PROTACTINIUM

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1. The Pattern of Development

PROTACTINIUM, element 91, falls between thorium and uranium, in the same vertical group as niobium and tantalum. It is one of the more intractable of the natural radioactive elements and it is only comparatively recently that a reasonably clear picture of its chemistry has begun to emerge. In the last fifteen years its study has been stimulated, on the one hand, by its possible importance in nuclear technology and, on the other, by an interest in the way in which the characteristics of the actinide elements gradually develop within the group.

Discovery.—The consequences of Soddy and Fajans's discovery of the chemical implications of radioactive decay—the displacement laws—were realised, independently, during December 1912 and January 1913 by Fajans,[1,2] Russell,[3] and Soddy.[4] The transformation of an element by β-decay into an isotope of its right-hand neighbour in the Periodic Classification required that the conversion of UI into UII must involve two successive β-decays. UX must, therefore, comprise two isotopes, one of thorium and one of the then missing element between thorium and uranium. A little later in the year Fajans and Göhring[5] identified the predicted UX_2 and found that it had a half-life of little more than one minute.

Experiments with such a short-lived species were very difficult, but chemical separation of UX_1 and UX_2 was achieved.[6] These observations were quickly confirmed and extended by Fleck[7] and by Hahn and Meitner,[8] who both found some similarities in the chemical behaviour of the UX_2 and tantalum. Because of the short half-life Göhring suggested the name brevium.[9]

Origin of the Actinium Series.—For the next quarter of a century, work on protactinium was closely connected with the origin of the actinium series. Already in 1913 work on the C members had demonstrated the possibility of branching in the natural-decay series, and Hahn and Meitner suggested[10] that branching at UX_1 might yield protactinium or an earlier

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[1] K. Fajans, *Ber.*, 1913, **46**, 422.
[2] K. Fajans, *Phys. Z.*, 1913, **14**, 126; *Radium*, 1913, **10**, 61.
[3] A. S. Russell, *Chem. News*, 1913, **107**, 49.
[4] F. Soddy, *Chem. News*, 1913, **107**, 97.
[5] K. Fajans and O. Göhring, *Naturwiss.*, 1913, **1**, 399.
[6] K. Fajans and O. Göhring, *Phys. Z.*, 1913, **14**, 877.
[7] A. Fleck, *Phil. Mag.*, 1913, **6**, 26.
[8] O. Hahn and L. Meitner, *Phys. Z.*, 1913, **14**, 758.
[9] O. Göhring, *Diss. Karlsruhe T.H.*, 1914, quoted by Gmelin.
[10] O. Hahn and L. Meitner, *Phys. Z.*, 1913, **14**, 752.

member of the actinium series. However, UY had already been reported and both Hahn and Meitner[11] and Soddy[12] confirmed its isotopy with UX_1. At about this time both groups began the search for such a longer-lived isotope of UX_2, probably formed as a branch product and parent of the actinium series. Paneth and Fajans[13] were unsuccessful in a search in an old preparation of radium, but in 1918 Hahn and Meitner,[14] and Soddy and Cranston,[15] independently isolated a long-lived isotope of UX_2 from pitchblende. It was quickly identified as the daughter of UY and parent of actinium[16] and named "protoactinium".* For the next ten years work was directed towards the development of a reliable analytical procedure in order to determine whether the ratio of the actinium to the uranium series in pitchblende was constant and where, if at all, branching occurred. Secondly, preparations were made to isolate macroscopic amounts of the longer-lived ^{231}Pa. The actinium problem itself was considerably confused by Hahn's discovery of UZ, the first example of nuclear isomerism[18] and the ground state of UX_2.

Macroscopic Studies.—By 1927 Von Grosse[19] obtained visible amounts of ^{231}Pa compounds and he quickly established an outline of the chemistry[20] of the element. In particular, a gravimetric analysis of K_2PaF_7 established[21] a value for the atomic weight of the element, 231, which suggested an independent origin for the series, possibly an isotope ^{235}U. This hypothesis was confirmed in the following year.

Work at the Curie Laboratory.—Methods for the isolation of the element were then available, although the reliability and reproducibility of the separations used were generally poor. Haissinsky and his collaborators at the Curie Laboratory in Paris now became interested in the element, first in its electrochemical behaviour and later, after separation of macroscopic amounts by improved methods, in its general chemistry.[22,23] These studies were especially fruitful immediately after the end of the Second World War and led to the discovery of the quadrivalent state of the element.[24] Subsequent work has dealt with the relation of pro-

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* Later condensed to "protactinium".[17]

[11] O. Hahn and L. Meitner, *Phys. Z.*, 1914, **15**, 236.

[12] F. Soddy, *Phil. Mag.*, 1914, **6**, 27.

[13] F. Paneth and K. Fajans, *Ber. Wien. Akad.*, 1914, **123**, IIa, 1627, 1633.

[14] O. Hahn and L. Meitner, *Z. Elektrochem.*, 1918, **24**, 169; *Phys. Z.*, 1918, **19**, 208.

[15] F. Soddy and J. A. Cranston, *Nature*, 1918, **100**, 498.

[16] F. Soddy and J. A. Cranston, *Proc. Roy. Soc.*, 1918, *A*, **94**, 384.

[17] XV Conf. Internat. Union Chem., 1949; see *Chem. Eng. News*, 1949, **27**, 2996.

[18] O. Hahn, *Naturwiss.*, 1921, **9**, 84.

[19] A. Von Grosse, *Naturwiss.*, 1927, **15**, 766; *Nature*, 1927, **120**, 621.

[20] A. Von Grosse, *J. Amer. Chem. Soc.*, (*a*) 1930, **52**, 1742; (*b*) 1934, **56**, 2200.

[21] A. Von Grosse, *J. Amer. Chem. Soc.*, 1934, **56**, 2501; *Proc. Roy. Soc.*, 1935, *A*, **150**, 363.

[22] G. Bouissières and M. Haissinsky, *Bull. Soc. chim. France*, 1951, **18**, 557.

[23] G. Bouissières and M. Haissinsky, Proc. XIth Internat. Congress Pure Appl. Chem., London, 1947, Vol. I, p. 17.

[24] M. Haissinsky and G. Bouissières, *Compt. rend.*, 1948, **226**, 573.

tactinium to niobium and tantalum on the one hand, and to its neighbouring elements on the other.

Work in the Manhattan Project.—The possibility of the eventual utilisation of thorium, by conversion into ^{233}U, as a nuclear fuel meant that information about the intermediate ^{233}Pa must be obtained. A good deal of tracer work with this isotope was carried out during 1944 and 1945. Two or three groups associated with the Manhattan project, and G. B. Cook in the Anglo-Canadian project, separated milligram amounts of ^{231}Pa.[25] In the late 1940's the American work culminated in Zachariasen's microcrystallographic characterisation of several solid protoactinium(IV) compounds.[26] The amounts of the element available were still not more than a few milligrams at each laboratory.

Recovery from Uranium Refinery Residues.—The large-scale industrial production of uranium from high-grade ores that was in full operation by the late 1940's led several laboratories to explore the possibility of recovering ^{231}Pa from the refinery wastes. Maddock and a group working at Cambridge thought a detailed study of the distribution of ^{231}Pa in the Springfield uranium plant desirable, in case its concentration in particular parts of the plant might constitute an additional health hazard. A pitchblende feed was being used, so that many grams of protactinium were passing into the plant. Some time was spent on the development of suitable analytical procedures and eventually (1951) a fairly complete picture of the distribution of the ^{231}Pa was obtained. This study revealed several potentially economic sources for the recovery of substantial amounts of the element. By 1955 a satisfactory procedure for the recovery of the ^{231}Pa from one of these sources, the ethereal sludge or residue separating at the original ether-extraction stage of the purification, had been developed.[27] During the next few years a pilot plant was operated sporadically at Cambridge, separating the ^{231}Pa in batches that yielded up to 100 mg. By this time a high-grade ore was no longer used as feed material in the Springfield plant, but more than 60 tons of the original ethereal sludge was still available. This material contained a valuable amount of residual uranium, and the industrial research and the development branch of the A.E.A. at Springfield and Windscale, in conjunction with A.E.R.E. Harwell and the Cambridge group, explored the possibility of processing these residues in such a way that both the uranium and ^{231}Pa content could be recovered economically. A process, essentially based on the Cambridge pilot-plant process, was eventually adopted[28]

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[25] R. E. Elson, "National Nuclear Energy Series," McGraw-Hill, New York, 1954, Div. IV, Vol. XIV*A*, p. 103.

[26] P. A. Sellers, S. Fried, R. E. Elson, and W. H. Zachariasen, *J. Amer. Chem. Soc.*, 1954, **76**, 5935.

[27] A. Goble, J. Golden, A. G. Maddock, and D. J. Toms, Progress in Nuclear Energy, Series 3, 1959, Vol. II, p. 86, ed. by F. R. Bruce, J. M. Fletcher, and H. H. Hyman, Pergamon Press, London, 1958.

[28] J. S. Nairn, D. A. Collins, H. A. C. McKay, and A. G. Maddock, Proc. U.N. Internat. Conf. Peaceful Uses At. En., Geneva, 1958, Vol. XVII, p. 216.

and in 1960 more than 130 g. of ^{231}Pa was separated in a substantially pure form.[29,30]

2. Isotopes

Twelve isotopes, ranging in mass from 225 to 237 are now known (Table 1). The references quoted and modes of preparation refer to their discovery. A detailed compilation by Hyde[31] is recommended for a full discussion of the numerous ways of obtaining the artificial nuclides, and in view of this recent publication we shall limit ourselves to a brief enunciation of the more pertinent data.

TABLE 1. *Protactinium isotopes*

Mass no.	Decay	Half-life	Prep.	Ref.
225	α	~ 2·0 s.	Th(p,8n)	33
226	α	1·8 m.	Th(d,8n)	34
227	α(85%); E.C.(15%)	38·3 m.	Th(d,7n)	35
228	α(2%); E.C.(98%)	22 h.	Th(d,6n)	35
229	α(0·25%); E.C.(99%+)	1·4 d.	Io(d,3n)	36
230	α(0·003%); E.C.(91%); β^-(9%)	17·7 d.	Th(d,4n)	37
231	α	3·28 × 10^5 yr.	Natural	14 — 16
232	β^-	1·32 d.	Th(d,2n)	38
233	β^-	27·4 d.	Th(n,γ)^{233}Th$\xrightarrow{\beta}$	39
234	UX$_2$.β^-(99·85%); I.T.(0.13%)	1·175 m.	Natural	5
	UZ.β^-	6·7 h.	Isomeric transition	32
235	β^-	23·7 m.	^{238}U(p,α)	40
237*	β^-	10·5 m. 39·0 m.	^{238}U(d,2p.n) ^{238}U(γ,p)	41 42

* The results quoted for ^{237}Pa represent the total available information on this isotope and it is apparent that further work is necessary to clarify the present situation.

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[29] (*a*) N. Jackson, 1960, unpublished information; (*b*) N. Jackson, F. J. G. Rogers, and J. F. Short, 1960, Report AERE-R 3311.

[30] D. A. Collins, J. J. Hillary, J. S. Nairn, and G. M. Phillips, *J. Inorg. Nuclear Chem.*, 1962, **24,** 441.

[31] E. K. Hyde, 1961 Rep. UCRL-9458.

[32] O. Hahn, *Ber.*, 1921, **54,** 1131.

[33] J. D. Keyes, Ph.D. Thesis, McGill University, 1951.

[34] W. W. Meinke, A. Ghiorso, and G. T. Seaborg, *Phys. Rev.*, 1949, **75,** 314.

[35] A. Ghiorso, W. W. Meinke, and G. T. Seaborg, *Phys. Rev.*, 1948, **74,** 695.

[36] E. K. Hyde, M. H. Studier, H. H. Hopkins, jun., and A. Ghiorso, Paper No. 19.17, "The Transuranic Elements", Nat. Nuclear Energy Ser., Div. IV, Vol. XIV*B*, McGraw-Hill, New York, 1949.

[37] M. H. Studier and E. K. Hyde, *Phys. Rev.*, 1948, **74,** 591.

