CHAPTER FOUR

PROTACTINIUM

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4.1 INTRODUCTION

Protactinium, element 91, is one of the most rare of the naturally occurring elements and may well be the most difficult of all to extract from natural sources. Protactinium is, formally, the third element of the actinide series and the first having a 5f electron. The superconducting properties of protactinium metal provide clear evidence that Pa is a true actinide element (Smith *et al.*, 1979). Its chemical behavior in aqueous solution, however, would seem to place it in group VB of the Mendeleev's table, below Ta and Nb.

The predominant oxidation state is 5+. Pa(v) forms no simple cations in aqueous solution and, like Ta, it exhibits an extraordinarily high tendency to undergo hydrolysis, to form polymers, and to be adsorbed on almost any available surface. These tendencies undoubtedly account for the many reports of erratic and irreproducible behavior of protactinium as well as for its frustrating habit of disappearing in the hands of inexperienced or unwary investigators. A useful review of the chemical properties of Pa important in an analytical context has been made by Pal'shin *et al.* (1970) and Myasoedov *et al.* (1978).

The most important natural isotope is ^{231}Pa, but the industrial importance of Pa stems chiefly from the role of its artificial isotope, ^{233}Pa, as an intermediate in the production of fissile ^{233}U in thorium breeder reactors. It was, in fact, the need for a relatively stable isotope that could be used for macroscopic chemical studies, which was responsible for the revival of interest in the recovery of ^{231}Pa from natural sources (Katzin, 1952). The result has been a rapid growth in our understanding of Pa chemistry, as summarized in numerous critical review articles (Gmelin, 1942, 1977; Elson, 1954; Katz and Seaborg, 1957; Haïssinsky and Bouissières, 1958; Kirby, 1959; Salutsky, 1962; Brown and Maddock, 1963; Sedlet, 1964; Guillaumont and deMiranda, 1966; Keller, 1966a; Brown and Maddock, 1967; Guillaumont *et al.*, 1968; Brown, 1969; Muxart *et al.*, 1969; Muxart and Guillaumont, 1974; Morgan and Beetham, 1990), books (Cotton *et al.*, 1999) and presentations (Weigel 1978; Jung *et al.*, 1993; Greenwood and Earnshaw 1997; Sime, 1997).

4.1.1 Discovery of protactinium

During the preparation of the periodic table Mendeleev (1872) placed in the vacant space in group V between Th(IV) and U(VI) an unknown hypothetical element No. 91 named 'eka-tantalum' with atomic mass of about 235, and chemical properties similar to Nb and Ta. Forty years later, Russell (1913), Fajans (1913a,b), and Soddy (1913a,b) independently proposed the radioactive displacement principles, i.e. two simple rules for reconciling the chemical and radioactive properties of the 33 radioelements known at that time: (1) if a radioelement emits an α particle, its position in the Mendeleev's table is shifted two places to the left, or (2) if it emits a β^--particle, its position is shifted one place to the right. When the rules were applied systematically, there was one obvious discrepancy: the only known link between ^{238}U and ^{234}U, both in group VI, was element UX, a β^--emitter whose chemistry was identical with that of thorium, in group IV. It was necessary to postulate the existence of an unknown β^--emitter, in the space in the periodic table reserved by Mendeleev (1872).

Before the end of 1913, Fajans and his student, Göhring, had shown that element UX was actually a mixture of two distinct radioelements: UX_1 (^{234}Th) and UX_2 (^{234m}Pa), which gave off hard β^--rays, had a half-life of 1.15 min, and was chemically similar to Ta (Göhring, 1914a,b). They named the new element, '*brevium*' (Bv) (*brĕvis* (Latin): short, brief), because of its short half-life (Göhring, 1914b).

An analogous problem existed with respect to the origin of actinium (Göhring, 1914a). It was clear that Ac could not be a 'primary' radioelement, because its half-life was only about 30 years (Curie, 1911). On the other hand, although there was a constant ratio of Ac to U in nature (Boltwood, 1906, 1908), Ac could not be part of the main U–Ra series, because the ratio was far too low. According to the displacement laws, Ac, in group III, could only be the product either of a β^--emitter in group II or of an α-emitter in group V. The first possibility was eliminated when Soddy (1913b) proved that Ra, the only group II element in the U–Ra series, was not the parent of Ac. The only remaining alternative was an α-emitting isotope of UX_2.

In 1913, Soddy had reported the growth of Ac in two lots of UX, separated from 50 kg of uranium 4 years earlier (Soddy, 1913a). This suggested that Ac was being produced from UX 'through an intermediate substance'. Five years later Soddy and Cranston (1918) [see also Sackett (1960)] had confirmed the growth beyond doubt and had separated the parent of Ac by sublimation from pitchblende in a current of air containing CCl_4 at incipient red heat. This method was later applied by Malm and Fried (1950, 1959) to the separation of ^{233}Pa from neutron-irradiated ^{232}Th.

Almost simultaneously, Hahn and Meitner (1918) reported their independent discovery of the parent of Ac in the siliceous residue resulting from the treatment of pulverized pitchblende with hot concentrated HNO_3. They proposed the name, *protactinium*. Preliminary estimates indicated that the half-life of the new isotope was between 1200 and 180 000 years. Since the name, *brevium*, was obviously inappropriate for such a long-lived radioelement, Fajans and Morris (1913) proposed that the name of element-91 be changed to *protactinium* (linguistic purists at first insisted on calling it *protoactinium*, because '*proto* is better Greek' (Grosse, 1975), but the name *protactinium* (Pa) was restored officially in 1949 (Anonymous, 1949)).

There was still no direct evidence as to the origin of protactinium. In 1911, Antonoff (1911) had separated uranium Y – UY (^{231}Th) from a purified U solution. UY was chemically similar to Th and Antonoff (1913) suggested that this might be the point at which the Ac series branched off from the U series. In 1917, Piccard (1917) suggested that, in addition to the two known isotopes of uranium, uranium I and II (UI and UII), there might also exist a third long-lived isotope, actinouranium (AcU). AcU would decay by α-emission to yield UY, which, in turn, would decay by β^--emission to give an isotope of *brevium*. Piccard's hypothesis was confirmed experimentally in 1935, when Dempster (1935) discovered AcU (^{235}U) by mass spectrography.

4.1.2 Isolation of protactinium

The new element was isolated for the first time in 1927, when Grosse (1927, 1928) reported that he had prepared about 2 mg of essentially pure Pa_2O_5. By the end of 1934, Grosse with Agruss had developed a process for the large-scale recovery and purification of Pa (Grosse, 1934a; Grosse and Agruss, 1934, 1935a). They had isolated more than 0.15 g of Pa_2O_5, reduced it to the metal, and determined its atomic weight to be 230.6 ± 0.5 (Grosse, 1934b). In the same year, Graue and Kading (1934a,b) recovered 0.5 g of pure Pa (as K_2PaF_7) from 5.5 tons of pitchblende residues, an achievement that would not be equaled, let alone surpassed, for the next quarter of a century.

The development of atomic energy led to the processing of most of the world's known reserves of high-grade uranium ores and to the accumulation of vast stockpiles of process wastes. Among these, at the Springfields refinery of the United Kingdom Atomic Energy Authority (UKAEA) was the '*ethereal sludge*', a siliceous precipitate that had separated during the ether extraction of U from dilute HNO_3 solution. This material, amounting to some 60 tons, contained about 4 ppm of Pa, or more than ten times its equilibrium concentration in unprocessed pitchblende. Since the sludge also contained about 12 tons of U, it was economically attractive to recover both elements, with most of the development and production cost being borne by the U recovery. The process that was finally adopted yielded 127 g of 99.9% pure ^{231}Pa (Goble *et al.*, 1958; Nairn *et al.*, 1958; Jackson *et al.*, 1960a,b; Collins *et al.*, 1962; Hillary and Morgan, 1964) at a cost of about US$500 000 (CRC Handbook, 1997).

The UKAEA has generously made its stockpile of Pa available to the rest of the world at nominal cost, thereby touching off intensive investigation of Pa chemistry at many laboratories. Thanks to this concentrated effort, the new era in Pa research that started in the mid-1950s has now reached maturity. Three international conferences were convened, devoted entirely to the chemical, physical, and nuclear properties of Pa (Oak Ridge National Laboratory, 1964; Bouissières and Muxart, 1966; Born, 1971).

4.2 NUCLEAR PROPERTIES

At present, there are 29 known isotopes of Pa (Table 4.1), but only three are of particular significance to chemists. They are the naturally occurring isotopes, ^{231}Pa and ^{234}Pa, and reactor-produced ^{233}Pa. The characteristics of α-decay of Pa isotopes with mass numbers (A) till 224 were presented by Andreev *et al.* (1996b). Hyde (1961, undated) and Hyde *et al.* (1964) had exhaustively reviewed the nuclear properties of all the isotopes with A ranging from 225 to 237.

A new nuclide ^{239}Pa produced recently by multi-nucleon transfer reactions ^{238}U(p,2n)^{239}Pa (Yuan *et al.*, 1996). Protactinium was chemically separated from the uranium target and other produced elements. From the ^{239}Pa β^--decay a half-life of (106 ± 30) min was observed.

For details concerning the more recently discovered isotopes, the reader should consult the original references (Meitner *et al.*, 1938; Ghiorso *et al.*, 1948; Gofman and Seaborg, 1949; Hyde *et al.*, 1949; Meinke *et al.*, 1949, 1951, 1952, 1956; Harvey and Parsons, 1950; Barendregt and Tom, 1951; Keys, 1951; Browne *et al.*, 1954; Crane and Iddings, 1954; Zijp *et al.*, 1954; Wright *et al.*, 1957; Hill, 1958; Arbman *et al.*, 1960; Takahashi and Morinaga, 1960; Albridge *et al.*, 1961; Baranov *et al.*, 1962; Bjørnholm and Nielsen, 1962, 1963; Subrahmanyam, 1963; Wolzak and Morinaga, 1963; McCoy, 1964; Bastin *et al.*, 1966; Bjørnholm *et al.*, 1968; Hahn *et al.*, 1968; Trautmann *et al.*, 1968; Briand *et al.*, 1969; Borggreen *et al.*, 1970; dePinke *et al.*, 1970; Laurens *et al.*, 1970; Varnell, 1970; Holden and Walker, 1972; Sung-Ching-Yang *et al.*, 1972; Lederer and Shirley, 1978; Folger *et al.*, 1995; Yuan *et al.*, 1995, 1996; Andreev *et al.*, 1996a; Nishinaka *et al.*, 1997).

4.2.1 Protactinium-231

^{231}Pa, an α-emitter with fixed atomic weight 231.03588 ± 0.0002 (Delaeter and Heumann, 1991), is a member of the naturally occurring ^{235}U decay ($4n + 3$) chain. It is the daughter of ^{231}Th and the parent of ^{227}Ac, from which it derives

Table 4.1 *Nuclear properties of protactinium isotopes.*

Mass number	*Half-life*	*Mode of decay*	*Main radiations* (MeV)	*Method of production*
212	5.1 ms	α	α 8.270	^{182}W(^{35}Cl,5n)
213	5.3 ms	α	α 8.236	^{170}Er(^{51}V,8n)
214	17 ms	α	α 8.116	^{170}Er(^{51}V,7n)
215	14 ms	α	α 8.170	^{181}Ta(^{40}Ar,6n)
216	0.2 s	α	α 7.865	^{197}Au(^{24}Mg,5n)
217	4.9 ms	α	α 8.340	^{181}Ta(^{40}Ar,4n)
	1.6 ms	α	α 10.160	
218	0.12 ms	α	α 9.614 (65%)	^{206}Pb(^{16}O,4n)
219	53 ns	α	α 9.900	^{204}Pb(^{19}F,4n)
220	0.78 μs	α	α 9.15	^{204}Pb(^{19}F,3n)
221	5.9 μs	α	α 9.080	^{209}Bi(^{16}O,4n)
222	5.7 ms	α	α 8.54 (~30%)	^{209}Bi(^{16}O,3n)
			~8.18 (50%)	^{206}Pb(^{19}F,3n)
223	6 ms	α	α 8.20 (45%)	^{208}Pb(^{19}F,4n)
			8.01 (55%)	^{205}Tl(^{22}Ne,4n)
224	0.9 s	α	α 7.49	^{208}Pb(^{19}F,3n)
225	1.8 s	α	α 7.25 (70%)	^{232}Th(p,8n)
			7.20 (30%)	^{209}Bi(^{22}Ne,α2n)
226	1.8 min	α 74%	α 6.86 (52%)	^{232}Th(p,7n)
		EC 26%	6.82 (46%)	
227	38.3 min	α ~85%	α 6.466 (51%)	^{232}Th(p,6n)
		EC ~15%	6.416 (15%)	
			γ 0.065	
228	22 h	EC ~98%	α 6.105 (12%)	^{232}Th(p,5n)
		α ~2%	6.078 (21%)	^{230}Th(p,3n)
			γ 0.410	
229	1.5 d	EC 99.5%	α 5.669 (19%)	^{230}Th(d,3n)
		α 0.48%	5.579 (37%)	^{229}Th(d,2n)
230	17.7 d	EC 90%	α 5.345	^{230}Th(d,2n)
		β^- 10%	β^- 0.51	^{232}Th(p,3n)
		α 3.2×10^{-3}%	γ 0.952	
231	3.28×10^4 yr	α	α 5.012 (25%)	nature
			4.951 (23%)	
			γ 0.300	
232	1.31 d	β^-	β^- 1.29	^{231}Pa(n,γ)
			γ 0.969	^{232}Th(d,2n)
233	27.0 d	β^-	β^- 0.568	^{233}Th daughter
			γ 0.312	^{237}Np daughter
234	6.75 h	β^-	β^- 1.2	nature
			γ 0.570	
234 m	1.175 min	β^- 99.87%	β^- 2.29	nature
		IT 0.13%	γ 1.001	
235	24.2 min	β^-	β^- 1.41	^{235}Th daughter
				^{235}U(n,p)
236	9.1 min	β^-	β^- 3.1	^{236}U(n,p)
			γ 0.642	^{238}U(d,α)
237	8.7 min	β^-	β^- 2.3	^{238}U(γ,p)
			γ 0.854	^{238}U(n,pn)
238	2.3 min	β^-	β^- 2.9	^{238}U(n,p)
			γ 1.014	
239	106 min	β^-		^{18}O + ^{238}U

its name (Fig. 4.1). Reported half-lives have ranged from 32 000 years ± 10% (Grosse, 1932) to (34 300 ± 300) years (Van Winkle *et al.*, 1949); three recent determinations (Kirby, 1961; Brown *et al.*, 1968a; Robert *et al.*, 1969) yield a weighted average of (32 530 ± 250) years (at the 95% confidence level). Therefore ^{231}Pa is the only isotope easy to access in multi-gram quantities. The thermal-neutron cross section is (211 ± 2) barn (Simpson *et al.*, 1962; Gryntakis and Kim, 1974). The spontaneous fission half-life is 1.1×10^{16} years (Segrè, 1952), which gives the correlation of 0.3 of a fission per 1 g Pa per min.

The complex fine structure of the ^{231}Pa alpha-spectrum can be resolved with a passivated implanted planar silicon detector (Fig. 4.2). Baranov *et al.* (1962, 1968), using a double-focusing magnetic spectrometer, found at least 19 α-groups with energies ranging from 4.51 to 5.06 MeV and additional low-abundance groups have been detected by α–γ coincidence measurements (Lange and Hagee, 1968). Predictably, the γ-ray spectrum, as recorded with a high-resolution Ge detector, is even more complex (Fig. 4.3): 92 γ-rays have been reported, with energies up to 609 keV (dePinke *et al.*, 1970; Leang, 1970). A detailed level scheme is given in the critical compilation by Artna-Cohen (1971). The prominent γ photopeak at 27.35 keV is easily detectable even with a NaI(Tl) crystal; it uniquely identifies ^{231}Pa in the presence of other naturally occurring γ-emitters (Fig. 4.4).

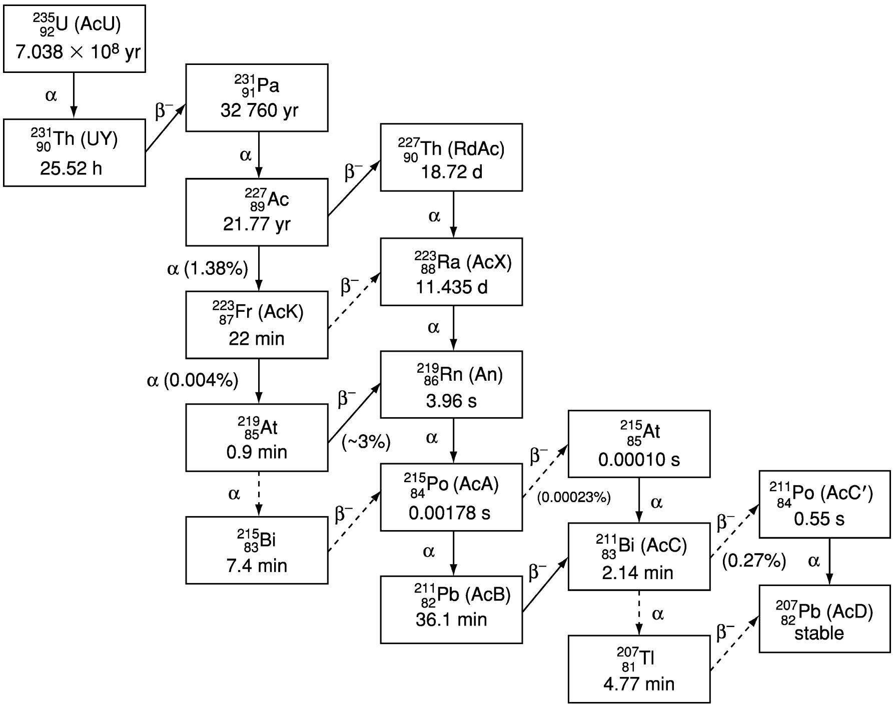


Fig. 4.1 *Uranium–actinium series* (4*n* + 3).

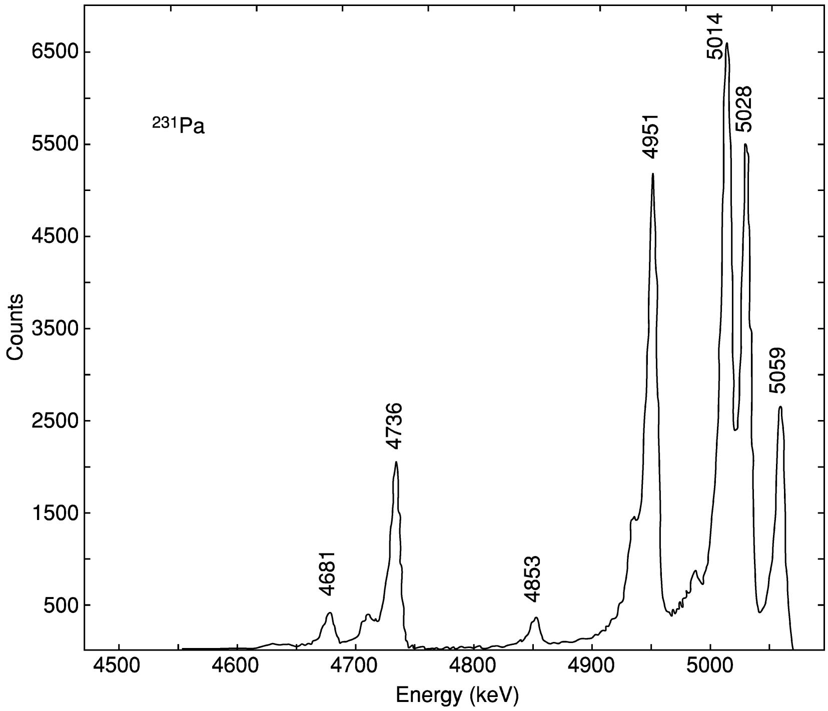


Fig. 4.2 *Alpha-spectrum of* ^{231}*Pa measured with a passivated implanted planar silicon detector* (*Ahmad,* 2004).

^{231}Pa can be separated from reprocessed U ores, or alternatively, produced by either of the two nuclear reactions: ^{232}Th(n,2n)^{231}Th (Nishina *et al.*, 1938) or ^{230}Th(n,γ)^{231}Th (Hyde, 1948). In principle, this would eliminate many of the problems attendant on the isolation of ^{231}Pa. However, neutron irradiation of ^{232}Th yields large amounts of ^{233}Pa and other undesirable contaminants, but relatively little ^{231}Pa (Table 4.2) (Schuman and Tromp, 1959; Codding *et al.*, 1964). The ^{230}Th route is only superficially more attractive, since the richest sources of ^{330}Th found thus far in U refinery waste streams and residues have always been associated with at least eight times as much ^{232}Th (Figgins and Kirby, 1966). Protactinium was not formed in the amalgam and could be also separated from thorium (David and Bouissières, 1966).

4.2.2 Protactinium-233

^{233}Pa is the only artificial isotope of Pa thus far produced in weighable amounts; the first gram was isolated in 1964 by a group at the National Reactor Testing Station in Idaho (Codding *et al.*, 1964). ^{233}Pa derives its importance from the

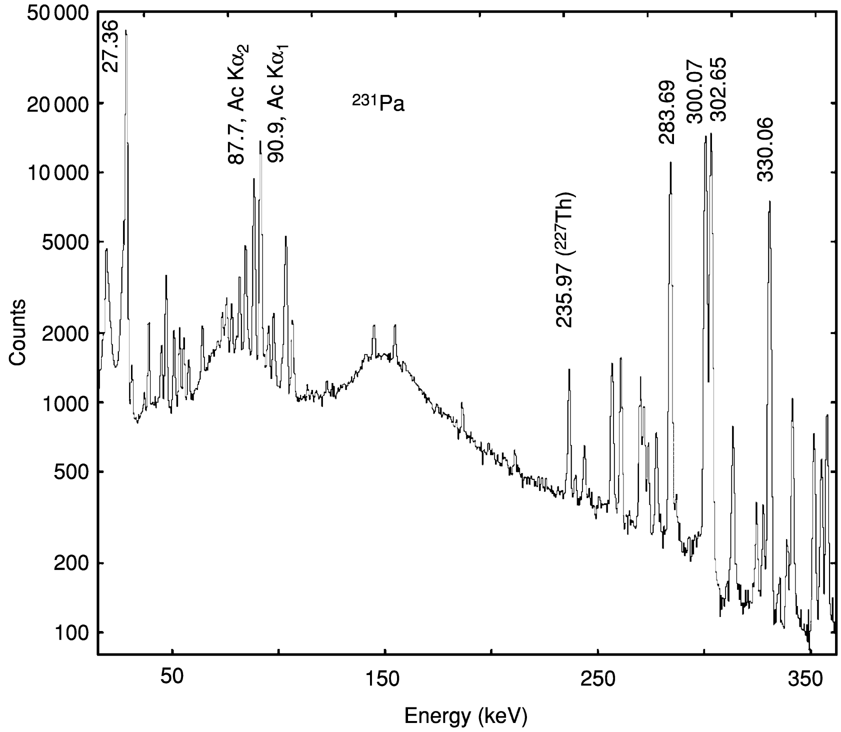


Fig. 4.3 *γ-Ray spectrum of* ^{231}*Pa measured with a 25% efficiency germanium detector* (*Ahmad*, 2004).

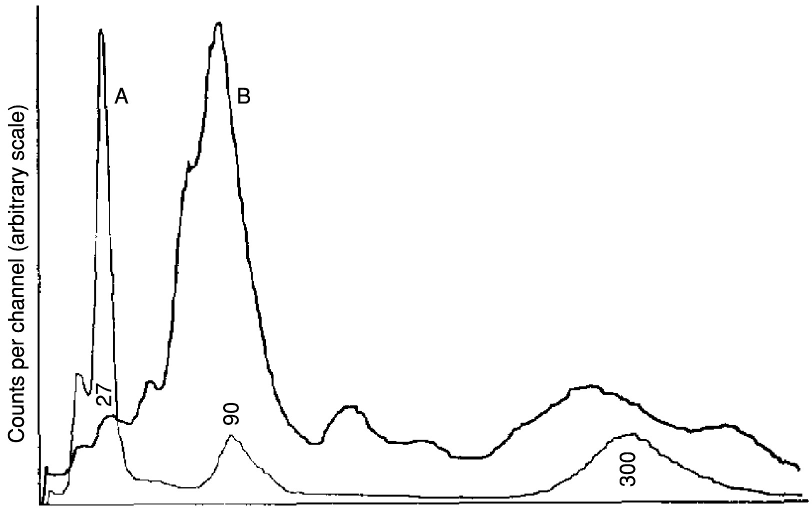


Fig. 4.4 *γ-Ray spectrum of* ^{231}*Pa observed with a NaI(Tl) crystal: curve A, freshly purified* ^{231}*Pa; curve B, raw material* (~0.3 *ppm* ^{231}*Pa*).

Table 4.2 *Calculated composition of* 100 g *of* ^{232}*Th after thermal-neutron irradiation* (*Codding* et al., 1964) (*thermal flux* = 5×10^{14} n cm^{-2}s^{-1}; *resonance flux* = (*thermal flux*)/12; *nvt* = 1.2×10^{21} n cm^{-2}).

Nuclide	*Amount*
^{231}Pa	98.6 g
^{232}Th	~1 mg
^{233}Pa	950 mg
^{233}U	320 mg
^{235}U	65 mg
^{235}U	5 mg
fission products	60 mg

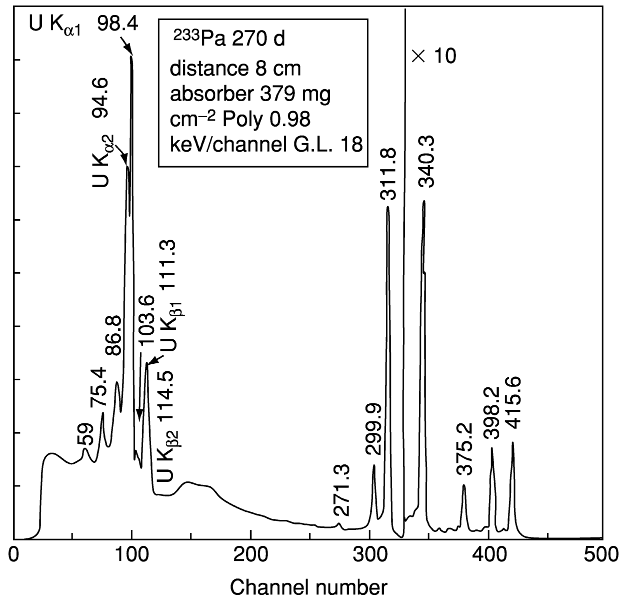


Fig. 4.5 *γ-Ray spectrum of* ^{233}*Pa observed with a Ge*(*Li*) *detector. Reproduced from Crouthamel* et al. (1970) *with permission from Pergamon Press.*

fact that it is an intermediate in the production of fissile ^{233}U. The reaction, discovered in 1938 by Meitner *et al.* (1938) (Sime, 1997) is:

$$^{232}\text{Th}\,(\text{n},\gamma)\,^{233}\text{Th}\,(\beta^-;\,22\ \text{min}) \rightarrow {}^{233}\text{Pa}(\beta^-;\,27\,\text{days}) \rightarrow {}^{233}\text{U}$$

^{233}Pa has largely replaced ^{234}Pa as a tracer because of its favorable half-life (26.95 ± 0.06) days (Wright *et al.*, 1957), its relative ease of preparation (cf. Table 4.2), and its readily detectable gamma spectrum (Fig. 4.5). Using this isotope a large volume of important data on protactinium chemistry had been provided.

