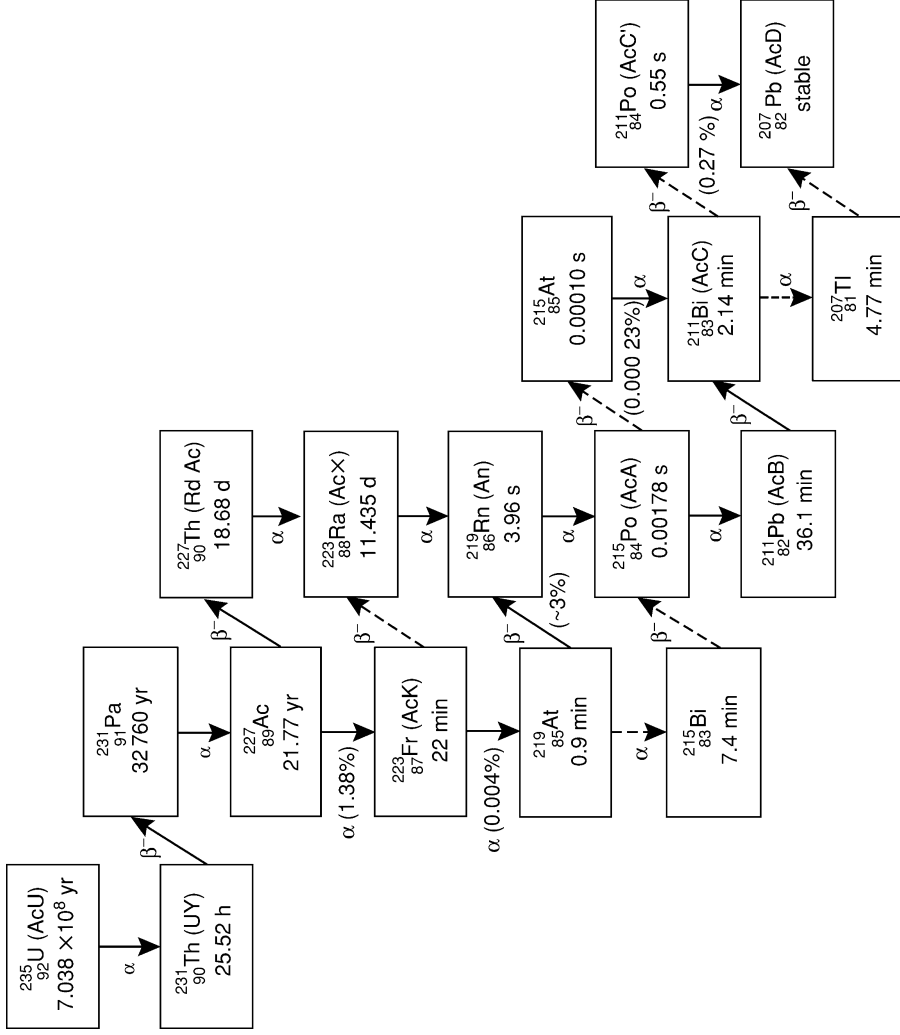
$^{235}_{92}$U (AcU) 7.038 ×10^8 yr — α → $^{231}_{90}$Th (UY) 25.52 h — β⁻ → $^{231}_{91}$Pa 32760 yr — α → $^{227}_{89}$Ac 21.77 yr

$^{227}_{89}$Ac — β⁻ → $^{227}_{90}$Th (Rd Ac) 18.68 d — α → $^{223}_{88}$Ra (AcX) 11.435 d — α → $^{219}_{86}$Rn (An) 3.96 s — α → $^{215}_{84}$Po (AcA) 0.00178 s — α → $^{211}_{82}$Pb (AcB) 36.1 min

$^{227}_{89}$Ac — α (1.38%) → $^{223}_{87}$Fr (AcK) 22 min — β⁻ → $^{223}_{88}$Ra (AcX)

$^{223}_{87}$Fr (AcK) — α (0.004%) → $^{219}_{85}$At 0.9 min — β⁻ → $^{219}_{86}$Rn (An)

$^{219}_{85}$At — α (~3%) → $^{215}_{83}$Bi 7.4 min — β⁻ → $^{215}_{84}$Po (AcA)

$^{219}_{86}$Rn (An) — α (0.000 23%) → $^{215}_{85}$At 0.00010 s — β⁻ → $^{211}_{83}$Bi (AcC) 2.14 min

$^{215}_{84}$Po (AcA) — β⁻ → $^{211}_{83}$Bi (AcC)

$^{211}_{83}$Bi (AcC) — α → $^{207}_{81}$Tl 4.77 min — β⁻ → $^{207}_{82}$Pb (AcD) stable

$^{215}_{85}$At — α → $^{211}_{84}$Po (AcC') 0.55 s — α (0.27 %) → $^{207}_{82}$Pb (AcD) stable

$^{211}_{83}$Bi (AcC) — β⁻ → $^{211}_{84}$Po (AcC')

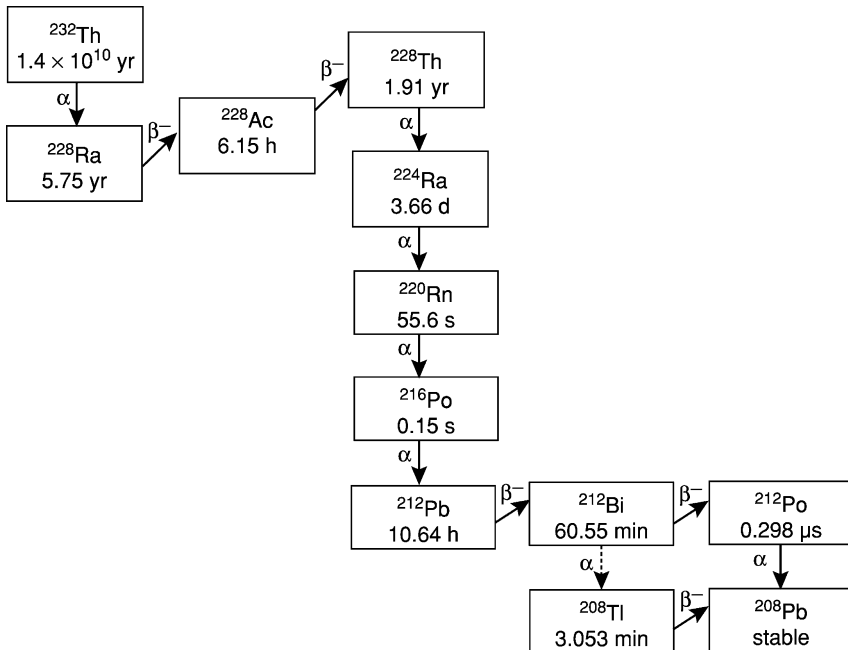**Fig. 2.1** *Uranium–actinium series (4n + 3).*

Table 2.1 *Nuclear properties of actinium isotopes.*[a]

Mass number	Half-life	Mode of decay	Main radiations (MeV)	Method of production
206	33 ms	α	α 7.750	^{175}Lu(^{40}Ar,9n)
	22 ms	α	α 7.790	
207	22 ms	α	α 7.712	^{175}Lu(^{40}Ar,8n)
208	95 ms	α	α 7.572	^{175}Lu(^{40}Ar,7n)
	25 ms	α	α 7.758	
209	0.10 s	α	α 7.59	^{197}Au(^{20}Ne,8n)
210	0.35 s	α	α 7.46	^{197}Au(^{20}Ne,7n)
				^{203}Tl(^{16}O,9n)
211	0.25 s	α	α 7.48	^{197}Au(^{20}Ne,6n)
				^{203}Tl(^{16}O,8n)
212	0.93 s	α	α 7.38	^{203}Tl(^{16}O,7n)
				^{197}Au(^{20}Ne,5n)
213	0.80 s	α	α 7.36	^{197}Au(^{20}Ne,4n)
				^{203}Tl(^{16}O,6n)
214	8.2 s	α ≥ 86%	α 7.214 (52%)	^{203}Tl(^{16}O,5n)
		EC ≤ 14%	7.082 (44%)	^{197}Au(^{20}Ne,3n)
215	0.17 s	α 99.91%	α 7.604	^{203}Tl(^{16}O,4n)
		EC 0.09%		^{209}Bi(^{12}C,6n)
216	~0.33 ms	α	α 9.072	^{209}Bi(^{12}C,5n)
216 m	0.33 ms	α	α 9.108 (46%)	
			9.030 (50%)	
217	69 ns	α	α 9.650	^{208}Pb(^{14}N,5n)
218	1.08 μs	α	α 9.20	^{222}Pa daughter
219	11.8 μs	α	α 8.66	^{223}Pa daughter
220	26.4 ms	α	α 7.85 (24%)	^{208}Pb(^{15}N,3n)
			7.68 (21%)	^{224}Pa daughter
			7.61 (23%)	
221	52 ms	α	α 7.65 (70%)	^{205}Tl(^{22}Ne,α2n)
			7.44 (20%)	^{208}Pb(^{18}O,p4n)
222	5.0 s	α	α 7.00	^{226}Ra(p,5n)
				^{208}Pb(^{18}O,p3n)
222 m	63 s	α > 90%	α 7.00 (15%)	^{208}Pb(^{18}O,p3n)
		EC ~ 1%	6.81 (27%)	^{209}Bi(^{18}O,αn)
		IT < 10%		
223	2.10 min	α 99%	α 6.662 (32%)	^{227}Pa daughter
		EC 1%	6.647 (45%)	
224	2.78 h	EC ~ 90%	α 6.211 (20%)	^{228}Pa daughter
		α ~ 10%	6.139 (26%)	
225	10.0 d	α	α 5.830 (51%)	^{225}Ra daughter
			5.794 (24%)	
			γ 0.100 (1.7%)	
226	29.37 h	β$^-$ 83%	α 5.399	^{226}Ra(d,2n)
		EC 17%	β$^-$ 1.10	
		α 6 × 10^{-3}%	γ 0.230 (27%)	
227	21.772 yr	β$^-$ 98.62%	α 4.950 (47%)	Nature
		α 1.38%	4.938 (40%)	
			β$^-$ 0.045	
			γ 0.086	

Table 2.1 (*Contd.*)

Mass number	Half-life	Mode of decay	Main radiations (MeV)	Method of production
228	6.15 h	β⁻	β⁻ 2.18 γ 0.991	Nature
229	62.7 min	β⁻	β⁻ 1.09 γ 0.165	^{229}Ra daughter ^{232}Th(γ,p2n)
230	122 s	β⁻	β⁻ 1.4 γ 0.455	^{232}Th(γ,pn)
231	7.5 min	β⁻	β⁻ 2.1 γ 0.282	^{232}Th(γ,p) ^{232}Th(n,pn)
232	119 s	β⁻		^{238}U + Ta
233	145 s	β⁻		^{238}U + Ta
234	44 s	β⁻		^{238}U + Ta

^{a} Appendix II.

Fig. 2.2 *Thorium series* (4*n*).

by α spectrometry (Fig. 2.4), and a computational technique has been described for its quantitative determination by this method (Kirby, 1970).

The γ spectrum of ^{227}Ac in equilibrium with its decay products is shown in Fig. 2.5. The 235.9-keV γ-ray, which has an intensity of (12.3 ± 1.3)% of ^{227}Th
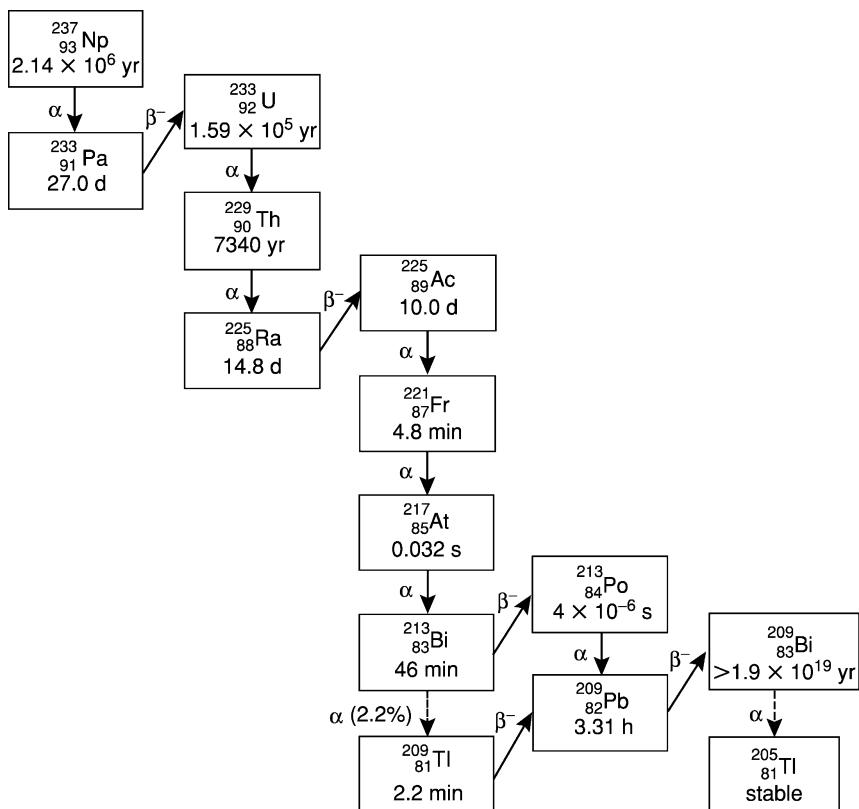
Fig. 2.3   *Neptunium series* $(4n + 1)$.

α decay, can be used for quantitative analysis of ^{227}Ac. For a detailed level scheme, see the most recent critical compilation (Firestone and Shirley, 1996).

2.2.2   Actinium–228 (MsTh II or MsTh₂)

The isotope ^{228}Ac (mesothorium II or MsTh$_2$) is a member of the naturally occurring ^{232}Th decay chain. It is the daughter of 5.77-year ^{228}Ra (mesothorium I or MsTh$_1$) and the parent of 1.9116-year ^{228}Th (radiothorium).