[38] S. W. Gofman and G. T. Seaborg, Paper No. 19.14, "The Transuranium Elements", Nat. Nuclear Energy Series, Div. IV, Vol. XIV*B*, McGraw-Hill, New York, 1949.

[39] L. Meitner, F. Strassman, and O. Hahn, *Phys. Z.*, 1938, **109,** 538.

[40] W. W. Meinke and G. T. Seaborg, *Phys. Rev.*, 1950, **78,** 475.

[41] W. T. Crane and G. M. Iddings, *Phys. Rev.*, 1954, **95,** 1703.

[42] K. Takahashi and H. Morinaga, *Nuclear Phys.*, 1960, **15,** 664.

Protactinium-234.—Apart from protactinium-231 the only naturally occurring isotope is protactinium-234, which has been shown to exist in two isomeric forms, UX_2 and UZ. The latter is produced to the extent of 0·13% by the branch decay of the metastable UX_2 (Fig. 1). Fajans and Göhring[5] first observed the occurrence of UX_2, before the discovery of protactinium-231, and later studies by Hahn[18,32] led to the isolation of the longer-lived isomeric UZ. During the earlier studies the separation procedures consisted in concentrating the UX_1 fraction of natural uranium ores and isolating protactinium-234 on tantalum carriers;[5,8,43,44] more recently ion-exchange,[45,46] solvent extraction,[47] and paper chromatography[48] have been utilised for the separation.

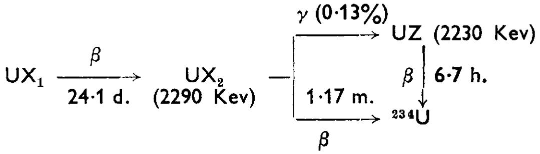

FIG. 1 (ref. 49).

Protactinium-233.—The most important artificial isotope is protactinium-233, produced by neutron irradiation of thorium, for

$$^{232}\text{Th}\ (n,\gamma)^{233}\text{Th} \xrightarrow[23\cdot5\ \text{m.}]{\beta} {}^{233}\text{Pa} \xrightarrow[27\cdot4\ \text{d.}]{\beta} {}^{233}\text{U}$$

protactinium-233 decays to the fissionable isotope uranium-233 as shown. Interest in the chemistry of protactinium was intensified by the discovery of this isotope, a potential source of fissile material greater than all the uranium-235 in Nature. The techniques applicable to the separation of thorium, protactinium, and uranium are dealt with below (pp. 300 *et seq.*). In addition, the results of the earlier investigations have been brought together in two volumes edited by Katzin[50,51] and Seaborg.[50]

Owing to its convenient half-life and nuclear properties, protactinium-233 is suitable for tracer studies on the chemistry of the element and, in fact, much of the information now available was obtained by using this isotope. The neutron-capture cross-section of ^{233}Pa is 140 ± 20 barns.[52] Like the long-lived protactinium-231, it possesses a metastable state of

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[43] W. G. Guy and A. S. Russell, *J.*, 1923, 2618.
[44] E. Jacobi, *Helv. Chim. Acta*, 1945, **28**, 757.
[45] F. Barendregt and S. Tom, *Physica*, 1951, **17**, 817.
[46] K. Kirmura, Y. Yokoyama, H. Sano, and H. Mabuchi, *Japan Analyst*, 1957, **6**, 637.
[47] G. Bouissières, N. Marty, and M. Teillac, *Compt. rend.*, 1953, **237**, 324.
[48] M. Lederer, Thesis (Paris), 1954.
[49] S. Bjoernholm and O. B. Nielson, *Nuclear Phys.*, 1962, **30**, 488.
[50] G. T. Seaborg and L. I. Katzin, 1951, Report T.I.D. 5222.
[51] L. I. Katzin, 1952, Report T.I.D. 5223.
[52] J. Halpern, R. W. Stoughton, D. Ferguson, C. V. Ellison, D. C. Overholt, and C. M. Stevens, Proc. U.N. Internat. Conf. Peaceful Uses Atomic Energy, Geneva, 1955, Vol. VII, p. 258.

half-life $3{\cdot}7 \times 10^{-8}$ second.[53] A suggested decay scheme is shown in Fig. 2.

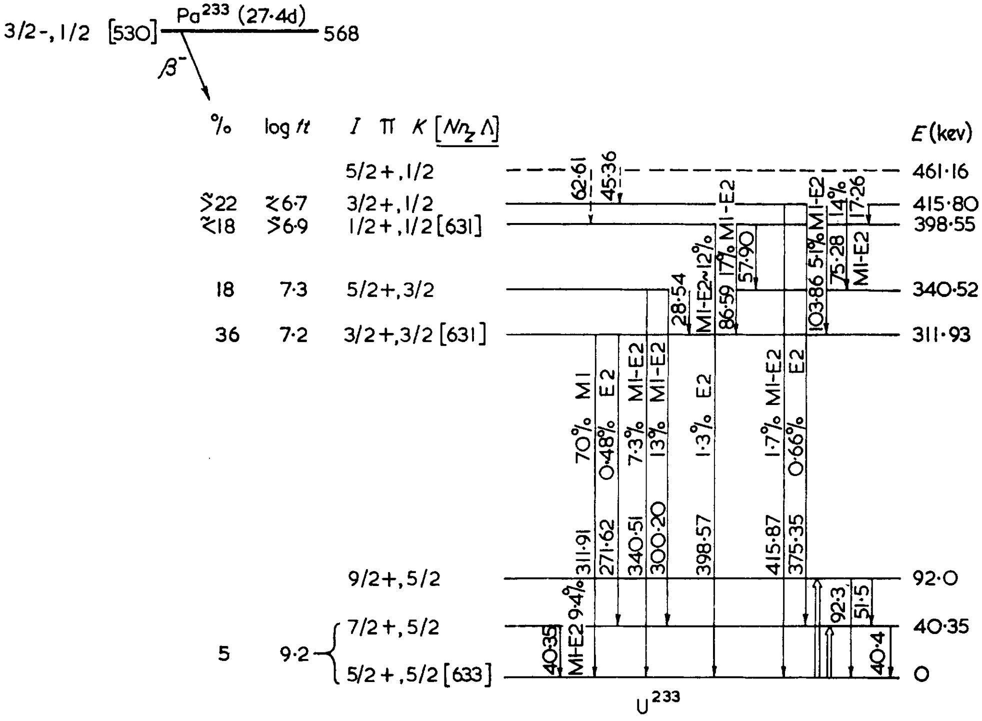

FIG. 2. *Decay scheme for protactinium*-233.

Protactinium-231.—(*a*) *General.* Protactinium-231, a member of the $(4n + 3)$ decay series has been extensively studied, both from a chemical

$$^{235}\text{U} \xrightarrow{\alpha} {}^{231}\text{Th} \xrightarrow{\beta} {}^{231}\text{Pa} \xrightarrow{\alpha} {}^{227}\text{Ac}$$

and from a nuclear aspect. The latter properties, which have been discussed by Katzin[54] and more recently by Hyde,[31] will only be outlined here. (All the data in this section refer to this isotope, unless otherwise stated.)

In the most recent investigation of the α-spectrum ten energy groups were identified[55] between 4·666 and 5·046 Mev, the principal peaks being 4·938 (22%), 5·001 (24%), and 5·017 Mev (23%). Details of studies concerning the α-spectrum, the complex γ-transitions, the conversion electrons, and the possible decay schemes (Fig. 3) are covered by Hyde.[31]

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[53] D. Engelkemier and L. B. Magnusson, *Phys. Rev.*, 1954, **94,** 1395.

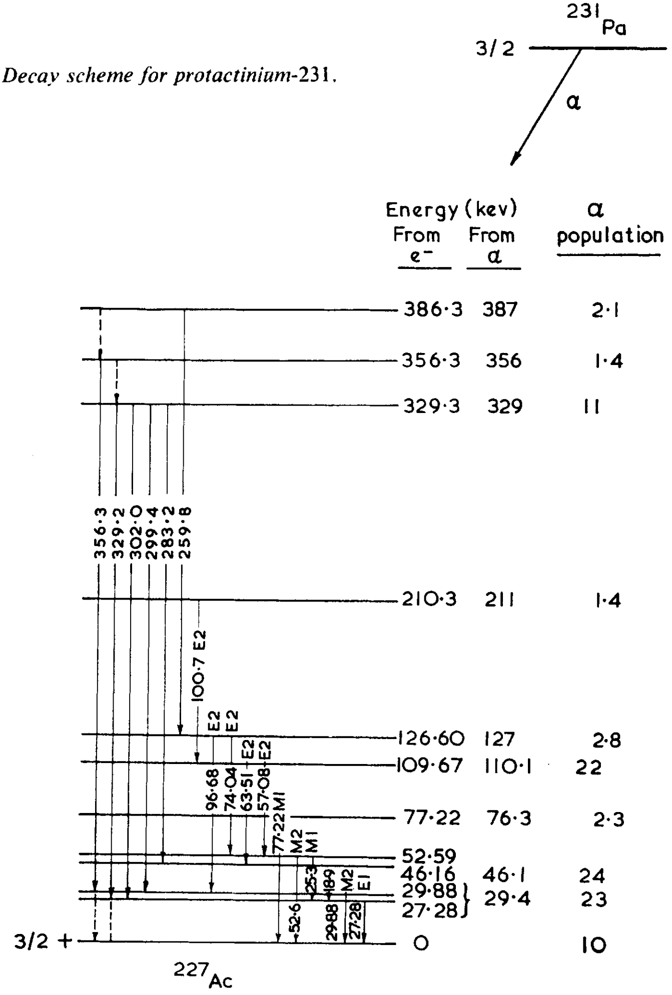
[54] L. I. Katzin, Nat. Nuclear Energy, Series Div. IV, Vol. XIV*A*, McGraw-Hill, New York, 1954, Chap. 3, p. 45.

[55] J. Hummel, F. Asaro, and I. Perlman, *Phys. Rev.*, 1955, **98,** 261; J. Hummel, Thesis, Report UCRL-3456, 1956.

In addition, protactinium-231 has a metastable state of half-life $4{\cdot}1 \times 10^{-8}$ seconds.[56]

Values ranging from 105 to 290 barns have been obtained for the thermal-neutron-capture cross-section;[57–61] the value now accepted is

FIG. 3. *Decay scheme for protactinium*-231.



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[56] D. Strominger and J. O. Rasmussin, *Phys. Rev.*, 1955, **100**, 844.

[57] Q. Van Winkle, 1949, Report ANL-4281.

[58] R. Elson, P. A. Sellers, and E. R. John, *Phys. Rev.*, 1953, **90**, 102; 1949, Report ANL-4282.

[59] A. H. Jaffey and Q. Van Winkle, 1949, Report ANL-4283; T.I.D. 5223 (2), 1952, 9.16, 604.

[60] Unpublished work.

[61] R. R. Smith, H. P. Alley, R. H. Lewis, and A. Vanderdoes, *Phys. Rev.*, 1956, **101**, 1053.

200 ± 15 b.[61] Further studies on the nuclear reactions of protactinium indicate that it is possible to prepare several protactinium, uranium, and neptunium isotopes by deuteron- or α-particle-bombardments.[62] Table 2 shows the products of bombardment by 21 Mev deuterons and 42 Mev alpha particles.

Von Grosse *et al.*[63] were the first to investigate the fission of protactinium. Their work indicated that fission occurred only with fast neutrons and that the threshold was ~1 Mev. More recent studies have confirmed the possibility of using protactinium as a threshold detector.[64,65] The capture cross-section rises sharply from threshold at 375 Kev to a value of 1·23 barns at 3·0 Mev. One unusual feature is its constant value in the region 600—700 Kev. Earlier measurements by Ghiorso and Van Winkle[66] showed that the thermal-neutron-fission cross-section could not exceed 0·01 barn; a study[67] of spontaneous fission indicated that protactinium gave 5 × 10^{-3} fiss. g.$^{-1}$ sec.$^{-1}$.