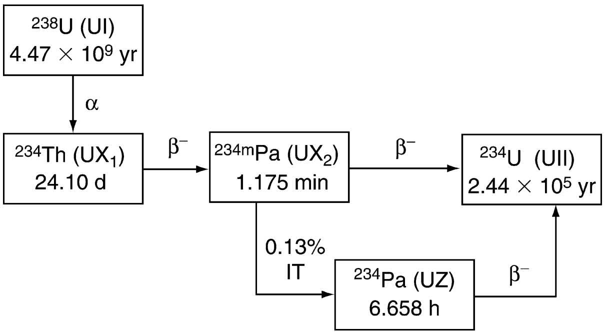


Fig. 4.6 *Genetic relationships of the* UX_1–UX_2–*UZ complex.*

4.2.3 Protactinium-234

The nuclide ^{234}Pa occurs naturally in two isomeric forms: ^{234m}Pa, discovered by Fajans and Göhring (1913a,b), and ^{234}Pa, discovered afterward by Hahn (1921). Their genetic relationships are indicated in Fig. 4.6. Both are β^--emitters, decaying to ^{234}U, but ^{234m}Pa is metastable and, in 0.13% of its disintegrations, it decays to its ground state by isomeric transition, yielding ^{234}Pa (Bjørnholm and Nielsen, 1963). The extraordinarily complex decay scheme of ^{234}Pa (Ellis, 1970; Ardisson and Ardisson, 1975) is difficult to study, because the intense sources needed for high-resolution spectrometry are not readily available. However, 0.8 Ci of ^{234}Th was extracted from several tons of ^{238}U, making possible the definitive study by Bjørnholm *et al.* (1967, 1968). The gamma-spectrum of ^{234}Pa (in equilibrium with ^{238}U and ^{234}Th) is shown in Fig. 4.7 (Crouthamel *et al.*, 1970).

4.3 OCCURRENCE IN NATURE

Since the half-life of ^{231}Pa is short in geological terms, its natural occurrence is closely tied to that of ^{235}U, its primordial ancestor. Uranium isotopes are widely distributed in the Earth's crust (Kirby, 1974). The average crustal abundance of U is 2.7 ppm (Taylor, 1964), of which 0.711 wt% is ^{235}U (Grundy and Hamer, 1961); therefore, the natural abundance of ^{231}Pa (calculated from its half-life and that of ^{235}U) is 0.87×10^{-6} ppm – only slightly less than that of ^{226}Ra. Assuming that the crustal mass (to a depth of 36 km) is 2.5×10^{25} g (Heydemann, 1969), the global inventory of ^{231}Pa is 2.2×10^7 metric tons.

The pronounced hydrolytic tendency of Pa is the basis of a method for dating marine sediments less than 10^6 years old (Sackett, 1960; Roshalt *et al.*, 1961, 1962; Sakanoue *et al.*, 1967; Thomson and Walton, 1971, 1972; Kirby, 1974). In an undisturbed geological formation, thematic Pa:U $= 3.2 \times 10^{-7}$, but this ratio

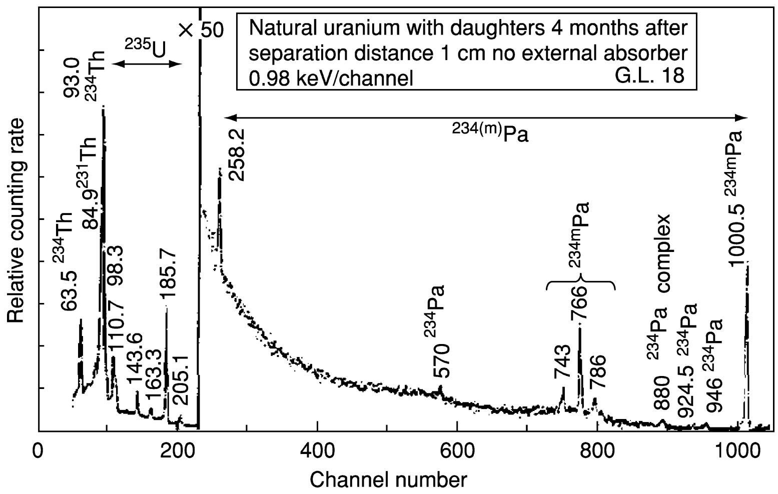


Fig. 4.7 *γ-Ray spectrum of UX_1–UX_2–UZ in equilibrium with ^{238}U. Reproduced from Crouthamel* et al. (1970) *with permission from Pergamon Press.*

is altered when the deposit is leached with groundwater and the U is carried to sea. At the pH of seawater, both Pa and Th hydrolyze and deposit together on the ocean floor, leaving the U in solution as UO$_2^{2+}$. Because ^{231}Pa and ^{230}Th decay moved at different rates, their ratio at various depths can be used to determine the rate of sedimentation.

^{231}Pa/^{235}U ages were also determined for 17 carnotites from two areas in Israel (Kaufman *et al.*, 1995). For the determination of ^{231}Pa in solids, a new method, more than ten times more precise than those determined by decay counting, based on thermal ionization mass spectroscopy (TIMS) of protactinium in carbonates was created. Carbonates between 10 and 250 000 years old can now be dated with this ^{231}Pa method. Barbados corals that have identical ^{231}Pa and ^{230}Th ages indicate that the timing of sea level change over parts of the last glacial cycle is consistent with the predictions of the Astronomical Theory (Edwards *et al.*, 1997).

^{233}Pa has not itself been detected in nature, but traces of both ^{237}Np, its parent, and ^{225}Ac, its descendant, have been identified in a U refinery waste stream (Peppard *et al.*, 1952). It may, therefore, be inferred that ^{233}Pa is being continually formed in nature by the reaction:

$$^{238}\text{U}\,(\text{n}, 2\text{n})\,^{237}\text{U}\,(\beta^-;\ 6.75\,\text{days}) \rightarrow {}^{237}\text{Np}\,(\alpha;\ 2.14 \times 10^6\,\text{years}) \rightarrow {}^{233}\text{Pa}.$$

The natural neutron output in pitchblende is about 0.05 ng^{-1} s^{-1}, attributable about equally to spontaneous fission of ^{238}U and (α,n) reactions of light elements (McKay, 1971).

4.4 PREPARATION AND PURIFICATION

No large-scale separation of ^{231}Pa has ever been made from virgin ores because the element has little commercial value. Weighable amounts of Pa have always been obtained from U refinery residues. Indeed, the economic realities are such that it is rarely possible even to optimize the segregation of Pa in a single waste stream or residue. More typically, the Pa is fractionated at every stage in the beneficiation and extraction of U from its ores.

Before the development of atomic energy, pitchblende ores were processed primarily for their Ra content. The pulverized ore, after being roasted with Na_2CO_3, was leached with aqueous solutions of H_2SO_4 or HNO_3 (or both) and the acid-insoluble material was digested with NaOH or Na_2CO_3 solutions. The residue was then leached with hydrochloric acid to recover the Ra (Curie, 1913). The final residue retained a greater or lesser fraction of the original Pa according to the relative proportions of the acids used in the digestion; a higher H_2SO_4 concentration and higher total acidity favored the dissolution of Pa (Reymond, 1931). This *Rückrückstände,* or 'residue of residues', was the raw material used by Hahn and Meitner (1918) for their discovery of ^{231}Pa, by Grosse (1927, 1928) in the isolation of the first milligram amounts, and by Graue and Kading (1934a) in the recovery of 0.5 g of the element. The analysis of one such residue is given in Table 4.3.

During and after World War II, an ether extraction process was used for the purification of U. The acid solution resulting from the ore digestion was treated with Na_2CO_3 to precipitate some of the less basic metals, while leaving the U in solution as a carbonate complex. Katzin *et al.* (1950) found that the carbonate precipitate contained 0.30–0.35 ppm of Pa and subsequent processing of this material yielded about 25 mg of pure Pa (Kraus and Van Winkle, 1952; Larson *et al.*, 1952; Thompson *et al.*, 1952). When the process was modified to eliminate the carbonate precipitation, the Pa passed through the ether extraction step into the aqueous raffinate, from which Elson *et al.* (1951) recovered 35 mg of pure material.

A later modification produced a precipitate in the aqueous waste stream, which, according to Salutsky *et al.* (1956), carried down nearly all the Pa. This material was periodically filtered off and eventually yielded a total of about 2 g of Pa (Kirby, 1959; Hertz *et al.*, 1974; Figgins *et al.*, 1975).

The aqueous raffinate from the ether extraction was treated with lime and the filtered precipitate was stored for future recovery of U and other commercially valuable metals. The accumulated material was later treated by a process of which the relevant steps were: digestion with sulfuric acid, followed by extraction with bis(2-ethylhexyl)phosphoric acid (HDEHP), and finally back-extraction with sodium carbonate solution. The waste solutions and residues were discharged to a tailings pond, where, for all practical purposes, much of the Pa and ^{230}Th were irretrievably lost. In 1972, the process was modified by

Table 4.3 *Analyses of some ^{231}Pa raw materials.*

Riickriickstände (*Grosse and Agruss*, 1935*a*)		*Ethereal sludge* (*Nairn* et al., 1958)		*Cotter concentrate* (*Ishida*, 1975)	
Constituent	*Amount (%)*	*Constituent*	*Amount (%)*	*Constituent*	*Amount (%)*
SiO_2	60	U	28.3	U_3O_8	13.8
Fe_2O_3	22	Fe	7.7	Fe	$\sim$30
PbO	8	Si	6.4	Si	$\sim$4
Al_2O_3	5	Ba	$\sim$3	Na	$\sim$60
MnO	1	Zr	2.7	Mo	$\leq$2
CaO	0.6	Mo	2.7	V	$\leq$1
MgO	0.5	F^-	1.8	Al	$\geq$0.3
Ti	0.3	NH_4^+	1.7	Th	0.15
Zr	0.1	Ca	1.5	Ti	0.1
HF and others	–	V	0.9	Ca	0.07
Graphite	0.1	Ti	0.44	Cu	0.05
Pa_2O_5	3×10^{-3}	Pb	0.4	Zr	0.04
		Al	0.27	Mg	0.04
		P	0.15	Ni	0.03
		Sr	0.09	Mn	0.01
		Nb, Ta	<0.1	Cr	0.01
		Mg, Ni, Cr,	<0.01	B	0.002
		Co, Mn, & Sn		Be	7×10^{-4}
		Pa	$3.7 \times I0^{-4}$	Pa	4×10^{-5}

adding enough sodium hydroxide to the Na_2CO_3 strip solution to cause total precipitation of the U, thus minimizing any further loss of Pa and ^{230}Th (Haubach, 1967; Figgins and Hertz, 1972a,b, 1973). The filtered precipitate ('*Cotter concentrate*') consists of some 2000 tons (dry weight) of mixed oxides and carbonates (Table 4.3) and contains an estimated 30 tons of U_3O_8, 14 kg of ^{230}Th, and 75 g of Pa. This material has been processed at Mound Laboratory.

At the Windscale refinery of the UKAEA, after removal of a sulfate precipitate containing the Ra, the solution was buffered to pH $\sim$2 and the U was precipitated by the addition of hydrogen peroxide. The peroxide precipitate carried down more than 80% of the Pa and, when it was redissolved in nitric acid, the low acidity encouraged the formation of a siliceous Pa-containing sludge, which deposited on the walls of the ether extraction plant and its ancillary vessels. This '*ethereal sludge*' was collected and drummed, pending future recovery of U. It proved to be the richest source of Pa ever found, ultimately yielding 127 g of the pure element (Goble *et al.*, 1958; Nairn *et al.*, 1958; Jackson *et al.*, 1960a; Collins *et al.*, 1962). The gross chemical composition of '*ethereal sludge*' is shown in Table 4.3.

4.4.1 Industrial-scale enrichment of siliceous residues

At ultra-micro concentrations with respect to other metals ions, Pa scarcely exhibits a chemistry of its own. Consequently, the procedure adopted to recover Pa from 'natural' sources is usually dictated less by the chemistry of Pa than by the gross chemical and physical characteristics of the source and, sometimes, by the sheer quantity of material to be processed.

The problems are magnified by the extreme complexity and variability of the sources from which ^{231}Pa is obtained, but one problem common to nearly all natural sources has been the ubiquitous presence of silica, and nearly all authors have resorted, at one stage or another, to alkaline fusion or digestion for its removal. Grosse (1934a) and Grosse and Agruss (1934, 1935a) recovered more than 100 g of pure Pa_2O_5 from 1.2 tons of *Rückrückstände,* a material composed largely of SiO_2 and Fe_2O_3 (Table 4.3). The principal steps in the enrichment process were: (1) leaching with hydrochloric acid to eliminate Fe and the more basic oxides; (2) fusing the residue with NaOH and leaching the cooled melt with water to remove soluble silicates and Pb; (3) dissolving the residue in hydrochloric acid and heating to coagulate the remaining SiO_2; (4) washing the precipitate with 20% NaOH solution and dissolving the residue in hydrochloric acid; (5) precipitating Zr (and Pa) by the addition of phosphoric acid; and (6) fusing the ZrP_2O_7 with KOH to eliminate PO_4^{3-} and the last of the SiO_2. The plant product contained more than 85% of the original Pa in a concentration of 1:5000 – an enrichment factor of about 600. Graue and Kading (1934a,b) recovered 700 mg of Pa from 5.5 tons of *Rückrückstände* by essentially the same process, except that the raw material was first fused with NaOH and then leached with hydrochloric acid. The large quantity of SiO_2 that remained in the residue was eliminated by fuming with hydrofluoric acid.

4.4.2 Enrichment of carbonate precipitates

Pa in trace amounts may fractionate unpredictably during dissolution or precipitation of a multi-component mixture. To inhibit such fractionation, many authors have introduced carriers such as Ta (Hahn and Meitner, 1918), Zr (Graue and Kading, 1934a; Grosse and Agruss, 1935a), or Ti (Zavizziano, 1935; Emmanuel-Zavizziano, 1936; Kirby, 1959), which carry Pa quantitatively when they are precipitated as phosphates or hydrated oxides.

Larson *et al.* (1952) leached a carbonate precipitate with nitric acid and digested the resultant SiO_2 gel with 10% NaOH solution to which La carrier was added to minimize losses of Pa in the alkaline solution. However, Thompson and co-workers (1952), by first digesting the carbonates with 40% NaOH, were able to remove enough SiO_2 to prevent gel formation when the metathesized residue was dissolved in 1 M HNO_3. There was no loss of Pa to the alkaline solution, probably because the residue already contained appreciable amounts of both Zr and Ti. The Pa was concentrated from the 1 M HNO_3

solution by adsorption on a MnO_2 precipitate formed *in situ* (Grosse and Agruss, 1935b; Katzin and Stoughton, 1956). Two additional cycles of MnO_2 precipitation and redissolution in HNO_3 were followed by a hydrolytic precipitation of Ti and Zr from 5 M HNO_3. The precipitate that carried down the Pa was taken up in hydrofluoric acid and evaporated to dryness in the presence of perchloric acid to eliminate SiO_2, giving a 1000-fold enrichment of the Pa with a 65% yield.

Carrying by MnO_2 is a key step in the recovery of Pa from *Cotter concentrate* (Hertz *et al.*, 1974). The solids are digested in HNO_3 solution and filtered to yield a solution that is 2–3 M in HNO_3. Essentially all the U and ^{230}Th and 50–85% of the Pa are dissolved; the undissolved residue is reserved for further digestion. The U is extracted with di-*S*-butylphenyl phosphonate (DSBPP) and the Pa and ^{230}Th are quantitatively extracted with tri-*n*-octylphosphine oxide (TOPO). ^{230}Th is stripped from the TOPO with 0.3 M H_2SO_4 and the Pa with 0.5 M $H_2C_2O_4$. Addition of potassium permanganate to the oxalic acid solution yields a precipitate of 5 g of MnO_2 containing 1–6 mg of Pa, for an enrichment factor of 500–2500.

4.4.3 Enrichment of aqueous raffinates

After the sodium carbonate precipitation step was omitted from the Mallinckrodt process, the aqueous raffinate from the diethyl ether extraction of U contained about 0.2 mg L^{-1} of Pa and 1–10 g L^{-1} for other elements (chiefly Ca, Fe, and rare earths). Elson *et al.* (1951) extracted this weakly acid solution of nitrates with 5% of its volume of tri(*n*-butyl)phosphate (TBP) and stripped the TBP with one-fourth of its volume of 0.5 M HF solution. Rare earths and Th isotopes precipitated, but the Pa remained in solution. Al^{3+} was added to complex the F^- and the solution was contacted with di-isopropylcarbinol (DIPC), which extracted 70–90% of the Pa. Back-extraction into 10% H_2O_2 gave another 20-fold volume reduction and yielded a product that contained about 4% Pa by weight, with Ca and U as the principal impurities. The overall yield was only 5–35%, however, primarily because of the poor extractability of Pa into TBP at low acidity. Peppard *et al.* (1957) later found that Pa is efficiently extracted by TBP from 5 M HCl.

In a Russian process (Shevchenko *et al.*, 1958b), the U ore is digested with nitric acid and extracted as slurry with a 10% solution of TBP in kerosene. About 75–85% of the ^{230}Th and 50–55% of the Pa pass into solution, but neither is appreciably extracted by the TBP. After phase separation and filtration, the aqueous solution is made 2 M in HNO_3 and contacted with a 15% solution of mixed mono- and di-isoamylphosphoric acids (DIAPA) in isoamylacetate. A single-stage extraction with an organic:aqueous volume ratio of 1:20 recovers 75–85% of the ^{230}Th and 82–89% of the Pa. After back-extraction with saturated aqueous $(NH_4)_2CO_3$, Fe and other heavy metals are precipitated as sulfides and the carbonate is decomposed by heating and acidification.

The ^{230}Th and Pa are precipitated with NH_4OH and calcined to yield a concentrate containing up to 1% ^{230}Th and about 0.01% Pa in a matrix of U, P, Ti, Zr, Sc, and other impurities. The Pa is separated from ^{230}Th and Sc by fluoride precipitation, which leaves Pa in the solution, from which it is coprecipitated with Zr as a phosphate in the presence of H_2O_2. The Pa:Zr ratio in the concentrate is usually 1:400 or higher.

The adsorption behavior of protactinium on zirconium phosphate cation exchanger from ammonium chloride, hydrochloric acid, and hydrochloric acid–alcohol media has been investigated (Souka *et al.*, 1975c). The distribution coefficients in solvent mixtures of hydrochloric acid and various alcohols depend on both alcohol content and acid concentration. Similar investigations have been carried out for nitric acid systems (Souka *et al.*, 1976a). Sorption of protactinium on silica gel has also attracted attention. Adsorption of ^{233}Pa on silica gel has been investigated as a possible procedure for obtaining isotopically pure uranium-233 (Chang and Ting, 1975a). Protactinium-233 sorption from oxalic acid system has been studied; a 1:1 complex of Pa and oxalate is formed in these systems and the observed adsorption is well correlated to the concentration of the oxalate complexes (Bykhovskii *et al.*, 1977). Hydrophobic silica gel has been prepared by silylation; uptake of protactinium from mixtures of hydrochloric acid and lower aliphatic alcohols increases with increasing molecular weight of the aliphatic alcohol (Caletka and Spěváčkova, 1975).

4.4.4 Enrichment of ethereal sludge

Aqueous hydrofluoric acid is the most consistently effective solvent for Pa(v), with which it forms strong anionic complexes (Guillaumont and deMiranda, 1966; Guillaumont *et al.*, 1968). It has the added advantage of dissolving the oxides of most of the elements with which Pa is normally associated in nature (Si, Fe, Ta, Zr, Ti, etc.). If Al^{3+} is added to such a solution in sufficient quantity to mask all the F^-, a precipitate forms, which carries the Pa quantitatively.

In an enrichment method reported by Goble *et al.* (1958), ethereal sludge was leached with 0.5 M HNO_3, which dissolved about 90% of the U. The residue, which retained more than 95% of the Pa, was leached with 0.5 M HF and Al sheets were suspended in the solution. After 5 days or more, the Pa separated quantitatively as a black deposit on the aluminum, from which it was loosened by treatment with 0.2 M NaOH. The precipitate was washed with dilute NaOH solution and dissolved in 8 M HCl, from which it was extracted with di-isobutylketone (DIBK). The DIBK was stripped with 8 M HCl containing a little HF. Addition of $AlCl_3$ permitted a second cycle of DIBK extraction and stripping. The crude HCl–HF product from 100 kg of sludge was 200 mg of Pa (77% yield) in 0.5 L of solution containing about 10 g of solids.

Unfortunately, this ingenious and inexpensive process failed when attempts were made to apply it on a tonnage scale, apparently because fluorides (from CaF_2 slag) had been dispersed throughout the sludge during a re-drumming operation. This resulted in unacceptable losses of Pa during the initial leaching with dilute HNO_3 solution. Furthermore, the deposition of Pa on Al plates proved too slow and cumbersome for operation on a tonnage scale.

The process that was finally adopted is outlined in Fig. 4.8 (Nairn *et al.*, 1958; Collins *et al.*, 1962). The U and Pa were dissolved by leaching the sludge with a mixture of HNO_3 and HF. After extraction of the U with TBP, Al^{3+} as chloride was added to the raffinate. A precipitate is formed, which carried down 80–95% of the Pa, with an enrichment factor of approximately 10. The precipitate was

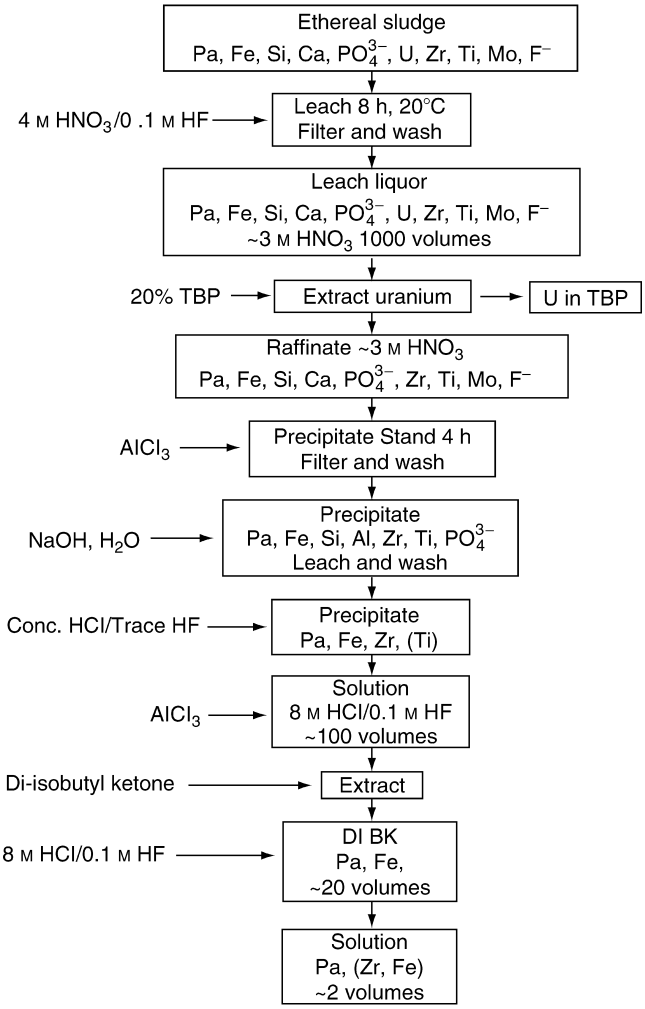


Fig. 4.8 *Recovery of protactinium and uranium from ethereal sludge* (*Nairn* et al., 1958).

digested with 10–35% NaOH to remove Si, Al, and, especially, PO_4^{3-}. The residue was dissolved in 8 M HCl and 0.1 M HF and aluminum chloride was added in a molar ratio of Al:F > 5. The solution was extracted with DIBK and stripped with 8 M HCl and 0.1 M HF. A second cycle of DIBK extraction and stripping yielded 52.4 L of an aqueous solution containing 126.75 g of Pa, 3.25 g of Zr, and 1.42 g of Fe (it was later learned that the product also contained 0.1–4% Nb) (Walter, 1963; Brown *et al.*, 1966a; Jenkins *et al.*, 1975).

Salutsky *et al.* (1956) recovered 0.5 mg of Pa from 5 kg of a material similar to ethereal sludge but only one-tenth as rich. The principal features of the method were: (1) dissolution in 1 M HCl, (2) saturation of the solution with sodium chloride, and (3) boiling to coagulate a small precipitate (chiefly Ca and Si), which quantitatively carried down the Pa. The precipitate was digested with NaOH solution to solubilize silicates and the residue was dissolved in 9 M HCl; this became the feed solution for purification of the Pa by anion exchange. However, attempts to apply this simple process to other batches of the same material failed because of the inhomogeneity of the raw material. Batchwise development and processing ultimately recovered approximately 2 g of Pa from 20 tons of residue, but only after substantial modification of the process, including (Kirby, 1959): addition of Ti as a carrier; dissolution of HCl-insoluble residues in sulfuric acid; extraction with isopropyl ether to reduce the Fe concentration to manageable proportions; and concentration of the Pa by several cycles of extraction into di-isobutylcarbinol (DIBC) and stripping with H_2O_2.

4.4.5 Purification of macroscopic amounts of ^{231}Pa

Preliminary enrichment processes such as those described above afford a high degree of decontamination from Si, Fe, U, Th, Ti, and most bivalent and trivalent elements, including the ^{231}Pa decay products (Fig. 4.1). However, Zr, Ta, and Nb are usually enriched along with the Pa and most recent work has been directed primarily at the separation of those elements, of which Nb is the most troublesome.

Methods reported for the purification of Pa after its enrichment from natural sources are so numerous that only a selected few can be mentioned here. For details of other methods, readers should consult the following reviews (Gmelin, 1942, 1977; Haïssinsky and Bouissières, 1958; Brown and Maddock, 1963, 1967; Pal'shin *et al.*, 1970) and the original publications cited therein.

(a) Precipitation and crystallization

The addition of KF to a solution of Pa(v) in hydrofluoric acid quantitatively precipitates K_2PaF_7 and separates Pa from Zr, Nb, Ti, and Ta (Grosse, 1928; Graue and Kading, 1934b; Bouissières and Haïssinsky, 1951; Cunningham, 1966).

On the other hand, during the fractional crystallization of the double ammonium fluorides, Pa crystallizes before Zr, but after Ti and Ta (Bachelet and Bouissières, 1947). Haïssinsky (Haïssinsky and Bouissières, 1951; Bouissières and Haïssinsky, 1951) separated Pa from Ta, Zr, and Ti by reducing Pa(v) to Pa(iv) with Zn amalgam in 2 M HF. The PaF_4 precipitate was redissolved in aqueous HF or H_2SO_4 in the presence of H_2O_2 or a current of air, which reoxidized the Pa.