All three nuclides were discovered by Otto Hahn (1905, 1907, 1908). The long-accepted half-life of ^{228}Ac (6.13 ± 0.03) h, reported in 1926 (Hahn and Erbacher, 1926), was redetermined to be (6.15 ± 0.02) h in 1985 (Skarnemark and Skalberg, 1985).

^{228}Ac has a complex β^- spectrum (Bjornholm *et al.*, 1957; Arnoux and Giaon, 1969; Dalmasso *et al.*, 1974), but, unlike ^{227}Ac, more than 99% of the β^- particles have maximum energies greater than 0.5 MeV so that its γ-ray spectrum (Novikova *et al.*, 1960) is a useful analytical tool. By contrast, the
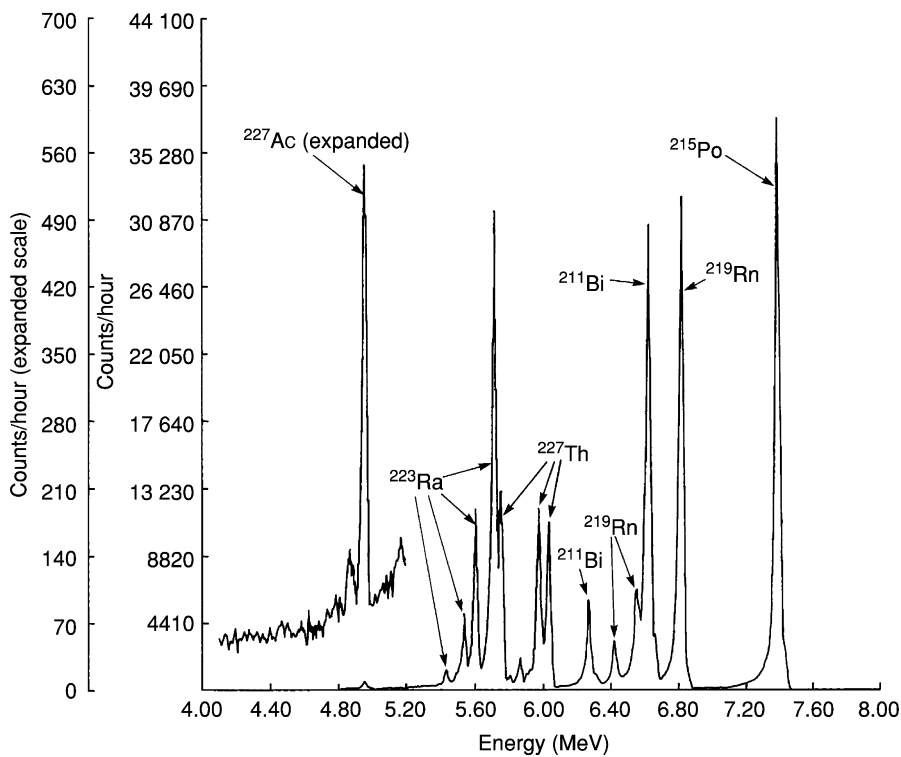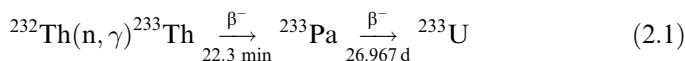
Fig. 2.4   *Alpha spectrum of* ^{227}Ac *in equilibrium with its decay products* (*Kirby,* 1970).

β^- and γ radiations from ^{228}Ra are too weak for routine detection; consequently, nearly all methods for the determination of ^{228}Ra are based on the isolation and counting of ^{228}Ac (Hahn and Erbacher, 1926). ^{228}Ac is frequently used as a tracer for other actinium isotopes (Bhatki and Adloff, 1964; Chayawattanangkur *et al.*, 1973).

A level scheme and a critical compilation of γ-ray energies for ^{228}Ac have been published (Horen, 1973).

2.2.3   Actinium-225

The isotope ^{225}Ac is an α emitter. It is a member of the $4n + 1$ decay series, of which ^{237}Np is the longest-lived member and progenitor (Fig. 2.3). In practice, however, ^{225}Ac is most easily obtained by milking a sample of ^{229}Th that was previously separated from aged ^{233}U (Valli, 1964). The latter isotope is itself produced by neutron bombardment of natural thorium (St. John and Toops, 1958; Hyde *et al.*, 1964):
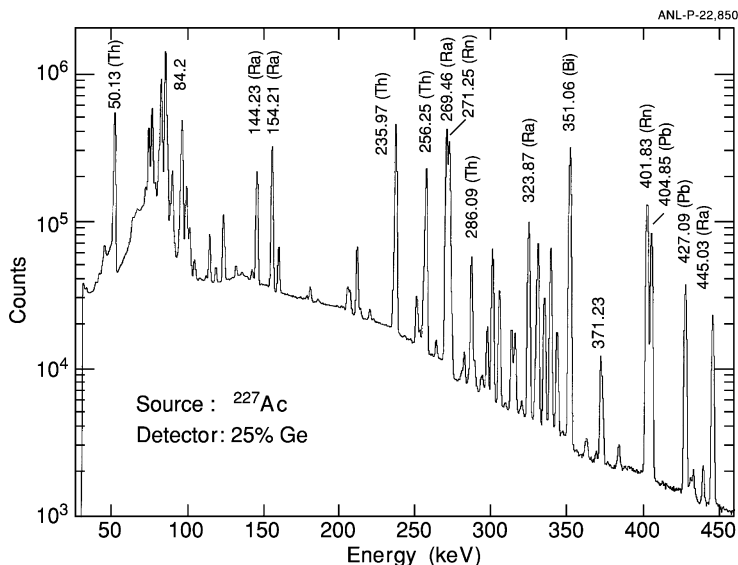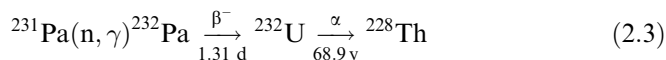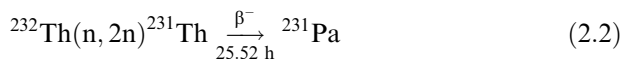
$$^{232}\text{Th}(n, \gamma)^{233}\text{Th} \xrightarrow[22.3\,\text{min}]{\beta^-} {}^{233}\text{Pa} \xrightarrow[26.967\,\text{d}]{\beta^-} {}^{233}\text{U} \qquad (2.1)$$

Fig. 2.5 *Gamma spectrum of* ^{227}*Ac in equilibrium with its decay products* (*I. Ahmad,* 2002).

Unfortunately, ^{229}Th is always more or less contaminated with ^{228}Th because of side reactions during the production of ^{233}U:

$$^{232}\text{Th}(n, 2n)^{231}\text{Th} \xrightarrow[25.52\text{ h}]{\beta^-} {}^{231}\text{Pa} \tag{2.2}$$

$$^{231}\text{Pa}(n, \gamma)^{232}\text{Pa} \xrightarrow[1.31\text{ d}]{\beta^-} {}^{232}\text{U} \xrightarrow[68.9\text{ y}]{\alpha} {}^{228}\text{Th} \tag{2.3}$$

To obtain pure samples of ^{225}Ac, the presence of ^{228}Th in ^{229}Th is not a serious problem, because the ^{224}Ra daughter of ^{228}Th can be chemically separated from he ^{225}Ac, together with ^{225}Ra, after its milking from thorium. The ^{224}Ra must be removed to ensure the absence of its progeny ^{208}Tl, which emits a 2.6-MeV γ-ray.
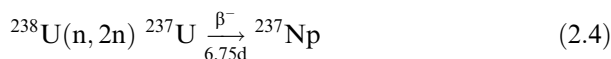
The complex fine structure of the ^{225}Ac α spectrum was thoroughly investigated by Dzhelepov *et al.* (1967) and by Bastin-Scoffier (1967). A level scheme is given in a critical compilation (Maples, 1973).

2.3   OCCURRENCE IN NATURE

The natural occurrence of ^{227}Ac is proportional to that of its primordial ancestor, ^{235}U, which is widely distributed in the Earth's crust (Kirby, 1974). The average crustal abundance of uranium is 2.7 ppm (Taylor, 1964), of which

0.720 mass% is ^{235}U (Holden, 1977). Therefore, the natural abundance of ^{227}Ac (calculated from its half-life and that of ^{235}U) is 5.7×10^{-10} ppm. Based upon a crustal mass of 2.5×10^{25} g (to a depth of 36 km) (Heydemann, 1969), the global inventory of ^{227}Ac is estimated to be 1.4×10^{4} metric tons.
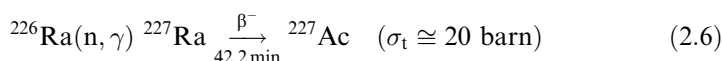
Although the $4n + 1$ family is not ordinarily considered to be 'naturally occurring' because its primordial ancestor has become extinct, both ^{237}Np and ^{225}Ac have been detected in uranium refinery wastes and ^{225}Ac has been found in ^{232}Th isolated from Brazilian monazite (Peppard *et al.*, 1952). These nuclides are believed to be formed continually in nature by the bombardment of natural thorium and uranium with neutrons arising from spontaneous fission of ^{238}U and from neutrons produced by (α,n) reactions on light elements:

$$^{238}\text{U}(\text{n}, 2\text{n})\ ^{237}\text{U} \xrightarrow[6.75\text{d}]{\beta^-}\ ^{237}\text{Np} \qquad (2.4)$$

$$^{232}\text{Th}(\text{n}, \gamma)\ ^{233}\text{Th} \xrightarrow[22.3\,\text{min}]{\beta^-}\ ^{233}\text{U} \qquad (2.5)$$
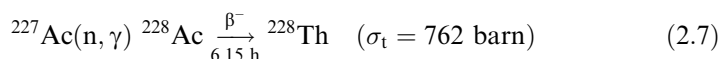
2.4 PREPARATION AND PURIFICATION

Uranium ores always contain large amounts of rare earths, and were thus generally unsatisfactory as sources of actinium before modern methods of rare earth separations were developed. The most concentrated actinium sample ever prepared from a natural raw material consisted of 0.5 mCi ($\sim$7 μg) of ^{227}Ac in less than 0.1 mg of La_2O_3 (Lecoin *et al.*, 1950).

In 1949, Peterson reported that ^{227}Ac could be synthesized by irradiating ^{226}Ra with thermal neutrons (Peterson, 1949):

$$^{226}\text{Ra}(\text{n}, \gamma)\ ^{227}\text{Ra} \xrightarrow[42.2\,\text{min}]{\beta^-}\ ^{227}\text{Ac} \quad (\sigma_t \cong 20 \text{ barn}) \qquad (2.6)$$

This reaction greatly simplified the chemical separations required to prepare macroscopic amounts of pure ^{227}Ac and, in 1950, Hagemann reported the isolation of 1.27 mg of ^{227}Ac from 1 g of neutron-irradiated ^{226}Ra (Hagemann, 1950).

Later work (Kirby *et al.*, 1956; Cabell, 1959; Monsecour and De Regge, 1975) showed that the neutron-capture cross section of ^{227}Ac is many times greater than that of ^{226}Ra (Fig. 2.6). A new problem is introduced, namely that of separating ^{227}Ac from the large amounts of 1.9-year ^{228}Th produced by the second-order reactions:
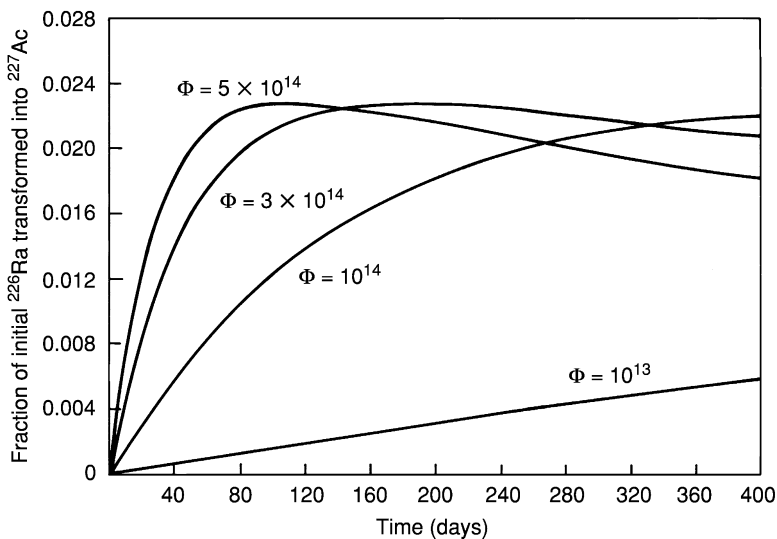
$$^{227}\text{Ac}(\text{n}, \gamma)\ ^{228}\text{Ac} \xrightarrow[6.15\,\text{h}]{\beta^-}\ ^{228}\text{Th} \quad (\sigma_t = 762 \text{ barn}) \qquad (2.7)$$

Fig. 2.6 *Growth of* ^{227}Ac *in neutron-irradiated* ^{226}Ra *at various thermal-neutron fluxes* Φ *(in* cm^{-2} s^{-1}*). The calculations assume* $\sigma_t(^{226}Ra) = 20$ *barn and* $\sigma_t(^{227}Ac) = 795$ *barn* (*Gomm and Eakins,* 1968).

Nevertheless, neutron irradiation of ^{226}Ra remains the method of choice for the preparation of ^{227}Ac at either the tracer or the macroscopic level.

The isotope ^{225}Ac is best generated by separating it from the generator ^{229}Th (Geerlings *et al.*,1993; Tsoupko-Sitnikov *et al.*, 1996; Khalkin *et al.*, 1997). The ^{229}Th generator must be separated from ^{233}U. The isotope ^{233}U is synthesized by neutron irradiation of ^{232}Th, which contaminates the ^{229}Th with some ^{228}Th and its daughters.