TABLE 2. *Nuclear reactions of protactinium*-231.[62]

21 Mev Deuterons		42 Mev Alpha Particles	
Reaction	Product	Reaction	Product
(d,p)	^{232}Pa	$(\alpha,\alpha n)$	^{230}Pa
$(d,p2n)$	^{230}Pa	$(\alpha,p4n)$	^{230}U
$(d,p3n)$	^{229}Pa	$(\alpha,p2n)$	^{232}U
$(d,4n)$	$^{229}\text{U}\rightarrow{}^{229}\text{Pa}$	$(\alpha,p3n)$	^{231}U
(d,n)	^{232}U	(α,n)	^{234}Np
$(d,2n)$	^{231}U		
$(d,3n)$	^{230}U		

After the discovery of protactinium its atomic weight was the subject of speculation[68–70] until the direct determination by Von Grosse[21] in 1934. Probably the most accurate value available is 231·05 calculated by Glass *et al.*[71] from nuclear disintegration data.

The earlier assessments of the half-life ranged from 12,000 to 32,000 years.[72–74] Recent studies have involved more direct techniques but there

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[62] D. W. Osborne, R. C. Thompson, and Q. Van Winkle, Report T.I.D. 5223 (2), 1952, 9.8, 558.

[63] A. Von Grosse, F. T. Booth, and J. R. Cummings, *Phys. Rev.*, 1939, **56**, 382.

[64] J. H. Williams, 1944, Report LA-150.

[65] Report AECU-2040, 1952.

[66] A. Ghiorso and Q. Van Winkle, Report T.I.D. 5223 (2), 1952, 9.12, 593.

[67] E. Segre, *Phys. Rev.*, 1952, **86**, 21.

[68] F. Lotze, *Naturwiss.*, 1928, **16**, 558.

[69] F. W. Aston, *Nature*, 1929, **123**, 313.

[70] F. Western and A. E. Ruark, *J. Chem. Phys.*, 1933, **1**, 717.

[71] R. A. Glass, S. G. Thompson, and G. T. Seaborg, *J. Inorg. Nuclear Chem.*, 1955, **1**, 3.

[72] (*a*) O. Hahn, *Phys. Z.*, 1920, **21**, 591; *Naturwiss.*, 1928, **16**, 454; 1932, **20**, 505; (*b*) A. Von Grosse, *Ber.*, 1928, **61**, 233; *Naturwiss.*, 1932, **20**, 505.

[73] J. H. Mennie, *Phil. Mag.*, 1923, **46**, 675.

[74] O. Hahn and E. Walling, *Naturwiss.*, 1927, **15**, 803.

is still some discrepancy between the reported values. Van Winkle *et al.*[75] obtained a value of 34,300 years by measuring the α-emission from a known quantity of an oxide believed to be Pa_2O_5. More recently Flegenheimer and Maddock[76] carried out studies using protactinium pentoxide, potassium heptafluoroprotactinate(V), and protactinium pentachloride as starting materials and report a value of 32,800 years, and Kirby,[77] using a calorimetric method, found the half-life to be 32,480 years. These discrepancies will probably be resolved by the combination of efficient counting and α-pulse analysis on a sample of protactinium metal.

(*b*) *Atomic properties.* Beuthe and Von Grosse,[78,79] using a sample of the pentoxide, measured 21 lines in the *L*-series of the *X*-ray spectrum having wavelengths between $1088{\cdot}5 \times 10^{-11}$ and $586{\cdot}6 \times 10^{-11}$ cm.; and Pierce and Von Grosse[80,81] reported 14 lines of the *M*-series with wavelengths ranging from $518{\cdot}2 \times 10^{-11}$ to $252{\cdot}2 \times 10^{-11}$ cm. Further information on the discontinuities in these two series are provided by Dolejsek and his co-workers.[82]

The emission spectrum has been investigated[83-85] and many of the lines were observed to possess hyperfine structure. Those useful in analysis range from 4291·3 to 2743 Å; the most sensitive and distinct lines being at 3957·8, 3054·6, and 3053 Å. During a study of the superconductivity of several elements de Launey and Dolecek[86] inferred that protactinium should be superconducting with a threshold temperature in excess of 2°K.

(*c*) *Analysis for protactinium*-231. Von Grosse[20a,21] was the first to report potentially useful analytical observations on pure samples of protactinium-231. Haissinsky and Bouissières, who reviewed the chemistry of protactinium several years ago,[87] investigated numerous precipitation reactions of protactinium(V) and compared their observations with the behaviour of zirconium(IV), tantalum(V), etc., under similar conditions.[22] Table 3 summarises these reactions which were carried out with $2{\cdot}1 \times 10^{-3}$M–^{231}Pa(V) in 2·5M-sulphuric acid solution.

The strong basic character observed for protactinium(V) is particularly characteristic of niobium and tantalum in the same valency state. Thus aqueous ammonia, sodium hydroxide, and potassium hydroxide cause

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[75] Q. Van Winkle, R. G. Larsen, and L. I. Katzin, *J. Amer. Chem. Soc.*, 1949, **71**, 2585.
[76] J. Flegenheimer and A. G. Maddock, unpublished work.
[77] H. W. Kirby, *J. Inorg. Nuclear Chem.*, 1961, **18**, 8.
[78] H. Beuthe and A. Von Grosse, *Phys. Z.*, 1930, **61**, 170.
[79] A. Von Grosse, *C.R. Acad. Sci. U.S.S.R.*, 1930, 42.
[80] W. E. Pierce and A. Von Grosse, *Phys. Rev.*, 1935, **47**, 532.
[81] A. Von Grosse, *Phys. Rev.*, 1939, **55**, 584.
[82] V. Dolejsek and V. Marek, *Phys. Z.*, 1935, **97**, 70; V. Dolejsek and V. Kunzl, *Nature*, 1936, **138**, 590.
[83] H. Schüller and H. Gollnow, *Naturwiss.*, 1934, **22**, 511.
[84] F. S. Tomkins and M. Fred, *J. Opt. Soc. Amer.*, 1949, **39**, 357.
[85] E. W. Richards and N. J. Atherton, 1962, Report AERE-R 3851.
[86] J. de Launey and R. L. Dolecek, *Phys. Rev.*, 1947, **72**, 141.
[87] M. Haissinsky and G. Bouissières, "Nouveau Traité de Chimie Mineral," ed. P. Pascal, Masson et Cie, Paris, 1958, Vol. XII, p. 617.

TABLE 3. *Some reactions of protactinium in dilute sulphuric acid.*

Reagent	Behaviour of Pa(V)	Pa(IV)	Behaviour of other elements* Ta(V)	Zr(IV)	Th(IV)
Aq. NH_3 excess	Insol.	+	+	+	+
NaOH–KOH excess	Insol.	+	—	+	+
H_2O_2	Insol.	—	—	+	—
K_2SO_4 sat. soln.	Insol.	+		+	+
Na_2CO_3 soln. excess	Insol.		—	—	—
H_3PO_4 in HCl	Insol.	+	+	+	—
$Na_2P_2O_6$ in H_2SO_4	Insol.	+		+	—
HIO_3 in HNO_3	Insol.	+		+	+
Na phenylarsonate	Insol.	+		+	+
Citric acid, pH 1–10	Sol.	+	+	+	+
Tartaric acid, pH 1–10	Sol.	+	+	+	+
Oxalic acid, pH 1–10	Sol.		+	+	—

* + Similar to Pa(v). — Unlike Pa(v).

immediate formation of a white, gelatinous, hydrated oxide which is insoluble in an excess of the reagent. Although Von Grosse has stated that such a precipitation is incomplete from fluoride media, the present authors have observed complete precipitation provided the solutions are sufficiently ammoniacal. The solubility of the hydroxide in various mineral acids was first studied by Thompson;[88] the results of such investigations, however, have little value, depending largely on the age of the precipitate and on the instability of the resulting solutions with respect to hydrolysis in the absence of fluoride ions (see section 4 below).

The peroxide, first mentioned by Von Grosse,[20a] has proved to be valuable during purification of the element (see section 3). The conditions of preparation from various mineral acid solutions were recently investigated.[89] The precipitate obtained on addition of potassium sulphate has been examined by Maddock and Miranda.[90] Their analytical results suggest that the compound is a double salt, $K_3PaO(SO_4)_3$, containing small amounts of hydrolysis products. To date, the only double salt which has been unambiguously characterised from aqueous solution is potassium heptafluoroprotactinate(v), K_2PaF_7, prepared by addition of a saturated solution of potassium fluoride to protactinium(v) in hydrofluoric acid.[21] However, co-precipitation on barium fluorozirconate reported by Meinke[91] indicates the probable existence of an insoluble barium fluoroprotactinate, whilst the ammonium double salt is soluble.

No analytical data are at present available for the peroxide, carbonate, phosphate, hypophosphate, iodate, or sodium phenylarsonate precipitate. All are readily soluble in dilute hydrofluoric acid.

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[88] R. C. Thompson, 1946, Report AECD-1897; 1946, AECD-2488.
[89] T. Stchouzkoy and R. Muxart, *Bull. Soc. chim. France*, 1962, 2176.
[90] A. G. Maddock and C. Miranda, unpublished work.
[91] W. Meinke, 1946, Report AECD-2738.

The soluble complexes observed with citrate and tartrate are extremely stable, *viz.*, neither of them is destroyed by acid or ammoniacal solution. The oxalate complex, investigated by Bouissières and Odiot,[92] proved to be less stable. Addition of aqueous ammonia to a solution of the hydroxide in 0·3M-oxalic acid reprecipitated the hydroxide at pH 8—9. The observations on protactinium(IV) are discussed in section 7 below.

One of the chief problems encountered with protactinium-231 has been that of analysis, particularly for the control of isolation procedures. Most methods have involved a rigorous chemical purification before each analysis, and only the most recent method has circumvented this troublesome task.[93] Recent articles by Kirby[94] and Salutsky[95] give details of numerous procedures. The earlier workers achieved radiochemical purification by the addition and subsequent elimination of various carriers, *e.g.*, zirconium or tantalum, the procedures being cumbersome and unreliable.[93–104] Katzin *et al.*[105] devised an involved method based on the separation of protactinium, radium, and polonium by selective co-precipitation with zirconium phosphate, barium sulphate, and manganese dioxide. However, chemical and radiochemical purity are better attained through solvent extraction, *e.g.*, by using di-isopropylcarbinol (2,4-dimethylpentan-3-ol),[106] di-isopropyl ketone,[107] or di-isobutyl ketone,[27] or by ion-exchange.[108] The chemical yield of a process has frequently been determined by establishing equilibrium between protactinium-231 and, as added tracer, the β-emitter protactinium-233. It is essential to use fluoride solutions for this in order to ensure that the protactinium is in true solution and that isotopic equilibrium is really achieved. In addition, all dilutions should be kept to a minimum if loss of protactinium, by hydrolysis, is to be avoided.

Salutsky *et al.*[109] reported a determination of < 1 p.p.m. of protactinium-231 in uranium ores by γ-spectrometry, based on the

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[92] G. Bouissières and Odiot, *Bull. Soc. chim. France*, 1951, **18**, 918.

[93] K. M. Glover and F. J. G. Rogers, Report AERE-R 2971, 1959.

[94] W. Kirby, "Radiochemistry of Protactinium," 1960, NAS-NS-3016.

[95] M. Salutsky, Chap. 5c in Vol. Ic of "Comprehensive Analytical Chemistry", ed. C. L. Wilson and D. W. Wilson, Elsevier, Amsterdam, 1962.

[96] A. S. Russell and W. B. Widdowson, *Phil. Mag.*, 1923, **46**, 915.

[97] J. E. Wildish, *J. Amer. Chem. Soc.*, 1930, **52**, 163.

[98] E. Gledisch and E. Foyn, *Compt. rend.*, 1932, **194**, 1571.

[99] A. Von Grosse, *Phys. Rev.*, 1932, **42**, 565.

[100] Tcheng-da-Tchang, *Ann. Chim. (France)*, 1934, **2**, 186; *Compt. rend.*, 1931, **193**, 167.

[101] M. Francis and Tcheng-da-Tchang, *Phil. Mag.*, 1935, **20**, 623.

[102] F. Reymond, *J. Chim. phys.*, 1931, **28**, 409.

[103] W. C. Schumb, R. D. Evans, and J. L. Hastings, *J. Amer. Chem. Soc.*, 1939, **61**, 3451.

[104] M. Blau and H. Sinason, *Science*, 1947, **106**, 400.