Precipitation by H_2O_2 has been widely used to separate Pa from Nb, Ta, and Ti (Grosse, 1930; Bachelet and Bouissières, 1944, 1947; Goble *et al.*, 1958). Walter (1963) decontaminated 500 mg of Pa of about 4% Nb by adding H_2O_2 to a 40% H_2SO_4 solution of the Pa and neutralizing with ammonium hydroxide. Pal'shin *et al.* (1968a) mixed 4.1 mg of Pa with 8 mg each of Nb, Ta, and Zr in 0.25–0.5 M $H_2C_2O_4$, then precipitated the Pa by adding H_2O_2 (to 7.5%) and HCl (to 1.2 M). The precipitate, which formed during an 8–12 h period at room temperature, contained less than 1% total impurities.

The hydrolytic behavior of Pa was used by Kirby (1966) and by Kirby and Figgins (1966) to separate it from up to 13 times as much Nb. When hydrochloric acid was added to a 1 M $H_2C_2O_4$ solution containing equal amounts of the two elements, the precipitate, which developed on heating, contained 94.4% of the Pa and 2.0% of the Nb. Final purification was achieved by dissolution of the precipitate in 7 m H_2SO_4 and evaporation to fumes of SO_3, yielding Pa crystals of undetermined composition, in which the Nb content was reduced from 0.3 to 0.05% in a single stage. According to Brown and Jones (1964) and Bagnall *et al.* (1965), Pa crystallizes quantitatively as $H_3PaO(SO_4)_3$ when Pa_2O_5 is dissolved in a mixture of HF and H_2SO_4 and the solution is evaporated until all F^- has been eliminated. Two recrystallizations of a 10 g batch of Pa reduced the Nb contamination from 4 to 0.18%.

Myasoedov *et al.* (1968c) reported that Pa is quantitatively precipitated by phenylarsonic acid (PAA) from 1 to 7 N HCl, HNO_3, or H_2SO_4. In the absence of $H_2C_2O_4$, Sn(iv), Zr, Nb, Ta, and Ti are also precipitated; however, Pa is separated from Nb and Zr (but not from Ta) when PAA is added to a 2.5 M H_2SO_4 solution containing 0.1 M $H_2C_2O_4$. Both trace and major amounts of Pa have been separated from Nb, Zr, and Fe by this method.

Protactinium was isolated from liquid radioactive waste by sodium silicate, potassium silicate, and an alumina sol mixed in ratios by volume of 1:0.1 to 1. As an example, 0.94 mL of water glass containing 200 g L^{-1} of sodium silicate, and 100 mL of liquid waste containing 20 ppm of uranium was stirred, then 0.94 mL of the same water glass was added and stirred into the mixture along with 1.88 mL of an alumina sol for 10 min. Negatively charged silica particles and positively charged alumina particles absorb U and β^--decay nuclides (Pa) (Mitsubishi, 1995).

The protactinium distribution in a fluoride melt in the presence of solid oxide phases has been calculated (Alekseev *et al.*, 1988, 1989).

(b) Ion exchange

Numerous studies have demonstrated that Pa(v) at trace levels can be separated from the usual contaminants by sorption on anion-exchange resins from hydrochloric acid solutions (Kraus and Moore, 1950, 1951, 1955; Kahn and Hawkinson, 1956; Kraus *et al.*, 1956; Maddock and Pugh, 1956; Hill, 1958; Bunney *et al.*, 1959; Lebedev *et al.*, 1961; D'yachkova *et al.*, 1962; El-Dessouky, 1966; Hicks *et al.*, 1978; Kluge and Lieser, 1980; Alhassanieh *et al.*, 1999; Raje *et al.*, 2001). Typically, the feed solution is 9–10 M HCl, from which Pa(v) is strongly sorbed in anion-exchange resins such as Dowex-1, along with Fe(iii), Ta(v), Nb(v), Zr(iv), U(iv), and U(vi); Th(iv) is only weakly sorbed and appears in the feed effluent. The eluent is a mixture of HCl and HF acids, the concentration of each depending upon the separation required. For example, Zr and Pa are both eluted with 9 M HCl and 0.004 M HF, but Zr may be eluted with 6–7 M HCl, without significant desorption of Pa (Fig. 4.9).

However, attempts to apply this procedure to the purification of weighable amounts of Pa have usually been unsatisfactory, primarily because of the low capacity of the resin (5–50 μg of Pa per gram of resin) and the strong tendency of Pa to hydrolyze in HCl solutions in the absence of complexing anions (Nairn *et al.*, 1958; Kirby, 1959; Collins *et al.*, 1962). Nevertheless, several authors (Jackson *et al.*, 1960a; Stein, 1966; Suzuki and Inoue, 1966) have reported the successful purification of gram quantities of Pa by anion-exchange procedures in which a stable feed solution was prepared by first dissolving the Pa in 9 M HCl

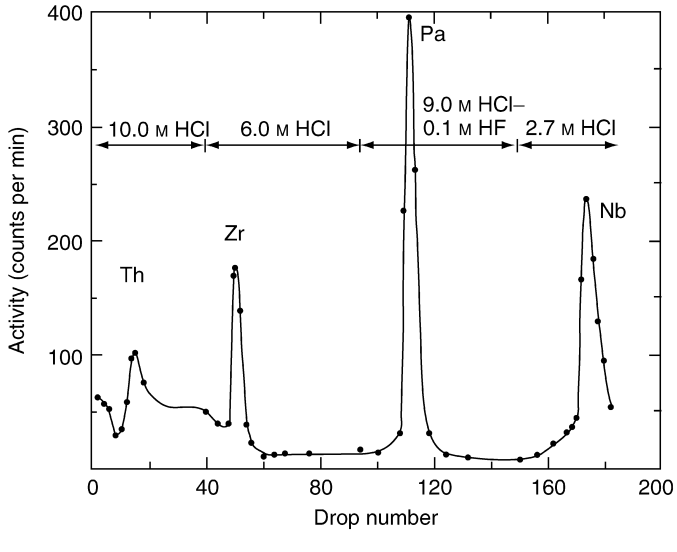


Fig. 4.9 *Separation of Th, Zr, Pa, and Nb on Dowex-*1 *anion-exchange column* (*Hill*, 1958).

containing some HF and then eliminating the F^- by complexing it with Al^{3+} or by evaporation. Sorption properties of Zr, HF, Nb, Ta, and Pa at trace levels towards a macroporous anion exchanger in HF and HCl media were investigated with two ion-exchange methods: static and dynamic. Variations of the distribution coefficients as a function of HCl and HF concentration in the range 0.02–0.8 M for both acids were presented in the form of contour plots and some of the most promising separation possibilities were pointed out (Trubert *et al.*, 1998).

Keller (1963) found that Pa(V), Nb(V), and Ta(V) are all strongly sorbed by an anion exchanger (Dowex-1) from pure hydrofluoric acid solution. However, an increase in $[H^+]$ suppresses the dissociation of HF and sharply reduces the distribution coefficient (K_d) of Pa. Chetham-Strode and Keller (1966) observed that, in >10 M HF, the K_d of Pa was more than an order of magnitude lower than that of Nb and they applied these observations to the separation of Nb and various alkali- and alkaline-earth metal ions from 1 g of Pa_2O_5. The impure Pa was loaded on Dowex-1-Ax10 in 2.5 M HF and eluted with 17 M HF; the product was contaminated only by ^{227}Th, a decay product of ^{231}Pa. Jenkins *et al.* (1975) have reported the purification of approximately 35 g of Pa by this method, with high decontamination factors for Si, Mg, Fe, Al, Cu, and Nb.

The separation of Zr, Ha, Nb, Ta, and Pa was performed on a macroporous anion-exchange resin BIO-RAD AG MP1® in HF media (Monroy-Guzman *et al.*, 1996) and a mixture of 0.01–4.0 M NH_4SCN and 0.05–3.0 M HF media to determine its analytical potential for the quantitative separation of these elements. It was found that the SCN^- concentration in mixtures NH_4SCN–HF had a strong influence on the adsorption of these ions. The K_d of these elements could be explained in terms of the formation of species: $[MF_x]^{(n-x)-}$, $[M(SCN)_y]^{(n-y)-}$, or $[MOF_x]^{(n-x-y)-}$ and $[MO(SCN)_y]^{(n-(2+y)-}$, and mixed fluorothiocyanates of the type $[M(F)_x(SCN)_y]^{(n-x-y)-}$ anionic complexes (Monroy-Guzman *et al.*, 1997).

El-Sweify *et al.* (1985) calculated the distribution of Pa, other actinides, and fission products between the chelating ion exchanger Chelex–100 and certain carboxylic acid solutions.

(c) Solvent extraction and extraction chromatography

Pal'shin *et al.* (1970) have exhaustively reviewed the analytical applications of solvent extraction and Guillaumont and deMiranda (1971) have reviewed the published data as they relate to the ionic species of Pa and the mechanism of its extraction. At tracer levels ($<10^{-4}$ M), Pa(V) is efficiently extracted from aqueous solutions by a wide variety of organic solvents (Hyde and Wolf, 1952; Elson, 1954; Sedlet, 1964); however, only a few have been found useful at macroscopic levels. Dimethyl sulfoxide (DMSO) and the related compounds, diphenyl sulfoxide, and dibenzyl sulfoxide, have received some scrutiny, but it is not clear whether these complexing agents have particular utility for protactinium separation (Reddy and Reddy, 1977; Reddy *et al.*, 1977; Chakravortty and Mohanly, 1979; Chakravortty *et al.*, 1986). As with ion exchange, the chief problems encountered in scaling up tracer-level procedures have been the low capacities of most solvents and the hydrolysis of Pa(v) in the aqueous phase, leading to the formation of 'inextractable polymers'. The most successful extractions of Pa at concentrations up to about 10 g L^{-1} have been with certain ketones, such as di-isopropylketone (DIPK) and DIBK (Goble and Maddock, 1958; Brown *et al.*, 1966a; Myasoedov *et al.*, 1966b) and long-chain alcohols, notably DIBC (Moore, 1955; Kirby, 1959; Brown and Jones, 1964; Scherff and Hermann, 1964; Brown *et al.*, 1966a; Sotobayashi *et al.*, 1977; Pathak *et al.*, 1999a,b).

DIBK was used in some studies for isolation of protactinium from raw materials (Katzin *et al.*, 1950; Katzin, 1952; Kraus and VanWinkle, 1952; Larson *et al.*, 1952; Thompson *et al.*, 1952) and from neutron-irradiated thorium (Meinke, 1946; Hyde and Wolf, 1952; Hill, 1958; Van Winkle and Kraus, 1959; Hyde *et al.*, 1951). Brown *et al.* (1966a) dealt with the problem of hydrolysis by precipitating Pa(v) from aqueous acid solutions with NH_4OH, redissolving the hydrated oxide in either 9 M H_2SO_4 and 0.5 M HF or 9 M HCI and 0.5 M HF, and then complexing the F^- with H_3BO_3. The use of sulfuric acid systems is preferred because of the greater stability of the Pa(v) complexes in that medium. In HCl and HF solutions, hydrolysis proceeds rapidly after the F^- is masked by reaction with $A1^{3+}$ or BO_3^{3-}. After adjustment of the aqueous phase to 4.5 M H_2SO_4 and 6 M HCl, the Pa(v) is extracted with DIBK, stripped with 9 M H_2SO_4 containing some H_2O_2, and re-extracted with DIBC (Fig. 4.10).

The method is said to give good decontamination from nearly all the usual impurities, including Si, Al, Fe, Nb, Zr, Ta, and ^{231}Pa decay products.

DIBC was also used for extraction studies of Pa, Nb, and element 105 – dubnium (Db) from aqueous HBr and HCl. It was shown that the extraction behavior of Db is closer to that of Nb than to Pa. The decreasing extractability from HBr (Pa $>$ Nb $>$ Db) is likely to be due to an increasing tendency of these elements to form a non-extractable polynegative complex species in concentrated HBr in the sequence Pa $<$ Nb $<$ Db (Gober *et al.*, 1992).

Milligram amounts of Pa(v) were extracted from H_2SO_4, HCl or HNO_3 acid solutions by isoamyl alcohol containing 1% PAA or 4% benzeneseleninic acid; good separation from many impurities was reported (Myasoedov *et al.*, 1966a, 1968a). Tetraphenylarsonium chloride has also been studied as a possible extractant for protactinium from hydrochloric or oxalic acid solutions (Abdel Gawad *et al.*, 1976; Souka *et al.*, 1976b). Other extraction agents have also been explored. Thus, l-phenyl-2-methyl-3-hydroxy-4-pyridone dissolved in chloroform (Tamhina *et al.*, 1976, 1978; Herak *et al.*, 1979) quantitatively extracted Pa from hydrochloric acid solution, and Pa can be separated from uranium and/or thorium by appropriate adjustment of the acidity. The antibiotic, tetracycline, was used in radiochemical analytical separations of protactinium from other actinide elements (Saiki *et al.*, 1981) and 5,7-dichloro-8-hydroxyquinoline

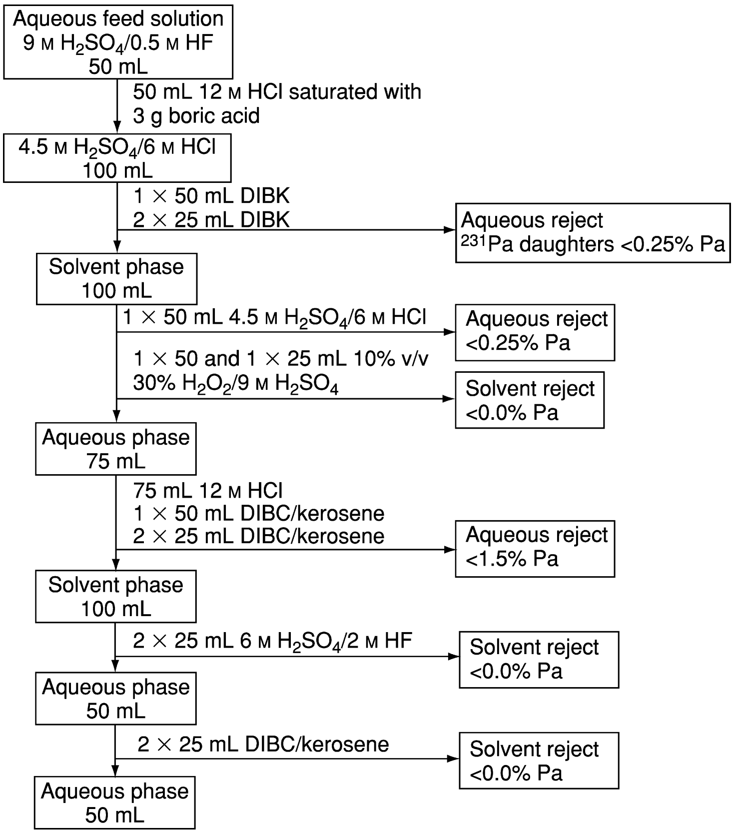


Fig. 4.10 *Purification scheme for* 555 mg *of Pa.* (*According to Brown* et al., 1966*a*.) *Reproduced with permission from Pergamon Press.*

was investigated for the separation of protactinium from niobium, tantalum, and zirconium by solvent extraction (Vaezi-Nasr *et al.*, 1979).

Myasoedov and Pal'shin (1963) and Davidov *et al.* (1966c) proposed an effective method for isolation of Pa from uranium ores and products of their reprocessing by liquid–liquid extraction with the chelating complexing reagent 3,6-bis-[(2-arsenophenyl)azo]-4,5-dihydroxy-2,7-naphthalene disulfo acid (Arsenazo-III) in isoamyl alcohol. It was shown that an effective extraction of Pa from strong acid media, even in the presence of a great amount of Al, Fe(III), Mn(II), rare earth metals, and other elements, took place. The growth of U, Zr, Th, and particularly Nb concentrations in the solutions led to a diminution of Pa isolation. This method was used for analytical control of the separation of gram amounts of Pa(V) under plant conditions.

Thenoyltrifluoroacetone (TTA) had been used for separation and purification of Pa from several elements (Meinke and Seaborg, 1950; Meinke, 1952; Bouissières *et al.*, 1953; Moore, 1955, 1956; Brown *et al.*, 1959; Moore *et al.*, 1959; Poskanzer and Foreman, 1961a,b; Myasoedov and Muxart, 1962a). TTA extraction has been applied to the extraction of Pa from 10 M HCI in which $PaOCl_6^{3-}$ appears to be a principal species (Duplessis and Guillaumont, 1979). Triphenylphosphine oxide (TPPO), triphenylarsine oxide (Maghrawy *et al.*, 1989), and mixtures of TTA and either TBP, TOPO, or TPPO have been investigated (Kandil *et al.*, 1980); a combination of TTA and TOPO has found use in the separation of protactinium and thorium by solvent extraction (Kandil and Ramadan, 1978). TBP (Peppard *et al.*, 1957; Souka *et al.*, 1975b; Svantesson *et al.*, 1979), HDEHP (Shevchenko *et al.*, 1958a; Brown and Maddock, 1963; Myasoedov and Molochnikova, 1968; Myasoedov *et al.*, 1968b; Maghrawy *et al.*, 1988), and di-2-ethyl-hexyl isobutylamide (D2EHIBA) (Pathak *et al.*, 1999a,b) have high capacities for Pa(v), but are relatively unselective.

The extraction by *N*-benzoylphenylhydroxylamine (BPHA) from HCl, and H_2SO_4 solutions was used for the separation of Pa(v) from other elements by Pal'shin *et al.* (1963) and Myasoedov *et al.* (1964). It was found that protactinium complexes with BPHA were extracted by benzene or other solvents from aqueous solutions with a wide range of acid concentrations. D'yachkova and Spitsyn (1964) studied the protactinium, zirconium, and niobium behavior by extraction with BPHA from sulfuric acid solutions. The isolation of the above elements was carried out with 0.2–0.5% solution BPHA in chloroform. The largest difference in extraction ability for these elements was observed with H_2SO_4 concentrations in the aqueous phase greater than 7 N. Rudenko *et al.* (1965) and Lapitskii *et al.* (1966) carried out the separation of protactinium from uranium and thorium by extraction with 0.1 M BPHA solution in chloroform from 4 M HCl.

The Pa(v) extraction by cupferron (CP) had been studied by Maddock and Miles (1949). It was found that Pa was easily extracted by CP in both oxygen-containing and inert solvents from inorganic acid media. Spitsyn and Golutvina (1960) used the extraction with CP for the separation of ^{233}Pa from large amounts of manganese. Rudenko *et al.* (1965) and Lapitskii *et al.* (1965) reported that the neocupferron (NCP), an analog of CP, can be also used for the separation of protactinium from uranium, thorium, and other elements. Uranium and thorium are not extracted by NCP from 2 M HCl solutions, whereas protactinium isolation by a 0.01 M solution of this reagent in chloroform is about 90%. These authors used NCP for isolation of ^{233}Pa from irradiated thorium.

The extraction of Pa by 1-phenyl-3-methyl-4-benzoylpyrazolone (PMBP) in benzene solution from H_2SO_4 media effectively isolated this element from large amounts of Fe(III), La, Nb(v), Th(IV), and U(VI) (Pal'shin *et al.*, 1970). Hence, Pa extraction and isolation by 0.1 M solution of PMBP in benzene from 5 N H_2SO_4 is greater than 98%. For the complete separation of Pa from Zr by this method, a 12% solution of H_2O_2 had been used.

The quantitative extraction of protactinium salicylate with acetone at pH 4 from saturated calcium chloride solutions was reported by Nikolaev *et al.* (1959). Under these conditions zirconium, thorium, uranium, and plutonium are extracted with protactinium. The extraction with salicylate can be used for the separation of protactinium from rare earth and other di- and tervalent elements. The quantitative extraction of protactinium oxychinolate with chloroform from solutions with pH 3–9 was described (Keller, 1966a).

Extraction by tertiary amines in early work was explored only at levels of 10^{-4} M or less, but this procedure shows promise because it permits the extraction of Pa(V) from HF-containing solutions (Moore, 1960; Muxart and Arapaki-Strapelias, 1963; Guillot, 1966; Muxart *et al.*, 1966b; Pal'shin *et al.*, 1971; Moore and Thern, 1974).

The extraction behavior of protactinium in mixtures of uranium, thorium, and neptunium with trilaurylamine from sulfonic acid solutions (Souka *et al.*, 1975c) indicates low distribution coefficients at high acid concentrations; the addition of hydrochloric acid appreciably enhances extraction. The extraction of protactinium (V) with trioctylamine (TOA) dissolved in xylene from thiocyanate solutions containing uranium and thorium have been successfully accomplished (Nekrasova *et al.*, 1975a); tracer amounts of Pa can exist in monomeric form in thiocyanate media for several months, but at Pa(V) concentrations greater than 10^{-6} M, polymers form and the efficacy of TOA as an extractant is seriously impaired (Nekrasova *et al.*, 1975b). Columns impregnated with TOA in a liquid chromatographic system were also used for the separation of ^{262,263}Db in HCl–HF media from Pa and Nb. The data obtained confirm the non-tantalum-like behavior of dubnium in 0.5 M HCl and 0.01 M HF media, and corroborate previously suggested structural differences between the halide complexes of dubnium, niobium, and protactinium, on the one hand, and those of tantalum on the other hand (Zimmerman *et al.*, 1993). Dubnium was shown to be adsorbed on the column from 12 M HCl and 0.02 M HF solutions together with its lighter homologs Nb, Ta, and the pseudohomolog Pa. In elutions with 10 M HCl and 0.025 M HF, 4 M HCl and 0.02 M HF, and 0.5 M HCl and 0.01 M HF, the extraction sequence Ta $>$ Nb $>$ Db $>$ Pa was observed (Paulus *et al.*, 1998, 1999).

The formation of polymers of Pa(V) in the extractions by quaternary ammonium base Aliquat 336 from strongly alkaline solutions can be minimized by the addition of a hydroxycarboxylic acid or aminopolycarboxylic acid (Myasoedov *et al.*, 1980). While the extractability of Pa(V) can be enhanced, the separations are poor. For the systematic study of halide complexation of the group V elements, new batch extraction experiments for Nb, Ta, and Pa were performed with the Aliquat 336 in pure HF, HCl, and HBr solutions. Based on these results, new chromatographic column separations were designed to study separately the fluoride and chloride complexation of Db with Automated Rapid Chemistry Apparatus II (ARCA II). In the system Aliquat 336-HF, after feeding the activity onto the column in 0.5 M HF, dubnium did not elute in 4 M HF (Pa fraction) but showed a higher distribution coefficient close to that of

Nb (and Ta). In the system Aliquat 336-HCl, after feeding onto the column in 10 M HCl, dubnium showed a distribution coefficient in 6 M HCl close to that of Nb establishing an extraction sequence Pa $>$ Nb greater than or equal to Db $>$ Ta, which was theoretically predicted by considering the competition between hydrolysis and complex formation (Paulus *et al.*, 1998, 1999). Separation of ^{231}Pa from U and other impurities has been provided by an extraction-chromatographic method using quaternary ammonium-Kel-F materials (Zhang Xianlu *et al.*, 1993).

Extraction of protactinium(V) chloro complexes by tricaprylamine and its separation from Th(IV), U(VI), and rare earths has been described (El-Yamani and Shabana, 1985).

(d) Large-scale recovery of protactinium-231

Brown and Whittaker (1978) have described a new, 'relatively simple' method for the recovery and purification of protactinium-231. It has been applied with signal success to the recovery of Pa from various residues containing 1.73 g of protactinium in a state of high chemical and radiochemical purity. Efficient separation of ^{231}Pa was readily effected by dissolving the ^{231}Pa-containing residues in 5 M hydrofluoric acid. Excess ammonia is added to precipitate the hydrous oxides, which after several washes with water are redissolved in 2 M nitric acid. This precipitate is considerably enriched in ^{231}Pa. Washing the precipitated hydrous oxides with 0.5–4.0 M HNO_3 and/or 0.5 M HNO_3 and 0.3 M H_2O_2, in which protactinium(V) hydrous oxide, is essentially insoluble, removes much of the impurities carried in the initial hydrous oxide precipitation. Repetition of this cycle twice more yields Pa_2O_5 of high purity. The final traces of silicon are then removed by dissolving the hydrous oxides in 20 M HF and evaporating the solution to dryness. Recovery yields range from 92 to 96% from initial samples containing 30–75 wt% ^{231}Pa. The purity of the product is generally greater than 99%; it is also radiochemically pure.

4.4.6 Preparation of pure ^{234}Pa and ^{234m}Pa

Because of its short half-life, 1.17 min ^{234m}Pa is frequently used for classroom demonstrations of radioactive decay and growth (Booth, 1951; Carsell and Lawrence, 1959; Overman and Clark, 1960). Pure ^{234m}Pa (and its ground-state isomer, 6.7 h ^{234}Pa) can be coprecipitated directly from a 6 M HCl solution of $(NH_4)_2U_2O_7$ with BPHA (Cristallini and Flegenheimer, 1963). The procedure is rapid and gives a high degree of decontamination from both U and Th.

However, most authors prefer to make a preliminary separation of 24.1 day ^{234}Th, from which the ^{234m}Pa (and ^{234}Pa) can be repeatedly 'milked'. The classical procedure of Crookes (1900) is still one of the most widely used for this purpose (Harvey and Parsons, 1950; Barendregt and Tom, 1951;

Bouissières *et al.*, 1953; Forrest *et al.*, 1960; Bjørnholm and Nielsen, 1963): 10–200 g of $UO_2(NO_3)_2 \cdot 6H_2O$ are dissolved in diethyl ether. The aqueous phase formed by the water of crystallization retains the ^{234}Th and some U. Repeated extraction with fresh ether removes the remaining U. Alternatively, the ^{234}Th is purified and concentrated by coprecipitation with $Fe(OH)_3$ in the presence of $(NH_4)_2CO_3$ (Hahn, 1921; Harvey and Parsons, 1950), by cation exchange from HCl solution (Zijp *et al.*, 1954; Suner *et al.*, 1974), by anion exchange from HNO_3 solution (Bunney *et al.*, 1959), or by extraction with tertiary amines (Moore and Thern, 1974; Carswell and Lawrence, 1959).

Once the ^{234}Th has been purified, the ^{234m}Pa and ^{234}Pa quickly regain equilibrium and can be isolated by any of the methods described above for the purification of ^{231}Pa, except, of course, carrier-free precipitation. Solvent extraction is the most suitable, because of its speed and selectivity, at tracer levels, Pa(v) is rapidly and quantitatively separated from Th(iv) by extraction from 6 M HCl solution with any number of organic solvents, notably DIPK, DIBK, DIPC, and DIBC (Moore, 1955; Myasoedov *et al.*, 1966a). The ^{234}Th remains in the aqueous phase. To prepare ^{234m}Pa free of ^{234}Pa, the first two or three organic extracts are discarded and, after 10–15 min, the re-grown ^{234m}Pa is extracted with fresh solvent (Bjørnholm and Nielson, 1963).