The isotope ^{228}Ac can be generated by separating it from the generator ^{228}Ra, which can be isolated from natural ^{232}Th (Gmelin, 1981). Detailed procedures were given by Sekine *et al.* (1967). Sani (1970) and Mikheev *et al.* (1995) removed ^{228}Ra from aged ^{232}Th by cocrystallization with $Ba(NO_3)_2$. The ^{228}Ac that grew into ^{228}Ra was removed by extraction or by adding $GdCl_3$ to an aqueous solution of the ^{228}Ra in $Ba(NO_3)_2$ and coprecipitating Ac^{3+} with Gd $(OH)_3$ using $NH_3(g)$.

2.4.1 Purification by liquid–liquid extraction

Hagemann (1950, 1954) isolated the first milligram of ^{227}Ac from neutron-irradiated ^{226}Ra by liquid–liquid extraction with 2-thenoyltrifluoroacetone (TTA). Experience has shown (Engle, 1950; Stevenson and Nervik, 1961; Kirby, 1967), however, that TTA is not a suitable reagent for quantitative extraction of actinium because a relatively high pH (≥ 5.5, Fig. 2.7) is required
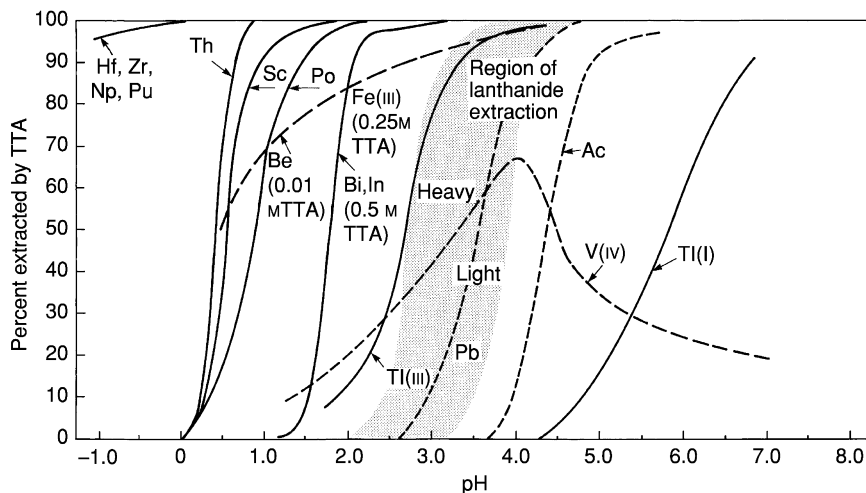
Fig. 2.7 *Extraction of various elements with thenoyltrifluoroacetone (TTA). (After Stevenson and Nervik, 1961).*

for efficient chelation but Ac^{3+} hydrolyzes above pH 7 and forms inextractable polymeric species when the pH is in the 'desirable' range, 6–7. The recovery of actinium requires tight pH control and speed of operation for satisfactory yields (Allison *et al.*, 1954; Tousset, 1961) that are usually not quantitative. The most effective application of TTA in the purification of ^{227}Ac is to remove ^{227}Th, which can be selectively and quantitatively extracted from moderately acid solutions. For this extraction, the pH_{50} (the pH at which 50% of the Th^{4+} is extracted or partitioned equally between the phases, i.e. $D = 1$) is 0.48 (Poskanzer and Foreman, 1961).

On the other hand, Sekine *et al.* (1967) found that, while the extraction of ^{228}Ac with TTA alone was not quantitative, a mixture of 0.1 M TTA and 0.1 M tri(*n*-butyl)phosphate (TBP) in CCl_4 gave reproducible distribution ratios and quantitative extraction of Ac^{3+} at $pH \geq 4$.

Solvent extraction systems that have been applied to other actinide and lanthanide separations have also been applied to actinium separations from thorium and radium. Thus, Karalova *et al.* (1977a) studied the extraction of Ac(III) in aqueous nitrate solution by trioctylphosphine oxide dissolved in cyclohexane, *o*-xylene, carbon tetrachloride, octyl alcohol, or chloroform. Optimum extraction conditions were: $[NaNO_3] \geq 2$ M, pH 2, and cyclohexane as the partition solvent. Making the aqueous phase 8 M in lithium chloride appears to facilitate extraction with 0.1 M trioctylphosphine oxide (Karalova *et al.*, 1977b).

Trialkylphosphine oxide in aliphatic hydrocarbon solvents was used by Xu *et al.* (1983) for the solvent extraction separation of Ac(III) from La(III) in nitric acid solution. Amines and quaternary ammonium bases have also been used in

solvent extraction systems for the separation of Ac(III) from rare earths and Am(III). Karalova *et al.* (1979a) examined the separation of Ac(III) from Eu(III) by extraction from aqueous solutions containing lithium nitrate at pH 2.5–3 with tri-*n*-octylamine in cyclohexane, and concluded that this partition system shows promise for the separation of Ac(III) from rare earths. A 0.5 M solution of the quaternary ammonium base Aliquat 336 (methyltrioctylammonium chloride) in xylene extracts Ac, Am, and Eu efficiently from aqueous alkaline (pH > 11) solutions containing ethylenediaminetetraacetic acid (EDTA) or 2-hydroxydiaminopropanetetraacetic acid; separation factors for Ac(III)/Am(III) and Ac(III)/Eu(III) greater than 100 were attained (Karalova *et al.*, 1978a, 1979b). A mixture of trialkylmethylammonium nitrate and TBP was reported by Mikhailichenko *et al.* (1982) to exert a weak synergistic effect on La(III) extraction and an antagonistic effect on Ac(III) extraction. Bis(2-ethylhexyl) phosphoric acid (HDEHP) has been successfully employed in the solvent extraction separation of ^{227}Ac(III), ^{227}Th(IV), ^{223}Ra(II), and ^{223}Fr(I) (Mitsugashira *et al.*, 1977). Karalova *et al.* (1978b) established that the actinium species extracted from 1 M perchloric acid is AcX$_3$·2HX, and at higher perchloric acid concentrations is HAc(ClO$_4$)$_4$·2HX.

The use of bis(2-ethylhexyl)phosphoric acid (HDEHP) as an extractant for Ac^{3+} has been little explored. Two studies have explored the fundamental mechanism of this extractant with Ac^{3+} (Szeglowski and Kubica, 1991) and the influence of colloidal rare earth particles on this extraction (Szeglowski and Kubica, 1990).

An unusual purification procedure is one in which actinium must be removed from rare earths on a commercial scale to minimize the level of radioactive contamination of the rare earth products (Kosynkin *et al.*, 1995). Uranium–rare earth phosphorites [fibrous apatites, generic formula Ca$_5$(PO$_4$)$_3$(OH,F,Cl)] have been processed commercially to remove both uranium and rare earths. After uranium was extracted from the dissolved phosphorite, cerium was removed by oxidation and precipitation from dilute acid. The trivalent rare earths and actinium remained in the aqueous phase and the actinium was removed from the rare earth fraction using mixer-settlers with mixtures of TBP and trialkyl amine (TAA) extractants in kerosene. Decontamination from a level of ~10^{-8} Ci/(g rare earth oxides) to a level of ~2 × 10^{-11} Ci/(g rare earth oxides) has been achieved on an industrial scale.

2.4.2 Purification by ion-exchange chromatography

Cation-exchange chromatography is the simplest and most consistently effective method of separating sub-milligram amounts of ^{227}Ac from its principal decay products, 18.68-day ^{227}Th and 11.43-day ^{223}Ra (Gmelin, 1981). The resin most commonly employed is a strong cation-exchange resin such as Dowex 50 (Andrews and Hagemann, 1948; Cabell, 1959; Farr *et al.*, 1961; Eichelberger *et al.*, 1964; Nelson, 1964; De Troyer and Dejonghe, 1966; Baetslé *et al.*, 1967;

Baetslé and Droissart, 1973; Kraus, 1979; Boll *et al.*, 2005), but inorganic ion exchangers have also been used successfully (Huys and Baetslé, 1967; Monsecour and De Regge, 1975). The method is applicable to milking of ^{228}Ac tracer from its parent, 5.76 year ^{228}Ra (Bjornholm *et al.*, 1956, 1957; Duyckaerts and Lejeune, 1960; Bryukher, 1963; Bhatki and Adloff, 1964; Gomm and Eakins, 1966; Arnoux and Giaon, 1969; Monsecour *et al.*, 1973). A typical separation is illustrated in Fig. 2.8.

Anion-exchange chromatography is now used for bulk separation of ^{225}Ac and ^{223}Ra from ^{229}Th. The ^{225}Ac and ^{223}Ra are eluted in 2–4 bed volumes of 8 M HNO_3 and then ^{229}Th is stripped from the resin in 0.1 M HNO_3, after which the ^{229}Th can be recycled (Boll *et al.*, 2004).

Partition chromatography by reverse-phase and ion-exchange chromatography has been explored (Sinitsyna *et al.*, 1977, 1979). The radioisotopes of actinium were separated from other elements using trioctylamine, bis(2-ethylhexyl)phosphoric acid, and TBP as stationary phases on Teflon. Chromatography on a Teflon support was also investigated by Korotkin (1981). He used a mixture of TTA and TBP impregnated in Teflon to sorb the metal ions. Elution
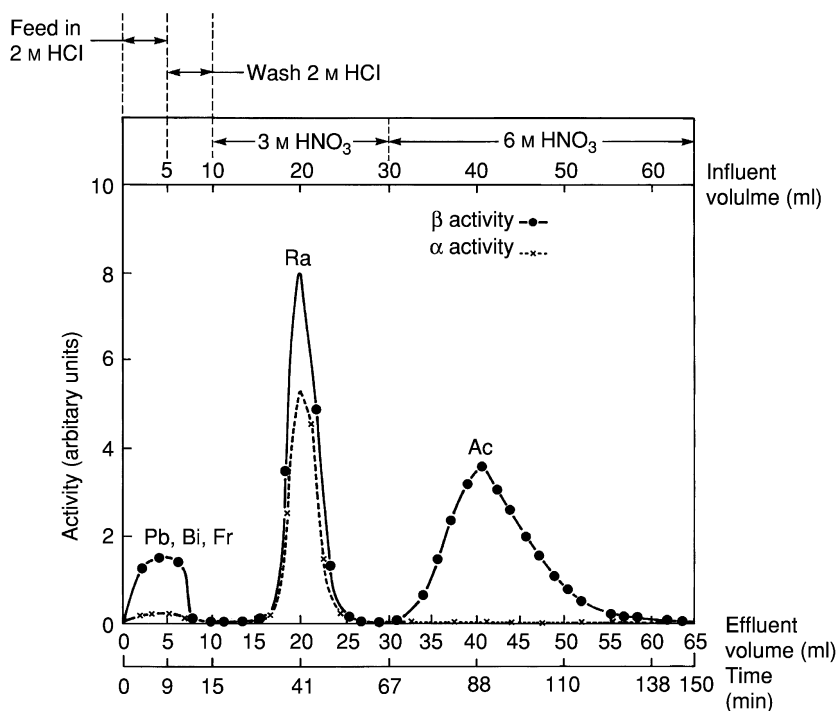

Fig. 2.8 *Separation of* ^{227}Ac *from its decay products by cation-exchange chromatography on Dowex* 50, *hydrogen form,* 200–400 *mesh,* 60°C (*Cabell,* 1959).

was by oxalate in a phthalate buffer. The procedure appears to have general utility for the rapid separation of actinides, lanthanides, and other metal ions. ^{227}Ac was separated from irradiated radium samples containing Pb, Tl, Bi, Po, and Th, and ^{225}Ac was separated from ^{233}U containing the same elements.

The inorganic cation exchanger, cryptomelane MnO_2 [a sorbent for large cations related to the mineral cryptomelane, $K(Mn^{4+},Mn^{2+})_8O_{16}$] is highly radiation-resistant and has distribution ratios (K_d values) for trivalent lanthanides and actinides that are orders of magnitude smaller than for Ra^{2+}. This ion exchanger has been used to separate ^{225}Ac^{3+} or ^{228}Ac^{3+} from ^{225}Ra^{2+} or ^{228}Ra^{2+} in radioisotope generators (Włodzimirska *et al.*, 2003).

2.4.3 Isolation of gram quantities of actinium

The history of large-scale actinium production is littered with the mutilated corpses of carefully designed processes, developed at the laboratory scale, which failed utterly, or required innumerable *ad hoc* modifications, when they were applied to the recovery of multi-Curie amounts of ^{227}Ac and ^{228}Th from multi-gram quantities of neutron-irradiated ^{226}Ra (Andrews and Hagemann, 1948; Engle, 1950; Kirby, 1951, 1952; Eichelberger *et al.*, 1964, 1965; De Troyer and Dejonghe, 1966; Foster, 1966; Baetslé *et al.*, 1967; Huys and Baetslé, 1967; Baetslé and Droissart, 1973).

Not the least of the problems is that posed by 3.824-day ^{222}Rn, a noble gas, which is evolved copiously and continuously by the decay of ^{226}Ra. The radioactive gaseous exhaust from the facility must be trapped and immobilized for several weeks while it decays to levels at which it can safely be released to the environment. (The maximum permissible concentration [inhalation derived air concentration (DAC)] of ^{222}Rn and its progeny in air in the workplace is very low, 3×10^{-8} μCi mL^{-1}) (U.S. Nuclear Regulatory Commission, 2005) Until now, this low level has been achieved by adsorbing the radon on activated charcoal at -75 to $-180°$C (Baetslé *et al.*, 1972), or by replacing the air at a sufficiently high rate, but chemical methods for removing radon and its daughters from the air by reaction with powerful fluorination reagents were also shown to bear promise for the removal of radon from air (Stein and Hohorst, 1982).