[105] L. I. Katzin, Q. Van Winkle, and J. Sedlet, *J. Amer. Chem. Soc.*, 1950, **72**, 4815.

[106] K. A. Kraus and A. Garen, Report T.I.D. 5223 (1), 1952, 6.12, 304.

[107] J. Golden and A. G. Maddock, *J. Inorg. Nuclear Chem.*, 1956, **2**, 46.

[108] M. K. Barnett, *J. Inorg. Nuclear Chem.*, 1957, **4**, 358.

[109] M. L. Salutsky, M. L. Curtis, K. Shaver, A. Elmlinger, and R. A. Miller, *Analyt. Chem.*, 1957, **29**, 373.

magnitude of the 300 Kev peak before and after removal of interfering γ-activity on a thorium tetrafluoride precipitate. However, the reproducibility of the behaviour of protactinium and other γ-emitters is doubtful. In particular, actinium-227, which along with its decay products shows a strong poorly resolved peak around 300 Kev, is not efficiently removed by the fluoride precipitation, and this method is not considered reliable.

Obviously for control analysis it is more satisfactory to omit the purification steps necessary in the above procedures. Thus, although Salutsky *et al.*[109] considered it impracticable, Glover and Rogers[93] have established a method involving α-spectrometry which does not necessitate purification of the samples. Using uniformly spread, thin sources to minimise self-absorption they were able to determine 0·1 p.p.m. of protactinium-231. The application of the γ-spectrometry method to such samples was less satisfactory and it appears that the two techniques are comparable in efficiency only when used with pure protactinium sources.

Chemical estimation is best accomplished either by ignition of the precipitated hydroxide at 800°, giving Pa_2O_5, or by a combination of total α-count and α-kick sorting. The latter procedure, however, is based on the value of the specific activity which, as mentioned elsewhere, is not firmly established.

Although Mjassoedov and Muxart[110] have claimed high precision when using a spectrophotometric technique based on the trifluorothenoylacetonate complex of protactinium(V) it is known that several elements interfere.[111,112] Other spectrophotometric techniques have proved unsatisfactory.[113]

3. Isolation and Purification Processes

Sources of Protactinium-231.—This isotope occurs in Nature to approximately the same extent as radium; 1 ton of uranium, at radioactive equilibrium, contains about 340 mg. of protactinium. The various residues from uranium and radium refineries have always constituted the chief source of the element. The distribution of protactinium in any plant is markedly affected by the method of treatment of the ore and by the behaviour of similar elements (*e.g.*, niobium, tantalum, and zirconium) during the processing. Consequently, several different residues have been used as sources of protactinium.

In the classical separations the siliceous residue remaining after the exhaustive mineral-acid treatment of the pitchblende ores was utilised by Grosse and Agruss[19,72b,99,114,115] and by Graue and Käding[116] who

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[110] B. Mjassoedov and R. Muxart, *Bull. Soc. chim. France*, 1962, **29**, 237.

[111] D. Brown and R. G. Wilkins, *J.*, 1961, 3804.

[112] E. S. Khopkar and A. K. De, *Chem. and Ind.*, 1959, 291, 854.

[113] A. Casey and A. G. Maddock, *J. Inorg. Nuclear Chem.*, 1959, **10**, 58.

[114] A. Von Grosse, *Science*, 1934, **80**, 512; *Ber.*, 1935, **68**, 307, 1511.

[115] A. Von Grosse and M. Agruss, *J. Amer. Chem. Soc.*, 1934, **56**, 2200; *Ind. Eng. Chem.*, 1935, **27**, 422.

[116] G. Graue and K. Käding, *Naturwiss.*, 1934, **22**, 386; *Angew. Chem.*, 1934, **47**, 650.

succeeded in obtaining several hundred milligrams from this highly intractable source. Reymond[102] showed later that the proportions of sulphuric and nitric acid in the initial leach had a profound effect on the quantity of protactinium extracted from the ores. Thus with a 1 : 5 mixture 38% of the protactinium was dissolved, whereas a 2 : 1 mixture effected dissolution of more than 90%. Katzin *et al.*[105] later showed that the "carbonate precipitate" resulting from addition of an excess of sodium carbonate to the acid extract constituted a more attractive source of protactinium. Several milligrams of the element have since been recovered from such residues.[117–119]

More recent practice has omitted the carbonate complexing of the uranium, and consequently the protactinium has penetrated further into the purification plants. In fact, the aqueous waste stream,[120] and later the waste-stream precipitate[121] from the Mallinckrodt process, were shown to be capable of yielding gram amounts of the element. However, the ethereal sludge obtained by the Springfield uranium refinery has proved to be the most tractable source of protactinium.

In addition to natural sources, protactinium-231 can be synthesised by neutron bombardment of ionium (^{230}Th).[122] The thorium-231 so formed decays by β emission:

$$^{230}\mathrm{Th}(n,\gamma)^{231}\mathrm{Th} \xrightarrow[25\cdot6\ \mathrm{hr.}]{\beta} {}^{231}\mathrm{Pa}$$

However, the product is contaminated with protactinium-233 owing to the large quantity of thorium-232 which is unavoidably present in the ionium sample.

Alternatively, fast-neutron bombardment (> 6·35 Mev) of thorium-232 results in the production of some protactinium-231:[123]

$$^{232}\mathrm{Th}(n,2n)^{231}\mathrm{Th} \xrightarrow{\beta} {}^{231}\mathrm{Pa}$$

but this is not suitable for the production of macroscopic amounts.

Isolation of Protactinium-231.—The development of isolation procedures was hindered by ignorance of the chemistry of protactinium and by the intractable nature of many of the starting materials. Furthermore, the difficulties experienced in maintaining protactinium(v) in true solution (see section 4) undoubtedly contributed to the low yields obtained. In the

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[117] K. A. Kraus and Q. Van Winkle, Report T.I.D. 5223 (1), (*a*) 1952, 6.2, 259; (*b*) 1952, 6.11, 296.

[118] G. Larsen, L. Katzin, and G. Hausemann, Report T.I.D. 5223 (1), 1952, 6.3, 272.

[119] R. C. Thompson, Q. Van Winkle, and J. G. Malm, Report T.I.D. 5223 (1), 1952, 6.4, 276.

[120] R. E. Elson, G. W. Mason, D. F. Peppard, P. A. Sellers, and M. H. Studier, *J. Amer. Chem. Soc.*, 1951, **73**, 4974.

[121] M. L. Salutsky, K. Shaver, A. Elmlinger, and M. L. Curtis, *J. Inorg. Nuclear Chem.*, 1956, **3**, 289.

[122] A. H. Jaffey and E. K. Hyde, Report T.I.D. 5223 (1), 1952, 9.3, 532.

[123] Y. Nishima, T. Yasaki, K. Kimura, and M. Ikawa, *Nature*, 1938, **142**, 874.

earlier processes the first stages of the treatment were acid leaches or large-scale fusions. The latter present obvious practical difficulties, whilst the former give irreproducible results owing to the troublesome tendency of protactinium(v) to undergo hydrolysis. The use of nitric acid solutions is not to be recommended since more reproducible behaviour is observed with the aqueous chloride and fluoride complexes. The co-precipitation of protactinium, particularly on manganese dioxide, is also very unreliable in the presence of large amounts of other elements. For these reasons it is not surprising that the earlier workers obtained so little pure material. With the availability of more information on the solvent-extraction and ion-exchange behaviour of protactinium(v) the suitability of such techniques became apparent, particularly for the production of radiochemically pure protactinium. A number of processes are described in this section and summaries are given in Table 4.

(*a*) *Co-precipitation techniques.* Protactinium(v) is readily carried from aqueous acid or alkaline solutions, particularly on zirconium, tantalum, titanium, and manganese, which were commonly used to concentrate protactinium from uranium ore residues. The first attempted isolations[14–16,124,125] were based on an assumed similarity to tantalum. For instance, Hahn and Meitner[14,124] treated pitchblende with nitric acid and dissolved the residue, after the addition of tantalum, in a sulphuric–hydrofluoric acid mixture. The residue from the evaporation of this solution was treated with *aqua regia* and then dissolved in hydrofluoric acid. The protactinium and tantalum were concentrated in this acid solution, whilst the radiochemical impurities were removed on appropriate carriers. The original nitric acid leaches contained up to 60% of the protactinium, which was recovered by hydroxide precipitation in the presence of ammonium carbonate followed by treatment as above after the addition of tantalum. Alternatively,[125] a siliceous pitchblende residue was mixed with tantalum and fused with sodium hydrogen sulphate. The residue, after treatment with water, was fumed with hydrofluoric acid and the protactinium and tantalum partially separated by fractional crystallisation of their fluorides. The final 525 g. of concentrate contained $\sim$6 mg. of protactinium, which was later isolated by Von Grosse.[19] Despite the small yields and low purity of the product many other workers have used a tantalum-carrier method to isolate natural protactinium isotopes (refs. 5, 6, 8, 32, 43, 44, 96–98, 100, 101, 126, 127).

Von Grosse was the first to suggest that protactinium might behave to some extent like zirconium. Thus, using zirconium phosphate as a carrier, he obtained the first pure samples of protactinium-231.[19] Several of his publications (refs. 19, 72*b*, 99, 114, 115) deal with the development of an

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[124] O. Hahn and L. Meitner, *Phys. Z.*, 1918, **19**, 221; 1918, **20**, 530; *Naturwiss.*, 1918, **6**, 324.

[125] O. Hahn and L. Meitner, *Ber.*, 1919, **52**, 1812.

[126] F. Reymond and Tcheng-da-Tchang, *Compt. rend.*, 1931, **192**, 1723; 1932, **195**, 143.

[127] O. Gratias and C. H. Collie, *J.*, 1932, 987.

isolation procedure suitable for the large-scale recovery of protactinium. Table 4 outlines the method due to Von Grosse and Agruss,[115] who used pitchblende residues from radium extractions which contained 300 mg. of protactinium per ton. After initial hydrochloric acid leaches and a sodium hydroxide fusion the residue was further treated with acid and alkali before being dissolved in 20% hydrochloric acid. Zirconium phosphate was then precipitated, carrying the protactinium, and after

TABLE 4. *Outline of isolation procedures*

Reference	Source	Principal isolation and purification stages
Von Grosse and Agruss[115]	Sulphate residues	Alkaline fusions, Zr phosphate carrier, and fractional crystn. of oxychlorides. Th oxalate carrier in final stage.
Kraus and Van Winkle[117]	Carbonate residues	Fluoride solution, Zr iodate carrier, and extraction into Pr^i_2CO.
Larsen *et al.*[118]	Carbonate residues	Nitrate solution and Pr^i_2CO extractions.
Thompson *et al.*[119]	Carbonate residues	Nitrate soln., MnO_2 carrier, ion-exchange from fluoride solns., and Pr^i_2CO extractions from nitric acid.
Spitsyn and D'Yachkova[136]		Fluoride soln., phosphate carrier, and adsorption on a MnO_2 column.
Elson *et al.*[120]	Mallinckrodt waste stream	Nitrate solution, Bu_3PO_4 and $Bu^i_2CH{\cdot}OH$ extractions. Peroxide and tannate precipitations followed by Pr^i_2CO extractions.
Salutsky *et al.*[121]	Mallinckrodt waste stream precipitate	M–HCl soln., silicate carrier, and anion-exchange from chloride soln.
Bouissières and Haissinsky[22]	Siliceous residue	Fluoride soln., peroxide pptn., reduction, and PaF_4 isolation. K_2PaF_7 pptn. and peroxide prepn.
Schevchenko *et al.*[137]	Aqueous raffinate	Alkyl phosphate extraction, sulphide pptns., and phosphate carrier from fluoride soln.
Goble *et al.*[27]	Ethereal sludge	Fluoride soln., deposition on Al, NaOH wash, Bu^i_2CO extraction from chloride solns., peroxide and K_2PaF_7 pptns.
Nairn *et al.*[28]	Ethereal sludge	Fluoride–nitrate solution, Bu_3PO_4 extractions, pptn. by $AlCl_3$, NaOH wash, Bu^i_2CO extractions, and anion-exchange from chloride solns.