Fajans and Göhring (1913b) first separated *brevium* by selective adsorption on lead plates and by coprecipitation with Ta_2O_5. The addition of ^{232}Th keeps the mixture of ^{234}Th and ^{234m}Pa more quantitatively in solution (Guy and Russell, 1923; Jacobi, 1945). Hahn (1921) coprecipitated the mixture of ^{234}Th and ^{234m}Pa with LaF_3, leaving ^{234}Pa in the filtrate. Zijp *et al.* (1954) concentrated ^{234}Pa by MnO_2 precipitations (Maddock and Miles, 1949), alternating with extraction by TTA (Meinke, 1952).

Bjørnholm *et al.* (1967) milked 0.5–1 mCi of ^{234}Pa from 0.8 mCi of ^{234}Th by extraction into hexone (methyl isobutyl ketone, MIK) from 6 M HC1 solution. It is noteworthy, however, that many of the same problems were encountered in the initial concentration of ^{234}Th from 2 tons of U metal as in scaling up laboratory procedures for the concentration of macroscopic amounts of ^{231}Pa from natural sources.

4.4.7 Preparation of pure ^{233}Pa

Irradiation of 1 g ^{232}Th (as metal, oxide, chloride, nitrate, or basic carbonate) for 1 day in a thermal-neutron flux of 2×10^{14} n cm^{-2} s^{-1} will produce approximately 5 Ci of ^{233}Pa (Schuman and Tromp, 1959). Detailed procedures for the isolation of ^{233}Pa from Th targets are given in several review articles (Hyde and Wolf, 1952; Hyde, 1954, 1956; Haïssinsky and Bouissières, 1958; Kirby, 1959; Pal'shin *et al.*, 1970). In general, the target is dissolved in concentrated HCl or HNO_3 (usually containing 0.01–0.1 M HF as a catalyst) and the ^{233}Pa is separated from Th and other impurities by one, or a combination, of the anion-exchange and solvent extraction methods described above. Alternatively, 3 g of Th metal irradiated in a reactor with an irradiation time of 1 day in a thermal flux of 3×10^{13} n cm^{-2} s^{-1} are dissolved in nitric acid. The ^{233}Pa is adsorbed on an anion-exchange column, eluted, then is extracted by TOPO (Kuppers and Erdtmann, 1992).

A preliminary concentration by coprecipitation (Katzin and Stoughton, 1956; Fudge and Woodhead, 1957; Katzin, 1958) is often used, and was, in fact, the method adopted by Codding *et al.* (1964) to isolate 1 gram of ^{233}Pa after solvent extraction with MIK or DIPK gave unaccountably poor yields. Leaching the MnO_2 with a mixture of HNO_3 and H_2O_2 removed the Mn without loss of ^{233}Pa, which was subsequently dissolved in 6 M H_2SO_4 and reprecipitated with HNO_3. On the other hand, Schulz (1972) reported good extraction of ^{233}Pa by DIBC from 7.4 M HNO_3 solutions containing 1.4 M Th $(NO_3)_4$ and 480 Ci L^{-1} of ^{233}Pa. Macroscopic amounts of ^{233}Pa have also been recovered from HNO_3 solutions of irradiated ThO_2 by adsorption on powdered unfired Vycor glass and silica gel (Moore and Rainey, 1964; Goode and Moore, 1967); at tracer levels, ^{233}Pa has been separated from Th targets by adsorption on silica gel (Davydov *et al.*, 1965; Spitsyn *et al.*, 1969; Chang *et al.*, 1974; Chang and Ting, 1975b), on quartz sand (Sakanoue and Abe, 1967), and on activated charcoal saturated with PAA (Pal'shin *et al.*, 1966). Separations with cation and chelating resins (Kurodo and Ishida, 1965; Myasoedov *et al.*, 1969), by paper chromatography and paper electrophoresis (Vernois, 1958, 1959; Myasoedov *et al.*, 1969), and by reversed-phase partition chromatography (Fidelis *et al.*, 1963) have also been reported.

4.4.8 Toxic properties

^{231}Pa is dangerous to organisms, similar to other α-emitters with comparatively short half-lives. Once in organisms it accumulates in kidneys and bones. The maximum amount of protactinium considered not harmful after absorption by an organism is 0.03 μCi. It corresponds to 0.5 μg ^{231}Pa. Protactinium-231, contained in the air as an aerosol, is 2.5×10^8-fold more toxic than hydrocyanic acid at the same concentrations (Bagnall, 1966a). Therefore all operations with weighable amounts of ^{231}Pa are carried out in special isolated boxes.

4.4.9 Applications of protactinium

Pa was used for the preparation of a scintillator for detecting X-rays, comprising complex oxides of Gd, Pa, Cs, rare earth metals and other elements. This scintillator, which can significantly increase relative light emission outputs without increasing background, is used in for detecting X-rays, particularly in an X-ray computed tomography apparatus (Hitachi Metals, 1999). The coating material for a color cathode ray tube with bright green fluorescence was created by doping wih Pa (Toshiba, 1995).

Mixed oxides of Nb, Mg, Ga and Mn, doped with 0.005–0.52% Pa_2O_5, were used as high temperature dielectrics (up to 1300°C) for ceramic capacitors (Fujikawa *et al.*, 1996).

One of the important applications of Pa can be in the determination of ancient subjects using a $^{231}Pa/^{235}U$ dating method. This method was used for the dating of one of the Qafzeh human skulls, Qafzen 6, excavated in 1934 by Neuville and Stekelis and conserved at the Institut de Paléontologie Humaine in Paris, by non-destructive gamma-ray spectroscopy. A long-term measurement resulted in an age of (94 ± 10) Ka and confirmed the great antiquity of the Proto-Cro-Magnons of the Near East, contributing to the establishment of modern man's chronology (Yokoyama *et al.*, 1997). The Neanderthal hominid Tabun C1, found in Israel by Garod and Bate, was attributed to either layer B or C of their stratigraphic sequence. Gamma-ray spectroscopy of the $^{231}Pa/^{235}U$ ratios of two bones from this skeleton was used to determine their age. Calculations gave the age of the Tabun C1 mandible as 345 Ka. This suggests that Neanderthals did not necessarily coexist with the earliest modern humans in the region. The early age determined for the Tabun skeleton would suggest that Neanderthals survived as late in the Levant as they did in Europe (Schwarcz *et al.*, 1998). Uranium-series dating of bones and teeth from the Chinese Paleolithic sites has also been used (Chen and Yuan, 1988).

As a result of the development of the nuclear industry (e.g. nuclear power engineering and nuclear powered fleets), a considerable amount of radioactive wastes and spent nuclear fuel is accumulating in the world. Geological disposal of solid and solidified nuclear waste is considered as being economical, technically and ecologically the most feasible approach to completion of the nuclear fuel cycle. Thus determination of chemical behavior of actinides elements, Pa included, is an important problem of environmental science.

The sorption behavior of Pa, which is a decay product of uranium, was studied on the principal rock types from the potential areas selected for construction of a repository. The sorption distribution coefficients (K_d) of Pa were determined under ambient conditions in oxic and anoxic (N_2) atmospheres using natural fresh and brackish groundwater; and the values obtained were 0.07–2.3 and 1.7–12 $m^3 kg^{-1}$, respectively (Kulmala *et al.*, 1998). Pickett and Murrell (1997) presented the first survey of $^{231}Pa/^{235}U$ ratios in volcanic rocks; such measurements were made possible by new mass spectrometric techniques. It was shown that the high $^{231}Pa/^{235}U$ ratios in basalts reflect a large degree of discrimination between two incompatible elements, posing challenges for modeling of melt generation and migration. Fundamental differences in $^{231}Pa/^{235}U$ ratios among different basaltic environment are likely related to differences in melting zone conditions (e.g. melting rate). Strong disequilibria in continental basalts demonstrate that Pa–U fractionation is possible in both garnet and spinel mantle stability fields.

4.5 ATOMIC PROPERTIES

Experimental measurements (Marrus *et al.*, 1961; Giaechetti, 1966; Richards *et al.*, 1968) and theoretical calculations (Judd, 1962; Wilson, 1967, 1968) agree that the ground state configuration of the neutral Pa atom is almost certainly [Rn] $5f^26d^17s^2$. However, some unpublished calculations by Maly (cited by Cauchois (1971)) indicated that the total relativistic energy of that structure was 0.9 eV higher than that of a $5f^16d^27s^2$ configuration, implying that the latter may be the more stable of the two. Giaechetti (1967) found that the ground state configuration of the first ion of Pa (Pa^{1+}) was $5f^27s^2$ and this was confirmed by theoretical calculations, which also yielded $5f^26d^1$, $5f^2$ and $5f^1$ as the ground state configurations of Pa^{2+}, Pa^{3+} and Pa^{4+}, respectively. Crystal structure stabilities and the electronic structure of Pa have been discussed by Wills and Ericsson (1992).

The emission spectrum of Pa was first recorded by Schüler and Gollnow (1934), who reported a large number of lines in the visible region, many of which showed hyperfine splitting patterns, indicating a nuclear spin of 3/2 for ^{231}Pa. Tomkins and Fred (1949) listed 263 lines in the ultraviolet region sensitive to copper spark excitation. The emission spectrum excited by a microwave discharge tube was measured by Richards and co-workers (1963, 1968), who recorded some 14 000 lines between 3 μm and 400 nm, about half of which were fitted into a level scheme of about 200 even and 300 odd levels.

Table 4.4 lists recommended X-ray atomic energy levels, based on the X-ray wavelengths re-evaluated by Bearden (1967) and by Bearden and Burr (1967).

The Mössbauer effect has been studied by Croft *et al.* (1968) with the 84.2 keV γ-ray of ^{231}Pa, following β^--decay of ^{231}Th; resonance absorption was detected

Table 4.4 *Recommended values of the atomic energy levels* (eV) *of Pa* (*measured values of the X-ray absorption energies are shown in parentheses*) (*Bearden and Burr*, 1967).

Level	*Energy* (eV)	*Level*	*Energy* (eV)
K	1 12 601.4 ± 2.4	N_I	1387.1 ± 1.9
L_I	21 104.6 ± 1.8 (21 128)	N_{II}	1224.3 ± 1.6
L_{II}	20 313.7 ± 1.5 (20 319)	N_{III}	1006.7 ± 1.7
L_{III}	16 733.1 ± 1.4 (16 733)	N_{IV}	743.4 ± 2.1
M_I	5366.9 ± 1.6	N_V	708.2 ± 1.8
M_{II}	5000.9 ± 2.3	N_{VI}	371.2 ± 1.6
M_{III}	4173.8 ± 1.8	N_{VII}	359.5 ± 1.6
M_{IV}	3611.2 ± 1.4 (3608)	O_I O_{II}	309.6 ± 4.3
M_V	3441.8 ± 1.4 (3436)	O_{III} O_{IV} O_V	222.9 ± 3.9 94.1 ± 2.8

with absorbers of both Pa_2O_5 and PaO_2. No isomer shift between the valence states was observed.

4.6 THE METALLIC STATE

Grosse (1934a) prepared metallic Pa by two methods: (1) Pa_2O_5 was bombarded for several hours with 35 kV electrons at a current strength of 5–10 mA and (2) the pentahalide (Cl, Br, I) was heated on a tungsten filament at a pressure of 10^{-6} to 10^{-5} torr. Later authors have prepared the metal by reduction of PaF_4 with the vapors of Ba (Sellers *et al.*, 1954; Bansal, 1966; Cunningham, 1966, 1971; Dod, 1972), Li (Fowler *et al.*, 1965; Cunningham, 1971), or Ca (Marples, 1966). A Zn–Mg reductant is said to yield an impure Pa product (Lee and Marples, 1973).

In the method used by Cunningham and his co-workers at Berkeley (Cunningham, 1971; Dod, 1972), PaF_4 is mixed with barium in a crucible fabricated from a single crystal of BaF_2 (or LiF) and supported in a tantalum foil cylinder. The assembly is evacuated to below 10^{-6} torr and heated inductively to 1250–1275°C for 4–5 min. The BaF_2 crucible is then melted by raising the temperature to 1600°C for 1.5 min and then molten Pa metal agglomerates as a small sphere at the bottom of the Ta support ring. Individual preparations are limited to about 15 mg.

Subsequently, individual preparations of Pa metal of up to 0.5 g have been successfully executed by a modified Van Arkel technique (Baybarz *et al.*, 1976; Brown *et al.*, 1977; Bohet and Muller, 1978; Brown, 1982; Spirlet, 1982). The starting material is protactinium carbide obtained by reduction of Pa_2O_5 with carbon. Heating the protactinium carbide with I_2 generates volatile PaI_5, which is then decomposed on a heated tungsten filament or, better, a sphere (Spirlet, 1979) using induction heating. Protactinium can be precipitated from diluted HF, H_2SO_4 solutions as a fine film on several metal plates (Zn, Al, Mn, and other) (Camarcat *et al.*, 1949; Haïssinsky and Bouissières, 1958; Stronski and Zelinski, 1964). The electrolytic reduction of Pa from NH_4F solutions in the presence of triethylamine at pH 5.8 and 10–20 mA cm^{-2} also has been realized (Emmanuel-Zavizziano and Haïssinsky, 1938). Preparation of a protactinium measurement source by the electroplating method also has been reported by Li Zongwei *et al.* (1998).

The availability of pure, single-crystal Pa metal has made possible the measurement of important physical parameters that cast light on the electronic structure of Pa and for the calculation of its optical properties (Gasche *et al.*, 1996). A theoretical calculation by Soderling and Eriksson (1997) predicted that protactinium metal will undergo a phase transition to the α-U orthorhombic structure below 1 Mbar (1 Mbar $\sim$100 GPa) pressure. At higher pressures, the β-phase re-enters into the phase diagram and at the highest pressures an ideal *hcp* structure becomes stable. Hence, Soderling and Eriksson expect Pa to undergo a sequence of transitions, with the first transition taking place at 0.25 Mbar and the subsequent ones above 1 Mbar. The β→α-U transition is triggered by the pressure-induced promotion of the spd-valence electrons to 5f states. In this regard Pa approaches uranium, which at ambient conditions has one more 5f electron than Pa at similar conditions. At higher compression of Pa, the 5f band broadens and electrostatic interactions in combination with Born–Mayer repulsion become increasingly important and drive Pa gradually to more close-packed structures. At ultra-high pressures, the balance between electrostatic energy, Born–Mayer repulsion, and one-electron band energy stabilizes the *hcp* (ideal packing) structure.

Recent experimental results (Haire *et al.*, 2003) confirm that the stable room temperature and pressure phase of Pa metal is the body-centered tetragonal (*bct*) phase. Under high pressure this phase is stable until 77(5) GPa (77 GPa ~0.77 Mbar) where it is converted to orthorhombic, the α-uranium phase, with a small (0.8%) volume collapse. The relative volume of the *bct* phase decreased smoothly from 1 atm down to a volume ratio of ~0.7 before the high-pressure phase transformation. Experiments continued to a pressure of 130 GPa with no further phase change but with a smooth decrease in the volume of the orthorhombic phase of ~0.62. Haire *et al.* (2003) attribute the structural phase change to an increase in 5f bonding at the higher pressures.

The superconducting properties of Pa metal have been described by Smith *et al.* (1979), who determined the superconducting transition temperature and upper critical magnetic field. Since the superconducting properties of Pa are markedly affected by its 5f electronic structure, it is now evident that Pa is a true actinide element. The heat capacity of a single Pa crystal in the temperature range 4.9–18 K has been reported (Stewart *et al.*, 1980). The unit cell volume of Pa metal first decreases and then increases on cooling from 300 to 50 K (Benedict *et al.*, 1979). The importance of the expansion coefficient in the explanation of specific-heat parameters has been discussed by Mortimer (1979). A Mössbauer resonance of ^{231}Pa at 84.2 keV in Pa metal has been reported; the electric field gradient in Pa metal is $|eq_Z| = (2.05 \pm 0.15) \times 10^{18}$ V cm^{-2} (Friedt *et al.*, 1978; Rebizant *et al.*, 1979). The vapor pressure of liquid Pa metal in the temperature range 2500–2900 K has been measured by a combination of mass spectrometry and Knudsen effusion techniques; the vapor pressure (in Pascals) is given (Bradbury, 1981) by:

$$\log[P(\text{Pa(liq)})] = -[(31\,328 \pm 375)/T] + (10.83 \pm 0.13).$$

Pa metal is malleable and ductile (Zachariasen, 1952; Sellers *et al.*, 1954). Other physical properties are summarized in Table 4.5. The enthalpy of sublimation of Pa(s) at 298 K has been calculated to be 660 (Bradbury, 1981) or 570 kJ mol^{-1} (Kleinschmidt *et al.*, 1983).

Metallic Pa is attacked by 8 M HCl, 12 M HF, or 2.5 M H_2SO_4, but the initial reaction ceases quickly, possibly because of the accumulation of a protective layer resulting from the hydrolysis of Pa(V) or Pa(IV) at the metal surface.

Table 4.5 *Some physical properties of protactinium metal.*

Property	*Observed or calculated value(s)*	*References*
crystal structure	body-centered tetragonal (14/*mmm*)	Zachariasen (1952); Asprey *et al*. (1971)
	high temp. form is fcc or bcc	
lattice parameters (Å)	$a = 3.925 \pm 0.005$, $c = 3.238 \pm 0.007$ (RT)	Zachariasen (1952); Sellers *et al*. (1954)
	$a = 3.924 \pm 0.001$, $c = 3.239 \pm 0.0005$ (18°C)	Marples (1966)
	(a/c approaches 1 with increased temperature)	
	$a = 3.929 \pm 0.001$, $c = 3.241 \pm 0.002$ (RT)	Cunningham (1966)
	$a = 3.921 \pm 0.001$, $c = 3.235 \pm 0.001$ (RT)	Bohet (1977)
	$a = 5.02$ (high temperature form fcc)	Asprey *et al*. (1971)
	$a = 5.018$ (high temperature form fcc)	Bohet (1977)
	$a = 3.81$ (high temperature form bcc)	Marples (1965)
X-ray density (g cm^{-3})	15.37 ± 0.08	Zachariasen (1952)
metallic radius (Å)	1.63 for coordination number 12	Zachariasen (1952)
melting point (°C)	1575 ± 20	Marples (1966)
	1560 ± 20	Cunningham (1966)
	1565 ± 20	Cunningham (1971)
	1562 ±15	Dod (1972)
vapor pressure (atm)	1×10^{-8} at ~2400 K	Cunningham (1971)
	5.1×10^{-5} at 2200 K	Murbach (1957)
magnetic susceptibility (emu mol^{-1}; 20–298 K)	$(250 \pm 50) \times 10^{-6}$ (temperature-independent)	Cunningham (1966)
	$(268 \pm 14) \times 10^{-6}$ (temperature-independent)	Bansal (1966)
	$(189 \pm 6.5) \times 10^{-6}$ (temperature-independent)	Dod (1972)
superconducting transition temperature (K)	1.4	Fowler *et al*. (1965, 1974)
	?	Smith *et al*. (1979)
	2	Francis and Theng-Da Tchang (1935)
	2	Launay and Dolechek (1947)

Table 4.6 *Preparation and structure of protactinium–noble-metal alloy phases* (*Erdmann*, 1971; *Erdmann and Keller*, 1971, 1973).

Compound	*Reduction temperature* (°C)	*Structure type*	*Lattice parameters* (Å) *a*	*c*
Pt_3Pa	1250 ± 50	Cd_3Mg (hex)	5.704	4.957
Pt_5Pa	1200 ± 50	Ni_5U	7.413	
Ir_3Pa	1550 ± 50	Cu_3Au	4.047	
Rh_3Pa	1550 ± 50	Cu_3Au	4.037	
$Be_{13}Pa$	1300 ± 50	$NaZn_{13}$	10.26	

The metal does not react with 8 M HNO_3 even in the presence of 0.01 M HF. The most effective solvent found thus far is a mixture of 8 M HCl and 1 M HF (Cunningham, 1971).

According to Dod (1972), metal samples exposed to air at room temperature show little or no tarnishing over a period of several months. A slight loss of metallic luster was observed when a sample of Pa metal was heated in air for 1 h at 100°C. Heating for 1 h at 300°C caused the sample to turn grayish white and begin to disintegrate. Pa metal exposed to O_2, H_2O, or CO_2 at 300 and 500°C yielded Pa_2O_5; reaction with NH_3 and H_2 produced PaN_2 and PaH_3, respectively. The metal reacts quantitatively with excess I_2 above 400°C to yield a sublimate of crystalline, black PaI_5 (Sellers *et al.*, 1954; Brown *et al.*, 1967b).

4.6.1 Alloys

Erdmann and Keller (Erdmann, 1971; Erdmann and Keller, 1971, 1973) have prepared Pa–noble-metal alloy phases by reduction of Pa_2O_5 with highly purified H_2 in the presence of Pt, Ir, and Rh. Preparation conditions and some properties of these intermetallic compounds are listed in Table 4.6. Reaction of Pa_2O_5 with beryllium metal has been reported by Benedict *et al.* (1975) to form $Be_{13}Pa$.

4.7 SIMPLE AND COMPLEX COMPOUNDS

4.7.1 Protactinium hydride

Perlman and Weisman (1951) and Sellers *et al.* (1954) reacted H_2 with Pa metal at about 250°C and a pressure of about 600 torr, and obtained a black flaky substance, isostructural with β-UH_3. The compound was cubic, with a unit cell constant $a = (6.648 \pm 0.005)$ Å. However, Dod (1972) reported the formation at 100, 200, and 300°C of a gray, powdered substance that is isostructural with α-UH_3. The unit cell constant of α-PaH_3 is (4.150 ± 0.002) Å for the product obtained at 100 and 200°C and (4.154 ± 0.002) Å at 300°C. Subsequently, Brown (1982) prepared α- and β-PaH_3 at 250 and 400°C, respectively.

4.7.2 Protactinium carbides

Lorenz *et al.* (1969) prepared PaC by reduction of Pa_2O_5 with graphite at reduced pressure and temperatures above 1200°C. The product obtained at 1950°C was face-centered cubic (*fcc*) (NaCl type) with $a = (5.0608 \pm 0.0002)$ Å. At 2200°C, some additional weak lines, attributable to PaC_2, were observed; this structure was body-centered tetragonal with $a = (3.61 \pm 0.01)$ Å and $c = (6.11 \pm 0.01)$ Å. According to Sellers *et al.* (1954), PaC was 'probably' prepared by the reduction of PaF_4 with Ba in a carbon crucible. The magnetic susceptibility of PaC between 4 K and room temperature was measured by Hery *et al.* (1977). The magnetic susceptibility of PaC is weak (about -50×10^6 (emu cg)·mol^{-1}) and essentially independent of temperature, which may be taken to indicate the absence of 5f electrons and the presence of Pa(v) in the compound. Theoretical calculations by Maillet (1982) suggest that in ThC 5f electron participation in the bonding is minimal, but that in PaC the 5f electron bonding contribution is important.

4.7.3 Protactinium oxides

The known binary oxides of Pa are listed in Table 4.7. White Pa_2O_5 is obtained when the hydrated oxide, $Pa_2O_5 \cdot nH_2O$, and a wide variety of protactinium compounds as well are heated in oxygen or air above 500°C (Kirby, 1961) or 650°C (Sellers *et al.*, 1954; Keller, 1977). Thermochemical studies (Kleinschmidt and Ward, 1986) and differential thermal analysis shows three endothermic peaks, with maxima at 80, 390, and 630°C, and an exothermic peak, whose maximum occurs at 610°C (Stchouzkoy *et al.*, 1968). Several crystal modifications can be prepared, depending on the temperature to which the Pa_2O_5 is heated (Stchouzkoy *et al.*, 1964, 1966b; Roberts and Walter, 1966).

Black PaO_2 is prepared by the reduction of Pa_2O_5 with H_2 at 1550°C (Sellers *et al.*, 1954). Pa dioxide did not dissolve in H_2SO_4, HNO_3, or HCl solutions but reacted with HF because of the Pa(iv) oxidation to the pentavalent state by O_2 (Pal'shin *et al.*, 1970). Four intermediate phases have been identified by reduction of the pentoxide and oxidation of the dioxide (Roberts and Walter, 1966). A monoxide has been claimed to exist as a coating on metal preparations (Sellers *et al.*, 1954).

The heat of formation of Pa_2O_5 is about 106 kJ mol^{-1} as calculated by Augoustinik (1947). Pa_2O_5 did not dissolve in concentrated HNO_3 (Jones, 1966), but dissolved in HF and in a HF + H_2SO_4 mixture (Codding *et al.*, 1964) and reacted at high temperatures with solid oxides of metals of groups I and II of the periodic table (Pal'shin *et al.*, 1970).

Ternary oxides and oxide phases of different compositions and structures have been prepared by reaction of PaO_2 and Pa_2O_5 with the oxides of other elements (Table 4.8) (Keller, 1964a,b, 1965a–c, 1966a,b, 1971; Keller and Walter, 1965; Keller *et al.*, 1965; Iyer and Smith, 1966).

Table 4.7 *Binary oxides of protactinium.*

Composition	*Symmetry*	*Lattice constants*				*Temp, range of existence* (°C)	*References*
		a (Å)	*b* (Å)	*c* (Å)	α (deg.)		
PaO	cubic (NaCl)	4.961					Sellers *et al.* (1954)
PaO_2	fcc (CaF_2)	5.509					Roberts and Walter (1966)
PaO_2	fcc	5.505					Sellers *et al.* (1954)
$PaO_{2.18}$–$PaO_{2.21}$	fcc	5.473					Roberts and Walter (1966)
$PaO_{2.33}$	tetragonal	5.425		5.568			Roberts and Walter (1966)
$PaO_{2.40}$–$PaO_{2.42}$	tetragonal	5.480		5.416			Roberts and Walter (1966)
$PaO_{2.42}$–$PaO_{2.44}$	rhombohedral	5.449			89.65		Roberts and Walter (1966)
Pa_2O_5	fcc	5.446				650–700	Sellers *et al.* (1954)
Pa_2O_5	tetragonal	5.429		5.503		700–1000	Roberts and Walter (1966)
Pa_2O_5	tetragonal	10.891		10.992		700–1050	Stchouzkoy *et al.* (1968)
Pa_2O_5	hexagonal	3.820		13.225		1050–1500	Stchouzkoy *et al.* (1968)
Pa_2O_5	hexagonal	3.817		13.220		1000–1500	Roberts and Walter (1966)
Pa_2O_5	orthorhombic	6.92	4.02	4.18		?	Sellers *et al.* (1954)
Pa_2O_5	rhombohedral	5.424			89.76	1240–1400	Roberts and Walter (1966)

Table 4.8 *Polynary oxides of protactinium* (*Keller*, 1966*a*, 1971; *Palshin* et al., 1970).