At the Belgian Nuclear Research Center (SCK-CEN, Mol), the irradiated $RaCO_3$ was dissolved in dilute nitric acid, and then precipitated as $Ra(NO_3)_2$ from 80% HNO_3, leaving nearly all the ^{227}Ac and ^{228}Th in solution. This step made the ^{226}Ra immediately available for recycling to the reactor; it also eliminated many of the severe radiolytic problems that develop when organic solvents or ion-exchange resins are in contact with large amounts of ^{226}Ra for extended periods of time.

The solution was then filtered, adjusted to 5 M HNO_3, and passed through a column of Dowex AG 1 × 8, an anion-exchange resin. ^{228}Th was quantitatively

adsorbed (Danon, 1956, 1958), while the non-complexing cations (Fe, Ni, Cr) passed through the column unimpeded. ^{227}Ac, which appeared to be adsorbed to a slight extent by the resin, followed after a brief delay. The actinium was finally purified by oxalate precipitation (Salutsky and Kirby, 1956) and ignited to Ac_2O_3 at 700°C. The process gave excellent Ac/Th separations (<0.01% ^{228}Th) and 'reasonable' Ac purifications (Baetslé *et al.*, 1972; Baetslé, 1973).

The production capacity at Mol was about 20 g ^{227}Ac and 4 g ^{228}Th per year. As of the end of 1972, 2 g of Ac_2O_3 had been encapsulated as a prototype 30 W heat source and about 700 mg had been purified for the preparation of Ac–Be neutron sources. The ^{227}Ac production and separation facility at Mol was dismantled a few years later (Deworm *et al.*, 1979).

2.5 ATOMIC PROPERTIES

Meggers, Fred, and Tomkins (Meggers *et al.*, 1951, 1957; Meggers, 1957; Sugar, 1984) examined the emission spectra of actinium excited in a hollow cathode and in arcs and sparks between copper or silver electrodes. They reported some 500 lines characteristic of actinium in the spectral range 2062.00–7886.82 Å. Of these about 140 lines were assigned to the neutral atom, Ac I, more than 300 to singly ionized actinium, Ac II, and eight to doubly ionized actinium, Ac III. The lowest energy levels for identified configurations are given in Chapter 16 of this work (Table 16.1). The electron configuration of the Ac I (neutral Ac) ground state was found to be [Rn]($6d7s^2$) $^2D_{3/2}$; that of Ac II (Ac^+), ($7s^2$) $^1S_0$; and that of Ac III (Ac^{2+}), ($7s$) $^2S_{1/2}$. The first two ionization potentials were estimated to be 5.17 and 11.87 eV (Sugar, 1973, 1984). Similar values were calculated by Eliav *et al.* (1998), who also calculated the third ionization potential to be 17.518 or 17.512 eV by relativistic coupled-cluster methods. The first ionization potential was recently measured to be 5.3807(3) eV by resonant excitation of ^{227}Ac by laser spectroscopy in an external electric field (Backe *et al.*, 2002).

Analysis of interference spectrograms of the ^{227}Ac nucleus yielded the nuclear spin $I = 3/2$ (Tomkins *et al.*, 1951), and values of $\mu = (1.1 \pm 0.1)$ nuclear magnetons and $Q = +1.7$ barns for the magnetic and electric quadrupole moments, respectively (Fred *et al.*, 1955).

The foregoing comprises essentially all the experimentally determined data presently available on the properties of isolated actinium atoms and ions in the gas phase (see also Chapters 16 and 19). Theoretical calculations on such properties as energy levels (Brewer, 1971a,b; Nugent and Vander Sluis, 1971; Vander Sluis and Nugent, 1972, 1974; Nugent *et al.*, 1973b), ionization potentials (Carlson *et al.*, 1970; Sugar, 1973; Eliav *et al.*, 1998), and electron affinities (Eliav *et al.*, 1998) of actinium atoms and its free ions have also been made. There remain some discrepancies among some of these calculations or estimates

that will only be resolved by better theoretical treatments and experimental measurements.

Consistent with the difference between the ionic radii of La^{3+} and Ac^{3+} (0.088 Å = 8.8 pm) (Shannon, 1976 and Section 15.7.5, Chapter 15), *ab initio* nonrelativistic and quasi-relativistic calculations of the bond lengths in mono-hydrides, monoxides, and monofluorides of all the lanthanide and actinide elements indicated a difference between La–X and Ac–X bond lengths of 10 pm (Küchle *et al.*, 1997). Another set of fully relativistic *ab initio* calculations of the bond lengths in monofluorides, monohydrides, and trihydrides revealed similar La–X and Ac–X bond-length differences; for LaH_3 and AcH_3 the bond-length difference calculated was also 10 pm (Laerdahl *et al.*, 1998).

2.6 THE METALLIC STATE

In 1953, Farr *et al.* (1953, 1961) prepared 10 μg of ^{227}Ac metal in an X-ray capillary by reduction of $AcCl_3$ with potassium vapor at 350°C. The diffraction pattern yielded two face-centered cubic (fcc) structures, which were attributed (by analogy to a parallel experiment with lanthanum) to actinium metal ($a_0 = 5.311 \pm 0.010$ Å) and actinium hydride ($a_0 = 5.670 \pm 0.006$ Å). The calculated densities were 10.07 and 8.35 g cm^{-1}, respectively. (The hydrogen in the 'actinium hydride' was of unknown origin.)

Milligram amounts of actinium metal were prepared by reduction of AcF_3 with lithium vapor in a molybdenum crucible (Stites *et al.*, 1955). The temperature range, 1100–1275°C, was critical for the reduction of AcF_3; at lower temperatures reduction was incomplete because the product metal did not melt, whereas at higher temperatures the yield was low because some of the AcF_3 was lost by volatilization.

The metal was reported to be silvery white in color, sometimes with a golden cast. It oxidizes rapidly in moist air to form a white coating of Ac_2O_3, which is somewhat effective in preventing further oxidation. Stites *et al.* (1955) estimated the melting point to be (1050 ± 50)°C. This melting point has been criticized as 'unreasonably low' (Matthias *et al.*, 1967) but is accepted in this work. A melting point of 1227°C has been estimated more recently (Arblaster, 1995). Based upon bonding contributions to the cohesive energy by 7s, 7p, and 6d electrons, Fournier (1976) estimated the melting point to be 1430°C and the enthalpy of sublimation ($\Delta_f H°$, Ac, g, 298 K) to be 396 kJ mol^{-1}. Other estimates of the enthalpy of sublimation are 406 kJ mol^{-1} (Wagman *et al.*, 1982) and 418 kJ mol^{-1} (David *et al.*, 1978; Ward *et al.*, 1986). The boiling point, estimated by extrapolation from vapor pressure measurements, is (3200 ± 300)°C (Foster and Fauble, 1960).

Subsequently, two metal preparations were made by the reduction of Ac_2O_3 with metallic thorium in high vacuum at 1750°C (Baybarz *et al.*, 1976), subliming the metal onto a tantalum condenser, and resubliming the metal to further

purify it. X-ray data on these preparations of Ac metal suggest an fcc lattice with a_0 parameter of (5.317 ± 0.009) and (5.314 ± 0.001) Å in the two preparations (Baybarz *et al.*, 1976). Arblaster (1995) predicted that actinium metal should parallel metallic lanthanum and americium, with a double close-packed hexagonal allotrope at lower temperature and a body-centered cubic (bcc) allotrope at higher temperature.

Farr *et al.* (1953, 1961) reported that the metallic radius of actinium is 1.88 Å, but Zachariasen (1961, 1973) regarded this value as unreasonably similar to that of lanthanum (1.87 Å), because, in all isostructural compounds, the bond distances for actinium compounds are approximately 0.1 Å greater than those for the corresponding lanthanum compounds. By interpolation between the metallic radii of Ra and Th (2.293 and 1.798 Å, respectively), he predicted a value of 1.977 Å for Ac. On the other hand, Hill (1972) suggested that the lack of an appreciable increase in the metallic radius is a manifestation of a pronounced relativistic shrinkage in the 7s orbital of the neutral Ac atom, relative to such an effect on the 6s orbital of lanthanum. The fcc Ac prepared by Baybarz *et al.* (1976) corresponded to a metallic radius of 1.878 Å, supporting Hill's argument.

2.7 COMPOUNDS

With the sole exception of the questionable hydride mentioned in Section 2.6, almost all the compounds of actinium that have been positively identified by X-ray diffraction analysis are the result of a single study by Fried, Hagemann, and Zachariasen (Fried *et al.*, 1950). Each of the compounds was prepared from 10 μg of actinium or less, which was purified by TTA extraction (Hagemann, 1950) immediately before the start of the preparation. The small sample size was chosen to minimize the radiation health hazard and to reduce the fogging of the X-ray film by γ radiation from the rapidly growing actinium decay products. Even, so, it was necessary to prepare and photograph the compound within 24 h after purification. After purification of actinium from neutron-irradiated ^{226}Ra (Baetslé and Droissart, 1973) by ion exchange, Weigel and Hauske (1977) precipitated actinium oxalate on the 10 μg scale and identified it as the decahydrate from its X-ray powder pattern. It is isomorphous with similar compounds of the rare earths, plutonium, and americium.

Table 2.2 summarizes the preparative work and some of the properties of the ten known compounds of actinium. In addition, compounds thought to be the iodide, hydroxide, oxalate, oxyiodide, phosphate, and double salt with potassium sulfate were prepared but could not be identified (Fried *et al.*, 1950). Other unidentified compounds, suggested by chemical or thermogravimetric evidence, include the basic carbonate (Butterfield and Woollatt, 1968), the 8-hydroxyquinolate (Mosdzelewski, 1966; Keller and Mosdzelewski, 1967), and a double salt with ammonium nitrate (Kirby, 1969).

Table 2.2 *Preparation and properties of actinium compounds (Fried et al., 1950; Weigel and Hauske, 1977; Gmelin, 1981).*

Compound	Preparation		Crystal structure data					
	Reaction	Temp. (°C)	Symmetry	Structure type	Lattice parameters			
					a_0 (Å)	b_0 (Å)	c_0 (Å)	β (deg)
AcF_3	$Ac(OH)_3 + 3HF \rightarrow$ $AcF_3 + 3H_2O$ $Ac^{3+} + 3F^- \rightarrow AcF_3$	700 25	trigonal	LaF_3	7.41 ± 0.01		7.53 ± 0.02	
$AcCl_3$	$2Ac(OH)_3 + 3CCl_4 \rightarrow$ $2AcCl_3 + 3CO_2 + 6HCl$	subl 960	hexagonal	UCl_3	7.62 ± 0.02		4.55 ± 0.02	
$AcBr_3$	$Ac_2O_3 + 2AlBr_3 \rightarrow$ $2AcBr_3 + Al_2O_3$	800	hexagonal	UCl_3	8.06 ± 0.04		4.68 ± 0.02	
$AcOF$	$AcF_3 + 2NH_3 + H_2O \rightarrow$ $AcOF + 2NH_4F$	900–1000	cubic	CaF_2	5.931 ± 0.002			
$AcOCl$	$AcCl_3 + H_2O \rightarrow$ $AcOCl + 2HCl$	1000	tetragonal	$PbClF$	$4.24 + 0.02$		7.07 ± 0.03	
$AcOBr$	$AcBr_3 + 2NH_3 + H_2O \rightarrow$ $AcOBr + 2NH_4Br$	500	tetragonal	$PbClF$	4.27 ± 0.02		7.40 ± 0.03	
Ac_2O_3	$Ac_2(C_2O_4)_3 \rightarrow Ac_2O_3$ $+ 3CO_2 + 3CO$	1100	hexagonal	La_2O_3	4.07 ± 0.01		6.29 ± 0.02	
Ac_2S_3	$Ac_2O_3 + 3H_2S \rightarrow Ac_2S_3$ $+ 3H_2O$	1400	cubic	Ce_2S_3	8.97 ± 0.01			
$AcPO_4 \cdot 1/2H_2O$	$Ac^{3+} + PO_4^{3-} \rightarrow AcPO_4$	25	hexagonal	$LaPO_4 \cdot 1/2H_2O$	7.21 ± 0.02		6.64 ± 0.03	
$Ac_2(C_2O_4)_3 \cdot 10H_2O^a$	$2Ac^{3+} + 3C_2O_4^{2-} \rightarrow$ $Ac_2(C_2O_4)_3 \cdot 10H_2O$	25	monoclinic	$La_2(C_2O_4)_3 \cdot$ $10H_2O$	11.26	9.97	10.65	111.3

[a] From Weigel and Hauske (1977).

2.8 SOLUTION AND ANALYTICAL CHEMISTRY

All available evidence supports the conclusion (Moeller and Kremers, 1945), derived primarily from tracer and coprecipitation studies, that actinium is a homolog of lanthanum, fitting into the 7th period in the periodic table. The Ac^{3+}(aq) ion is more basic (less subject to hydrolysis) than the La^{3+}(aq) ion. As such, Ac^{3+} is the most basic tripositive ion known.

Aqueous solutions of actinium are colorless. In the only reported spectro-photometric study (Hagemann, 1954), no absorption was observed over the range 400–1000 nm. There was a slight amount of absorption between 300 and 400 nm, and a pronounced absorption maximum at 250 nm.

There has been limited work on the fundamental properties of Ac^{3+}(aq). Abramov *et al.* (1998) calculated the hydration Gibbs energy of Ac^{3+} to be -3034.7 kJ mol^{-1}.