fusion with potassium carbonate the resulting oxides were fused with sodium hydrogen sulphate to facilitate dissolution in hydrochloric acid. The oxychlorides were fractionally crystallised from this solution and, after a further precipitation of the phosphate, this cycle was repeated until the precipitate contained 10% of protactinium by weight. The remaining zirconium was then separated by sublimation of the tetrachloride and the protactinium was finally precipitated by hydrogen peroxide.[115] Alternatively,[19] the protactinium was precipitated, from dilute acid solution, as the oxalate or on thorium oxalate. In the latter instance, thorium was later removed as the insoluble tetrafluoride. Graue and Käding[116] isolated 500 mg. of protactinium by a slightly modified process involving a preliminary sodium hydroxide fusion of the residue from radium production at Joachimstal; the precipitation on zirconium phosphate carrier was improved by reduction of the iron present to the ferrous state and, after a tantalum-carrier step, potassium fluoroprotactinate was precipitated from hydrofluoric acid solution. There are a number of other processes based on zirconium carriers,[101,103,104,128,129] the most interesting of which uses zirconium mandelate.[128,129]

The use of titanium as carrier has been investigated by Zavizziano[130] and Tcheng-da-Tchang.[131] Mineral ores were treated with a sulphuric–nitric acid mixture, and two separate batches of titanium were added and precipitated by hydrolysis.[130] The protactinium which dissolved (60%) was almost quantitatively recovered on these precipitates and it was claimed that this carrier was superior to either tantalum or zirconium. After radiochemical purification the protactinium was concentrated with respect to titanium by precipitations from boiling sulphuric acid solution containing hydrogen peroxide. During the elimination of tin, lead, bismuth, etc., it was observed that the protactinium was co-precipitated with their sulphides.[131,132]

The co-precipitation on manganese dioxide, first observed by Von Grosse and Agruss[133] and since examined in detail by others,[134,135] has frequently been utilised in isolation procedures. Thus Maddock and his co-workers reported two processes. In one[135] the co-precipitation was carried out from nitric acid solution ($\sim$3M) and coupled with the extraction of the protactinium cupferronate into pentyl acetate. Alternatively,[107] a siliceous sulphate residue was treated with concentrated hydrofluoric acid, and the dissolved protactinium was carried on a

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[128] I. E. Starik, A. P. Rather, M. A. Pasvik, and L. D. Sheidina, *Zhur. analit. Khim.*, 1957, **12**, 85.

[129] I. Starik and L. D. Sheĭdina, *Zhur. neorg. Khim.*, 1958, **3**, 139.

[130] E. Zavizziano, *Compt. rend.*, 1935, **200**, 1843; 1936, **202**, 1052.

[131] Tcheng-da-Tchang, *J. Chinese Chem. Soc.*, 1935, **3**, 381; *Bull. Soc. chim. France*, 1936, **3**, 271.

[132] M. M. Tcheng-da-Tchang and Li Houang, *Bull. Soc. chim. France*, 1936, **3**, 326.

[133] A. Von Grosse and M. Agruss, *J. Amer. Chem. Soc.*, 1935, **57**, 438.

[134] L. I. Katzin and R. W. Stoughton, Report T.I.D. 5223 (1), 1952, 3.2, 126; *J. Inorg. Nuclear Chem.*, 1956, **3**, 229.

[135] A. G. Maddock and G. L. Miles, *J.*, 1949, S 253.

precipitate formed by the addition of barium chloride ($BaF_2 + BaPaF_7$?). Dissolution in nitric acid containing aluminium nitrate allowed further concentration of the protactinium on manganese dioxide, after which it was purified by extracting the chloride complex into di-isopropyl ketone.

After the recommendation of Katzin *et al.*[105] several groups[117-119] attempted to isolate milligram quantities of protactinium from the carbonate residue remaining after the treatment of acid extracts of pitchblende with an excess of sodium carbonate. Thompson *et al.*[119] carried out a manganese dioxide precipitation from the nitric acid solution obtained after an initial sodium hydroxide treatment of this residue. Sodium nitrite was added to assist dissolution of the precipitate and further concentration was effected on successively smaller dioxide precipitations. The final manganous solution was boiled with concentrated nitric acid, and the hydrolysis products were fumed to remove silica. The residue was dissolved in hydrofluoric acid, and the protactinium adsorbed on an anion-exchange resin from 4M-hydrofluoric acid. After elution with M-nitric acid, the acidity was adjusted to 8M and the protactinium purified by extraction into di-isopropyl ketone. A trace of added hydrogen peroxide prevented the extraction of titanium. An interesting variation on the use of manganese dioxide was recently reported.[136] After a dioxide precipitation, followed by the removal of silica and further concentration on zirconium phosphate, the protactinium and remaining impurities (zirconium, titanium, and niobium) in 10M-nitric acid solution, were passed through a column of manganese dioxide on which only the niobium and protactinium were adsorbed. The protactinium was preferentially eluted with 0·5M-nitric acid–0·2M-ammonium fluoride and further purified from traces of manganese by passage through an anion-exchange column.

(*b*) *Solvent extraction and ion-exchange procedures.* Elson *et al.*[120] utilised the waste stream from the Mallinckrodt process for uranium recovery, and Salutsky *et al.*[121] examined a waste-stream precipitate. The waste stream contained essentially all the acid-soluble compounds in concentrated nitrate solution. The first step in the isolation of protactinium was an extraction with tributyl phosphate which was not very efficient. After further extractions with 2,4-dimethylpentan-3-ol the material was precipitated as peroxides, and the uranium was then extracted from a highly salted nitrate solution. Protactinium was purified from the remaining elements by precipitation from oxalic acid solution as tannate and by extraction of the nitrate complexes into di-isopropyl ketone. The overall yield varied between 5% and 35%.

The waste-stream precipitate[121] was leached with M-hydrochloric acid, and the protactinium was concentrated on the siliceous precipitate formed on the addition of sodium chloride to the leach solution. This precipitate was treated with sodium hydroxide, and the product was

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[136] V. I. Spitsyn and R. A. D'Yachkova, *Doklady. Akad. Nauk S.S.S.R.*, 1960, **134**, 1111.

dissolved in 9M-hydrochloric acid from which the protactinium was adsorbed on an anion-exchange column. Elution with a mixture of hydrochloric and hydrofluoric acid gave protactinium of high chemical and radiochemical purity.

A Russian report[137] describes the recovery of protactinium from a nitric acid solution of the "slimes" remaining after the extraction of uranium into tributyl phosphate. The protactinium and ionium were extracted into mono- or di-isopentyl hydrogen phosphate in pentyl acetate and recovered into aqueous ammonium carbonate. Heavy-metal sulphides were precipitated from this strip solution before precipitation of the protactinium as hydroxide. A separation from ionium was achieved by treating this concentrate with hydrofluoric acid and the protactinium in the resulting solution was carried on zirconium phosphate. Only the earlier stages are described and the report suggests that purification could be achieved by the use of anion-exchangers.

In the older uranium recovery processes an "ethereal sludge" was formed which has proved a useful source of substantial quantities of protactinium. A satisfactory process, developed by Maddock and his co-workers,[27] involved initial treatment with 0·5M-hydrochloric acid to extract protactinium; when aluminium sheets were suspended in the latter solution, a black deposit, containing nearly all the protactinium, was formed on them (the nature of the chemical process involved is not known). The deposit was washed from the sheets, leached with sodium hydroxide, and dissolved in hydrochloric acid. The protactinium was further concentrated and purified by cycles involving extraction into di-isobutyl ketone and stripping into hydrochloric–hydrofluoric acid mixtures. The final stages of purification comprised hydroxide, peroxide, and fluoroprotactinate precipitations along with further extraction cycles. The use of fluoride ions and the aluminium necessary to complex them can be avoided in the latter stages by using oxalic acid strip solutions.[138,139]

A very similar process was used in the recent isolation of over 130 g. of protactinium. An outline of the method was first presented by Nairn *et al.*[28] whilst full details of the work are contained in recent reports.[29,30] In distinction from the method employed by Goble *et al.*,[27] the uranium and protactinium were leached together from the sludge by 4M-nitric acid–0·5M-hydrofluoric acid.[29a] Uranium was then quantitatively extracted into 20% tributyl phosphate–kerosene, after which addition of aluminium chloride to the aqueous phase precipitated a mixture of hydrous oxides and phosphates which carried the protactinium quantitatively. This product was treated with sodium hydroxide to remove the phosphate and dissolved in a mixture of hydrochloric and hydrofluoric acid. Purification

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[137] V. B. Schevchenko, S. I. Zolotukha, H. F. Kascheyev, S. A. Tsaryov, V. A. Mikhailov, and G. A. Toropchenova, Progr. Nuclear Energy, Series III, Pergamon Press Ltd., London, 1961, Vol. III, p. 52.

[138] Cambridge University Group Report, 1961, AERE-EMR/PR 1024.

[139] F. L. Moore and S. A. Reynolds, *Analyt. Chem.*, 1957, **29**, 1596.

was then achieved by cyclic extraction with di-isobutyl ketone and, finally, by anion exchange[29b] from hydrochloric acid solution. The overall yield was greater than 81%, the main losses occurring before the solvent-extraction and ion-exchange stages. The final product, however, was recently[140] shown to contain 4% of niobium, probably owing to lack of control of the conditions during the ion-exchange. The niobium is most efficiently removed by peroxide treatment of dilute sulphuric acid solutions when the protactinium is precipitated.

(*c*) *Final purification procedures.* There are several interesting reports dealing with the separation of specific elements from protactinium. Some of these are dealt with in the following sections and others in the paragraphs on protactinium-233.

(i) Solvent extraction. Niobium[141] is easily separated from protactinium by extracting it into di-isobutylcarbinol (2,6-dimethylheptan-4-ol) from a mixture of sulphuric, hydrofluoric, and oxalic acid, and zirconium can be extracted from nitric acid solutions in the presence of hydrogen peroxide to inhibit protactinium(V) extraction, by trifluorothenoylacetone (T.T.A.)–benzene.[142] Peppard *et al.*[143] used tributyl phosphate extractions to achieve a separation from uranium(VI) and thorium(IV), and the extraction of protactinium(V) from very acid (chloride or nitrate) solutions by T.T.A.–benzene has been shown to give excellent decontamination from almost all other elements.[92,144,145] In the latter case repetitive extractions are necessary since the distribution coefficient is not very favourable.

(ii) Ion exchange. The existence of anionic complexes of protactinium(V) in solutions greater than 4M in hydrochloric acid[146] has been used repeatedly as the basis for the separation of protactinium from other elements.[147–156] Much of the work has been carried out with protactinium-233 tracer, but the processes are obviously applicable during the later stages of the isolation of natural protactinium and will accordingly be summarised here.

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[140] L. J. Roberts and A. Walter, *J. Inorg. Nuclear Chem.*, in the press.

[141] F. L. Moore, *Analyt. Chem.*, 1955, **27**, 70.

[142] F. L. Moore, *Analyt. Chem.*, 1956, **28**, 997.

[143] D. F. Peppard, G. W. Mason, and M. V. Gergel, *J. Inorg. Nuclear Chem.*, 1957, **3**, 370.

[144] D. Brown, R. G. Wilkins, and A. J. Smith, *J.*, 1959, 1463.

[145] See Chapter 4 in "The Chemistry of the Actinide Elements", ed. by J. J. Katz and G. T. Seaborg, Methuen & Co. Ltd., London, 1957.

[146] K. A. Kraus and G. E. Moore, *J. Amer. Chem. Soc.*, 1950, **72**, 4293.

[147] K. A. Kraus and G. E. Moore, *J. Amer. Chem. Soc.*, 1955, **77**, 1383.

[148] K. A. Kraus and G. E. Moore, 1949, Report ORNL-330; 1959 U.S.Pt. 2,872,284.

[149] K. A. Kraus, G. E. Moore, and F. Nelson, *J. Amer. Chem. Soc.*, 1956, **78**, 2692.

[150] A. G. Maddock and W. Pugh, *J. Inorg. Nuclear Chem.*, 1956, **2**, 114.

[151] K. A. Kraus and G. E. Moore, 1949, Report ORNL-336.

[152] K. A. Kraus and G. E. Moore, *J. Amer. Chem. Soc.*, 1951, **73**, 2900.