		Lattice constants			
Compound	*Structure type*	*a* (Å)	*b* (Å)	*c* (Å)	*β* (deg.)
$LiPaO_3$	unknown				
Li_3PaO_4	tetragonal (Li_3UO_4)	4.52		8.48	
Li_7PaO_6	hexagonal (Li_7BiO_6)	5.55		15.84	
(2–4)$Li_2O \cdot Pa_2O_5$	cubic (fluorite phase)				
(2–4)$Na_2O \cdot Pa_2O_5$					
$NaPaO_3$	orthorhombic ($GdFeO_3$)	5.82	5.97	8.36	
Na_3PaO_4	tetragonal (Li_3SbO_4)	6.68			
$KPaO_3$	cubic ($CaTiO_3$)	4.341			
$RbPaO_3$	cubic ($CaTiO_3$)	4.368			
$CsPaO_3$	unknown				
$BaPaO_3$[a]	cubic ($CaTiO_3$)	4.45			
$SrPaO_3$[a]	unknown				
$Ba(Ba_{0.5}Pa_{0.5})O_{2.75}$	cubic (Ba_3WO_6)	8.932			
$GaPaO_4$	unknown				
$(La_{0.5}Pa_{0.5})O_2$	cubic (CaF_2)	5.525			
$Ba(LaO_{0.5}Pa_{0.5})O_3$	cubic (Ba_3WO_6)	8.885			
α-$PaGeO_4$	tetragonal ($CaWO_4$)	5.106		11.38	
β-$PaGeO_4$[a]	tetragonal ($ZrSiO_4$)	7.157		6.509	
α-$PaSiO_4$[a]	tetragonal ($ZrSiO_4$)	7.068		6.288	
β-$PaSiO_4$[a]	monoclinic ($CePO_4$)	6.76	6.92	6.54	104.83
Pa_2O_5/ThO_2	cubic (fluorite phase)				
$PaO_2 \cdot 2Nb_2O_5$[a]	tetragonal ($Th_{0.25}NbO_3$)	7.76		7.81	
$PaO_2 \cdot 2Ta_2O_5$[a]	tetragonal ($Th_{0.25}NbO_3$)	7.77		7.79	
$Pa_2O_5 \cdot 3Nb_2O_5$	hexagonal ($UTa_3O_{0.67}$)	7.48		15.81	
$Pa_2O_5 \cdot 3Ta_2O_5$	hexagonal ($UTa_3O_{10.67}$)	7.425		15.76	

[a] Could not be prepared in the pure state; always contained varying amounts of Pa(v).

The pale yellow product, which precipitates upon addition of H_2O_2 to a solution of Pa(v) in 0.25 M H_2SO_4, has been assigned the formula $Pa_2O_9 \cdot 3H_2O$ (Stchouzkoy *et al.*, 1966b). It is considered to be an unstable peroxide with a composition that varies with time over the range $Pa_2O_x \cdot 3H_2O$ with $5 < x < 9$.

4.7.4 Protactinium halides

Methods for preparing all the binary halides and many of the oxyhalides of Pa(iv) and Pa(v) are summarized schematically in Figs. 4.11, 4.12, and 4.13; those compounds which have been fully characterized are listed in Table 4.9. The preparative methods shown in Figs. 4.11 and 4.12 use an aqueous acid solution of Pa(v) as the starting material for the synthesis of binary protactinium halides. PaF_5 can be prepared by fluorination of PaC at 570 K or $PaCl_5$ at 295 K. The reaction products are isostructural with β-UF_5 (Brown *et al.*, 1982a). $PaF_5 \cdot 2H_2O$ is prepared by the evaporation of Pa solution in 30% HF

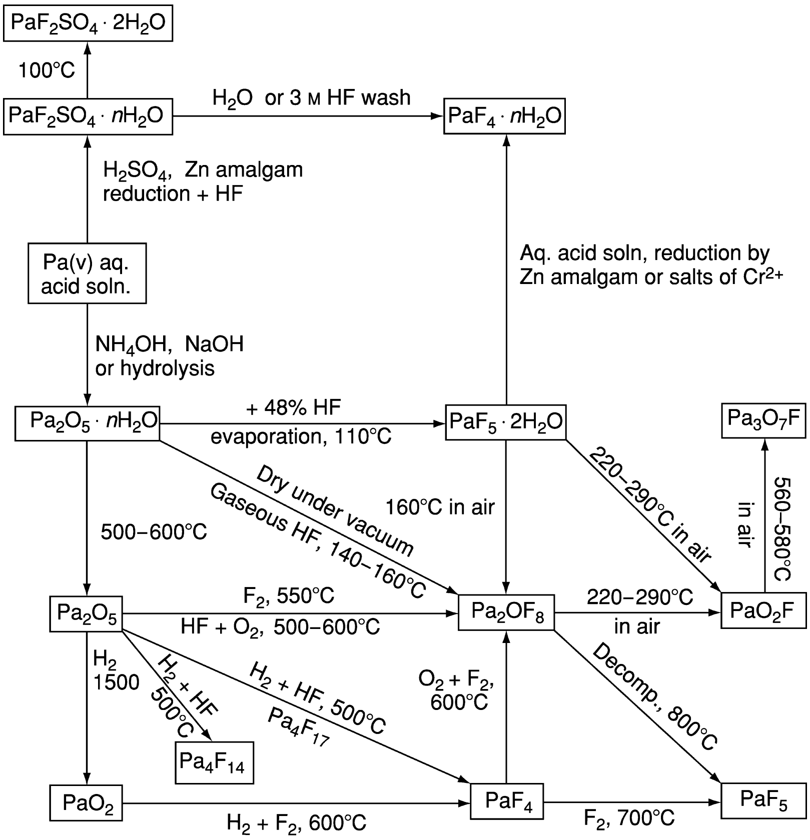


Fig. 4.11 *Preparation of some fluoride derivatives of Pa(IV) and Pa(V) (Muxart and Guillaumont,* 1974; *Pal'shin* et al., 1968a).

(Grosse, 1934c). Protactinium carbide is also useful in the preparation of other binary penta- and tetrahalides. Brown *et al.* (1976a) treated PaC with I_2 at 400°C, Br_2 at 350°C, and $SOCl_2$ at 200°C to obtain PaI_5, $PaBr_5$, and $PaCl_5$, respectively. PaI_4 was obtained by reaction of PaC with PaI_5 at 600°C or by the treatment with HgI_2 at 500°C. These compounds were also prepared by reactions of Pa_2O_5 with $Cl_2 + CCl_4$ at 300°C (→$PaCl_5$) (Pissot *et al.*, 1966); CCl_4 at 400°C (→$PaCl_4$) (Sellers *et al.*, 1954); $AlBr_3$ at 317°C (→$PaBr_5$); and AlI_3 at $\leq$300°C (→PaI_5) (D'Ege *et al.*, 1963) and so on.

Protactinium pentafluoride is reduced to PaF_4 by PF_3 but no reaction occurs with AsF_3. $PaCl_5$ and $PaCl_4$ are formed from PaF_5 and PaF_4 by reaction with PCl_3 and $SiCl_4$, respectively. PaF_5 reacts with CCl_4 to give $PaCl_xF_{5-x}$ (x probably 1), but no reaction is observed with PaF_4 (O'Donnell *et al.*, 1977). Whereas UF_5 is very soluble in acetonitrile, PaF_5 forms a sparingly soluble complex. An adduct $PaF_5 \cdot 2Ph_3PO$ forms on addition of TPPO to PaF_5 in acetonitrile

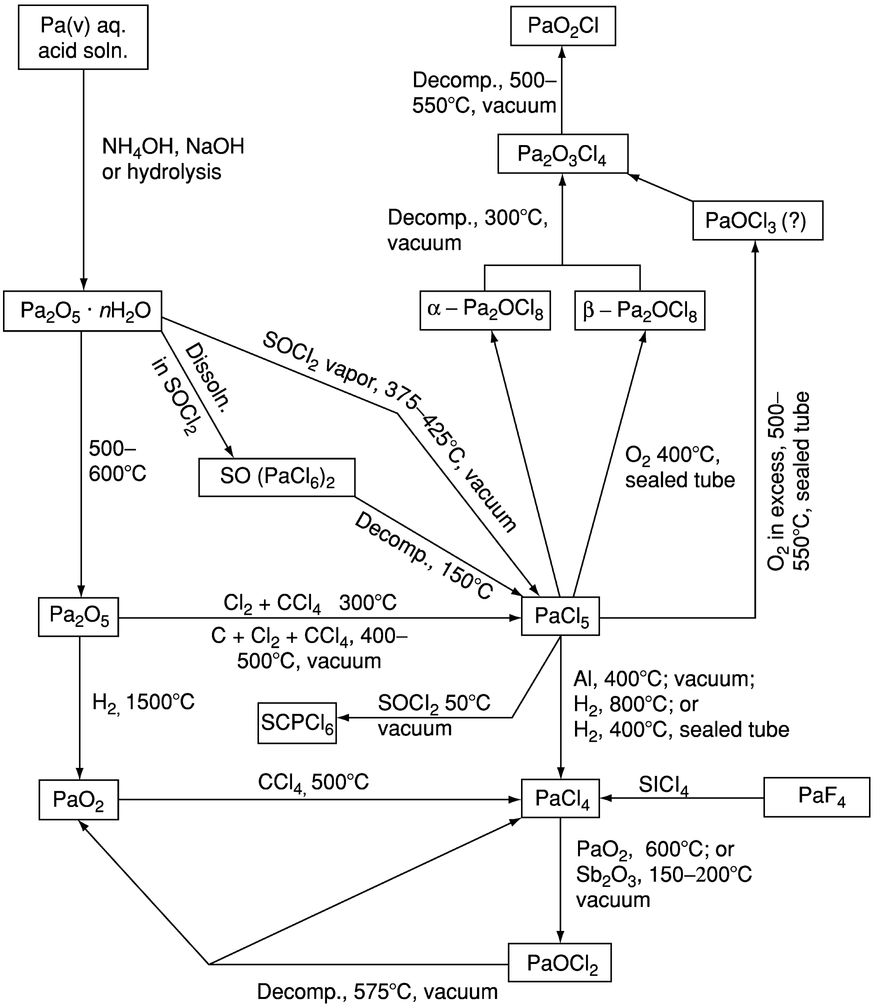


Fig. 4.12 *Preparation of some chlorides and oxychlorides of Pa*(IV) *and Pa*(V) (*Muxart and Guillaumont*, 1974; *Pal'shin* et al., 1968*a*).

(Brown *et al.*, 1982b). Brown (1979) found still another $PaBr_5$ crystal structure, designated γ, isostructural with β-UCl_5.

Of the possible halides of Pa(III), only PaI_3 has been reported so far (Scherer *et al.*, 1967). It is a dark brown compound (not black as originally reported) (Wilson, 1967), prepared by heating PaI_5, for several days at 10^{-6} torr and 360–380°C. Its tentative identification is based primarily on the similarity of its X-ray powder pattern to that of CeI_3.

All the binary halides are volatile at moderate temperatures, a property that has been used for the separation of ^{233}Pa from irradiated ThO_2 as well as for the

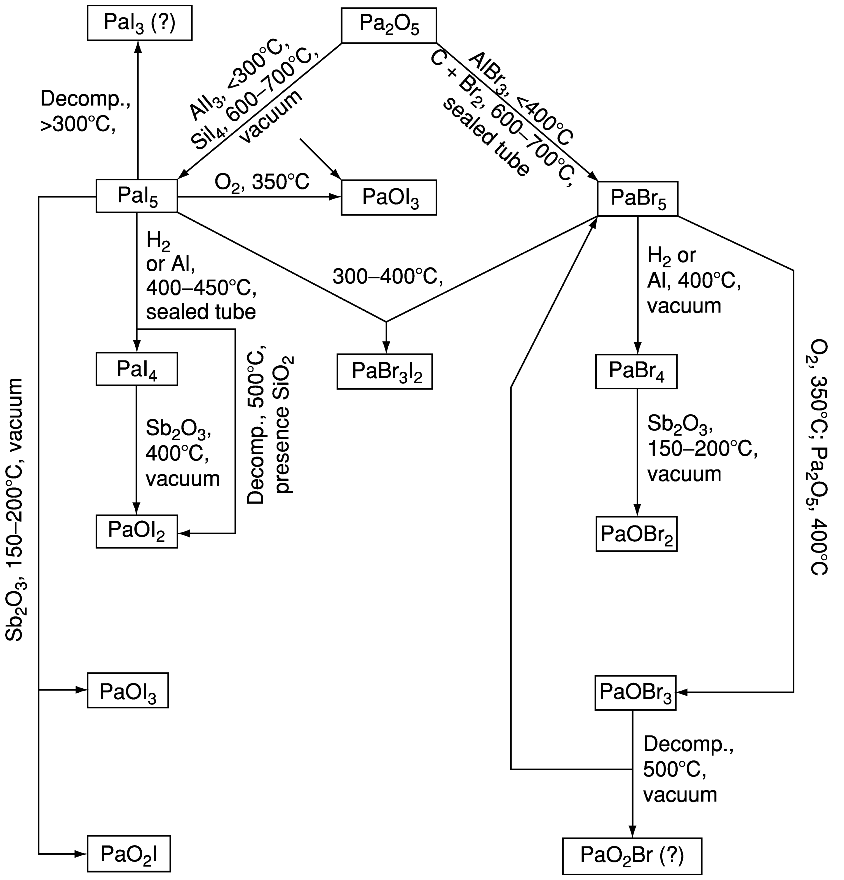


Fig. 4.13 *Preparation of some bromide and iodide derivatives of Pa*(*IV*) *and Pa*(*V*) (*Muxart and Guillaumont*, 1974; *Pal'shin* et al., 1968*a*).

preparation of radiochemically pure ^{231}Pa and ^{234}Pa (Malm and Fried, 1950; Merinis *et al.*, 1966; Brown, 1971). The vapor pressures of $PaCl_5$ and $PaBr_5$ have been measured by Weigel *et al.* (1969, 1974) in the temperature range 490–635 K; the boiling points, extrapolated to 760 torr, were 420 and 428°C, respectively. The thermal stability studies of Brown and co-workers (1976b) show that PaI_4 is stable up to a temperature of 330°C, and that PaI_5 is stable to 200–300°C.

Numerous alkali fluoro complexes of Pa(v) have been identified (Table 4.10) . The first, K_2PaF_7, was prepared by Grosse (1934a) for use in determining the atomic weight of ^{231}Pa. Complexes of the form $MPaF_6$ (M = Li, Na, K, Rb, Cs, Ag, NH_4) can be prepared by crystallization from aqueous HF solutions containing equimolar amounts of Pa(v) and the alkali fluorides, but $LiPaF_6$ and $NaPaF_6$ are best prepared by evaporating the equimolar mixture to dryness and

Table 4.9 *Halides and oxyhalides of protactinium.*

Compound	*Symmetry*	*Structure type or space group*	*Lattice constants*				*References*
			a (Å)	*b* (Å)	*c* (Å)	*Angle* (deg.)	
PaF_4	monoclinic	UF_4	12.86	10.88	8.54	$\beta = 126.34$	Soddy and Cranston (1918); Sellers *et al.* (1954); Asprey *et al.* (1967)
Pa_2F_9 (or Pa_4F_{17})	bcc cubic	U_2F_9	8.507				Brown (1966); Stein (1966)
PaF_5	tetragonal	β-UF_5	11.525		5.218		Brown (1971)
			11.53		5.19		Stein (1964)
Pa_2OF_8	bcc	U_2F_9	8.406				Stein (1964)
							Brown and Easey (1970)
PaO_2F	orthorhombic	–	6.894	12.043	4.143		Brown and Easey (1970)
Pa_3O_7F	orthorhombic	$Cmm2(C_{20}^{11})$	6.947	12.030	4.203		Brown and Easey (1970)
$PaCl_4$	tetragonal	UCl_4	8.377		7.479		Brown and Jones (1967c)
					7.482		Sellers *et al.* (1954)
$PaCl_5$	monoclinic	C2/*c*	10.35	12.31	8.82	$\beta = 111.8$	Brown and Maddock (1963)
$PaOCl_2$	orthorhombic	*Pbam*	15.332	17.903	4.012		Dodge *et al.* (1968); Bagnall *et al.* (1968a)
$PaBr_4$	tetragonal	UCl_4	8.824		7.957		Brown and Jones (1967c)
α-$PaBr_5$	monoclinic	$P2_1/c$	12.69	12.82	9.92	$\beta = 108$	Brown and Petcher (1969)
β-$PaBr_5$	monoclinic	$P2_1/n$	8.385	11.205	8.950	$\beta = 91.1$	Brown *et al.* (1968b); Brown and Petcher (1969)
γ-$PaBr_5$	triclinic	P1	7.52(1)	10.21(1)	6.74(1)	$\alpha = 89.27(5)$; $\beta = 117.55(6)$; $\gamma = 109.01(5)$	Merinis *et al.* (1966)
			9.25	12.12	9.13		D'Ege *et al.* (1963)
$PaOBr_3$	monoclinic	C2	16.911	3.871	9.334	$\beta = 113.67$	Brown *et al.* (1968b)
PaI_3(?)	orthorhombic	CeI_3	4.33	14.00	10.02		Scherer *et al.* (1967)
PaI_4							Brown *et al.* (1976b)
PaI_5	orthorhombic	–	7.22	21.20	6.85		Maddock (1960)
PaO_2I	hexagonal	–	12.64		4.07		Brown *et al.* (1967b)

Table 4.10 *Some fluoro complexes of Pa(IV) and Pa(V).*

Compound	*Symmetry*	*Structure type or space group*	*Lattice constant* *a* (Å)	*b* (Å)	*c* (Å)	*Angle* (deg.)	*References*
$LiPaF_5$	tetragonal	$LiUF_5$	14.96		6.58		Asprey *et al.* (1967)
$Na_7Pa_6F_{31}$	rhombohedral	$Na_7Zr_6F_3$,	9.16			$\alpha = 107.09$	Asprey *et al.* (1967)
$K_7Pa_6F_{31}$	rhombohedral	$Na_7Zr_6F_3$,	9.44			$\alpha = 107.15$	Asprey *et al.* (1967)
$Rb_7Pa_6F_{31}$	rhombohedral	$Na_7Zr_6F_{31}$	9.64			$\alpha = 107.00$	Asprey *et al.* (1967)
$(NH_4)_4PaF_8$	monoclinic	–	13.18	6.71	13.22	$\beta = 17.17$	Asprey *et al.* (1967)
$NaPaF_6$	tetragonal	–	5.35		3.98		Asprey *et al.* (1966)
NH_4PaF_6	orthorhombic	$RbPaF_6$	5.84	11.90	8.03		Asprey *et al.* (1966); Brown (1973)
$KPaF_6$	orthorhombic	$RbPaF_6$	5.64	11.54	7.98		Asprey *et al.* (1966); Brown (1973)
$RbPaF_6$	orthorhombic	*Cmca*	5.86	11.97	8.04		Asprey *et al.* (1966); Brown (1973)
$CsPaF_6$	orthorhombic	$RbPaF_6$	6.14	12.56	8.06		Asprey *et al.* (1966); Brown (1973)
K_2PaF_7	monoclinic	*C2/c*	13.760	6.742	8.145	$\beta = 125.17$	Brown and Easey (1966)
Cs_2PaF_7	monoclinic	K_2PaF_7	14.937	7.270	8.266	$\beta = 125.32$	Brown *et al.* (1967a)
Li_3PaF_8	tetragonal	$P4_22_12(D^6)$	10.386		10.89		Brown and Easey (1965, 1966)
Na_3PaF_8	tetragonal	14 *mmm*	5.487		10.89		Brown and Easey (1965, 1966)
K_3PaF_8	fcc	F*m3m*	9.235				Brown and Easey (1966)
Cs_3PaF_8	fcc	F*m3m*	9.937				Brown and Easey (1966)
Rb_3PaF_8	fcc	F*m3m*	9.6				Asprey *et al.* (1966); Brown (1973)

fluorinating the dried residue (Asprey *et al.*, 1966). The heptafluoroprotactinates, M_2PaF_7 (M = K, NH_4, Rb, Cs), are precipitated by the addition of acetone to a 17 M HF solution containing Pa(V) and an excess of the appropriate alkali fluoride. NaF in a 3:1 molar ratio to Pa(V) yields Na_3PaF_8, but the other octafluoroprotactinates (V) are most easily prepared by the reaction:

$$M_2PaF_7 + MF \rightarrow M_3PaF_8$$

at 450°C in an atmosphere of dry argon or by fluorination of the product obtained by evaporation of an HF solution containing 3:1 MF and Pa(V) (Brown and Easey, 1966).

The fluoro complexes of Pa(IV) are prepared either by H_2 reduction of a Pa(V) complex at 450°C or by heating stoichiometric amounts of the alkali fluoride with PaF_4 in a dry argon atmosphere (Asprey *et al.*, 1967).

$Pa_2O_5 \cdot nH_2O$ reacts vigorously with $SOCl_2$ at room temperature to yield stable solutions containing up to 0.5 M Pa(V). The product is probably $SO(PaCl_6)_2$ which decomposes at 150°C under vacuum. Hexa- and octachloroprotactinates (V) are precipitated when CS_2 is added to $SOCl_2$ solutions containing equal amounts of $PaCl_5$ and MCl (M = $N(CH_3)_4$, $N(C_2H_5)_4$, $NH_2(CH_3)_2$, and $(C_6H_5)_4As$). Hexachloro complexes with Cs^+ and NH_4^+ precipitate when the component halides are reacted in $SOCl_2$/ICl mixtures (Bagnall and Brown, 1964). Hexabromoprotactinate (V) complexes, $MPaBr_6$ (M = $N(CH_3)_4$, $N(C_2H_5)_4$), have been prepared by vacuum evaporation of stoichiometric quantities of $PaBr_5$ and the tetraalkylammonium bromide dissolved in anhydrous CH_3CN (Brown and Jones, 1967b).

Axe and co-workers (Axe, 1960, Axe *et al.*, 1960, Axe *et al.*, 1961) observed the paramagnetic resonance spectrum of Pa^{4+} in single crystal of Cs_2ZrCl_6, crystallized from a melt containing approximately 500 μg of $^{231}PaCl_4$. The $5f^1$ structure was confirmed, as was the nuclear spin of 3/2. The resonance spectrum was found to be isotropic, with a spectroscopic splitting factor $g = -1.14$. Hendricks *et al.* (1971) measured the magnetic susceptibility of $PaCl_4$ from 3.2 to 296 K and found a ferromagnetic transition at about 182 K.

$PaCl_4$ is virtually insoluble in $SOCl_2$, but hexachloro- and hexabromoprotactinates (IV), M_2PaX_6 (X = Cl, Br; M = $N(CH_3)_4$ and $N(C_2H_5)_4$), have been prepared by reaction of PaX_4 with the tetraalkylammonium halide in CH_3CN. Cs_2PaCl_6 is precipitated on the addition of CsCl to a solution of $PaCl_4$ in concentrated HCl. The hexaiodo complex, $[(C_6H_5)_3CH_3As]_2PaI_6$, was also prepared from the component iodides dissolved in CH_3CN (Brown and Jones, 1967a). The electronic structures and optical transition energies of PaX_6^{2-} (X = F, Cl, Br, I) were calculated by quasi-relativistic density functional methods (Kaltsoyannis and Bursten 1995; Kaltsoyannis 1998). Analysis of the $5f^1 \rightarrow 6d^1$ transitions in PaX_6^{2-} (X = Cl, Br) and $ThBr_4:Pa^{4+}$ was reported by Edelstein *et al.* (1988), and the EPR spectra of $ThBr_4:Pa^{4+}$ in the incommensurate phase was detected (Zwanenburg *et al.*, 1988). The fluorescence and absorption spectra between the ground $5f^1$ and the excited $6d^1$ configurations of

Pa^{4+} diluted into a single crystal of Cs_2ZrCl_6 were analyzed (Piehler *et al.*, 1991; Edelstein *et al.*, 1992).

Numerous halide complexes of Pa(IV) and Pa(V) are formed with oxygen donor ligands, such as substituted phosphine oxides (Brown *et al.*, 1966b, 1970a,b), hexamethylphosphoramide (Brown and Jones, 1966a), DMSO (Bagnall *et al.*, 1968b), tropolone (Brown and Rickard, 1970), *N*,*N*-dimethylacetamide (Bagnall *et al.*, 1969), acetylacetone (Brown and Rickard, 1971b), and *N*,*N*-diethyldithiocarbamate (Heckley *et al.*, 1971). In addition, complexes with sulfur and selenium donors have been reported (Brown *et al.*, 1971).

The ground state electronic structures of PaX_6^{2-} (X = F, Cl, Br, I), UX_6^- (X = F, Cl, Br), and NpF_6 have been calculated using both non-relativistic and relativistic implementations of the discrete-variational X alpha (DV-X alpha) method. A significant amount of metal–ligand covalent bonding is found, involving both 6d and 5f metal orbitals. The 5f contribution to the bonding levels increases significantly from PaX_6^{2-} to UX_6^- to NpX_6 but remains approximately constant as the halogen is altered in PaX_6^{2-} and UX_6^-. In contrast, the 6d atomic orbital character of the halogen-based levels increases from UF_6^- to UBr_6^- and a similar, though less marked, trend is observed in PaX_6^{2-}. The electronic transition energies have been calculated using the transition-state method. The relativistic calculations are far superior to the non-relativistic ones in both qualitatively and quantitatively describing the electronic spectra. The stabilization of the metal 5f atomic orbitals with respect to the halogen *n*p levels from Pa to Np results in the more energetic f→f transitions in NpF_6 being masked by the onset of a ligand-to-metal charge transfer band. In the remaining molecules, the f→f transitions occur well removed from charge transfer bands (Kaltsoyannis, 1998).

Several chloro complexes and one bromo complex for which crystallographic data are available are listed in Table 4.11.

4.7.5 Protactinium pnictides

Protactinium pnictide compounds have been prepared and constitute a new category of Pa compounds that have several features of more than usual interest. The protactinium phosphide, PaP_2, was prepared by reaction of elemental phosphorus with protactinium hydride; thermal dissociation of PaP_2 forms Pa_3P_4 (Table 4.12) (Wojakowski *et al.*, 1982). The diarsenide, $PaAs_2$, can be obtained by heating together PaH_3 and elemental arsenic at 400°C; heating $PaAs_2$ to 840°C results in decomposition of $PaAs_2$ to form Pa_3As_4 (Hery *et al.*, 1978). $PaAs_2$ has a tetragonal structure of the anti-Fe_2As type, and Pa_3As_4 crystallizes in a body-centered structure of the Th_3P_4-type (Table 4.12). Single crystals of $PaAs_2$, Pa_3As_4, PaAs, and Pa_3Sb_4 were prepared from the elements by a Van Arkel procedure using vapor transport; iodine was the transporting agent and deposition occurred on an induction-heated tungsten support (Calestani *et al.*, 1979a,b). Hery and co-workers (1979) have obtained Pa_3Sb_4 and $PaSb_2$ by heating PaH_3 with antimony.