2.8.1 Redox behavior

The only stable oxidation state of actinium in aqueous solution is 3+. A transitory Ac(II) ion has been postulated by Bouissières, David, and coworkers (Bouissières *et al.*, 1961; Bouissières and Legoux, 1965; David and Bouissières, 1965, 1968; David, 1970a) to account for the amalgamation behavior of actinium, which resembled that of Eu(II) and Sm(II) more than that of La(III). This hypothesis was reinforced by polarographic evidence: David (1970b,c) reported two waves in the polarogram of ^{228}Ac in $HClO_4$ at pH 1.9–3.1. He attributed the first wave to the reversible reaction:

$$Ac^{2+} + 2e^- + Hg \leftrightarrows Ac(Hg) \qquad (2.8)$$
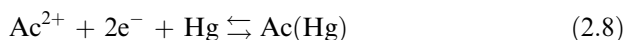
and the second to the irreversible reaction:

$$Ac^{3+} + 3e^- + Hg \rightarrow Ac(Hg) \qquad (2.9)$$
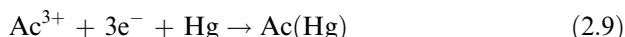
From the half-wave potentials, he estimated the formal potential of the Ac(III)/Ac(II) couple to be -1.6 V and that of the Ac(III)/Ac(0) couple to be -2.62 V. A later estimate was $E^\circ(Ac^{3+}/Ac) = -2.13$ V (David *et al.*, 1978). However, Maly (1969) performed extractions of actinium and other elements from sodium amalgam in sodium acetate solutions as a function of pH and found that actinium extraction behavior was similar to that of the elements thorium to berkelium, i.e. that actinium reduction did not show evidence of the Ac(II) ion.

Yamana *et al.* (1983) attempted to increase the stability of Ac^{2+}(aq) by complexing it with 18-crown-6. They noted a shift of the half-wave potential of about 0.15 V due to a complex, which they attributed to formation of an Ac^{2+}–crown complex and an Ac^{2+}(aq) ion with electronic configuration [Rn]6d^1 and ionic radius 1.25 Å. The [Rn]6d^1 configuration lies only 801 cm^{-1} above the [Rn]7s state in the free ion, so that the change of configuration is plausible.

However, Mikheev *et al.* (1995) noted that Nugent *et al.* (1973a) and Bratsch and Lagowski (1986) had calculated $E°(Ac^{3+}/Ac^{2+})$ to be -4.9 and -3.3 V, respectively; the value $E°(Ac^{3+}/Ac^{2+}) = -4.9$ V is adopted in Chapter 19 of this work. Either of these much more negative $E°$ values would preclude the observation of $Ac^{2+}(aq)$. Mikheev *et al.* (1994) found no evidence for Ac^{2+} in co-crystallization experiments with Gd_2Cl_3 clusters or with Sm^{2+} in aqueous ethanol solution, a medium that should enhance the stability of Ac^{2+}. They recommended that the polarographic reduction of $Ac^{3+}(aq)$ (David, 1970b,c) was actually reduction of water but they recommended further research on the Ac^{3+}/Ac^{2+} couple.

The electrolysis of actinium at a mercury cathode has been used to separate tracer amounts of ^{228}Ac and 1.24 µg of ^{227}Ac from 3.10 mg of ^{231}Pa and an equilibrium amount of ^{227}Th. After 50 min of electrolysis in 0.17 M lithium citrate solution at a current density of 15 mA cm^{-2} the actinium was recovered by washing the amalgam with 0.1 M HCl. The overall yield was 85% and the decontamination factor was greater than 10^8 with respect to protactinium and thorium (David and Bouissières, 1966; Monsecour *et al.*, 1973).

2.8.2   Solubility

At the tracer level, actinium is carried quantitatively by any quantitative lanthanum precipitate, as well as by a wide variety of isomorphous and non-isomorphous carriers. The coprecipitation behavior of actinium was summarized in a useful table by Kahn (1951) and was exhaustively discussed in reviews (Bouissières, 1960; Sedlet, 1964; Kirby, 1967; Gmelin, 1981).

The relative amounts of actinium in partial precipitations of actinium tracer with lanthanum or other carriers are consistent with the relative solubilities of the compounds precipitated, where these are known or predictable. Unfortunately, however, with only two exceptions, quantitative solubility information is generally unavailable, because the dissolutions and precipitations that have been reported were usually incidental to some other objective, e.g. the preparation of compounds for crystallographic analysis (Table 2.2) (Weigel and Hauske, 1977).

Salutsky and Kirby (1956) precipitated tens of milligrams of ^{227}Ac from homogeneous solution with dimethyl oxalate and estimated the solubility of $Ac_2(C_2O_4)_3$ in 0.25 M $H_2C_2O_4$ (pH 1.2) to be 24 mg L^{-1}. That result is consistent with a more detailed study by Ziv and Shestakova (1965a), which shows, as expected, that the solubility of $Ac_2(C_2O_4)_3$ varies with both the acidity and the oxalate concentration (Table 2.3). In a parallel study, the authors found that the solubility of $La_2(C_2O_4)_3$ in 0.01 M HNO_3 (pH 2.2) was 4.28×10^{-5} M, about half that of $Ac_2(C_2O_4)_3$ under the same conditions. This unusual solubility of $Ac_2(C_2O_4)_3$ may be due to radiolysis.

Ziv and Shestakova (1965b) also studied the solubility of $Ac(OH)_3$ in NH_4NO_3 solutions ($\mu = 0.001$ M). They observed a pronounced aging effect

Table 2.3 *Solubility of actinium oxalate in aqueous media at 25°C (Ziv and Shestakova, 1965a).*

| Solvent	pH	Solubility		Activity product
		Ac^{3+} (mg L^{-1})	$Ac_2(C_2O_4)_3$ (M)	
0.01 M HNO_3	1.85	41.0	9.0×10^{-5}	7.5×10^{-27}
0.01 M HNO_3	2.00	40.0	8.8×10^{-5}	6.7×10^{-27}
0.01 M HNO_3	2.00	34.0	7.5×10^{-5}	2.1×10^{-27}
0.01 M HNO_3	2.00	30.0	6.5×10^{-5}	1.5×10^{-27}
H_2O	–	0.86	1.9×10^{-6}	2.7×10^{-27}
H_2O	–	1.5	3.3×10^{-6}	4.2×10^{-26}
H_2O	–	1.7	3.7×10^{-6}	8.0×10^{-26}
5×10^{-5} M $H_2C_2O_4$	3.4	2.5	5.5×10^{-6}	–
5×10^{-4} M $H_2C_2O_4$	3.0	1.2	2.6×10^{-6}	–
5×10^{-3} M $H_2C_2O_4$	2.3	0.96	2.1×10^{-6}	–
5×10^{-1} M $H_2C_2O_4$	0.9	7.85	1.73×10^{-5}	–

on both its solubility and the pH of its saturated solutions. For example, 1 h after precipitation the solubility was 3.6×10^{-8} g L^{-1} (1.59×10^{-8} M) and the pH was 10.4; 15 h later, the solubility had increased to 1.73×10^{-4} g L^{-1} and the pH had decreased to 9.1. After 27 days, the pH was 4.2. The authors attributed this decrease in pH to radiolysis of the solution by adsorbed ^{227}Th. Gamma radiation of aerated water also causes the pH to decrease: radiolysis by γ-rays produces nitric acid from dissolved O_2 and N_2 (Barkatt *et al.*, 1982). Another reason for the decrease of pH is that radiolysis of air by α particles at an air–water interface (Burns *et al.*, 1982) oxidizes nitrogen to acidic nitrogen oxides, which slowly acidifies the adjacent aqueous solution.

When ^{227}Ac was radiochemically purified before precipitation, the pH declined from 10.4 to only 8.3 in 166 days. From the activity product in various concentrations of NH_4NO_3, the solubility of aged $Ac(OH)_3$ was calculated to be 0.74 mg L^{-1}, which is higher than that for $La(OH)_3$. The corresponding equilibrium constants

$$M(OH)_3(s) + 3H^+(aq) \rightarrow M^{3+}(aq) + 3H_2O \quad *K_{s,0} \qquad (2.10)$$
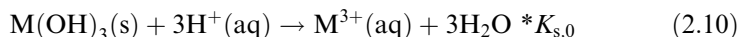
(see Chapter 19, section 9, this book, for further discussion of $*K_{s,0}$) at ionic strength 0.1 are $(1.26 \pm 0.04) \times 10^{24}$ for $Ac(OH)_3$ and 2.0×10^{20} for $La(OH)_3$. The higher solubility of $Ac(OH)_3$ can be attributed to the more basic character of the large Ac^{3+} ion, radiation damage of the crystallites, and/or to the tendency of radiolysis to produce more acidic conditions (Barkatt *et al.*, 1982; Burns *et al.*, 1982). A comparison of some solubility products for rare earth and actinide hydroxides is given in Chapter 19. The above evidence that $Ac(OH)_3$ is the most soluble of all f-element trihydroxides is consistent with Ac^{3+} being the most basic tripositive cation.

More recently, Kulikov *et al.* (1992) used electromigration to determine that
^{225}Ac is unhydrolyzed in aqueous solution of ionic strength 0.1 at 298 K until
pH > 10. They determined the $*K_{s,0}$

$$Ac(OH)_3(s) + 3H^+(aq) \rightarrow Ac^{3+}(aq) + 3H_2O \quad *K_{s,0} \qquad (2.11)$$
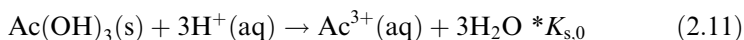
to be 7.9×10^{31}. This value is much higher than that derived by Ziv and
Shestakova or that expected by extrapolating from trivalent rare earths
and actinide hydroxides.

2.8.3 Complexation

As in all its reactions, actinium closely resembles lanthanum in its behavior
toward complexing agents. To the extent that they have been determined
experimentally, the stability constants of actinium complexes (a selection is
given in Table 2.4) are the same as, or slightly smaller than, those of the
corresponding lanthanum complexes (Rao *et al.*, 1968, 1970; Shahani *et al.*,
1968; Sekine *et al.*, 1969; Sekine and Sakairi, 1969; Gmelin, 1981), in agreement
with prediction from the similarity in their electronic configurations and their
ionic radii (Kirby, 1967; Section 15.7.5). There is a linear dependence of log
(formation constant) upon ionic radius, with Ac^{3+} always having the extreme
position of largest ionic radius (Gmelin, 1981 and Section 15.7.5).

The hydrolysis of Ac^{3+}(aq) is the smallest of all 3+ ions. Moutte and
Guillaumont (1969) determined the equilibrium constant for the reaction

$$AcOH^{2+}(aq) + H_2O \rightarrow Ac(OH)_2^+(aq) + H^+(aq) \qquad (2.12)$$
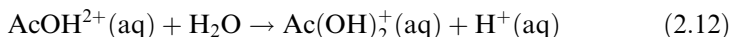
to be 3.5×10^{-9} mol L^{-1}. Using the isotope ^{228}Ac, they determined that, at pH
8, 74% of the actinium in solution exists as $Ac(OH)^{2+}$ and 26% exists as
$Ac(OH)_2^+$.

The Ac^{3+}–citrate complexes are sufficiently strong that citrate complexes
almost all Ac^{3+} in 0.001 M citrate even at pH 8.1 (Moutte and Guillaumont,
1969). In addition to the complexes listed in Table 2.4, Ac^{3+} complexes have
been studied with *trans*-1,2-diaminocyclohexanetetraacetic acid (DCTA), TTA
and other diketones, arsenazo III, and other organic ligands (Gmelin, 1981).

Fukusawa *et al.* (1982) determined stability constants for chloro and bromo
complexes of Ac(III), among many others, by a solvent extraction procedure.
A much larger contribution from inner-sphere complex formation was observed
in chloro than in bromo complexes for tripositive actinide ions. An empirical
approach for predicting the stability of metal-ion complexes has been applied to
actinium (Kumok, 1978).

On the basis of known and estimated ionic radii, Abramov *et al.* (1998)
calculated the extraction constant K_{ex} of Ac^{3+} with bis(2-ethylhexyl)phosphoric
acid (HDEHP) into toluene. The calculated K_{ex} value for Ac^{3+} is nearly an
order of magnitude smaller than that for La^{3+}.

Table 2.4 *Cumulative stability constants of selected actinium complexes.*

Ligand	Ionic strength (μ)	$[H^+]$ (M)	Stability constant[a]	Reference
F^-	0.5	0.00025	$\beta_1 = 529 \pm 8$ $\beta_2 = (1.67 \pm 0.09) \times 10^5$ $\beta_3 = 8 \times 10^7$	Aziz and Lyle (1970)
F^-	0.1	0.016	$\beta_1 = 885$	Makarova *et al.* (1973)
Cl^-	1.0	1.0	$\beta_1 = 0.80 \pm 0.09$ $\beta_2 = 0.24 \pm 0.08$	Shahani *et al.* (1968)
Cl^-	4.0	0.01	$\beta_1 = 0.9$ $\beta_2 = 0.09$ $\beta_3 = 0.05$	Sekine and Sakairi (1969)
Br^-	1.0	1.0	$\beta_1 = 0.56 \pm 0.07$ $\beta_2 = 0.30 \pm 0.06$	Shahani *et al.* (1968)
NO_3^-	1.0	1.0	$\beta_1 = 1.31 \pm 0.12$ $\beta_2 = 1.02 \pm 0.12$	Shahani *et al.* (1968)
SO_4^{2-}	1.0–1.16	1.0	$\beta_1 = 15.9 \pm 1.3$ $\beta_2 = 71.4 \pm 7.3$	Shahani *et al.* (1968)
SO_4^2	1.0	pH 3–3.5	$\beta_1 = 22.9$ $\beta_2 = 479$	Sekine and Sakairi (1969)
SCN^-	1.0	pH 2	$\beta_1 = 1.11 \pm 0.07$ $\beta_2 = 0.82 \pm 0.08$	Rao *et al.* (1968)
SCN^-	5.0	pH 3–3.5	$\beta_1 = 0.18$ $\beta_2 = 0.35$	Sekine and Sakairi (1969)
$C_2O_4^{2-}$	1.0	pH 3–3.5	$\beta_1 = 3.63 \times 10^3$ $\beta_2 = 1.45 \times 10^6$	Sekine and Sakairi (1969)
$H_2PO_4^-$	0.5	pH 2–3	$\beta_1 = 38.8 \pm 5$	Rao *et al.* (1970)
Citrate	0.1	pH 2–3	$\beta_1 = 9.55 \times 10^6$	Makarova *et al.* (1974)
NTA^{-b}	0.1	pH ≈ 5	$\beta_3 = 4.3 \times 10^{14}$	Keller and Schreck (1969)
$EDTA^c$	0.1	pH 2.8	$\beta_1 = 1.66 \times 10^{14}$	Makarova *et al.* (1972)

[a] $\beta_n = [MLn]/[M][L]^n$.