[153] Yang Jeng-Tsong, *Compt. rend.*, 1950, **231**, 1059.

[154] S. Kahn and D. F. Hawkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 155.

[155] M. Gasior and J. Mikulski, *Nukleonika*, 1961, **6**, 757.

[156] L. R. Bunney, N. E. Ballou, J. Paschal, and S. Foti, *Analyt. Chem.*, 1959, **31**, 324.

Protactinium(V) is readily adsorbed by anion-exchange resins from relatively concentrated hydrochloric acid, and it is usual to elute it with a mixture of hydrochloric and hydrofluoric acid rather than with dilute hydrochloric acid as in the latter solution hydrolysis tends to occur very readily. The details of separations achieved are shown in Table 5, where the elements are arranged in order of elution from the column. Further results on the separation of protactinium(V) and zirconium(IV) were obtained by Kahn and Hawkinson,[154] and the purification and concentration of protactinium(V) have been described by Barnett.[108] In addition Bunney *et al.*[156] have provided data on numerous elements, including protactinium(V), in hydrochloric, nitric, and sulphuric acid solutions; on the basis of their results it is possible to postulate several separations.

TABLE 5. *Separation of protactinium*(V) *from other elements by anion-exchange.*

Feed solution	Element	Eluant	Ref.
9·0M-HCl	Pa(V)	3·8M-HCl	147
	Fe(III)	3·8M-HCl	
9·0M-HCl	Pa(V)	9·0M-HCl–0·5M-HF	147
	Fe(III)	0·5M-HCl	
8·0M-HCl	Th(IV)	8·0M-HCl	148
	Pa(V)	3·8M-HCl	
	U(VI)	3·8M-HCl	
10·0M-HCl	Th(IV)	10·0M-HCl	149
	Pa(V)	9·0M-HCl–1·0M-HF	
	U(VI)	0·1M-HCl	
7·0M-HCl	Zr(IV)	6·0–7·0M-HCl	150
	Pa(V)	3·0M-HCl	
8·0M-HCl	Zr(IV)–Nb(V)	8·0M-HCl	151
	Pa(V)		
—	Pa(V)	9·0M-HCl–0·05M-HF	152
	Nb(V)	9·0M-HCl–0·05M-HF	
	Ta(V)	9·0M-HCl–0·05M-HF	
—	Zr(IV)	9·0M-HCl–0·004M-HF	152
	Pa(V)	9·0M-HCl–0·004M-HF	
	Nb(V)	9·0M-HCl–0·18M-HF	
	Ta(V)	1·0M-HF –4·0M-NH_4Cl	
Citrate soln.	Ta(V)	6·5M-HF at pH 3·0	153
	Pa(V)	6·5M-HF at pH 3·0	

Information on separations on cation-exchangers is limited to sparse data on thorium(IV) and protactinium(V) in nitric acid solutions. Protactinium(V) is adsorbed quantitatively from 0·1—2M-nitric acid and can be eluted with a saturated solution of oxalic acid[157] or ammonium fluoride solution.[158] Alternatively, the separation is achieved by removing

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[157] R. Elson, P. Sellers, and R. John, 1948, Report ANL-4176.
[158] R. W. Stoughton, 1958, U.S.Pt. 2,856,262.

the adsorbed thorium(IV) with an ammonium sulphate solution at pH 3·5.[159] The former method has recently been applied to the separation of UX_1 and UX_2.[46]

(iii) Paper chromatography. A number of investigations have been reported.[160–168] Lederer and Vernois[161–166] have used both paper chromatography and electrophoresis. Such a combination was successfully applied to the separation of protactinium(V), niobium(V), tantalum(V), titanium(IV), zirconium(IV), iron(III), and uranium(VI).[164] By using a butanol–hydrochloric acid–hydrofluoric acid–water mixture (50: 25: 1: 24) protactinium(V) can be separated from niobium(V) and tantalum(V) which move close to the solvent front. Zirconium(IV), which moves with the protactinium(V) in this system, and iron(III) are satisfactorily removed by electrophoresis in 1% hydrofluoric acid, whilst freedom from uranium(VI), titanium(IV), and zirconium(IV) is obtained by using 5% hydrochloric acid–5% hydrofluoric acid solutions. Further separations from these and other elements are described elsewhere by Vernois.[165] Use of chromatography paper impregnated with the Dowex-50 resin for separating protactinium(V) and numerous other metal ions has been examined.[166] In a 2% v/v hydrofluoric acid solution protactinium(V), which moves with the liquid front, with niobium, tantalum, and titanium, is separated from a number of bivalent transition elements. With oxine-treated paper hydrofluoric acid–5% hydrochloric acid solution removes protactinium and leaves zirconium behind.[164]

(iv) Miscellaneous. Various methods of removing titanium, tantalum, and zirconium from solutions of protactinium have been reported. For instance, alkaline carbonate fusions remove tantalum, and titanium remains in solution when protactinium is carried on zirconium phosphate.[169] Alternatively, fractional crystallisation of the ammonium double fluorides of the above elements concentrates protactinium in the mother-liquor,[170,171] and similarly zirconium oxychloride can be preferentially crystallised from hydrochloric acid solutions.[19,114] This observation is surprising in the light of current knowledge of solutions of protactinium in such a medium (section 4). Electrolytic techniques for separating protactinium from these elements are discussed in section 5.

Bouissières and Haissinsky[22] have reported a method which utilises

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[159] J. C. Sullivan and M. H. Studier, 1949, Report ANL-4286; 1959, U.S.Pt. 2,894,807.
[160] A. Fudge and J. L. Woodhead, *Analyst*, 1956, **81**, 417.
[161] M. Lederer, *Analyt. Chim. Acta*, 1953, **8**, 134.
[162] M. Lederer, *Actualités Sci. et Ind.*, 1956, No. 1240.
[163] M. Lederer, *J. Chromatog.*, 1958, **1**, 172.
[164] J. Vernois and M. Lederer, *Compt. rend.*, 1957, **244**, 2388.
[165] J. Vernois, *J. Chromatog.*, 1958, **1**, 52; 1959, **2**, 155.
[166] M. Lederer, *J. Chromatog.*, 1959, **2**, 210.
[167] C. E. Crouthamelt and A. J. Fudge, *J. Inorg. Nuclear Chem.*, 1958, **5**, 240.
[168] C. Keller, *J. Chromatog.*, 1962, **7**, 535.
[169] M. Batchelet and G. Bouissières, *Bull. Soc. chim. France*, 1944, **11**, 169.
[170] M. Batchelet, *J. Chim. Phys.*, 1946, **43**, 106.
[171] M. Batchelet and G. Bouissières, *Bull. Soc. chim. France*, 1947, **14**, 281.

the insoluble protactinium tetrafluoride. An oxide mixture containing titanium, tantalum, zirconium, and iron as main impurities was dissolved in hydrofluoric acid, the solution was converted into a sulphate medium, and the protactinium and zirconium were precipitated by addition of aqueous ammonia and hydrogen peroxide (tantalum and titanium remained in solution). The precipitate was dissolved in hydrochloric acid, and the hydrolysis products obtained on addition of acetone were dissolved in sulphuric acid. This leaves the iron chloride complexes in the acetone solution. Protactinium was then precipitated by aqueous ammonium hydroxide and carbonate (zirconium remaining in solution), after which traces of tantalum were eliminated by sodium carbonate fusion. The residue was dissolved in hydrofluoric acid, and protactinium tetrafluoride was precipitated after reduction with zinc amalgam. The more soluble fluorides of titanium, tantalum, and zirconium remained in solution during this treatment. Final purification was accomplished by precipitation of potassium fluoroprotactinate and then protactinium peroxide.

Potassium fluoroprotactinate is extremely useful during the later purification stages,[22,27] since the above elements and niobium form soluble salts. The protactinium can be recovered in greater than 99% yield by precipitation from ice-cold concentrated hydrofluoric acid with saturated potassium fluoride solution. Similarly, peroxide formation in dilute sulphuric acid is useful for the elimination of niobium, tantalum, and titanium.[27,140] However, traces of iron follow the protactinium. Other insoluble salts, namely, the iodate and phosphate, are accompanied by several impurities and the latter, when dissolved in hydrofluoric acid, provides a solution from which the protactinium is not readily recovered.[138]

Isolation of Protactinium-233.—It is impossible to give full details here of all processes, but an attempt will be made to give a reasonably complete literature coverage. Several applicable procedures have been dealt with elsewhere (see refs. 134, 143, 148, 149, 157–159).

The earlier work on the production of uranium-233 has been summarised by Stoughton[172] and Hyde[173] who record most of the techniques used during the "Manhattan project".[50,51] After irradiation, the thorium metal or salt is brought into solution by treatment with hydrochloric or nitric acid, usually with a trace of added fluoride ion to assist dissolution. Initial concentration may be achieved by the use of suitable carriers, followed by solvent-extraction or ion-exchange, but the majority of recent processes omit the carrier stage.

Of the carrier reagents, manganese dioxide has been subjected to the most intensive study.[134,135] Katzin and Stoughton[134] examined the conditions for radiochemical purification of protactinium-233 by forming the

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[172] R. W. Stoughton, Report T.I.D. 5222, 1951, 1.1, 3.

[173] E. K. Hyde, Nat. Nuclear Energy Series, Div. IV, Vol. XIV*A*, McGraw-Hill Ltd., New, York, 1949, Chap. 15, p. 558.

dioxide *in situ* in solutions 1—4M in nitric acid by the addition of potassium permanganate to a manganous nitrate solution. Recycling, with consequent reduction in bulk, was achieved by dissolving the precipitate with the aid of hydroxylamine, sodium nitrite, hydrogen peroxide, or formic acid. Although tracer thorium was carried, macroquantities (up to 0·65M) did not interfere and more than 95% of the protactinium was carried with less than 1% of uranium.

This technique has been used as a basis for several procedures[38,91,174–183] and usually allows good recovery provided chloride, fluoride, and citrate are absent.[135] It is of historical interest to note the details of the first isolation of pure samples of uranium-232[33] and uranium-233.[174] The protactinium parent was concentrated by precipitation with zirconium phosphate and manganese dioxide, the final zirconium concentrate being converted into the sulphate and dissolved in 0·33M-ammonium fluoride. After adjustment of the hydrogen-ion concentration to the Methyl Red end-point by ammonia, the protactinium was plated on to a copper cathode. Other workers have followed the initial separation by solvent-extraction. For instance, Meinke[91] dissolved the precipitate in hydrochloric or nitric acid and purified the protactinium by extractions with di-isopropyl ketone and trifluorothenoylacetone. A similar procedure was adopted by Hagemann *et al.*[175] after they had removed the uranium-233 by ether-extraction from highly salted M-nitric acid; Maddock and Miles[135] achieved purification by extracting the cupferron complex into pentyl acetate (see also ref. 176). A recent investigation[184] has shown that the dioxides of tin and lead are also useful carriers. Again, high concentrations of nitric acid and of thorium are detrimental and the co-precipitation is impaired by the presence of fluoride, phosphate, or zirconium.

Fudge and Woodhead[160] have employed niobium as a carrier, in addition to manganese dioxide. However, simple acid hydrolysis of the niobium in the presence of hold-back carriers did not yield protactinium-233 free from fission products. Purification was achieved by precipitating the protactinium with niobium tannate from a solution containing ethylenediaminetetra-acetic acid to hold back zirconium.The niobium and protactinium were then separated by paper chromatography with hydrofluoric acid–ethyl methyl ketone as developer or by carrying

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[174] G. T. Seaborg, J. W. Gofman, and R. W. Stoughton, Report T.I.D. 5223 (1), 1952, 1.1, 1.

[175] F. Hagemann, W. H. Studier, and A. Ghiorso, Report CF-3769, quoted by E. K. Hyde (ref. 173).

[176] V. I. Spitsyn and M. M. Golutvina, *Atomnaya Energ.*, 1960, **8**, 117.

[177] D. E. Ferguson, Progr. Nuclear Energy Series III, Pergamon Press Ltd., London, 1958, Vol. I, p. 219.

[178] G. T. Seaborg, J. W. Gofman, and R. W. Stoughton, 1958, U.S.Pt. 2,831,750.

[179] L. I. Katzin, U.S.Pt. 2,847,273.