Table 4.11 *Some chloro and bromo complexes of Pa(IV) and Pa(V).*

		Lattice constants				
Compound	*Symmetry*	*a* (Å)	*b* (Å)	*c* (Å)	*Angle* (deg.)	*References*
Cs_2PaCl_6	trigonal	7.546		6.056		Brown and Jones (1967a)
$(NMe_4)_2PaCl_6$	fcc	13.08				Brown and Jones (1967a)
$(NEt_4)_2PaCl_6$	orthorhombic	14.22	14.75	13.35		Brown and Jones (1966a,b)
$(NMe_4)_2PaBr_6$	fcc	13.40				Brown and Jones (1967a,b)
$Pa(Trop)_4Cl,DMSO$	triclinic	9.87	12.60	15.96	$\alpha = 119.8$; $\beta = 103.6$; $\gamma = 103.0$	Brown and Rickard (1970)
$(NEt_4)_2PaOCl_5$	monoclinic	14.131	14.218	13.235	$\beta = 91.04$	Brown and Rickard (1971a); Brown *et al.* (1972)
$Pa(Acac)_2Cl_3$	monoclinic	8.01	23.42	18.63	$\beta = 98.9$	Bagnall *et al.* (1969)

Me, methyl; Et, ethyl; Trop, tropolonate; DMSO, dimethyl sulfoxide; Acac, acetylacetonate.

Table 4.12 *Crystallographic data for some miscellaneous compounds of protactinium.*

Compound	*Symmetry*	*Lattice parameters*				*References*
		a (Å)	*b* (Å)	*c* (Å)	γ (deg.)	
$H_3PaO(SO_4)_3$	hexagonal	9.439		5.506		Bagnall *et al*. (1965)
$H_3PaO(SeO_4)_3$	hexagonal	9.743		5.679		Bagnall *et al*. (1965)
PaOS	tetragonal	3.832		6.704		Sellers *et al*. (1954)
$[N(C_2H_5)_4]_4Pa(NCS)_8$	tetragonal	11.65		23.05		Al-Kazzaz *et al*. (1972)
$[N(C_2H_5)_4]_4Pa(NCSe)_8$	tetragonal	11.82		23.49		Al-Kazzaz *et al*. (1972)
$Pa(HCOO)_4$	tetragonal	7.915		6.517		Bohres (1974); Greis *et al*. (1977)
$HPaOP_2O_7$	fcc	5.92				LeCloarec (1974)
$(PaO)_4(P_2O_7)_3$	monoclinic	12.23	13.44	8.96	113.88	LeCloarec (1974); Lux *et al*. (1980)
$Pa_2O_5{\cdot}Pa_2O_5$	orthorhombic	5.683	12.06	14.34		LeCloarec (1974); Lux *et al*. (1980)
PaP_2	tetragonal	3.898		7.845		Bhandari and Kulkarni (1979)
[a]$Pa(Trop)_5$	tetragonal	9.759		9.46		Bhandari and Kulkarni (1979)

[a] Trop, tropolone.

The magnetic susceptibility of $PaAs_2$ and $PaSb_2$ has been measured from 4 K to room temperature. PaAs, $PaAs_2$, and $PaSb_2$ exhibit temperature-independent paramagnetism (Hery *et al.*, 1978). Self-consistent band structure calculations show that PaN and PaAs have about one f-electron, and hence they are expected to be paramagnetic; these results have been confirmed by experiment (Hery, 1979; Brooks *et al.*, 1980).

4.7.6 Miscellaneous compounds

Pa_2O_5 is insoluble in nitric acid but the freshly prepared hydroxide, the pentachloride, the pentabromide, and the complex $SO(PaCl_6)_2$ all dissolve in fuming HNO_3 to form stable solutions of at least 0.5 M Pa(V). Vacuum evaporation of such solutions yields $PaO(NO_3)_3 \cdot xH_2O$ $(1 < x < 4)$. The reaction of Pa(V) halides with N_2O_5 in anhydrous CH_3CN yields $Pa_2O(NO_3)_4 \cdot 2CH_3CN$. Complexes of the type $MPa(NO_3)_6$ ($M = Cs$, $N(CH_3)_4$, $N(C_2H_5)_4$) have been prepared by reaction of the hexachloroprotactinates (V) with liquid N_2O_5 at room temperature (Brown and Jones, 1966b; Jones, 1966).

When a solution of Pa(V) in a mixture of HF and H_2SO_4 is evaporated until all F^- ion has been eliminated, $H_3PaO(SO_4)_3$ crystallizes almost quantitatively. The analogous selenato complex, more stable in acid (6 M HCl) or basic (NH_4OH) media, is obtained from HF/H_2SeO_4 mixtures. The sulfato-complex decomposes to $HPaO(SO_4)$ at 375°C (Bagnall *et al.*, 1965; Bagnall, 1966b) and to Pa_2O_5 at 750°C (Pal'shin *et al.*, 1968b). The binary chalcogenides, β-PaS_2 and γ-$PaSe_2$, have been prepared by Hery (1979). PaOS was obtained by the reaction of $PaCl_5$ with a mixture of H_2S and CS_2 at 900°C (Sellers *et al.*, 1954). $PaF_2SO_4 \cdot 2H_2O$ is precipitated when a solution of Pa(IV) in 4.5 M H_2SO_4 is added to 3 M HF (Stein, 1966). Crystallographic data for some S and Se compounds are given in Table 4.12.

The addition of hydrochloric acid to a solution of Pa(V) oxalate causes the precipitation of $PaO(C_2O_4)(OH) \cdot xH_2O$ ($x \sim 2$) (Muxart *et al.*, 1966a). On the other hand, the addition of acetone instead of acid yields $Pa(OH)(C_2O_4)_2 \cdot 6H_2O$ (Davydov and Pal'shin, 1967).

Phenylarsonic acid forms a white flocculent precipitate with Pa(V) in neutral or acid solutions. The compound is believed to have the composition $H_3PaO_2(C_6H_6AsO_3)_2$ (Myasoedov *et al.*, 1968c).

Complexes of the type $[N(C_2H_5)_4]_4PaR_8$ (R = NCS or NCSe) have been prepared by reaction of $PaCl_4$ with stoichiometric amounts of KCNS or KCNSe in anhydrous CH_3CN (Table 4.12) (Al-Kazzaz *et al.*, 1972). The bis(phthalocyaninato)complexes of Pa(IV), $(C_{32}H_{16}N_8)_2Pa$, have been prepared by neutron irradiation of the corresponding thorium $^{233}ThPc_2$ complex by the reactions (Lux *et al.*, 1970, 1971):

$$^{232}ThPc_2(n,\gamma)\,^{233}ThPc_2 \rightarrow {}^{233}PaPc_2 + \beta^-$$

Spectroscopically pure bis(phthalocyaninato)protactinium(IV) ($PaPc_2$) was prepared by reaction between $PaI_4 \cdot 4CH_3CN$ and *o*-phthalic dinitrile in

1-chloronaphthalene followed by purification by sublimation. $PaPc_2$ is isostructural with $ThPc_2$ and UPc_2 (Lux *et al.*, 1980). Tetrakis(cyclopentadienyl)Pa(IV), $(C_5H_5)_4Pa$, was prepared by treating Pa_2O_5 with a mixture of $Cl_2 + CCl_4$ in an argon stream at 600°C, then fusing the reaction product with $Be(C_2H_5)_2$ at 65°C (Keller, 1964b; Baumgartner *et al.*, 1969). Protactinium(IV) tropolone, $Pa(Trop)_4$, has been prepared by reaction of $PaCl_4$ or $PaBr_4$ with lithium tropolonate, Li(Trop) in methylene chloride; in the presence of excess Li (Trop) in dimethyl formamide, $LiPa(Trop)_5$ is formed (Brown and Richard, 1970). However, when protactinium pentethoxide, which is obtained by reaction of $PaCl_5$ with sodium ethoxide in anhydrous alcohol (Maddock and Pires deMatos, 1972; Bagnall *et al.*, 1975), is treated with tropolone, the complex Pa $(Trop)_5$ is obtained. $Pa(Trop)_5$ has been crystallized and its crystal structure parameters are determined (Table 4.12) (Bhandari and Kulkarni, 1979). Complexes of the actinide elements with cyclooctatetrene have been obtained by reaction of an actinide halide with cyclooctatetrene anion. The bis(η^8-tetramethylcyclooctatetradiene) complex of Pa has been prepared by reaction of Pa borohydride, $Pa(BH_4)_4$, with tetramethylcyclooctatetrene dianion (Solar *et al.*, 1980). The preparation of the anhydrous tetraformate, $Pa(HCOO)_4$, has been reported by the reaction of $PaCl_4$ with O_2-free HCOOH at 60°C in an argon atmosphere for 4 h (Table 4.12) (Bohres, 1974; Bohres *et al.*, 1974).

Freshly precipitated Pa(V) hydroxide or peroxide dissolves readily in 14 M H_3PO_4. However, upon aging, the hydrated orthophosphate, $PaO(H_2PO_4)_3 \cdot 2H_2O$, crystallizes out. Calcination of this product yields, successively: the anhydrous orthophosphate, $PaO(H_2PO_4)_3$ between room temperature and 300°C; the trimetaphosphate, $PaO(PO_3)_3$, stable to 900°C; the pyrophosphate, $(PaO)_4(P_2O_7)_3$, at 1000°C; and an unidentified phase with the gross composition $Pa_2O_5 \cdot P_2O_5$ at 1200°C (LeCloarec *et al.*, 1970, 1976; LeCloarec and Muxart, 1971; LeCloarec, 1974). Crystallographic data for several phosphates are given in Table 4.12. Protactinium(V) perrhenate, $PaO(ReO_4)_3 \cdot xH_2O$, has been prepared by reaction of Pa_2O_5 and Re_2O_7 (Silvestre *et al.*, 1977).

Protactinium(IV) borohydride, $Pa(BH_4)_4$, has been prepared by treating PaF_4 with aluminum borohydride, $Al(BH_4)_3$. It is a relatively unstable solid at 20°C, but exhibits high volatility as do other actinide borohydrides. $Pa(BH_4)_4$ is isostructural with $U(BH_4)_4$ (Banks *et al.*, 1978; Banks, 1979; Banks and Edelstein, 1980). The molecular compound, $Pa(BH_3CH_3)_4$, has been synthesized from the reaction of $PaCl_5$ or $PaCl_4$ with $Li(BH_3CH_3)$. Its optical and NMR spectra have been obtained. Because of the T_d symmetry at the Pa^{4+} site, the dipolar shift is zero and the temperature-dependent proton and ^{11}B shifts are attributed to spin delocalization mechanisms. The ^1H NMR peaks of both the bridging and terminal protons shift to lower field as the temperature is decreased. These observations are inconsistent with a spin-polarization mechanism, which assumes that the temperature-dependent shifts are proportional to the average value of the electron spin in the 5f orbitals. In addition, new synthetic routes to $Pa(BH_4)_4$ and $Pa(MeCp)_4$ (MeCp = methylcyclopentadienyl) are described. They are simpler and more convenient than the earlier published methods and take advantage of the unexpected solubility of $PaCl_5$ in aromatic hydrocarbons (Kot and Edelstein, 1995). The 5f–6d absorption spectrum of $Pa^{4+}/CsZrCl_6$ (Edelstein *et al.*, 1992) and magnetic data of tetravalent protactinium(IV) (Edelstein and Kot, 1993) also were reported.

4.8 SOLUTION CHEMISTRY

Two oxidation states, Pa(IV) and Pa(V), have been definitely established in aqueous solution (Haïssinsky and Bouissières, 1948, 1951; Bouissières and Haïssinsky, 1949), but all attempts to demonstrate the existence of Pa(III) in solution have led to negative or inconclusive results (Elson, 1954; deMiranda and Maddock, 1962; Musikas, 1966). Both Pa(IV) and Pa(V) show strong tendencies to hydrolyze in the absence of complexing agents and most studies of the ionic species of Pa in aqueous solution have therefore been carried out at the tracer level. Furthermore, the instability of Pa(IV) toward reoxidation has made it difficult to obtain reproducible data on this oxidation state, so that, until quite recently, little quantitative information has been available about the aqueous chemistry of Pa(IV).

The behavior of protactinium in aqueous solution has been very thoroughly reviewed by Guillaumont, Bouissières, and Muxart (Guillaumont *et al.*, 1968; Bouissières, 1971; Muxart and Guillaumont, 1974) and by Pal'shin *et al.* (1970); those reviews should be consulted for more detail than can be given here. For a general discussion of the techniques used in the determination of stability constants, see Rossotti and Rossotti (1961), Fronaeus (1963), or Ahrland *et al.* (1973).

4.8.1 Hydrolysis of Pa (V) in non-complexing media

The hydrolytic behavior of Pa(V) has been studied by a large number of investigators (Jakovac and Lederer, 1959; Guillaumont, 1966a, 1971; Liljenzin and Rydberg, 1966; Scherff and Hermann, 1966; Suzuki and Inoue, 1966, 1969; Kolarich *et al.*, 1967; Mitsuji and Suzuki, 1967; D'yachkova *et al.*, 1968a; Mitsuji, 1968; Liljenzin, 1970; Cazaussus *et al.*, 1971) whose conclusions are summarized schematically in Figs. 4.14 and 4.15 (Bouissières, 1971).

The hydrolysis of Pa(V) is usually studied in perchloric acid solutions, because ClO_4^- is considered to be a non-complexing anion. However, the presence of small amounts of weakly complexing anions does not affect the results. Thus, <0.5 M HNO_3, <1 M HCl, <0.01 M H_2SO_4, or <0.01 M $H_2C_2O_4$, are all equivalent to $HClO_4$ of the same acidity.

In solutions of constant ionic strength ($\mu = 3$; 10^{-5} M< $[H^+] < 3$ M), the least hydrolyzed cation is $PaOOH^{2+}$. At $[H^+] < 1$ M, $PaO(OH)_2^+$ begins to form and becomes predominant at pH ~3. At higher pH values, the neutral species, $Pa(OH)_5$, is formed. At tracer levels these species are in equilibrium (Fig. 4.14), but, at concentrations of Pa(V) close to saturation, polymers are

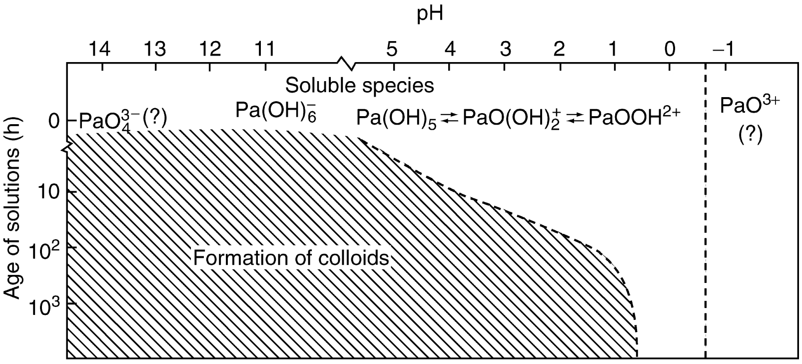
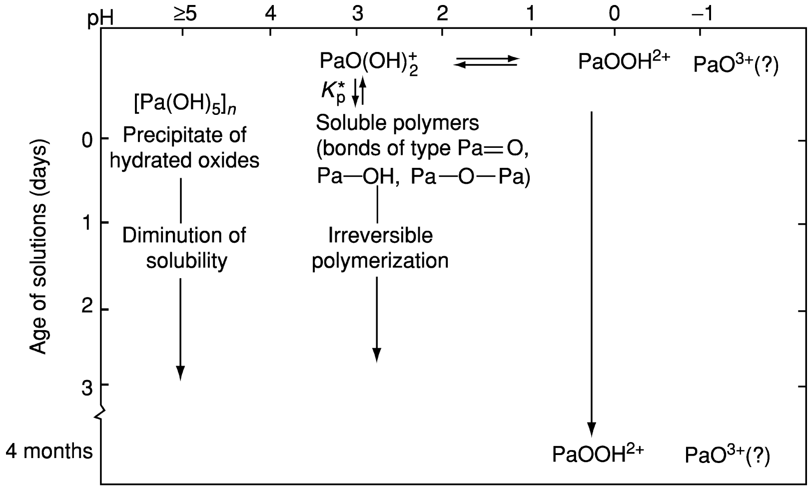


Fig. 4.14 *Hydrolysis of tracer-level Pa(V) in $HClO_4$ solution (Bouissières, 1971).*



$K_p^* = [Pa_p]/[Pa_{p-1}][PaO(OH_2^+)] \approx 3 \times 10^7$, with $Pa_p \equiv$ polymers of p atoms

Fig. 4.15 *Hydrolysis of Pa(V) in $HClO_4$ solution at $[Pa(V)] = 10^{-5}$ M (Bouissières, 1971).*

formed, a process that rapidly becomes irreversible (Fig. 4.15). At pH 5–6, the hydrated oxide is precipitated. In alkaline solution ($\mu = 0.1$) minute concentrations of $Pa(OH)_6^-$ are formed, and at $[H^+] \geq 3$ M the existence of PaO^{3+} has been suggested.

The hydrolysis reactions of Pa(V) may be written as:

$$PaO^{3+} + H_2O \leftrightarrow PaO(OH)^{2+} + H^+ \qquad (4.1)$$

$$\mathrm{PaO(OH)^{2+} + H_2O \leftrightarrow PaO(OH)_2^+ + H^+} \quad (4.2)$$

$$\mathrm{PaO(OH)_2^+ + 2H_2O \leftrightarrow Pa(OH)_5 + H^+} \quad (4.3)$$

with the corresponding equilibrium reaction constants K_1, K_2, and K_3. Since the species $\mathrm{PaO^{3+}}$ has only been suggested but never proven, only the latter two hydrolysis reactions and corresponding hydrolysis constants can be measured. Early studies on Pa(v) hydrolysis were reported by Guillaumont (1966a) and Bouissières (1971).

Recently Trubert *et al.* (Le Naour *et al.*, 2003; Trubert *et al.*, 1998, 2002, 2003) have obtained the hydrolysis constants for Pa(v) at the tracer level ($\sim 10^{-12}$ M using ^{233}Pa) from the variations of the partition coefficient of Pa(v) in the system: TTA/toluene/Pa(v)/$\mathrm{H_2O/H^+/Na^+/ClO_4^-}$. These experiments were performed as a function of the concentrations of TTA and $\mathrm{H^+}$ at ionic strengths of $0.1 \leq \mu \leq 3$ M and temperatures of $10°\mathrm{C} \leq T \leq 60°\mathrm{C}$. From the hydrolysis constants obtained under these conditions extrapolations to zero ionic strength were performed using the specific ion interaction theory (SIT) (Grenthe and Puigdomenech, 1997). The equilibrium constants obtained are given in Table 4.13. Thermodynamic data related to the hydrolysis equilibria were derived from the temperature dependence of the hydrolysis constants at infinite dilution and are given in Table 4.14.

Table 4.13 *Equilibrium constants for the hydrolysis of Pa(*v*) at zero ionic strength (from Trubert* et al., 2003).

T	$\log K_2^0$	$\log K_3^0$
(°C)	$PaO(OH)^{2+} + H_2O \leftrightarrow PaO(OH)_2^+ + H^+$	$PaO(OH)_2^+ + 2H_2O \leftrightarrow Pa(OH)_5 + H^+$
10	–1.32 ± 0.15	–6.7 ± 0.4
25	–1.24 ± 0.02	–7.03 ± 0.15
40	–1.22 ± 0.1	–5.3 ± 1.0
60	–1.19 ± 0.12	–5.4 ± 0.9

Table 4.14 *Standard thermodynamic data at* 25°C *derived from the experimental hydrolysis equilibria of Pa(*v*). The thermodynamic values for the hydrolysis reaction forming* $Pa(OH)_5$ *are considered to be estimates (from Trubert* et al., 2003).

$PaO(OH)^{2+} + H_2O \leftrightarrow PaO(OH)_2^+ + H^+$	$PaO(OH)_2^+ + 2H_2O \leftrightarrow Pa(OH)_5 + H^+$
$\Delta_r H° = (5.7 \pm 1.3)$ kJ mol^{-1}	$\Delta_r H° = (61 \pm 31)$ kJ·mol^{-1}
$\Delta_r C_p° = (-200 \pm 89)$ J K^{-1} mol^{-1}	
$\Delta_r G° = (7.1 \pm 0.1)$ kJ mol^{-1}	$\Delta_r G° = (36.3 \pm 4)$ kJ mol^{-1}
$\Delta_r S° = (-4.5 \pm 4.7)$ J K^{-1} mol^{-1}	$\Delta_r S° = (81 \pm 118)$ J K^{-1} mol^{-1}

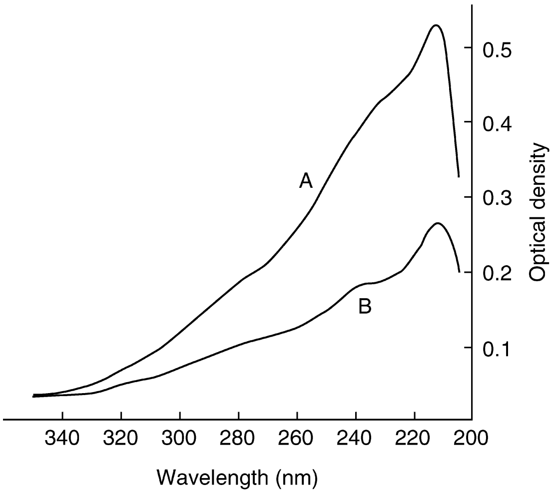


Fig. 4.16 *Absorption spectra of Pa(v) in* 11.5 M *$HClO_4$. The solution was prepared by dissolution of the hydroxide. Curve A, fresh solution; curve B, solution aged for* 1 *day or longer.* [*Pa*(v)] $\sim 10^{-5}$ M (*Guillaumont*, 1966*c*).

The absorption spectrum of Pa(v) in 11.5 M $HClO_4$ is shown in Fig. 4.16 (Guillaumont, 1966c); similar spectra are obtained at lower acidities. The absorption maximum at about 200–210 nm is attributed to the Pa=O bond in $PaO(OH)_2^+$ and $PaOOH^{2+}$; this bond persists even in sulfuric acid media up to 4 M concentration.

4.8.2 Complexes of Pa(v) in mineral acid solutions

In the absence of strong complexing agents, such as F^- and certain organic reagents, the aqueous complexes of Pa(v) are all oxo- or hydroxo complexes. Consequently, Pa(v) in aqueous solution is rarely present as a single species but rather exists as a mixture of several complexes or hydrolyzed species. These may be characterized by solvent extraction or ion-exchange methods, which, because of differences in the experimental conditions, such as ionic strength, acidity, concentration of the ligand, age of the solution, etc., may yield ambiguous or mutually contradicting interpretations.

The relative complexing tendencies of inorganic anions with respect to Pa(v) are:

$$F^- > OH^- > SO_4^{2-} > Cl^- > Br^- > I^- > NO_3^- \geq ClO_4^-$$

(a) Ionic species of Pa(v) in nitric acid solution

In general, NO_3^- is a poor complexing anion for Pa(v) but freshly prepared solutions, in which [Pa(v)] $\leq 10^{-5}$ M and [HNO_3] $\geq$ 1 M, are fairly stable. Such systems contain monomeric nitratohydroxo complexes of the form $[Pa(OH)_n(NO_3)_m]^{5-n-m}$, where $n \geq 2$ and $m \leq 4$ (Hardy *et al.*, 1958). The transition from cationic to anionic forms occurs at $[HNO_3] \approx 4$–5 M. Stability constants for several suggested species in this medium are listed in Table 4.15.

(b) Ionic species of Pa(v) in hydrochloric acid solution

Solutions of Pa(v) in hydrochloric acid are generally unstable with respect to hydrolytic condensation when $[Pa] \geq 10^{-3}$ M, although complete precipitation may take as long as several weeks (Kirby, 1966). If the freshly precipitated hydroxide is dissolved in 12 M HCl and then diluted to $[Pa] \leq 10^{-4}$ M and 1 M < [HCl] < 3 M, the solution is reasonably stable and will then contain a mixture of monomeric chloro complexes in thermodynamic equilibrium. It is generally agreed that, for [HCl] < 1 M and $[Pa] < 10^{-5}$ M, the species present are the same as those described above for perchloric acid media, while, for [HCl] ≈ 3 M, the predominant species is $PaOOHCl^+$. The complexes that have been proposed to explain the solvent extraction and ion-exchange behavior of Pa(v) at higher acidities are summarized in Table 4.16. The study of complex formation of Pa in aqueous HCl solutions of medium and high concentrations and the electronic structures of anionic complexes of $[PaCl_6]^-$, $[PaOCl_4]^-$, $[Pa(OH)_2Cl_4]^-$, and $[PaOCl_5]^{2-}$ have been calculated using the relativistic Dirac–Slater discrete-variational method. The charge density distribution analysis has shown that protactinium has a slight preference for the $[PaOCl_5]^{2-}$ form or for the pure halide complexes with coordination number higher than six under these conditions. On the other hand, Ta occupies a specific position in the group and has the highest tendency to form the pure halide complex $[TaCl_6]^-$; niobium has equal tendencies to form the $NbCl_6$ and $[NbOCl_5]^{2-}$ species (Pershina *et al.*, 1994).

There are no data on the species of protactinium in HBr and HI solutions. Goble and co-workers (1956, 1958) suggested on the basis of ^{231}Pa extraction from HBr and HI aqueous solutions that bromide and iodide complexes of protactinium are less stable than the chloride complexes.

(c) Fluoro complexes of Pa(v)

The solubility of Pa(v) is relatively high at all concentrations of hydrofluoric acid; thus, 0.05 M HF dissolves 3.9 g L^{-1} of ^{231}Pa and 20 M HF dissolves at least 200 g L^{-1} of the pentoxide (Bagnall *et al.*, 1965). The solubility of Pa(v) is estimated to be 11.2 g L^{-1} in 8 M HCl and 0.6 M HF and at least 125 g L^{-1} in 8 M HCl and 5 M HF (Chilton, 1964). Solutions of Pa(v) in aqueous HF are very stable with respect to hydrolysis and are probably the only systems that contain no polymeric species.

A great many complexes have been proposed to explain the behavior of Pa(v) in aqueous HF (deMiranda and Muxart, 1965; Bukhsh *et al.*, 1966a,b;

Table 4.15 *Stability constants for some suggested nitrate complexes of Pa(v).*

μ	$[H^+]$ (M)	$[NO_3^-]$ (M)	*Suggested species*	*Stability constants*	*References*
1	1	≤1	$[PaO_x(OH)_{4-2x}NO_3]^\circ$	$K_1 = 0.68$	Nowikow and Pfrepper (1963)[a]
			$[PaO_x(OH)_{4-2x}(NO_3)_2]^-$	$K_2 = 3.0$	
			$[PaO_x(OH)_{2-2x}(NO_3)_3]^-$	$K_4 = 11.93$	
2	2	≤1		$K_1 = 0.79$	
				$K_2 = 0.74$	
4	4	≤1		$K_1 = 0.63$	
				$K_2 = 0.21$	
1	1	≤1	$(PaNO_3)^{4+}$	$K_1 = 1.43$	Kolarich *et al.* (1967)
			$[Pa(NO_3)_2]^{3+}$	$K_2 = 0.07$	
6	6	1–3	$[Pa(NO_3)_5]^0$		Stanik and Ilmenkova (1963)
6	6	3–6	$[Pa(NO_3)_6]^-$	$K_6 = 0.141$	
			$[Pa(NO_3)_7]^{2-}$	$K_7 = 1.09$	
5–6	5	0.4–5	$[Pa(OH)_2(NO_3)]^{2+}$	$K_1 = 17$	Spitsyn *et al.* (1964); Khlebnikov *et al.* (1966)
			$[Pa(OH)_2(NO_3)_2]^+$	$K_2 = 127$	
			$[Pa(OH)_2(NO_3)_3]^0$	$K_3 = 540$	
			$[Pa(OH)_2(NO_3)_4]^-$	$K_4 = 1380$	

[a] Only the ratio $[Pa]:[NO_3^-]$ was determined.