[b] HNTA, 2-naphthoyltrifluoroacetone.

[c] EDTA, ethylenediaminetetraacetic acid.

2.8.4 Radiocolloid formation

Kirby (1969) noted that when acidic aqueous solutions containing tracer amounts of Ac^{3+} and its progeny $^{227}Th^{4+}$ and $^{223}Ra^{2+}$ are dried on platinum disks, the actinium can be separated by redissolution in dilute NH_4NO_3(aq) and the radium by redissolution in dilute HF(aq), leaving the thorium on the disk. He described this separation as an application of 'residue adsorption'; it may represent radiocolloid formation and selective redissolution at the metal surface.

Rao and Gupta (1961) studied the adsorption of ^{228}Ra and ^{228}Ac onto sintered glass and paper, and found that the adsorption of ^{228}Ac onto the glass increased with pH and time of aging. They studied the phenomenon by

centrifugation; the ^{228}Ac fraction could be centrifuged at pH $\geq$ 5. Paper chromatography showed that the ^{228}Ac was immobile at a pH of 3 and higher, whereas Ba remained in solution. They concluded that the ^{228}Ac formed radiocolloids at pH $\geq$ 5.

2.8.5   Analytical chemistry of actinium

Sedlet (1964) published a complete set of procedures for analytical chemistry of actinium, primarily radiochemical procedures for ^{227}Ac. Kirby (1967) published a review that selected published and unpublished procedures that "will be of most value to the modern analytical chemist." Kirby also wrote the section on analytical chemistry in Gmelin (1981). Karalova (1979) reviewed the analytical chemistry of actinium. The analytical procedures that they described were based upon separation of actinium from other radioelements and then determination by measurement of the α, β, or γ radioactivity of a sample that has reached secular equilibrium with its daughters. The techniques suitable for tracer-level determination of ^{227}Ac are neutron activation analysis, by which ^{227}Ac can be determined at the level of 10^{-17} g, and total α, β, and γ radioactivity of a sample that has reached secular equilibrium with its daughters, by which ^{227}Ac can be determined at the level of 10^{-20} g. Recently a procedure for determination of ^{227}Ac in environmental samples by coprecipitation with lead sulfate, ion exchange, and α spectrometry after allowing the daughter isotopes ^{227}Th and ^{223}Ra to reach secular equilibrium (2–3 months) has been published (Martin *et al.*, 1995). The method requires the use of a short-lived actinium yield tracer, ^{225}Ac or ^{228}Ac. The lower limit of detection is ~0.2 mBq per sample (7.5×10^{-16} g) at 95% confidence level.

The isotope ^{225}Ac, which is useful for tumor radiotherapy (see below), can be determined by α-spectrometric measurement of its α-emitting progeny ^{217}At (Martin *et al.*, 1995) or by γ spectrometry of the progeny ^{221}Fr and ^{213}Bi (McDevitt *et al.*, 2001).

2.9   APPLICATIONS OF ACTINIUM

2.9.1   Heat sources for radioisotope thermoelectric generators

The first practical use of actinium was to produce multi-Curie amounts of ^{227}Ac in order to take advantage of the energy released from the five α particles that are generated during its decay (Fig. 2.1) to produce electrical power for spacecraft and other devices that must operate for long periods of time in remote locations. An ambitious radioisotope thermoelectric generator (RTG) program was undertaken in Belgium to produce a 250 W_{th} thermoelectric generator fueled with 18 g of ^{227}Ac (Baetslé and Droissart, 1973). A prototype heat source that contained 2 g of ^{227}Ac was prepared but was not put into use (Baetslé and

Droissart, 1973). Kirby (Gmelin, 1981) listed the radioisotopes that can be used as thermoelectric heat sources. Of these, ^{238}Pu has been the most suitable; it has been used in almost all U.S. spacecrafts that utilized RTGs, beginning with 2.7-W SNAP–3B (Space Nuclear Auxiliary Power) generators for Transit 4A and 4B satellites in 1961 (Lange and Mastal, 1994; U.S. Department of Energy, 1987) and continuing to the three 276-W general purpose heat source (GPHS) RTGs in the Cassini probe, which was launched in 1997 and reached Saturn in 2004. (See also relevant sections in Chapter 7 and Chapter 15, section 11.2, this book.)

2.9.2 Neutron sources

Isotopes of elements with $Z \leq 20$ emit neutrons when they are bombarded by $\sim$5 MeV α particles. Kirby (Gmelin, 1981) listed the properties of important (α,n) generators. The advantages of ^{227}Ac as a heat source are also those that make it attractive as an (α,n) generator. A few ^{227}Ac (α,n) generators have been constructed and used (Gmelin, 1981).

2.9.3 Alpha-particle generators for tumor radiotherapy

The 10-day α emitter ^{225}Ac has desirable properties for destroying rapidly growing cancer cells. After decay of ^{225}Ac to ^{221}Fr, four additional high-energy α decays and two β^- decays occur rapidly (Fig. 2.3), delivering $\sim$40 MeV of high linear-energy-transfer radiation over a range of less than 100 μm. None of the decay events emits hard γ-rays, so that ^{225}Ac can deliver large doses to a tumor cell and negligible doses to surrounding healthy tissue (Tsoupko-Sitnikov *et al.*, 1996; Khalkin *et al.*, 1997; Boll *et al.*, 2005). To utilize this isotope for therapy, the principal challenges are to generate the isotope free of other radioisotopes, to deliver it to the cancer cell for a long enough period of time, to bind it firmly to the target call, and to retain the daughter radioisotopes (especially the ^{221}Fr$^+$ ion) at the target site. The *in vivo* stability of several macrocyclic complexes of ^{225}Ac have been evaluated. Deal *et al.* (1999) found the most promising complex to be that with 1,4,7,10,13,16-hexaazacyclohexadecane-N,N',N'',N''',N''''-hexa-acetic acid (HEHA); Ouadi *et al.* (2000) bifunctionalized an isothiocyanate derivative of HEHA for good covalent bonding to biomolecules. A procedure for delivering ^{225}Ac to tumors via bifunctional chelators related to the ligand 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (DOTA) has been described (McDevitt *et al.*, 2001). Kennel *et al.* (2000, 2002) evaluated radio-immunotherapy of mice with lung and other tumors using ^{225}Ac–HEHA conjugates with monoclonal antibodies; their studies concluded that the radio-toxicity of ^{225}Ac can only be controlled if conjugates that bind strongly with the daughters as well as with Ac$^+$ can be discovered.

As described in the earlier paragraph and in Section 2.2.3, ^{229}Th (α, $t_{1/2} = 7340$ years) is an appropriate generator from which ^{225}Ac can be removed periodically. At the time of writing, Oak Ridge National Laboratory is producing

50–60 mCi of ^{225}Ac from ^{229}Th every 8 weeks. Additional shipments of 5–20 mCi of ^{225}Ac are produced by ORNL every 2 weeks from the decay of the ^{225}Ra parent. The ^{225}Ac is shipped to hospitals and other research facilities (Boll *et al.*, 2005).

The isotope ^{225}Ac can also serve as a ^{213}Bi generator, which decays with a 45.6-min half-life (97.8% β, 2.2% α). The decay is accompanied by a 440-keV γ-ray, so that ^{213}Bi can be delivered to tumors with a bifunctional chelating agent for radioimmunotherapy as well as for imaging (Pippin *et al.*, 1995; Nikula *et al.*, 1999). Generators have been delivered to hospitals, where radio-isotopically pure, chemically active ^{213}Bi can be eluted for radiotherapy, with minimum shielding every 5–6 h for at least 10 days. At the time of writing, the Institute for Transuranium Elements (Joint Research Centre of the European Commission, located at Karlsruhe, Germany) is producing and distributing ^{225}Ac/^{213}Bi generators.

2.9.4   Actinium-227 as a geochemical tracer

Nozaki (1984) demonstrated that the concentration of ^{227}Ac is higher than that of its progenitor ^{231}Pa in deep seawater; he proposed the use of natural ^{227}Ac as a tracer for circulation and mixing of seawater in deep ocean basins. Geibert *et al.* (2002) confirmed this phenomenon in several other oceanic locations and proposed that ^{227}Ac be used as a tracer for deep seawater circulation (diapycnal mixing, i.e. mixing across lines of equal density).

REFERENCES

Abramov, A. A., Eliseeva, O. V., and Iofa, B. Z. (1998) *Radiochemistry,* **40**, 302–5; *Radiokhimiya*, **40**, 292–5.
Adloff, J. P. (2000) *Radiochim. Acta,* **88**, 123–7.
Ahmad, I. (2002) Unpublished; personal communication to L. Morss.
Allison, M., Moore, R. W., Richardson, A. E., Peterson, D. T., and Voight, A. F. (1954) *Nucleonics,* **12**(5), 32–4.
Andrews, H. C. and Hagemann, F. (1948) in *Summary Report for April, May, and June 1948. Chemistry Division, Section C-I, ANL–4176* (eds. W. M. Manning and D. W. Osborne), pp. 13–6.
Arblaster, J. W. (1995) *Calphad,* **19**, 373.
Arnoux, M. and Giaon, A. (1969) *C. R. Acad. Sci. Paris,* **269B**, 317–20.
Aziz, A. and Lyle, S. J. (1970) *J. Inorg. Nucl. Chem.,* **32**, 1925–32.
Backe, H., Dretzke, A., Eberhardt, K., Fritsche, S., Grüning, C., Gwinner, G., Haire, R. G., Huber, G., Kratz, J. V., Kube, G., Kunz, P., Lassen, J., Lauth, W., Passler, G., Repnow, R., Schwalm, D., Schwamb, P., Sewtz, M., Thörle, P., Trautmann, N., and Waldek, A. (2002) *J. Nucl. Sci. Technol.*, (Suppl. 3), 86–9.
Baetslé, L. H., Dejonghe, P., Demildt, A. C., De Troyer, A., Droissart, A., and Dumont, G. (1967) *Ind. Chim. Belge,* **32** (2), 56–60.

Baetslé, L. H., Brabers, M. J., Dejonghe, P., Demildt, A. C., De Troyer, A., Droissart, A., and Poskin, M. (1972) *Proc. 4th UN Int. Conf. on Peaceful Uses of Atomic Energy*. A/CONF.49/P/287, United Nations, New York, pp. 191–203.

Baetslé, L. H. (1973) in *CEN-SCK Annual Scientific Report, 1972, Belgian Report BLG–481* (eds. R. Billiau, K. Bobin, W. Drent, and L. Hespeels), ch. 6.

Baetslé, L. H. and Droissart, A. (1973) Production and Applications of [227]Ac. Belgian Report BLG 483.

Bagnall, K. W. (1957) in *Chemistry of the Rare Radioelements: Polonium–Actinium*, Butterworths, London, pp. 15–45.

Barkatt, A., Barkatt, A., and Sousanpour, W. (1982) *Nucl. Technol.,* **60**, 218–27.

Bastin-Scoffier, G. (1967) *C. R. Acad. Sci. Paris,* **265B**, 863–5.

Baybarz, R. D., Bohet, J., Buijs, K., Colson, L., Müller, W., Reul, J., Spirlet, J. C., and Toussaint, J. C. (1976) *Transplutonium Elements. Proc. 4th Int. Transplutonium Elements Symp., 1975* (eds. W. Müller and R. Lindner), North Holland, Amsterdam, pp. 61–8.

Beckmann, W. (1955) *Z. Phys.,* **142**, 585–601.

Bhatki, K. S. and Adloff, J. P. (1964) *Radiochim. Acta,* **3**, 123–6.

Bjornholm, S., Nielsen, B., and Sheline, R. K. (1956) *Nature,* **178**, 1110–1.

Bjornholm, S., Nathan, O., Nielsen, O. B., and Sheline, R. K. (1957) *Nucl. Phys.,* **4**, 313–24.

Boll, R. A., Malkemus, D., and Mirzadeh, S. (2004) *Appl. Radiat. Isot.*, **62**, 667–9.

Bouissières, G. (1960) in *Nouveau Traité de Chimie Minérale* (ed. P. Pascal), Masson, Paris 7, pp. 1413–46.

Bouissières, G., Haïssinsky, M., and Legoux, Y. (1961) *Bull. Soc. Chim. Fr.*, 1028–30.

Bouissières, G. and Legoux, Y. (1965) *Bull. Soc. Chim. Fr.*, 386–8.

Bratsch, S. G. and Lagowski, J. J. (1986) *J. Phys. Chem.,* **90**, 307–12.

Brewer, L. (1971a) *J. Opt. Soc. Am.,* **61**, 1101–11.

Brewer, L. (1971b) *J. Opt. Soc. Am.,* **61**, 1666–82.

Browne, E. (2001) *Nucl. Data Sheets,* **93**, 763.

Bryukher, E. (1963) *Sov. Radiochem.,* **5**, 123–5; *Radiokhimiya*, **5**, 142–3.

Burns, W. G., Hughes, A. E., Marples, J. A. C., Nelson, R. S., and Stoneham, A. M. (1982) *J. Nucl. Mater.,* **107**, 245–70.

Butterfield, D. and Woollatt, R. (1968) *J. Inorg. Nucl. Chem.,* **30**, 801–5.

Cabell, M. J. (1959) *Can. J. Chem.,* **37**, 1094–1103.

Carlson, T. A., Nestor, C. W. J., Wasserman, N., and McDowell, J. F. (1970) Comprehensive Calculation of Ionization Potentials and Binding Energies for Multiply-Charged Ions, US Report ORNL-4562.