[180] R. W. Stoughton and F. L. Steahly, U.S.Pt. 2,849,283.

[181] B.Pt. 810,542.

[182] B.Pt. 860,753.

[183] B.Pt. 863,845.

[184] C. A. Goodall and R. L. Moore, *J. Inorg. Nuclear Chem.*, 1959, **11**, 290.

the protactinium on barium fluorozirconate. This separation is better achieved by solvent-extraction with tributyl phosphate[185] or 2,6-dimethylheptan-4-ol[141] or by ion-exchange.[151,152]

Precipitation on zirconium iodate from hydrochloric or nitric acid solutions has also been investigated,[88,186–188] but in the presence of large amounts of thorium the concentrate was contaminated with thorium iodate. Zirconium phosphate,[88,174,178,189,190] barium zirconium hexafluoride,[91] and zirconium mandelate,[191] however, have been employed with more success. In the latter case, after two successive precipitations, the protactinium was adsorbed from nitric acid solution on glass filters. Recovery was accomplished by washing the filters with 0·3M-oxalic acid and, although radiochemical purity was attained, the adsorption stages are highly irreproducible and losses of protactinium are inevitable. It is claimed that protactinium has also been recovered on aluminium chromate precipitates.[192,193]

Uranium and protactinium are best separated from irradiated thorium by solvent-extraction, the chief advantages being the specific nature of certain solvents, the relative ease of remote operation, and the high overall efficiency. Hyde and Wolf[194] conducted one of the earliest surveys of suitable solvents. Their data, on extractions from salted M-nitric acid, showed that the most satisfactory extractions of protactinium were obtained with the higher ketones, particularly di-isopropyl ketone. Many workers have since employed this solvent,[91,107,175,195–197] which provides radiochemical purity without the use of carrier agents. The protactinium can be stripped into 2M-hydrochloric acid, or hydrochloric–hydrofluoric acid mixtures, and either recycled with the solvent[107] or purified by anion-exchange.[195]

Of the higher alcohols, 2,4-dimethylpentan-3-ol[198] and 2,6-dimethylheptan-4-ol[199] are extremely efficient extractants both from highly acid solutions and from salted phases. Oliver *et al.*[199] have shown that extraction from salted nitric acid solutions and recovery of the protactinium into nitric–hydrofluoric acid mixtures gives better than 99%

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[185] A. Fudge and J. L. Woodhead, *Chem. and Ind.*, 1957, **17**, 1122.

[186] K. A. Kraus and Q. Van Winkle, 1945, Report CC-3365, quoted by E. K. Hyde (ref. 173).

[187] R. W. Stoughton, Report CC-384, quoted by E. K. Hyde (ref. 173).

[188] J. E. Hugdens, B. Warren, and F. L. Moore, Report MON-N-234, 1947.

[189] K. A. Kraus and A. Garen, Report CNL-37, quoted by E. K. Hyde (ref. 173).

[190] G. T. Seaborg, J. W. Gofman, and R. W. Stoughton, 1958, U.S.Pt. 2,861,866.

[191] Y. Starik and L. D. Sheĭdina, *Radiokhymia*, 1959, **1**, 270.

[192] A. Gretsky, Progr. Nuclear Energy Series III, Pergamon Press Ltd., London, 1952, Vol. I, p. 212.

[193] French Pat. 188,528.

[194] E. K. Hyde and M. J. Wolf, Report T.I.D. 5223 (1), 1952, 3.12, 197.

[195] M. W. Hill, 1958, Report UCRL-8423.

[196] Q. Van Winkle and K. A. Kraus, 1959, U.S.Pt. 2,910,345.

[197] E. K. Hyde, L. I. Katzin, and J. Wolf, U.S.Pt. 2,978,294.

[198] R. E. Elson, U.S.Pt. 2,894,806.

[199] J. R. Oliver, J. R. Meriwether, and R. H. Rainey, 1959, Report ORNL-2668,

yield with good decontamination from thorium, uranium, zirconium, niobium, and fission products. Moore and Reynolds[139] had earlier reported that protactinium can be quantitatively extracted from a 6M-hydrochloric acid solution containing 4% of oxalic acid, almost all contaminants remaining in the aqueous phase.

Chelation by fluorinated β-diketones has been used successfully.[91,175,200,201] The procedure developed by Meinke[201] is of interest to workers handling short-lived isotopes of protactinium. The irradiated material was added to a 4M-nitric acid phase in contact with a 0·25M-solution of trifluorothenoylacetone in benzene. The protactinium was extracted into the organic phase, which was rapidly washed with nitric acid solution and aliquot parts from it were then mounted on trays. To offset the small yield (20%) the total time taken was only 1 minute.

Using Amberlite LA-1 (a secondary-amine resin), Ichikawa and Urono[202] successfully separated uranium and protactinium.

Tributyl phosphate can also be used since uranium will be extracted from a 5M-hydrochloric acid solution which is 0·5M in hydrofluoric acid while the protactinium remains in the aqueous phase.[143] More recently, tributylphosphine oxide has been used.[203–205]

Volatilisation techniques have been examined,[206–210a] but they will probably prove to be relatively inefficient for large-scale separations. Schulze[206] showed it was possible to volatilise protactinium from irradiated thorium compounds by passing a stream of hydrogen fluoride at temperatures in excess of 450°C. Further studies[207–209] have clarified the optimum conditions for isolating the protactinium and uranium fractions by using hydrogen–fluorine or hydrogen fluoride–fluorine mixtures. The chloride method has been demonstrated by Malm and Fried[210a] who used carbon tetrachloride (600°), phosphorus pentachloride (200°), and carbonyl chloride (400°) as chlorinating agents.

4. Protactinium(V): Species in Solution

Practical Difficulties.—There are still hardly any aqueous systems in which the nature of the protactinium species is rigorously established. This lack of accurate information is probably not so much due to the

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[200] Q. Van Winkle, U.S.Pt. 2,895,791.

[201] W. Meinke, *J. Chem. Phys.*, 1952, **20**, 754.

[202] F. Ichikawa and S. Urono, *Bull. Chem. Soc. Japan*, 1960, **33**, 569.

[203] T. Ishimori, K. Watanare, and K. Kimura, *J. Atom. Energy Soc. Japan*, 1960, **2**, 750.

[204] T. Ishimori and M. Sammour, *J. Atom. Energy Soc. Japan*, 1961, **3**, 410.

[205] T. Ishimori, K. Watamare, and T. Fujino, *J. Atom. Energy Soc. Japan*, 1961, **3**, 19.

[206] P. Schulze, Report T.I.D. 5223 (1), 1952, 3.1, 121.

[207] F. T. Miles, R. H. Wiswall, R. H. Heus, and L. P. Hatch, *Nucleonics*, 1954, **12**, 26.

[208] L. P. Hatch, F. T. Miles, T. V. Sheehan, R. H. Wiswall, and R. J. Heus, U.S.Pt. 2,893,936.

[209] G. T. Seaborg, J. W. Gofman, and R. W. Stoughton, U.S.Pt. 2,887,357.

[210] (*a*) J. G. Malm and S. Fried, quoted by R. Elson (ref. 25); 1959, U.S.Pt. 2,893,825; (*b*) K. W. Bagnall and D. Brown, 1962, unpublished observation.

scarcity of the element until recent years, as a natural consequence of the similarity of the chemical properties of this valency state to the corresponding states of niobium and tantalum. Indeed, existing information on the water-soluble species formed by the last two elements is limited and frequently inaccurate.

The properties of all three elements are such that the interpretation of tracer experiments is more than usually difficult. It is most unlikely that any appreciable concentration of uncomplexed Pa^{5+} ions can exist in water, even in quite acid media, although Elson believed it might be present in strong perchloric solutions.[25] Further, the majority of the complex ions formed by the element seem to be thermodynamically unstable with respect to hydrolysis. Hydrolysis is followed by condensation to polynuclear species which generally have low solubility products. At high concentrations of the element visible amounts of these products soon separate. In most cases these precipitates are chemically ill-defined because the solid phase separates before the condensation reaches completion. For example, the solid has been shown to be a hydroxy- or oxo-complex still containing some of the anionic groups present in the solution from which it separated, rather than a hydrated protactinium(V) oxide[210b] (this property is most inconvenient during the analysis of protactinium compounds).

Since a convenient tracer species, ^{233}Pa, and a longer-lived species, ^{231}Pa, are readily available, the protactinium concentration in a system can be varied over many more orders of magnitude than is possible for most elements. The concentration range 10^{-2}—10^{-14}M can easily be covered. As the concentration of protactinium in the aqueous system is reduced the amount of the hydrolytic condensation product decreases until there is insufficient to aggregate to a visible precipitate, but it will then separate as a colloidal suspension. At the same time, since the reactions involve the formation of polynuclear species, the rate of formation of the insoluble products decreases. At still lower concentrations of the element the amounts may be too small even for aggregation to the size of colloidal micelles, and there is then a strong tendency for the protactinium compounds to be adsorbed, either on other colloidal particles fortuitously present in the system, to form pseudocolloids, or on the walls of the containing vessel. Such systems display all the complexities characteristic of colloidal behaviour: thus, factors determining the sign of the charge on the electrical double layer on the surfaces will be important.

Although small, the solubility products of these solids cannot be infinitesimal, so that at some sufficiently low concentration of the protactinium the species will remain in solution. These true solutions can indeed be investigated by using ^{233}Pa, but their behaviour really has little bearing on the macroscopic properties of the element, because at higher concentrations the proportion of protactinium in true solution becomes negligible. It is very likely that many of the studies of the solution chemistry of protactinium, made by using ^{233}Pa in not too concentrated solution in weakly complexing acids, such as perchloric and, possibly, even nitric acid, suffer from this disadvantage.

Soluble Species at Tracer Concentrations.—Starik and his collaborators have applied a number of classical radiochemical techniques to the determination of the state of protactinium in dilute solutions in the mineral acids (^{233}Pa at 10^{-12}—10^{-13}M). They have studied the adsorption of the element from such solutions on glass,[211] polytetrafluoroethylene,[212] paraffin wax,[212] and various metals[211] as a function of the acidity of the solution. For the first two materials the adsorption shows a maximum at pH ~5·0 and for metals a similar maximum at a rather lower pH ~3—4. Centrifugation experiments[213] indicated that above pH 5·0 the protactinium formed a true colloid, that is, a colloidal system in which the disperse phase is entirely composed of the protactinium compound. If we suppose the disperse phase to be a hydrated protactinium(v) oxide this would correspond to a solubility product of 10^{-55}.[214] Although this is a likely order of magnitude for this quantity it is by no means clear what such a measurement really means. The identity of the solid phase is not established; it is not possible to determine very precisely the pH at which the solid begins to be formed; and finally the thermodynamic meaning to be attached to a solubility product for such a substance and under such conditions of particle size demands a much more elaborate investigation.

At a little below pH 5 the protactinium seems to be present as a negatively charged pseudocolloid, and in still more acid solutions electrolytic-migration experiments prove that cationic species are present in true solution. At very high pH (12—14) the protactinium again forms a pseudocolloid.[213] How far this pattern of behaviour is dependent on the anionic species present, which in the above studies were NO_3^- and Cl^-, is unknown.

Cationic Species.—By consideration of the charge : radius ratio of simple aquated ions of known hydrolytic behaviour Mikhaĭlov, who has reviewed recent developments in protactinium chemistry,[215] has estimated the first hydrolysis constant[216] of Pa^{5+} aq. at $10^{3\pm1}$, confirming the impression of most investigators that no appreciable concentration of such a species can be found. Although it was suggested, on the basis of some earlier cation-exchange studies, that moderately acid solutions

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[211] I. E. Starik, L. D. Sheĭdina, and L. I. Il'Menkova, *Radiokhimiya*, 1959, **1**, 391; 1961, **4**, 44.

[212] I. R. Starik and I. A. Skul'skiĭ, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1958, 1278.

[213] I. E. Starik, L. D. Sheĭdina, and L. I. Il'Menkova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1961, 690.

[214] I. E. Starik, L. D. Sheĭdina, and L. I. Il'Menkova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1959, 168.

[215] V. A. Mikhaĭlov, *Russ. Chem. Rev.*, 1960, **29**, 419.