Table 4.16 *Suggested chloro complexes of Pa(*v*) as a function of HCl concentration (after Guillaumont* et al., 1968).

[*HCl*] (M)	$Pa(OH)_nCl_m^{5-n-m}$			
1	$PaOOH^{2+}$	$PaOOH^{2+}$		
2	$PaOOHCl^{+}$	$PaOOHCl^{+}$		$Pa(OH)Cl_3^{+}$
3	$PaO_2Cl_2^{-}$	$PaOOHCl_2$ $PaOCl_3$	$Pa(OH)Cl_3^{+}$ $Pa(OH)_2Cl_3$	$Pa(OH)_3Cl^{+}$ $Pa(OH)_2Cl_2^{+}$
4	PaO_3^{+}	$POOHCl_3^{-}$	$Pa(OH)Cl_4$	$Pa(OH)_2Cl_3$ $Pa(OH)Cl_4$
5	$PaOCl_4^{-}$	$PaOCl_4^{-}$	$Pa(OH)_2Cl_4^{-}$	$Pa(OH)_2Cl_4^{-}$
6	$PaOHCl_6^{2-}$	$PaOCl_5^{2-}$	$Pa(OH)Cl_5^{-}$	$Pa(OH)Cl_5^{-}$
7	$PaCl_6^{-}$		$PaCl_6^{-}$	$PaCl_6^{-}$
8	$PaCl_7^{2-}$		$PaCl_7^{2-}$	
>8	$PaCl_8^{3-}$ or $POHCl_7^{3-}$	$PaOCl_6^{3-}$		
References	Scherff and Herrman (1966)	Guillaumont (1966c); Muxart *et al.* (1966a,b)	Casey and Maddock (1959a,b)	Shankar *et al.* (1963)

deMiranda, 1966; Guillaumont, 1966a,c; Guillaumont and deMiranda, 1966; Guillot, 1966; Kolarich *et al.*, 1967; Bonnet and Guillaumont, 1969; Plaisance and Guillaumont, 1969); their regions of existence are summarized in Fig. 4.17. Those for which stability constants have been determined are listed in Table 4.17. Only two species exist in a pure state: PaF_7^{2-}, which is present over the range 10^{-3} M < [HF] < 4–8 M, and PaF_8^{3-}, which can exist only when $[F^-] > 0.5$ M and 10^{-7} M < $[H^+] < 10^{-2}$ M. In more acid media, 1 M < $[H^+]$ < 3 M and $[F^-] \approx 10^{-4}$ M, the dominant heptafluoro complex is $HPaF_7^{-}$; this species would also exist in 10–12 M HF, because the $[F^-]$ is limited to about 10^{-2} M by the equilibrium constants: $K_1 = ([HF]/([H^+] \cdot [F^-])) = 935$ M^{-1} and $K_2 = ([HF_2]/([HF] \cdot [F^-])) = 3.12$ M^{-1} (Plaisance and Guillaumont, 1969). At [HF] < 10^{-3} M, PaF_7^{2-} is replaced by complexes of successively lower F:Pa ratios, then by oxo and hydroxyfluoro complexes and, finally, by uncomplexed species.

(d) Behavior of Pa(v) in sulfuric acid solution

Freshly precipitated Pa(v) hydroxide is readily soluble in moderately concentrated H_2SO_4 and permanently stable solutions, containing up to 90 g L^{-1} of ^{231}Pa in approximately 2.5 M H_2SO_4, have been reported (Thompson, 1952; Kirby, 1959, 1966; Brown *et al.*, 1961; Campbell, 1964; Bagnall *et al.*, 1965; Takagi and Shimojima, 1965; Kirby and Figgins, 1966). The solubility falls off sharply at both ends of the acid concentration range, yielding amorphous hydrated oxides or colloids in <1 M H_2SO_4 and crystalline $H_3PaO(SO_4)_3$ in

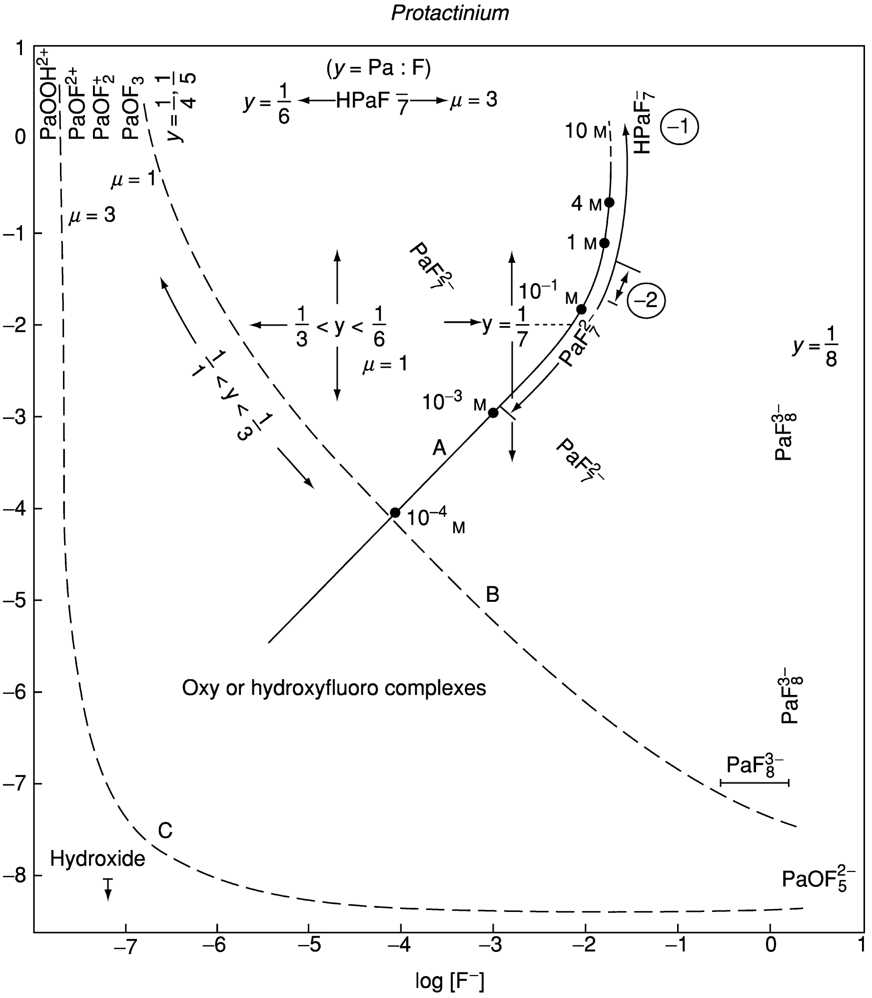


Fig. 4.17 *Fluoro complexes of Pa(*v*) as a function of* [*HF*], [H^+], *and* [F^-] (*Guillaumont* et al., 1968).

concentrated H_2SO_4 (Bagnall *et al.*, 1965; Takagi and Shimojima, 1965; Stchouzkoy *et al.*, 1966b, 1968).

The sulfate complexes of Pa(v) that have been deduced from tracer-level studies ([Pa] $\leq 10^{-4}$ M) are listed in Table 4.18. The absorption spectra of Pa(v) in H_2SO_4 are shown in Fig. 4.18 (Guillaumont *et al.*, 1960; Guillaumont, 1966c).

Table 4.17 *Stability constants for some suggested fluoride complexes of Pa(v).*

μ	$[H^+]$ (M)	$[F^-]$ (M)	*Suggested species*	*Stability constants*	*References*
1	≤0.1	≤0.1	PaF_3^{2+}	$\log K_3 = 4.9$	Bukhsh *et al.* (1966a)
			PaF_4^+	$\log K_4 = 4.8$	
			PaF_5	$\log K_5 = 4.5$	
			PaF_6^-	$\log K_6 = 4.4$	
			PaF_7^{2-}	$\log K_7 = 3.7$	
			PaF_8^{3-}	$\log K_8 = 1.7$	
3	1–3	$\leq 10^{-6}$	$Pa(OH)_2F^{2+}$	$K_1 = 3.6 \times 10^3$	Guillaumont (1966a,c)
			$Pa(OH)_2F_2^+$	$K_2 = 4.45 \times 10^7$	
			$Pa(OH)_2F_3$	$K_3 = 8.2 \times 10^{10}$	
1	1	$\leq 10^{-6}$	PaF^{4+}	$K_1 = 9 \times 10^3$	Kolarich *et al.* (1967)
			PaF_2^{3+}	$K_2 = 3 \times 10^3$	
			PaF_3^{2+}	$K_3 = 1.1 \times 10^3$	

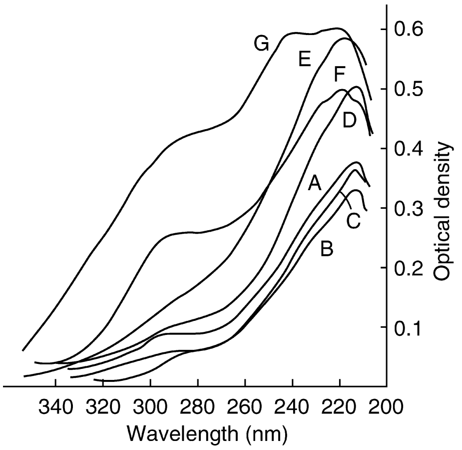
Table 4.18 *Stability constants for some suggested sulfate complexes of Pa(v).*

μ	$[H^+]$ (M)	$[SO_4^{2-}]$ (M)	*Suggested species*	*Stability constants*	*References*
1	1	≤1	$[PaO_x(OH)_{4-2x}SO_4]^-$	$K_1 = 0.94$	Nowikow and Pfrepper (1963)[a]
				$K_2 = 7.39$	
2	2	≤1	$[PaO_x(OH)_{2-2x}(SO_4)_2]^-$	$K_1 = 1.14$	
				$K_2 = 14.70$	
3	1–3	≤3	$PaOSO_4^+$	$K_1 = 19.3$	Guillaumont (1966c)
			$PaO(SO_4)_2^-$	$K_2 = 320$	
1	1	≤1	$PaSO_4^{3+}$	$K_1 = 120$	Kolarich *et al.* (1967)[a]
			$Pa(SO_4)_2^+$	$K_2 = 1.7$	
1.38	0.3	≤0.4	$Pa(OH)_2SO_4^+$	$K_1 = 6.4$	Mitsuji and Suzuki (1967c)
1	0.1–1	≤0.2	$PaOOH(HSO_4)^+$	$K_1 = 31$	LeCloarec *et al.* (1973)
		≤0.2	$PaO(HSO_4)_2^+$	$K_2 = 250$	

[a] Only the ratio $[Pa]:[SO_4^{2-}]$ was determined.

(e) Miscellaneous complexes of Pa(v) with inorganic ligands

The absorption spectra and the formation constants of complexes formed by tracer-level Pa(v) in phosphoric acid solution have been reported by LeCloarec and Muxart (1973), LeCloarec *et al.* (1973), and LeCloarec (1974). The species identified were $PaO(OH)\ ^-(H_2PO_4)^+$, $HPaO(H_2PO_4)_2^{2+}$, $PaO(H_2PO_4)_2^+$, and $PaO(H_2PO_4)_3$.



Curve	$[H_2SO_4]$ (M)	[Pa(v)] (M)
A	0.7	0.35×10^{-4}
B	1.32	0.40×10^{-4}
C	2.2	0.45×10^{-4}
D	4.1	0.42×10^{-4}
E	6.5	0.49×10^{-4}
F	9	0.18×10^{-4}
G	18	0.19×10^{-4}

Fig. 4.18 *Absorption spectra of Pa(v) in H_2SO_4 solution (Guillaumont,* 1966*c).*

The addition of ≤1 M H_2O_2 to a solution of ^{233}Pa in aqueous $HClO_4$ (1 M ≤ $[H^+]$ ≤3 M) leads to the formation of the following peroxy complexes: $PaO(OH)(HO_2)^+$, $PaO(OH)(HO_2)_2$, $PaO(HO_2)^{2+}$, and $PaO(HO_2)_2^+$, according to Stchouzkoy *et al.* (1969). Association constants for the 1:1 and 1:2 complexes of Pa(v) with IO_3^- have been reported by Kolarich *et al.* (1967).

Pa(v) forms mixed complexes in solutions containing more than one type of ligand. For example, a species identified as $PaO(H_2PO_4)_3(HSO_4)^-$ is found in a mixture of 0.35 M H_3PO_4 and 0.22 M H_2SO_4 (LeCloarec *et al.*, 1973). Mixed complexes are also formed in hydrochloric or nitric acid solutions containing $\leq 10^{-2}$ M HF (Hardy *et al.*, 1958; Casey and Maddock, 1959b; Shankar *et al.*, 1963; Plaisance and Guillaumont, 1969). Formation constants have been determined for the unidentified mixed complexes formed by Pa(v) in 3–6 M HNO_3 to which HCl, $(NH_4)_2SO_4$, $(NH_4)_2HPO_4$, or H_3AsO_4 was added (Davydov *et al.*, 1966b).

Finally, the existence of a perprotactinate ion with a charge of 3– is suggested by the fact that Pa(v) ($\sim 3 \times 10^{-4}$ M) is soluble in alkaline media in the presence of H_2O_2 (Stchouzkoy *et al.*, 1966a).

4.8.3 Organic complexes of Pa(v) in aqueous solution

Only a few systematic studies have been done of the aqueous complexes of Pa(v) with organic reagents. Galateanu and co-workers (1962a,b, 1966), Moskvin *et al.* (1963) used the ion-exchange method to determine the stability constants of the complexes formed with a number of organic acids (Table 4.19). Stability constants have also been reported for complexation by acetylacetone (Liljenzin and Rydberg, 1966; D'yachkova *et al.*, 1968b; Liljenzin, 1970),

Table 4.19 *Stability constants of complexes formed by Pa(v) with various organic acids* ($\mu = 0.25$) (*Galateanu and Lapitskii,* 1962*a,b*; *Moskvin* et al., 1963; *Galateanu*, 1966; *Lapitskii and Galateanu*, 1963).

		Stability constant for Pa:ligand ratio		
Acid	*pH*	1:1	1:2	1:3
lactic (≤0.1 м)	1.5–2.7	1.75×10^2		
α-hydroxyisobutyric (≤0.5 м)	0.98–1.2		3.0×10^3	1.0×10^7
mandelic (≤0.5 м)	1.0–1.1	9.1×10^2		
malic (≤0.65 м)	0.8–0.87	8.3×10^2	6.3×10^4	
tartaric (≤0.65 м)	0.75–0.8	1.7×10^2	2.1×10^4	
trihydroxyglutaric (≤0.7 м)	0.95–1.2	9.1×10^2	7.7×10^7	
oxalic (≤0.7 м)[a]	0.7–0.8	3.6×10^2	8.0×10^5	1.1×10^6
citric (≤0.7 м)[b]	0.7–0.95	4.5×10^3	2.3×10^5	6.3×10^8
aconitic (≤0.7 м)	0.75–0.8	1.5×10^2		
ethylenediaminetetraacetic acid (≤0.02 м)[c]	2.4–2.7	1.5×10^8	9.1×10^{11}	
amygdalic (≤0.5 м)	1.1	8.5×10^2		

[a] cf. Carrere (undated); Davydov *et al.* (1966a,b); Guillaumont (1966a,c).

[b] cf. Guillaumont (1968).

[c] cf. Shiokawa *et al.* (1969).

DIAPA (Mikhailov, 1960), and TTA (Guillaumont, 1965a; D'yachkova *et al.*, 1968a).

Oxalic acid has been singled out for special attention because of its importance in the analytical and process chemistry of ^{231}Pa. Davydov and Pal'shin (1967) found that the solubility of Pa(v) at 25°C remained low in <0.05 м $H_2C_2O_4$, but increased sharply from 0.33 to 4 g L^{-1} or more between 0.05 and 0.5 м $H_2C_2O_4$. The low solubility was attributed to the formation of hydroxy complexes with a Pa:C_2O_4 ratio of 1:1, while the higher solubility was explained by the formation of complexes with a 1:2 ratio. Casey and Maddock (1959b) suggested the existence of complexes of the form $Pa(C_2O_4)_3^-$, and $Pa(C_2O_4)_4^{3-}$, but Guillaumont (1966a,c) suggested that these were preceded by the formation of $PaOC_2O_4^+$ and $PaO(C_2O_4)_2^+$.

It was shown that protactinium(v) forms a colored compound with Arsenazo-III in highly acidic solutions with a 1:1 ratio (Pal'shin *et al.*, 1962). Complex compounds formed with a large number of other organic reagents, such as 8-oxyquinoline (Maddock and Miles, 1949; Vernois *et al.*, 1963), BPHA (Cristallini and Flegenheimer, 1963; D'yachkova and Spitsyn, 1964), tannin (Elson *et al.*, 1951; Casey and Maddock, 1959a), 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 (Myasoedov and Molochnikova, 1968), pyrogallol, catechol, and gallic acid (Casey and Maddock, 1959a), and are used in the analytical chemistry of protactinium. However, literature data on the composition and stability of these compounds are absent.

4.8.4 Redox behavior in aqueous solution

The standard electrode potential of the Pa(v)/Pa(iv) couple has been estimated to be –0.1 V (vs. normal hydrogen electrode [NHE]) by Fried and Hindman (1954) and –0.25 V by Haïssinsky and Pluchet (1962), the latter value being based on a measured electrochemical potential of –0.29 ± 0.03 V in 6 M HCl.

Pa(iv) was prepared by Haïssinsky (Haïssinsky and Bouissières, 1948, 1951; Bouissières and Haïssinsky, 1949), who reduced 0.1–2 mg of ^{231}Pa(v) with solid Zn amalgam or $CrCl_2$ in 1–3 N HCl or H_2SO_4. Brown *et al.* (1959) found that Zn amalgam gave complete reduction in 5–6 h only if the initial solution was $\geq$6 M in HCl; lower acidities led to the formation of colloidal Pa(v), which was difficult to reduce. Mitsuji (1967a,b) used liquid Zn amalgam to obtain complete reduction in a few minutes of 4×10^{-4} M ^{231}Pa(v) in 1–11 M HCl or 0.05–9 M H_2SO_4. Tracer-level Pa(v) could not be completely reduced unless Cr(iii) was added to the system. ^{233}Pa(iv) has also been obtained by dissolution of neutron-irradiated ^{232}Th metal in 1 M HCl by Manier and co-workers (1969, 1970) or of neutron-irradiated $^{232}ThX_4$ (X = Cl, Br, I) in 0.02 M $ThCl_4$ (Carlier, 1971; Carlier and Genet, 1972a,b). In the first case, the yield of Pa(iv) was about 20%; in the second, it varied with the nature of the irradiated halogen and the pH of dissolution, ranging from less than 20% at pH $\leq$ 3 to approximately 80% for $ThCl_4$ at pH 5.5.

Musikas (1966) has described the electrolytic reduction of 10^{-3} M ^{231}Pa(v) in 8 M HCl, 0.5 M H_2SO_4, and 5 M NH_4F (pH 7.2). Electrolysis at 50 mA for 5 h completely reduced Pa(v) in 8 M HCl to Pa(iv). The reduction of 10^{-13} M Pa(v) on a Pt–H_2 electrode in aqueous solutions of acetylacetone at pH > 7 has also been reported (Liljenzin and Rydberg, 1966).

The polarography of Pa has been studied in various aqueous media (Elson, 1954; deMiranda and Maddock, 1962; Musikas, 1966; Schwochau and Astheimer, 1970; Astheimer and Schwochau, 1973). All solutions gave at least one wave, corresponding to the one-electron change, Pa(v)→Pa(iv), and in some cases a second wave, which might represent either the reduction, Pa(iv)→Pa(iii), or, more probably, the catalytic reduction of H^+. For example, with $[NH_4F] = 3.84$ M, pH 7.2, $[^{231}\text{Pa(v)}] = (2.3\text{–}9.5) \times 10^{-4}$ M, the wave height at $E_{1/2} = -1.29$ V (vs. standard calomel electrode [SCE]) was proportional to [Pa], but that of the second wave ($E_{1/2} = -1.57$ V) was not (deMiranda and Maddock, 1962). In DMSO, the reduction of $PaCl_4$ led directly to Pa(0) in a single step ($E_{1/2} = -1.49$ V), with the 3+ oxidation state omitted (Astheimer and Schwochau, 1973).

The behavior of protactinium in the TmI_2–TmI_3–THF system (THF, tetrahydrofuran) was studied by the cocrystallization method. In the presence of Tm^{2+}, microamounts of Pa cocrystallize with the solid phase of TmI_3 solvate, the cocrystallization coefficient (K_c) being nearly 1. A similar K_c for this system was obtained with Ce. Thus, in THF in the presence of Tm^{2+}, protactinium is probably reduced to the oxidation state 3+ (Kulyukhin *et al.*, 1996, 1997). Attempts to reduce Pa(v) to the trivalent state by Sm(ii) or Tm(ii) in chloride melts at high temperatures were reported by Mikheev *et al.* (1992). Using a cocrystallization method of Pa with the Sm(II) and Tm(II) system, the authors proposed that under these conditions the stabilization of the Pa(III) species was obtained. In the system with PrOCl, the Pa(III) reduction to Pa(II) has been detected. The standard redox potential of Pa(III)/Pa(II) couple has been calculated as –2.59 ± 0.1 V (vs. NHE) (Mikheev *et al.*, 1993a,b). Pa(II) also was produced by interaction of ^{233}Pa(V) with the cluster PrI_2 (Kazakevich *et al.*, 1993). It was shown that An = Pa, U, Np, Pu with the electronic configuration ($5f^{n-1}6d$) in the divalent state, were stabilized in clusters of the type $(Pr,An)I_2$ in the $LiI–PrI_2–PrI_3$ system (Kulyukhin and Mikheev, 1998). The influence of the electronic configurations of Pa^{2+} (f^3 and f^2d) and Pa^{3+} (f^2 and fd) upon the stability of divalent and trivalent protactinium and their redox potentials was examined by Guillaumont *et al.* (1996). An analysis of the stabilization of the configuration $5f^26d$ (Pa^{2+}) led to predictions of the relative scale for the $E^{\circ}_{Pa(III)/Pa(II)}$ potentials which depend on the medium and on ligands. For this purpose the relation between the energy ($f^3 \rightarrow f^2d$) for Pa(II) in water ($Pa^{2+}\cdot aq$) and in solid ($Pa^{2+}:CaF_2$) was established. The values of the redox potentials were discussed on the basis of the 6d electron stabilization of Pa^{2+} and destabilization of Pa^{3+} ions. The standard redox potential $E^{\circ}_{Pa(III)/Pa(II)}$ was estimated to be around −4.0 V, and for the couple Pa(IV)/Pa(III) about –2.1 V (vs. NHE). This result was confirmed by a measurement of E_{fd} in Pa^{4+}(aq) and by correlation of E_{fd} for Pa^{2+}(aq), Pa^{3+}(aq), and Pa^{4+}(aq) with the corresponding redox potentials (Guillaumont *et al.* 1996). Standard reduction potentials are given in Chapter 19, Fig. 19.9.

Pa(IV) in aqueous solution is rapidly oxidized by air, but the rate of oxidation is decreased by the exclusion of O_2 and by the presence of complexing anions (Brown *et al.*, 1959; Brown and Wilkins, 1961; Guillaumont, 1966b; Bagnall and Brown, 1967; Mitsuji, 1967a). Guillaumont *et al.* (1960) found that the stability of ^{231}Pa(IV) increased with increase in $[H_2SO_4]$ or [HCl], but Myasoedov *et al.* (1966b) reported the opposite effect. The oxidation rate was increased by ultraviolet light or heat. In the absence of air, Pa(IV) in a neutral solution of 2.2 M $N(CH_3)_4F$ was oxidized at the rate of about 1% per day (deMiranda and Muxart, 1964). Mitsuji (1967a) has proposed the reaction:

$$2Pa^{4+} + 2H^+ \leftrightarrow 2Pa^{5+} + H_2$$

The half-life for the oxidation of ^{233}Pa(IV) in the absence of redox buffers decreases exponentially with increase in $[H^+]$, but the formation of complexes tends to stabilize the 4+ oxidation state. The stability of Pa(IV) is greatly enhanced by a decrease in the dielectric constant; thus, in 0.6 M $HClO_4$ (10% H_2O/90% C_2H_5OH), the half-life for oxidation was 40 h, as compared with $\tau_{1/2} \sim 1$ h in a pure aqueous solution (Manier *et al.*, 1969; Manier, 1970; Manier and Genet, 1970). The oxidation of Pa(IV) by molecular halogens is first-order with respect to both [^{233}Pa(IV)] and [Cl_2, or Br_2, or I_2] (Carlier, 1971; Carlier and Genet, 1972a).

4.8.5 Aqueous chemistry of Pa(iv)

The most characteristic property of Pa(iv) in aqueous solution is that, unlike Pa(v), it is precipitated by hydrofluoric acid (Haïssinsky and Bouissières, 1948; Bouissières and Haïssinsky, 1949). It is also precipitated by IO_3^-, PO_4^{3-}, $P_2O_6^{4-}$, phenylarsonate, and saturated K_2SO_4, but forms soluble carbonate, citrate, and tartrate complexes (Haïssinsky and Bouissières, 1951). PaF_4 is soluble in 15 M NH_4F (Haïssinsky *et al.*, 1961).

The spectrophotometry of Pa(iv) has been investigated in perchloric (Brown and Wilkins, 1961), hydrochloric (Fried and Hindman, 1954; Brown *et al.*, 1959; Guillaumont *et al.*, 1960; Brown and Wilkins, 1961; Bagnall and Brown, 1967; Mitsuji, 1967a), hydrobromic (Brown and Wilkins, 1961), and sulfuric (Guillaumont *et al.*, 1960; Brown and Wilkins, 1961; Myasoedov *et al.*, 1966b; Mitsuji, 1967a) acid solutions and in neutral fluoride media (Haïssinsky *et al.*, 1961; deMiranda and Muxart, 1964; Asprey *et al.*, 1967). The reduction of Pa(v) in acid solutions is accompanied by the disappearance of the prominent absorption band at 210–215 nm (Figs. 4.16 and 4.18) and the appearance of bands at 225–230, 255–265, and 275–290 nm. Beer's law is not followed in hydrochloric acid solutions, but, for (0.65–1.5) × 10^{-4} M Pa(iv) in 0.5–6 M H_2SO_4, the molar extinction coefficient (ε) is about 1500 L M^{-1} cm^{-1} at 290 nm (Myasoedov *et al.*, 1966b). In neutral fluoride media, the spectrum is different according to the nature of the medium: in NH_4F, bands are observed at 355 and 250 nm (Haïssinsky *et al.*, 1961); but in $N(CH_3)_4F$, the absorption maxima are at 344 and 323 nm, with $\varepsilon = 0.08$ and 0.037 M^{-1} cm^{-1}, respectively (deMiranda and Muxart, 1964).