Chayawattanangkur, K., Herrmann, G., and Trautmann, N. (1973) *J. Inorg. Nucl. Chem.,* **35**, 3061–73.

Clarke, R. W. (1954) Actinium. A Bibliography of Unclassified and Declassified Atomic Energy Project Reports and References to the Published Literature (1906–1953), UK Report AERE Inf/Bib 95.

Clarke, R. W. (1958) Abstracts of Atomic Energy Project Unclassified Reports and Published Literature on the Actinide Elements (Papers dated 1957 noted up to February, 1958), Part I. Actinium, Protactinium, Neptunium, UK Report AERE C/R 2472.

Dalmasso, J., Herment, M., and Ythier, C. (1974) *C. R. Acad. Sci. Paris,* **278B**, 97–100.

Danon, J. (1956) *J. Am. Chem. Soc.,* **78**, 5953–4.

Danon, J. (1958) *J. Inorg. Nucl. Chem.,* **5**, 237–9.

David, F. (1970a) *Rev. Chim. Minér.,* **7**, 1–11.

David, F. (1970b) *C. R. Acad. Sci. Paris,* **271**, 440–2.

David, F. (1970c) *Radiochem. Radioanal. Lett.,* **5**, 279–85.

David, F. and Bouissières, G. (1965) *Bull. Soc. Chim. Fr.*, 1001–7.

David, F. and Bouissières, G. (1966) in *Physico-Chimie du Protactinium,* Colloques internationaux du CNRS, Paris, No. 154, pp. 301–6.

David, F. and Bouissières, G. (1968) *Inorg. Nucl. Chem. Lett.,* **4**, 153–9.

David, F., Samhoun, K., Guillaumont, R., and Edelstein, N. (1978) *J. Inorg. Nucl. Chem.,* **40**, 69–74.

Deal, K. A., Davis, I. A., Mirzadeh, S., Kennel, S. J., and Brechbiel, M. W. (1999) *J. Med. Chem.,* **42**, 2988–92.

Debierne, A. (1899) *C. R. Acad. Sci. Paris,* **129**, 593–5.

Debierne, A. (1900) *C. R. Acad. Sci. Paris,* **130**, 906–8.

Debierne, A. (1904) *C. R. Acad. Sci. Paris,* **139**, 538–40.

Dempster, A. J. (1935) *Nature,* **136**, 180.

De Troyer, A. and Dejonghe, P. (1966) in *Large Scale Production and Applications of Radioisotopes,* US Report DP–1066, edn 1, session III, pp. 63–9.

Deworm, J. P., Fieuw, G., and Marlein, J. (1979) *Ann. Belg. Ver. Stralingsbescherming,* **4**, 107–28; *Chem. Abstr.*, 93, 83093b.

Duyckaerts, G. and Lejeune, R. (1960) *J. Chromatogr.,* **3**, 58–62.

Dzhelepov, B. S., Ivanov, R. B., Mikhailova, M. A., Moskvin, L. N., Nazarenko, O. M., and Rodionov, V. F. (1967) *Bull. Acad. Sci. USSR, Phys. Ser.,* **31**, 563–74; *Dokl. Akad. Nauk USSR, Fiz. Ser.*, **31**, 568–80.

Eichelberger, J. F., Grove, G. R., and Jones, L. V. (1964) Mound Laboratory Progress Report for April, 1964. US Report MLM-1196, pp. 9–11.

Eichelberger, J. F., Grove, G. R., and Jones, L. V. (1965) Mound Laboratory Progress Report for November, 1964. US Report MLM-1227.

Eliav, E., Shmulyian, S., and Kaldor, U. (1998) *J. Chem. Phys.,* **109**, 3954–8.

Engle, P. M. (1950) Preliminary Report on the Actinium Separation Project. US Report MLM-454.

Farr, J. D., Giorgi, A. L., Money, R. K., and Bowman, M. G. (1953) The Crystal Structure of Actinium Metal and Actinium Hydride. US Report LA-1545, Los Alamos National Laboratory.

Farr, J. D., Giorgi, A. L., Bowman, M. G., and Money, R. K. (1961) *J. Inorg. Nucl. Chem.,* **18**, 42–7.

Firestone, R. B. and Shirley, V. S. (eds.) (1996) *Table of Isotopes,* Wiley, New York.

Foster, K. W. (1966) Radioisotopes for Heat Sources. II. Calculations for preparation of Ac-227 by Neutron Irradiation of Ra-226. US Report MLM-1297.

Foster, K. W. and Fauble, L. G. (1960) *J. Phys. Chem.,* **64**, 958–9.

Fournier, J. M. (1976) *J. Phys. Chem. Solids,* **37**, 235–44.

Fred, M., Tomkins, F. S., and Meggers, W. F. (1955) *Phys. Rev.,* **98**, 1514.

Fried, S., Hagemann, F., and Zachariasen, W. H. (1950) *J. Am. Chem. Soc.,* **72**, 771–5.

Fukusawa, T., Kawasuji, I., Mitsugashira, T., Sato, A., and Suzuki, S. (1982) *Bull. Chem. Soc. Jpn.,* **55**, 726–9.

Geerlings, M. W., Kaspersen, F. M., Apostolidis, C., and Van Der Hout, R. (1993) *Nucl. Med. Commun.,* **14**, 121–5.

Geibert, W., Rutgers van der Loeff, M. M., Hanfland, C., and Dauelsberg, H.-J. (2002) *Earth Planet. Sci. Lett.,* **198**, 147–65.

Giesel, F. (1902) *Ber. Dtsch. Chem. Ges.,* **35**, 3608–11.

Giesel, F. (1903) *Ber. Dtsch. Chem. Ges.,* **36**, 342–7.

Giesel, F. (1904a) *Ber. Dtsch. Chem. Ges.,* **37**, 1696–9.

Giesel, F. (1904b) *Ber. Dtsch. Chem. Ges.,* **37**, 3963–6.

Giesel, F. (1905) *Ber. Dtsch. Chem. Ges.,* **38**, 775–8.

Gmelin (1942) *Handbuch der Anorganischen Chemie, 8. Auflage, System-Nummer 40, Actinium und Isotope (MsTh2),* Verlag Chemie, Berlin, (English translation by G. A. Young (1954)). U.S. Report AEC-tr-l734.

Gmelin (1981) *Handbook of Inorganic Chemistry, Actinium*, 8th edn, System Number 40 Suppl. vol. 1, Springer-Verlag, Berlin.

Godlewski, T. (1904–5) *Nature,* **71**, 294–5.

Godlewski, T. (1905) *Phil. Mag.,* **10**, 35–45.

Gomm, P. J. and Eakins, I. D. (1966) The Determination of Actinium-227 in Urine. UK Report AERE-R 4972.

Gomm, P. J. and Eakins, J. D. (1968) *Analyst,* **93**, 228–34.

Hagemann, F. (1950) *J. Am. Chem. Soc.,* **72**, 768–71.

Hagemann, F. T. (1954) The Chemistry of Actinium, in *The Actinide Elements, Nat. Nucl. En. Ser. Div. IV, 14A* (eds. G. T. Seaborg and J. J. Katz), McGraw-Hill, New York, pp. 14–44.

Hahn, O. (1905) *Jahrb. Radioaktivitat Elektronik,* **2**, 233–66.

Hahn, O. (1906a) *Ber. Dtsch. Chem. Ges.,* **39**, 1605–7.

Hahn, O. (1906b) *Phys. Z.,* **7**, 855–64.

Hahn, O. (1907) *Ber. Dtsch. Chem. Ges.,* **40**, 1462–9.

Hahn, O. (1908) *Phys. Z.,* **9**, 146–8.

Hahn, O. and Meitner, L. (1918) *Phys. Z.,* **19**, 208–18.

Hahn, O. and Erbacher, O. (1926) *Phys. Z.,* **27**, 531–3.

Heath, R. L. (1974) Gamma-ray Spectrum Catalogue. Ge(Li) and Si(Li) Spectrometry. US Report ANCR-1000-2, 3rd edn, vol. 2.

Heydemann, A. (1969) in *Handbook of Geochemistry* (ed. K. H. Wedepohl), Springer-Verlag, New York, vol. 1, pp. 276–412.

Hill, H. H. (1972) *Chem. Phys. Lett.,* **16**, 114–8.

Holden, N. E. (1977) *Isotopic Composition of the Elements and Their Variation in Nature – A Preliminary Report, BNL-NCS–50605*; (1979) *Pure Appl. Chem.,* **52**, 2371.

Horen, D. J. (1973) *Nucl. Data Sheets,* **10**, 387–90.

Huys, D. and Baetslé, L. H. (1967) Separation of ^{226}Ra, ^{227}Ac and ^{228}Th by Ion Exchange. Belgian Report BLG 422.

Hyde, E. K., Perlman, I., and Seaborg, G. T. (1964) *The Nuclear Properties of the Heavy Elements*, vol. 2, Prentice-Hall, Englewood Cliffs, NJ, pp. 584–6.

Ihde, A. J. (1964) *The Development of Modern Chemistry,* Harper & Row, New York, p. 492.

Jordan, K. C. and Blanke, B. C. (1967) in *Standardization of Radionuclides, IAEA Proc. Series STI/PUB/139.* IAEA, Vienna, pp. 567–78.

Kahn, M. (1951) in *Radioactivity Applied to Chemistry* (eds. A. C. Wahl and N. A. Bonner) Wiley, New York, pp. 403–33.

Karalova, Z. K., Rodionova, L. M., Pyzhova, Z. I., and Myasoedov, B. F. (1977a) *Soviet Radiochem.,* **19**, 31–3; *Radiokhimiya*, **19**, 38–41.

Karalova, Z. K., Rodionova, L. M., Pyzhova, Z. I., and Myasoedov, B. F. (1977b) *Sov. Radiochem.,* **19**, 34–7; *Radiokhimiya,* **19**, 42–5.

Karalova, Z. K., Nekrasova, V. V., Pyzhova, Z. I., Rodionova, L. M., and Myasoedov, B. F. (1978a) *Radiokhimiya,* **20**, 845–50.

Karalova, Z. K., Rodionova, L. M., Pyzhova, Z. I., and Myasoedov, B. F. (1978b) *Sov. Radiochem.,* **20**, 30–3; *Radiokhimiya,* **20**, 42–6.

Karalova, Z. K. (1979) *Sov. Radiochem.,* **20**, 712–20; *Radiokhimiya,* **20**, 834–44.

Karalova, Z. K., Rodionova, L. M., Pyzhova, Z. I., and Myasoedov, B. F. (1979a) *Sov. Radiochem.,* **21**, 7–10; *Radiokhimiya*, **21**, 11–4.

Karalova, Z. K., Rodionova, L. M., Pyzhova, Z. I., and Myasoedov, B. F. (1979b) *Sov. Radiochem.,* **21**, 335–9; *Radiokhimiya*, **21**, 394–9.

Katz, J. J. and Seaborg, G. T. (1957) in *The Chemistry of the Actinide Elements*, Methuen, London, pp. 5–15.

Keller, C. and Mosdzelewski, K. (1967) *Radiochim. Acta,* **7**, 185–8.

Keller, C. and Schreck, H. (1969) *J. Inorg. Nucl. Chem.,* **31**, 1121–32.

Keller, C. (1977) *Chem.-Z.,* **101**, 500–7.

Kennel, S. J., Chappell, L. L., Dadachova, K., Brechbiel, M. W., Lankford, T. K., Davis, I. A., Stabin, M., and Mirzadeh, S. (2000) *Cancer Biotherapy Radiopharm.,* **15**, 235–44.

Kennel, S. J., Brechbiel, M. W., Milenic, D. E., Schlom, J., and Mirzadeh, S. (2002) *Cancer Biotherapy Radiopharm.,* **17**, 219–31.

Khalkin, V. A., Tsupko- Sitnikov, V. V., and Zaitseva, N. G. (1997) *Radiochemistry,* **39**, 481–90; *Radiokhimiya,* **39**, 483–92.

Kirby, H. W. (1951) Mound Laboratory Report for General Research. December 11, 1950 to April 2, 1951 (Actinium volume). US Report MLM-558, pp. 13–4.

Kirby, H. W. (1952) Tentative Procedure for the Analysis of Mixtures Containing Radium-226, Actinium-227 and Thorium-228. US Report MLM-773.

Kirby, H. W., Grove, G. R., and Timma, D. L. (1956) *Phys. Rev.,* **102**, 1140–1.

Kirby, H. W. (1967) *Prog. Nucl. Energy, Ser. IX,* **8(1)**, 89–139.

Kirby, H. W. (1969) *J. Inorg. Nucl. Chem.,* **31**, 3375–85.

Kirby, H. W. (1970) *J. Inorg. Nucl. Chem.,* **32**, 2823–37.

Kirby, H. W. (1971) *Isis,* **62**, 290–308.

Kirby, H. W. (1974) Geochemistry of the Naturally Occurring Radioactive Series. US Report MLM-2111.

Korotkin, Y. S. (1981) *Sov. Radiochem.,* **23**, 145–9; *Radiokhimiya,* **23**, 181–5.

Kosynkin, V. D., Moiseev, S. D., and Vdovichev, V. S. (1995) *J. Alloys Compds.,* **225**, 320–3.

Kraus, K. A. (1979) *J. Chromatogr.,* **178**, 163–8.

Küchle, W., Dolg, M., and Stoll, H. (1997) *J. Phys. Chem. A,* **101**, 7128–33.

Kulikov, E. V., Novgorodov, A. F., and Schumann, D. (1992) *J. Radioanal. Nucl. Chem., Lett.,* **164**, 103–8.

Kumok, V. N. (1978) *Sov. Radiochem.,* **20**, 590–4; *Radiokhimiya*, **20**, 691–4.

Laerdahl, J. K., Faegri, J., Visscher, L., and Saue, T. (1998) *J. Chem. Phys.,* **109**, 10806–17.