Pa(iv) hydrolyzes less readily than Pa(v). In 3 M $HClO_4$, the dominant species are Pa^{4+} and $PaOOH^{2+}$ (cf. Fig. 4.14). As the acidity is decreased at constant ionic strength ($\mu = 3$), $Pa(OH)^{3+}$, PaO^{2+} or $Pa(OH)_2^{2+}$, and $PaO(OH)^+$ or $Pa(OH)_3^-$ appear successively; their hydrolysis constants, as determined by Guillaumont (1965b, 1966b), are 0.725, 0.302, and 0.017, respectively. Estimates of the relative amounts of these species as a function of $[H^+]$ are indicated in Fig. 4.19.

Mitsuji (1968), however, finds that $Pa(OH)_2^2+$ is the most probable ionic species at pH 0.4–1.1 ($\mu = 0.5$). Lundqvist (1974c,d, 1975) believes that PaO^{2+} is more probable, because of the high stability of that ion toward both ethylenediaminetetraacetic acid (EDTA) and acetylacetone. He finds no evidence for species either more or less hydrolyzed than $Pa(OH)_2^{2+}$ at pH 0–10.

There is, as yet, little information about the complexes formed by Pa(iv). Guillaumont (1966a,c) has calculated the formation constants of the following complexes at $\mu = 3$, $[H^+] = 3$ M, and $[Cr^{2+}] = 10^{-2}$ M: $PaCl^{3+}$ ($K_1 < 1$). $PaCl_2^{2+}$ ($K_2 = 1$), $PaSO_4^{2+}$ ($K_1 = 42$), $Pa(SO_4)_2$ ($K_2 = 153$), PaF^{3+} ($K_1 = 5.34 \times 10^4$), and PaF_2^{2+} ($K_2 = 1.8 \times 10^3$). Muxart *et al.* (1966b) found no anionic chloro complexes except at high acidity, e.g. $PaCl_6^{2-}$ in ~8 M HCl. Mitsuji (1968) finds that $Pa(SO_4)(OH)^+$ ($K = 320$) is the most probable ionic species formed by HSO_4^- at

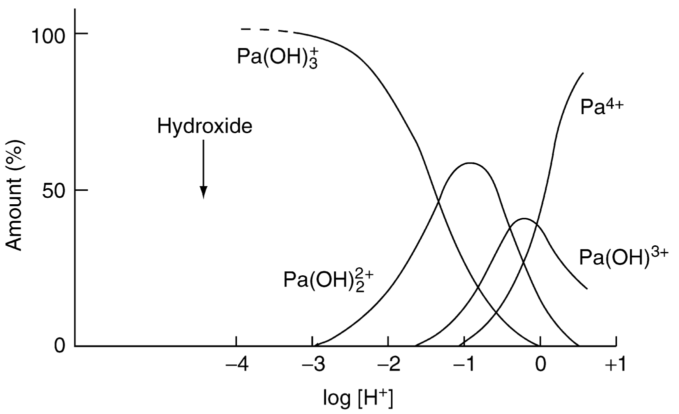


Fig. 4.19 *Distribution of the ionic species of* ^{233}*Pa(IV) as a function of* [H^+] *in non-complexing media of ionic strength* $\mu = 3$ (*Guillaumont*, 1966*a*).

pH 0.4–1.1, $\mu = 0.5$, 10°C. A comparable value is reported by Lundqvist (1974c), who has also determined stability constants for the complexes formed by ^{233}Pa(IV) with acetylacetone (Lundqvist, 1974a; Lundqvist and Rydberg, 1974), TOPO (Lundqvist, 1974b), EDTA (Lundqvist and Andersson, 1974), and benzoylacetone (Lundqvist, 1975).

Recently, the $6d^1 \rightarrow 5f^1$emission spectrum of Pa^{4+} in aqueous acidic solution was reported. The peak maximum was at 460 nm with a half-width of (61.6 ± 1.4) nm and a lifetime of (16 ± 2) ns (Marquardt *et al.*, 2004).

4.9 ANALYTICAL CHEMISTRY

Protactinium determination in natural materials is very complicated because of the extremely small content of Pa in the samples, as well as its tendency to hydrolyze. The presence of other elements, with chemical properties similar to protactinium, highly influences the behavior of protactinium in solutions.

Spectral, spectrophotometric, gravimetric, and other methods are used for the determination of macroquantities of protactinium. However, they are often invalid for the analysis of natural objects that contain very small amounts of protactinium. In these cases radiometric methods are preferable but they need careful purification of protactinium from macroelements and other radioactive materials.

4.9.1 Radiometric methods

The basis of the simplest methods for the determination of the long-lived protactinium isotope, ^{231}Pa, in natural objects (the ores, rocks, waste products), various solutions, and other samples is the measurements of α-activity and

γ-rays. The determination of the artificial protactinium isotope, ^{233}Pa, also is usually carried out by measurements of its γ-rays or β-particles.

(a) The determination of ^{231}Pa by α-counting

The large specific activity of ^{231}Pa isotope, equal to 10^6 alpha decays min^{-1} mg^{-1} of element (Bagnall, 1966a) allows the use of this method for the determination of submicrogram amounts of protactinium after its isolation in the radiochemically pure state.

α-Counters, such as ionization chambers, scintillation or proportional counters, are utilized for the measurements of α-activity of protactinium samples. Absolute quantities of protactinium are determined by comparison of the α-activity of the protactinium sample without other α-emitting isotopes with the activity of standard samples of ^{231}Pa, ^{239}Pu, RaD (^{210}Pb) + RaE (^{210}Bi) + RaF (^{210}Po), ^{210}Po, measured under the same conditions.

Usually protactinium samples for α-counting are prepared by evaporation of a known aliquot of the solution under investigation, after placing it on a platinum, stainless steel, or glass plate.

Thin layers are formed by placing the organic phase directly on a plate for counting, for instance, after extraction of protactinium with DIBK (Scherff and Hermann, 1964; Rona *et al.*, 1966).

Multichannel alpha-spectrometers are used for control of radiochemical purity of isolated samples (Salutsky *et al.*, 1957; Spitsyn and D'yachkova, 1960; Myasoedov and Pal'shin, 1963; Suzuki and Inoue, 1966). ^{231}Pa also can be characterized with enough reliability by its γ-rays spectrum (Salutsky *et al.*, 1956, 1957; Barnett, 1957; Suzuki and Inoue, 1966). Samples for alpha-spectrometers can be prepared by the electrolytic technique (Ko, 1956, 1957; Shimojima and Takagi, 1964; Smith and Barnett, 1965).

The application of alpha-spectrometers with high resolution ($\sim$0.5%) in some cases allows the determination of protactinium without separation from other α-emitters (Glover *et al.*, 1959; Jackson *et al.*, 1960b; Brown and Maddock, 1967). The alpha-spectrum of ^{231}Pa has the following main groups of α-particles: 5.046 (10%), 5.017 (23%), 5.001(24%), 4.938 (22%), and 4.722–4.666 MeV (13%) (Hyde, 1961). So 79% of ^{231}Pa α-particles emitted have energies within the interval 4.85–5.15 MeV. Measurements in this energy range with the alpha-spectrometer, previously calibrated with a pure ^{231}Pa sample, allow the determination of protactinium in the presence of other radioactive elements. Only ^{227}Ac (α-particles energy is 4.947 MeV) slightly influences measurements in this case. The effect of ^{227}Ac may be excluded completely if the protactinium α-particle energies in the interval 5.001–5.041 MeV are measured with a spectrometer that has a silicon detector with resolution of about 0.1%. The alpha-spectrometric method, developed by Glover *et al.* (1959), allows the determination of up to 10^{-4}% of protactinium in various natural objects with a relative precision of ±5%.

(b) The determination of ^{231}Pa by the γ-rays

The measurement of ^{231}Pa γ-rays is widely used for the quick determination of the protactinium concentration in the absence of other radioactive admixtures in solutions, in salts, and compounds of protactinium after their dissolution, and also for control of the protactinium behavior during its separation from waste solutions and solid residue (Barnett, 1957, 1958; Guillaumont *et al.*, 1960; Haïssinsky *et al.*, 1961; Stchouzkoy and Muxart, 1962; Miranda and Muxart, 1964a,b; Guillaumont, 1966a,c; Pissot *et al.*, 1966; Stchouzkoy *et al.*, 1966a,b).

In the γ-ray spectrum of ^{231}Pa there are three maxima, corresponding to the energies of γ-rays 27, 95, and 300 keV. The quantitative determination of protactinium is carried out with γ-spectrometers by comparison of γ-ray intensities from the sample under investigation in the region 300 keV with the intensity of the standard, containing a known amount of radiochemically pure protactinium. The sensitivity of this method is approximately 1×10^{-6} g Pa. So, for instance, it can determine 1.4×10^{-6} g Pa in a 5 g sample. The precision of this method is $\pm 5\%$ (Salutsky *et al.*, 1957). ^{227}Ac (0.095 and 280 keV) and ^{226}Ra (0.080 and 320 keV) prevent the determination.

(c) The determination of ^{234}Pa

The immediate short-lived daughters of U-238 are Th-234 and Pa-234. These nuclides are β^--emitters having energy bands that overlap the uranium bands in a liquid scintillation spectrum. ^{234}Pa is a high-energy β^--emitter that can be further identified and quantified from its Cerenkov radiation. Energy spectra were collected on the Packard 2500AB liquid scintillator analyzer for uranium solutions in diisopropylnaphthalene and pseudocumene-based scintillator cocktails. Calibration curves were prepared for nitric, hydrochloric, and sulfuric acid media (Huntley *et al.*, 1986; Grudpan *et al.*, 1990; Bower *et al.*, 1994).

(d) The determination of ^{233}Pa

Quantitative determination of ^{233}Pa is carried out by β^--particles (Fudge and Woodhead, 1956; McIsaak and Freinling, 1956; McCormac *et al.*, 1960; Sakanoue *et al.*, 1964) as well as γ-rays (Fudge and Woodhead, 1956; Moore and Reynolds, 1957; Arden *et al.*, 1962; Stricos, 1966) by comparison of the intensity of the sample under investigation with the intensity of a standard containing a known amount of ^{233}Pa.

The absolute amount of ^{233}Pa in a standard is determined by the β^--activity measurement on 4π-counters (Fudge and Woodhead, 1956; McCormac *et al.*, 1960).

A method, developed for the determination of absolute amounts ^{233}Pa in irradiated metallic thorium, consists of the measurement of ^{233}Pa β-particles after its chemical separation (McCormac *et al.*, 1960). This method is quick and simple and provides 70–80% protactinium yield and high degree of purification of protactinium from fission elements (10^6 times). For the separation of ^{233}Pa in a radiochemically pure state for its determination in neutron-irradiated thorium, Moore and Reynolds (1957) used the extraction with DIBC from 6 M HCl in the presence of oxalic acid, with almost all admixtures remaining in aqueous phase.

Fudge and Woodhead (1956) carried out the radiochemical purification of protactinium by ^{233}Pa precipitation with niobium tannate in the presence of EDTA. The separation of niobium and protactinium was carried out by paper chromatography or by protactinium precipitation with barium fluorozirconate.

4.9.2 Radioactivation methods

A quite large value of the thermal-neutron cross-section (^{231}Pa, 211 barns) (Smith *et al.*, 1956; Holtzman, 1962) allows the use of the nuclear reaction $^{231}\mathrm{Pa}(n,\gamma)^{232}\mathrm{Pa}$ for protactinium determination. In some cases it is better to measure ^{232}U, the daughter of the ^{232}Pa decay product, after the separation of uranium in a radiochemically pure state. This method allows the determination of 10^{-8} to 10^{-10} g of ^{231}Pa (Sakanoue *et al.*, 1965).

4.9.3 Spectral and X-ray methods

Spectral methods are not practical for the direct determination of protactinium in natural samples and other materials because of the low sensitivity and experimental complications. Usually emission spectral analysis is applied only for the detection of admixtures (Nb, Fe, Mg, Al, Sn, Cu, Si, and others) in pure samples of protactinium (Sackett, 1960; Spitsyn and D'yachkova, 1960; Walter, 1963; Birks *et al.*, 1965; Cunningham, 1966; Kirby and Figgins, 1966; Roberts and Walter, 1966).

The emission spectrum of protactinium has been investigated (Schüller and Gollnow, 1934; Thompson, 1951; Richards and Atherton, 1961, 1963; Richards *et al.*, 1961; Giaechetti, 1966). There are a few thousand lines in the range 2650–25 000 Å, and many of them have hyperfine structure. Tomkins and Fred (1949) observed 263 lines in the range 2640.3–4371.4 Å; the most sensitive and definite lines are at 3957.8, 3054.6, and 3053 Å. The sensitivity of protactinium determination is 0.2 μg Pa by use of these lines with the copper spark method. According to the data of Spitsyn and D'yachkova (1960), lines at 2732.2, 2743.9, and 2755.9 Å are also characteristic for protactinium. The X-ray spectrum of Pa_2O_5 has been investigated by Russell (1913) and Grosse and co-workers (Beuthe and Grosse, 1930; Pierce and Grosse, 1935; Grosse, 1939). Twenty-one lines of the L-series were found in the range 1088.5×10^{-11} to 586.6×10^{-11} cm and 14 lines of M-series in the range 518.2×10^{-11} to 252.2×10^{-11} cm. The information about other lines in these series has been reported in the literature (Dolejsek and

Kunzl, 1936; Cauchois and Hulubel, 1947; Cauchois and Bonnelle, 1966). A more recent compilation is given in Browne *et al.* (1954).

A comparative study of the photoacoustic spectra of lanthanide and actinide oxides (protactinium included) has been given by Heinrich *et al.* (1986).

4.9.4 Electrochemical methods

(a) Polarographic

The application of the polarographic method for the determination of protactinium is limited by the irreversibility of the Pa reduction process on the mercury drop electrode in many media.

(b) Potentiometric and amperometric

An oxidimetric method for Pa(IV) determination in chloride and sulfate solutions by titration with 6.7×10^{-2} M $FeCl_3$ solution was described by Musikas (1966). The final point was determined by a potentiometric method at a given current of 5 μA and an amperometric method at a given potential of 0.2 V. The platinum electrode was used as the indicator electrode, and a saturated calomel electrode was used as reference electrode. The titration was carried out in a special cell with a magnetic stirrer under nitrogen atmosphere.

The relative error for 3.65×10^{-2} to 4.08×10^{-2} M Pa in 6–8 N HCl or 1.0–1.8 N H_2SO_4 was nearly ±3%. The method is used for determination of the extent of Pa(V) reduction by an electrolytic method with the application of an amalgamated silver electrode.

4.9.5 Spectrophotometric methods

(a) Methods based on the Pa light absorption in mineral acids solutions

The absorption spectra of penta- and tetravalent protactinium in aqueous solutions of hydrochloric acid (Fried and Hindman, 1954; Nairn *et al.*, 1958; Brown *et al.*, 1959; Casey and Maddock, 1959a; Guillaumont *et al.*, 1959, 1960; Guillaumont, 1966c), sulfuric (Guillaumont *et al.*, 1960; Brown *et al.*, 1961; Brown and Wilkins, 1961; Guillaumont, 1966c; Myasoedov *et al.*, 1966b), perchloric (Guillaumont *et al.*, 1960; Brown and Wilkins, 1961; Guillaumont, 1966a,c) acids, and in neutral fluoride solutions (Miranda and Muxart, 1964a,b) have been studied rather completely. Protactinium complexes with inorganic ligands highly absorb in the ultraviolet part of spectrum at wavelength <250 nm. Protactinium determination by light absorption in solutions of inorganic acids is used very rarely because of the low sensitivity and selectivity of these methods, and also because of complications connected with work in ultraviolet part of the spectrum. Nevertheless the existence of characteristic bands in the absorption spectra of protactinium allow their use for the determination of protactinium concentration and for identification of protactinium valence state in some cases.

(b) Methods based on reactions with organic reagents

Effective spectrophotometric methods for the determination of microgram amounts of protactinium with application of organic reagents have been described. The advantage of such methods is their high sensitivity and the possibility of protactinium determination without previous separation from other radioactive elements that usually prevent radiometric determination of protactinium. Spectrophotometric methods for the determination in very acidic solutions are especially worthwhile. In this case complications connected with the hydrolysis of protactinium ions are excluded, and the selectivity of determination, reproducibility, and reliability of the methods increase considerably.

Pentavalent protactinium forms a stable complex with Arsenazo-III, hence this reaction is accompanied by the change of the red color of the reagent to green after mixing. The formation of the colored compound takes place in a wide interval of acidity: from slightly acidic media to 10 N H_2SO_4 or HCl and even in more concentrated solutions. Absorbance of the solution of protactinium complex compound reaches a maximum immediately after the reagent addition and does not change for at least 24 h. The reaction of Pa with the reagent is rather sensitive; the molar extinction coefficient at 660 nm is equal to 2.2×10^4 L· M^{-1} cm^{-1}. The error of the protactinium determination at the concentration 0.3–3.1 mg L^{-1} in the absence of interfering elements is ±3.5% (Pal'shin *et al.*, 1962).

According to the data of Pal'shin *et al.* (1962) the complex compound of protactinium with Arsenazo-III is quantitatively extracted by an equal volume of isoamyl alcohol from solutions with sulfuric acid concentration >2 M. The extraction of the protactinium compound from very acidic solutions of sulfuric acid gave high selectivity. In addition there is no necessity for the previous separation of contaminants. The error of the protactinium determination at a concentration 3 mg L^{-1} is less than 3% in the presence of a 10^4-fold amounts of Fe(III), Al, Ni; 10^3-fold amounts of Cr(III), La, Mn(II); 200-fold amounts of Bi(III), Sn(IV), Zr, Nb, Mo(VI), U(VI); and 100-fold amounts of Th and Ti(IV).

Pa(V) forms with TTA a colored complex compound, slightly soluble in aqueous solutions, but very soluble in many organic solvents (Myasoedov and Muxart, 1962a,b; Pal'shin and Myasoedov, 1963). The extraction-photometric method of protactinium determination with TTA is rather sensitive (~1 mg L^{-1} Pa) and highly selective. The molar extinction coefficient of protactinium complex with TTA is equal to 1.4×10^4 and 0.9×10^4 L· M^{-1} cm^{-1} at 430 and 440 nm, respectively. Beer's law is followed for concentrations of Pa in the solution over the range from 1.3 to 8.7 mg L^{-1}.

4.9.6 Gravimetric methods

Gravimetric methods of protactinium determination are used relatively rarely because of their low sensitivity. Nowadays this method is applied mainly for the determination of milligram amounts of Pa in solutions and in compounds. Protactinium is isolated from solutions in the form of insoluble compounds with inorganic or organic reagents. The choice of reagent for precipitation depends on the presence of other elements in solution.

The weighing of Pa_2O_5 is the final operation in most gravimetric determinations of protactinium after its precipitation in the form of hydroxide, peroxide, iodate, phenylarsonate, cupferronate, and following calcinations at 600–1000°C under air for 1–2 h. Pa_2O_5 is suitable and stable weight form for the determination, but it has a large conversion coefficient to protactinium, equal to 0.852. This limits the application of the determination to relatively large amounts of protactinium. The use of phenylarsonate of protactinium is more preferable as the weight form (Myasoedov *et al.*, 1968a). In this case the conversion coefficient is equal to 0.346. The calcinations of the protactinium compounds usually are carried out in platinum crucibles in order to regenerate the element. Concentrated HF or a mixture of HF + H_2SO_4 is used for dissolution of Pa_2O_5.

(a) Protactinium hydroxide

For weight determination protactinium hydroxide is obtained usually by precipitation of protactinium ions from solutions of mineral acids or their mixtures with ammonium hydroxide. The composition of the formed precipitate depends on precipitation conditions and can be represented as $Pa_2O_5 \cdot xH_2O$. Under precipitation by NaOH or KOH solutions it is necessary to wash thoroughly the precipitate to remove the adsorbed alkali metal ions. The precipitation of protactinium hydroxide is often used for analysis of some protactinium compounds (Grosse, 1934c; Sellers *et al.*, 1954; Bagnall and Brown, 1964; Bagnall *et al.*, 1965; Bukhsh *et al.*, 1966a,b; Stchouzkoy *et al.*, 1966a; Davydov and Pal'shin, 1967).

(b) Protactinium phenylarsonate

Phenylarsonic acid precipitates Pa(v) practically quantitatively from neutral solutions and from solutions of HCl, HNO_3, H_2SO_4, and $HClO_4$ at acids concentration <5 N. The precipitate composition, dried at 120–180°C, corresponds to the formula $H_3PaO_2(C_6H_5AsO_3)_2$. The precipitate is stable and is not changed in weight during heating for few hours at the above-mentioned temperature. As described above, protactinium phenylarsonate can be used for gravimetric determination. This compound may also be converted to Pa_2O_5 by calcination at 1000°C.

The precipitation of protactinium as phenylarsonate from acid solutions can be carried out in the presence of Ni, Co, Cr, La, Fe(III), Mn, Cu, Ti, Th, U, and other elements. Zr, Nb, Ta, fluoro-, and phosphate ions prevent the determination (Myasoedov *et al.*, 1968a).

(c) Protactinium peroxide

Hydrogen peroxide precipitates protactinium from solutions of mineral acids (HNO_3, HCl, H_2SO_4, and $HClO_4$) in the form of amorphous white protactinium peroxide, $Pa_2O_5 \cdot 3H_2O$ (Stchouzkoy and Muxart, 1962; Marples, 1965; Stchouzkoy *et al.*, 1966b). This compound is not stable in air, therefore, the protactinium determination is performed with the calcination of the precipitate to Pa_2O_5. The precipitation of protactinium peroxide from acid solutions can be carried out in the presence of Ni, Co, Cr, Mg, Mn, and other elements, and small quantities of iron. La, Th, U, Zr, and F^- ions prevent the determination. Stchouzkoy and Muxart (1962) recommend carrying out the $Pa_2O_5 \cdot 3H_2O$ precipitation from 0.25 M H_2SO_4 solution, obtained by dissolution of freshly precipitated protactinium hydroxide in sulfuric acid or by some other method.

Pal'shin *et al.* (1968a) applied oxalic acid to increase the selectivity of precipitation with hydrogen peroxide. It was shown that the extent of precipitation of protactinium peroxide from oxalic acid solutions increases with increasing HCl concentration. When the molar relation $H_2C_2O_4$:HCl is equal to 1:5 the extent of precipitation reaches a steady value, and at sufficient excess of hydrogen peroxide the precipitation is quantitative. The method allows determining protactinium in complex solutions and also in the presence of large amounts of zirconium, niobium, and tantalum.

(d) Protactinium iodate

Iodic acid and its salts precipitate Pa(V) from acid solutions in the form of a white volumetric precipitate. Upon standing, especially after heating on a water bath, the precipitate is compressed and is transformed into crystalline form. The composition of protactinium iodate precipitate is not established. According to the data of Kirby (1959) the quantitative precipitation of protactinium (~99.5%) occurs from previously heated solution of protactinium in 0.7 M H_2SO_4 under the addition of a drop at a time of excess 15% HNO_3. The weight determination is performed by calcination of the precipitate to Pa_2O_5 at 800°C (Codding *et al.*, 1964; 1966).

(e) Protactinium cupferronate

There is an indication that CP quantitatively precipitates protactinium from tartaric acid solutions (SalesGrande, 1950) and from solutions of mineral acids (Maddock and Miles, 1949). However, conditions of protactinium precipitation and composition of the formed precipitate have not been investigated in detail. The calcination of protactinium cupferronate at 1000°C leads to the formation of Pa_2O_5 that can be used for weight determination of protactinium.

4.9.7 Determination of protactinium in the environment

High-sensitivity mass spectrometric measurements of the naturally occurring radionuclides ^{231}Pa and ^{230}Th in the deep Canada Basin and on the adjacent shelf indicate high particle fluxes and scavenging rates in this region. The data obtained suggest that offshore advection of particulate material from the shelves contributes to scavenging of reactive materials in areas of permanent ice cover (Edmonds *et al.*, 1998). The scavenging of ^{231}Pa and ^{230}Th was investigated also in the Atlantic Sector of the Pacific Ocean (Yang *et al.*, 1986), and Southern Ocean by combining results from sediment trap and *in situ* filtration studies (Walter *et al.*, 2001). The U–Th–Pa model was realized for environment samples aging (Cheng *et al.*, 1998).

A new technique for the determination of ^{231}Pa in silicate rocks by isotope dilution mass spectroscopy was described (Bourdon *et al.*, 1999). This technique permits the determination down to a 100 fg of ^{231}Pa with a 1–2% uncertainty at the 2 sigma level. The first high-precision ^{231}Pa measurements in a manganese crust applying TIMS using the double filament techniques were described (Pickett *et al.*, 1994). The detection limit using TIMS is at least one order of magnitude lower, and the statistical uncertainty – six to eight times better than for alpha-spectroscopy. Thus, the older section of manganese crust from the Northern Equatorial Pacific could be measured precisely for their Pa-231 activity. The data described by Fietzky *et al.* (1999) reveal significant variations in ^{231}Pa activity for the last 150 ka, which corroborate existing alpha-spectroscopy results. If the growth rate was constant between 0 and 450 ka, the protactinium flux from the water column into manganese encrustations must have been variable. Thus, ^{231}Pa is not suitable for dating marine Mn/Fe deposits.

The determination of ^{231}Pa in environmental and soil materials (Harbottle and Evans, 1997) and in uranium ore samples is provided by gamma-ray spectrometer with high-purity germanium (Zhang Qingwen *et al.*, 1991).

LIST OF ABBREVIATIONS

Arsenazo-III	3,6-bis-[(2-arsonophenyl)azo]-4,5-dihydroxy-2,7-naphthalene disulfo acid
BPHA	*N*-benzoylphenylhydroxylamine
CP	Cupferron
HDEHP	bis(2-ethylhexyl)phosphoric acid
DIAPA	di-isoamylphosphoric acids
DIBC	di-isobutylcarbinol

DIBK	di-isobutylketone
DIPC	di-isopropylcarbinol
DIPK	di-isopropylketone
DMSO	dimethyl sulfoxide
DSBPP	di-*S*-butylphenyl phosphonate
EDTA	ethylenediaminetetraacetic acid
fg	femtogram
Hexone (or MIK)	methyl isobutyl ketone
Ka	thousand years ago
ng	nanogram
NCP	neocupferron
NHE	normal hydrogen electrode
PAA	phenylarsonic acid
Pc	phthalocyaninato
PMBP	1-phenyl-3-methyl-4-benzoylpyrazolone
SCE	standard calomel electrode
TBP	tri(*n*-butyl)phosphate
THF	tetrahydrofuran
TIMS	thermal ionization mass spectroscopy
TOA	trioctylamine
TOPO	tri-*n*-octylphosphine oxide
TPPO	triphenylphosphine oxide
TTA	thenoyltrifluoroacetone
UKAEA	United Kingdom Atomic Energy Authority

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