Lange, R. G. and Mastal, E. F. (1994) A tutorial review of radioisotope power systems in *A Critical Review of Space Nuclear Power and Propulsion, 1984–1993* (ed. M. S. El‑Genk), American Institute of Physics, New York, pp. 1–20.

Lecoin, M., Perey, M., Riou, M., and Teillac, J. (1950) *J. Phys. Radium.,* **11**, 227–34.

Maly, J. (1969) *J. Inorg. Nucl. Chem.,* **31**, 1007–17.

Makarova, T. P., Sinitsyna, G. S., Stepanov, A. V., Shestakova, I. A., and Shestakov, B. I. (1972) *Sov. Radiochem.,* **14**, 555–8; *Radiokhimiya,* **14**, 538–41.

Makarova, T. P., Stepanov, A. V., and Shestakov, B. I. (1973) *Russ. J. Inorg. Chem.,* **18**, 783–785; *Zh. Neorg. Khim.,* **18**, 1845–9.

Makarova, T. P., Sinitsyna, G. S., Stepanov, A. V., Gritschenko, I. A., Shestakova, I. A., and Shestakov, B. I. (1974) *Chem. Abs.,* **82**, 176644.

Maples, C. (1973) *Nucl. Data Sheets,* **10**, 643–71.

Marckwald, W. (1909) *Am. Chem. J.,* **41**, 515–57.

Martin, P., Hancock, G. J., Paulka, S., and Akber, R. A. (1995) *Appl. Radiat. Isot.,* **46**, 1065–70.

Matthias, B. T., Zachariasen, W. H., Webb, G. W., and Engelhardt, J. J. (1967) *Phys. Rev. Lett.,* **18**, 781–4.

McDevitt, M. R., Ma, D., Lai, L. T., Simon, J., Borchardt, P., Frank, R. K., Wu, K., Pellegrini, V., Curcio, M. J., Miederer, M., Bander, N. H., and Scheinberg, D. A. (2001) *Science,* **294**, 1537–40.

Meggers, W. F., Fred, M., and Tomkins, F. S. (1951) *J. Opt. Soc. Am.,* **41**, 867–8.

Meggers, W. F. (1957) *Spectrochim. Acta,* **10**, 195–200.

Meggers, W. F., Fred, M., and Tomkins, F. S. (1957) *J. Res. NBS,* **58**, 297–315.

Mikhailichenko, A. I., Goryacheva, E. G., Aksenova, N. M., and Denisov, A. F. (1982) *Sov. Radiochem.,* **24**, 173–5; *Radiokhimiya,* **24**, 207–9.

Mikheev, N. B., Kamenskaya, A. N., Rumer, I. A., Kulyukhin, S. A., and Novichenko, V. L. (1994) *Radiokhimiya,* **36**, 160–2; *Radiochemistry,* **36**, 173–5.

Mikheev, N. B., Veleshko, I. E., Kamenskaya, A. N., and Rumer, I. A. (1995) *Radiokhimiya,* **37**, 322–5; *Radiochemistry,* **37**, 297–9.

Mitsugashira, T., Yamana, H., and Suzuki, S. (1977) *Bull. Chem. Soc. Jpn,* **50**, 2913–6.

Moeller, T. and Kremers, H. E. (1945) *Chem. Rev.,* **37**, 97–159.

Moeller, T. (1963) *The Chemistry of the Lanthanides*, Reinhold, New York.

Monsecour, M., De Regge, P., and Demildt, A. (1973) *Radiochem. Radioanal. Lett.,* **14**, 365–71.

Monsecour, M., De Regge, P., Demildt, A., and Baetslé, L. H. (1974) *J. Inorg. Nucl. Chem.,* **36**, 719–23.

Monsecour, M. and De Regge, P. (1975) *J. Inorg. Nucl. Chem.,* **37**, 1841–3.

Mosdzelewski, K. (1966) Die Extraktion der Elemente Radium, Actinium, Protactinium, Americium, und Curium mit 8‑Hydroxychinolin, Thesis. German Report KFK–432.

Moutte, A. and Guillaumont, R. (1969) *Rev. Chim. Minér.,* **6**, 603–10.

Nelson, F. (1964) *J. Chromatogr.,* **16**, 538–40.

Nikula, T. K., McDevitt, M. R., Finn, R. D., Wu, C., Kozak, R. W., Garmestani, K., Brechbiel, M. W., Curcio, M. J., Pippin, C. G., Tiffany‑Jones, L., Geerlings, M. W., Sr., Apostolidis, C., Molinet, R., Geerlings, M. W. Jr., Gansow, O. A., and Scheinberg, D. A. (1999) *J. Nucl. Med.,* **40**, 166–76.

Novikova, G. I., Volkova, E. A., Gol'din, L. L., Ziv, D. M., and Tret'yakov, E. F. (1960) *Sov. Phys. JETP,* **37**, 663–9; *Zh. Eks. Teor. Fiz.,* **37**, 928–37.

Nozaki, Y. (1984) *Nature,* **310**, 486–8.

Nugent, L. J., Baybarz, R. D., Burnett, J. L., and Ryan, J. L. (1973a) *J. Phys. Chem.,* **77**, 1528–39.

Nugent, L. J., Burnett, J. L., and Morss, L. R. (1973b) *J. Chem. Thermodyn.,* **5**, 665–78.

Nugent, L. J., and Vander Sluis, K. L. (1971) *J. Opt. Soc. Am.,* **61**, 1112–5.

Ouadi, A., Loussouarn, A., Remaud, P., Morandeau, L., Apostolidis, C., Musikas, C., Fauve-Chauvet, A., and Gestin, J.-F. (2000) *Tetrahedron Lett.,* **41**, 7207–9.

Partington, J. R. (1964) *A History of Chemistry*, Macmillan, London, vol. 4, p. 938.

Peppard, D. F., Mason, G. W., Gray, P. R., and Mech, J. F. (1952) *J. Am. Chem. Soc.,* **74**, 6081–4.

Perey, M. (1939a) *C. R. Acad. Sci. Paris,* **208**, 97–9.

Perey, M. (1939b) *J. Phys. Radium,* **10**, 435–8.

Peterson, S. (1949) *Natl. Nucl. En. Ser., Div. IV*, in *The Transuranium Elements* (eds. G. Seaborg, J. J. Katz, and W. M. Manning), McGraw-Hill, New York, vol. 14B, pp. 1393–4.

Pippin, C. G., Gansow, O. A., Brechbiel, M. W., Koch, L., Molinet, R., van Geel, J., Apostolidis, C., Geerlings, M. W., and Scheinberg, D. A. (1995) in *Chemist's Views of Imaging Centers* (ed. A. M. Emran), Plenum Press, New York, pp. 315–25.

Poskanzer, A. M. and Foreman, B. M. J. (1961) *J. Inorg. Nucl. Chem.,* **16**, 323–36.

Rao, C. L. and Gupta, A. R. (1961) *J. Chromatogr.,* **5**, 147–52.

Rao, C. L., Shahani, C. I., and Mathew, K. A. (1968) *Inorg. Nucl. Chem. Lett.,* **4**, 655–9.

Rao, V. K., Shahani, C. J., and Rao, C. L. (1970) *Radiochim. Acta,* **14**, 31–4.

Rutherford, E. (1904) *Phil. Trans. R. Soc. Lond.,* **204A**, 169–219.

Rutherford, E. (1911) in *Encyclopaedia Britannica*, 11th edn, vol. 22, pp. 795–802.

Salutsky, M. L. (1962) in *Comprehensive Analytical Chemistry* (eds. C. L. Wilson and D. W. Wilson), Elsevier, Amsterdam, 1C, pp. 492–6.

Salutsky, M. L. and Kirby, H. W. (1956) *Anal. Chem.,* **28**, 1780–2.

Sani, A. R. (1970) *J. Radioanal. Chem.,* **4**, 127–9.

Seaborg, G. T. (1994) Origin of the Actinide Concept, in *Handbook on the Chemistry and Physics of the Rare Earths* (eds. K. A. Gschneidner, L. Eyring, G. R. Choppin, and G. Lander), North-Holland, Amsterdam, 18, 1–27.

Sedlet, J. (1964) Actinium, Astatine, Francium, Polonium, and Protactinium, in *Treatise on Analytical Chemistry*, Part II, vol. 6 (eds. I. M. Kolthoff, P. J. Elving, and E. B. Sandell), Wiley, New York, pp. 435–610.

Sekine, T., Koike, Y., and Sakairi, M. (1967) *J. Nucl. Sci. Technol.,* **4**, 308–11.

Sekine, T., Koike, Y., and Hasegawa, Y. (1969) *Bull. Chem. Soc. Japan,* **42**, 432–6.

Sekine, T. and Sakairi, M. (1969) *Bull. Chem. Soc. Jpn.,* **42**, 2712–3.

Shahani, C. J., Mathew, K. A., Rao, C. L., and Ramaniah, M. V. (1968) *Radiochim. Acta,* **10**, 165–7.

Shannon, R. D. (1976) *Acta Crystallogr.,* **A32**, 751–67.

Sinitsyna, G. S., Shestakova, I. A., Shestakov, B. I., Plyushcheva, N. A., and Malyshev, N. A., Belyatskii, A. F. (1977) *Tezisy Dokl.-Konf. Anal. Khim. Radioakt.*, Nauka, Moscow.

Sinitsyna, G. S., Shestakova, I. A., Shestakov, B. I., Plyushcheva, N. A., Malyshev, N. A., Belyatskii, A. F., and Tsirlin, V. A. (1979) *Sov. Radiochem.,* **21**, 146–51; *Radiokhimiya,* **21**, 172–7.

Skarnemark, G. and Skalberg, M. (1985) *Int. J. Appl. Radiat. Isot.,* **36**, 439–41.

Soddy, F. and Cranston, J. A. (1918a) *Nature,* **100**, 498–9.

Soddy, F. and Cranston, J. A. (1918b) *Proc. R. Soc. Lond.,* **94A**, 384–404.

Stein, L. and Hohorst, F. A. (1982) *Envir. Sci. Technol.,* **16**, 419–22.

Stevenson, P. C. and Nervik, W. E. (1961) The Radiochemistry of the Rare Earths, Scandium, Yttrium and Actinium. US Report NAS-NS 3020. All the volumes of the series "The Radiochemistry of..." can be found on the site http://lib-www.lanl.gov/radiochemistry/elements.htm

Stites, J. G. Jr., Salutsky, M. L., and Stone, B. D. (1955) *J. Am. Chem. Soc.,* **77**, 237–40.

St. John, D. S. and Toops, E. C. (1958) Formation of U-232 During the Irradiation of Thorium. US Report DP-279.

Sugar, J. (1973) *J. Chem. Phys.,* **59**, 788–91.

Sugar, J. (1984) Personal communication to L. R. Morss.

Szeglowski, Z. and Kubica, B. (1990) *J. Radioanal. Nucl. Chem.,* **143**, 389–95.

Szeglowski, Z. and Kubica, B. (1991) *J. Radioanal. Nucl. Chem. Lett.,* **153**, 67–74.

Taylor, S. R. (1964) *Geochim. Cosmochim. Acta,* **28**, 1273–85.

Tomkins, F. S., Fred, M., and Meggers, W. F. (1951) *Phys. Rev.,* **84**, 168.

Tousset, J. (1961) Les Spectres Béta de Faible Energie de Que1ques Eléments Lourds, Thesis, Univ. Lyon (F.) French Report NP-13367.

Tsoupko-Sitnikov, V., Norseev, Y., and Khalkin, C. (1996) *J. Radioanal. Nucl. Chem.,* **205**, 75–83.

U.S. Department of Energy (1987) Atomic Power in Space: a History (excerpted in *Nuclear News,* May 2003, pp. 37–44).

U.S. Nuclear Regulatory Commission (2005) U.S. Code of Federal Regulations, 10 CFR 20.

Valli, K. (1964) *Ann. Acad. Sci. Fenn.*, *Ser. A*, VI, no. 165.

Vander Sluis, K. L. and Nugent, L. J. (1972) *Phys. Rev. A,* **6**, 86–94.

Vander Sluis, K. L. and Nugent, L. J. (1974) *J. Opt. Soc. Am.,* **64**, 687–95.

Wagman, D. D., Evans, W. E., Parker, V. B., Schumm, R. H., Halow, I., Bailey, S. M., Churney, K. L., and Nuttall, R. L. (1982) *J. Phys. Chem. Ref. Data*, **11**, Suppl. No. 2.

Ward, J. W., Kleinschmidt, P. D., and Peterson, D. E. (1986) in *Handbook on the Physics and Chemistry of the Actinides*, vol. 4 (eds. A. J. Freeman and C. Keller), ch. 7.

Weeks, M. E. and Leicester, H. M. (1968) *Discovery of the Elements*, Journal of Chemical Education, Easton, PA, p. 794.

Weigel, F. and Hauske, H. (1977) *J. Less-Common Met.,* **55**, 243–7.

Włodzimirska, B., Bartoś, B., and Bilewicz, A. (2003) *Radiochim. Acta,* **91**, 553–6.

Xu, J., He, P., and Zhu, Y. (1983) *He Huaxue Yu Fangshe Huaxue,* **5**, 202–10; *Chem. Abstr.*, **99**, 192397.

Yamana, H., Mitsugashira, T., and Shiokawa, Y. (1983) *J. Radioanal. Nucl. Chem.,* **76**, 19–26.

Zachariasen, W. H. (1961) in *The Metal Plutonium* (eds. W. N. Miner and A. S. Coffinberry), University of Chicago Press, Chicago, pp. 99–107.

Zachariasen, W. H. (1973) *J. Inorg. Nucl. Chem.,* **35**, 3487–97.

Ziv, D. M. and Shestakova, I. A. (1965a) *Sov. Radiochem.,* **7**, 168–75; *Radiokhimiya,* **7**, 166–75.

Ziv, D. M. and Shestakova, I. A. (1965b) *Sov. Radiochem.,* **7**, 176–86; *Radiokhimiya,* **7**, 175–87.