[216] V. A. Mikhaĭlov, *Zhur. fiz. Khim.*, 1958, **32**, 1421.

of the element contained PaO_2^+ aq.,[217] it is now clear that if such an ion exists it is certainly quite different in properties and much more susceptible to further hydrolysis than UO_2^+ aq. or NpO_2^+ aq.[218] In solutions between 1M and 3M in the mineral acids, cation-exchange[25,157–159,219–223] and electrolytic-migration[25,211,212,222] experiments prove that cationic species are present. Probably these should be represented as $Pa(OH)_nX_m^{(5-n-m)}$ aq., where X is the mineral-acid anion. It is extremely difficult to obtain reproducible behaviour in these systems and the cationic species all seem to be liable, or indeed may be intermediate steps, to hydrolytic condensation to products of very low solubility. Such behaviour is, of course, not very different from that shown by niobium or tantalum. No really stable cationic complex has yet been reported for protactinium.

Anionic Complexes, Fluoroprotactinates.—The cationic species readily co-ordinate anionic ligands. Presumably, neutral complexes are formed before the anionic species are reached, but there is little direct evidence for their existence, except for those formed with chelating ligands (see below). For >3M-solutions the electrolytic-migration experiments indicate increasing amounts of anionic complexes in solution in nitric, hydrochloric, sulphuric, and hydrofluoric acid, as well as in the presence of many organic ligands such as oxalate, tartrate, and citrate.[222] With the possible exception of the sulphate complex, only the fluoro-complexes, among the inorganic complexes, are resistant to hydrolysis.

The fluoroprotactinate anion, PaF_7^{2-}, is distinguished as the first complex ion whose composition was certainly established. As early as 1931 Von Grosse analysed potassium fluoroprotactinate, K_2PaF_7, for the potassium and protactinium contents.[21] Within the limits of the accuracy of this analysis, however, the possibility remained that the compound was really K_2PaF_6OH, but more recently the analysis has been completed by the determination of the fluorine content which confirms the formulation, K_2PaF_7.[224]

Nonetheless, it is by no means certain PaF_7^{2-} is the only, or even the dominant, anionic species present in fluoride solutions containing protactinium. If the conductivity of a suspension of the hydrated oxide of protactinium is measured as increasing quantities of hydrofluoric acid are added, a plot of the observations reveals that a sharp change in the slope of curve takes place around F : Pa ratio of 8 : 1, suggesting that the first large change in the magnitude of successive association constants for F^- addition occurs when the PaF_8^{3-} ion is reached.[225]

[217] G. A. Welch, *Nature*, 1953, **172**, 458.

[218] Y. A. Zolotov, *Radiokhimiya*, 1960, **2**, 192.

[219] C. J. Hardy, D. Scargill, and J. M. Fletcher, *J. Inorg. Nuclear Chem.*, 1958, **7**, 257.

[220] I. E. Starik, L. D. Sheĭdina, and Il'Menkova, *Radiokhimiya*, 1961, **3**, 150.

[221] G. A. Welch, Thesis, London University, 1956.

[222] A. G. Maddock and L. Miles, *J.*, 1949, S 248.

[223] D. Brown, T. Sato, A. J. Smith, and R. G. Wilkins, *J. Inorg. Nuclear Chem.*, 1961, **23**, 91.

[224] J. Flegenheimer, Thesis, Cambridge University, 1959.

[225] C. Miranda, Thesis, Cambridge University, 1961.

Solvent Extraction of Protactinium.—Studies of the solvent extraction of protactinium have provided a great deal of information concerning the species existing in both aqueous and organic phases. Most of the empirical work on solvent extraction and its application to the separation of protactinium is described above (section 3).

(*a*) *Ion-pair solute systems.* Since quinquevalent protactinium readily gives anionic complexes it is not surprising that it can be extracted from many aqueous acid systems by donor solvents.[226] In such cases the extracting solute is an ion pair, comprising the anionic complex and an onium-type cation formed by the solvent. Protactinium(V) can be extracted in this way from solutions in nitric,[194,219,227] hydrochloric,[107,141,226–229] hydrobromic,[227,229] oxalic,[139,229] thiocyanic,[226] or even sulphuric acid.[141,226,229] In none of these systems has the identity of the extracted complex been rigorously demonstrated, but certain conclusions about their nature seem to be reasonably secure.

For a given organic solvent the extraction coefficient generally increases continuously with the concentration of hydrogen and ligand ions in the aqueous phase (Fig. 4). In principle, it is possible to derive information about the difference in composition between the species present in the two phases from data on such systems, but in practice the information about the relevant activity coefficients in the concentrated solutions concerned is usually insufficient to validate rigorous deductions.[229] However, the extraction coefficient is independent of the protactinium concentration over a wide range of concentrations, between 10^{-13} and

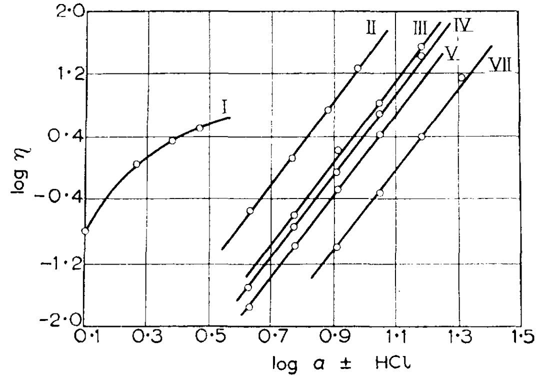

FIG. 4. *Relation between the extraction coefficient,* η, *and the activity,* $a^{\pm}$, *of hydrochloric acid in the aqueous phase for a number of ketones. Aqueous phases were initially between* 4 *and* 6 × 10^{-10}M *in* ^{233}Pa. *Solvents:* I *cyclohexanone,* II *mesityl oxide,* III *diethyl ketone,* IV *acetophenone,* V *methyl n-hexyl ketone,* VII *di-isobutyl ketone.* [Reproduced, by permission, from *J. Inorg. Nuclear Chem.*, 1958, **7**, 94.]

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[226] A. G. Goble and A. G. Maddock, *J. Inorg. Nuclear Chem.*, 1958, **7**, 94.
[227] A. G. Goble, J. Golden, and A. G. Maddock, *Canad. J. Chem.*, 1956, **34**, 284.
[228] A. G. Maddock and L. H. Stein, *J.*, 1949, S 258.
[229] A. Casey and A. G. Maddock, *J. Inorg. Nuclear Chem.*, 1959, **10**, 289.

10^{-8}M, so that the species present in the two phases must contain the same number of protactinium atoms per molecule. Since the total concentration is so small it seems reasonable to assert that all these species are in fact mononuclear complexes.

If we denote the average aqueous species by $Pa(OH)_mX_n^{5-m-n}$ and the organic species by $Pa(OH)_MX_N^{5-M-N}$, where X represents the unidentate anionic ligand, the changes in extraction coefficient with concentration of acid and X in the aqueous phase show that $M < m$ and $N > n$. From our knowledge of other systems of this kind it may be expected that M will be small, very possibly 0 and, further, that $M + N = 6$. These conclusions, which permit different proportions of cationic, neutral, and anionic complexes of varying degrees of hydrolysis in the aqueous phase, the proportions depending on the acidity and concentration of free ligand, are generally compatible with the conclusions from the other methods of investigation.[219,229]

In both oxalic and sulphuric acid solutions the extraction coefficient begins to decrease if the ligand concentration exceeds a limiting value (Fig. 5).[139,229] This is because protactinium then increases its co-ordination number and forms multicharged inextractable anionic complexes. Thus $PaOx_3^-$, or a slightly hydrolysed derivative thereof, is converted into

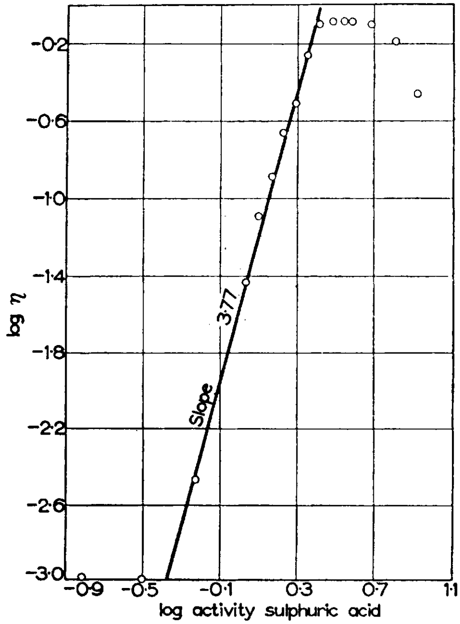

FIG. 5. *Extraction of protactinium-*233 *into di-isopropylcarbinol from sulphuric acid solutions. Variation of the logarithm of the extraction coefficient with the logarithm of the mean ionic activity of the sulphuric acid.* [Reproduced, by permission, from *J. Inorg. Nuclear Chem.*, 1959, **10**, 289.]

$PaOx_4^{3-}$, and $Pa(SO_4)_3^-$ gives $Pa(SO_4)_4^{3-}$. These conclusions are substantiated by ion-exchange data reported below.

Precise quantitative studies have been seriously hampered by the liability of the Pa–X group to replacement by Pa–OH. This reaction is probably generally reversible, but it may be followed by an irreversible condensation of the hydrolysed species to give inextractable polynuclear complexes that soon separate as a colloidal dispersion.[113,229] Reproducibility of the solvent-extraction behaviour on re-partition of the separated phases, after an initial extraction, with similar aqueous and organic phases free from protactinium, is indeed one of the most stringent tests for the absence of the condensed species. The condensation generally takes place rather rapidly, after an extremely variable induction period. The length of this induction period is related to the acidity, ligand concentration, and, especially, the protactinium concentration of the aqueous phase, decreasing as the latter increases. The formation of the inextractable condensed hydrolysis products is accompanied by changes in the absorption spectrum (see below) which parallel the changes in extraction behaviour.[113]

All ligands so far investigated, including hydroxyl, are readily replaced by fluoride and this ligand induces the protactinium to assume a co-ordination number greater than six, so that the anionic complex assumes a charge greater than two. Thus protactinium can always be extracted from the organic phase into aqueous solutions containing free fluoride ions.

Since at a low enough concentration the ion pairs will dissociate in almost any solvent, it is characteristic of these ion-pair extraction systems that at some low-enough concentration of protactinium the extraction coefficient will rise because of dissociation in the organic phase. In these systems there will be regions of constant extraction coefficient, for a fixed acidity and ligand concentration in the aqueous phase, for both low and high protactinium concentrations, the value in the low-concentration region being greater than in the high range. Between these extremes the extraction coefficient will be a function of the protactinium concentration, notwithstanding the fact that the protactinium species are all mononuclear complexes in either phase. With normal amounts of radioactivity, studies in which ^{233}Pa is used will involve solutions between 10^{-13}M and 10^{-11}M in the element and those with the long-lived ^{231}Pa will generally involve 10^{-3}—10^{-5}M-solutions. These two concentration regions generally correspond to parts of the low- and the high-concentration region referred to above, so that the extraction coefficients measured with ^{233}Pa are generally larger than those found for ^{231}Pa in these systems.[226]

Purity of solvent is important in quantitative studies since mixtures of solvents depart widely from additive behaviour,[230] and some trace impurities, such as organic peroxides[142,222] in ethers, will almost suppress extraction.

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[230] A. G. Goble and A. G. Maddock, *Trans. Faraday Soc.*, 1959, **55**, 591.

The extraction of protactinium by dodecylbenzenesulphonic acid may also be an ion-pair type of extraction.[231]

(*b*) *Extraction by the higher amines.* Closely related to the above processes are those in which the protactinium-containing anions are extracted from an aqueous phase by an organic solution of one of the higher amines (refs. 139, 219, 223, 226, 232–236). For instance, solutions of trioctylamine[233] or tributylamine[226] in benzene, or better in a more polar solvent such as dichloroethylene, extract protactinium, not only from solutions in hydrochloric,[226,232,233] sulphuric,[223] and nitric acid,[219,235] but also from phosphate solutions.[139] In the phosphate system it seems possible that the anionic part of the extracting complex may carry a charge greater than unity. However, in the relatively simpler nitrate, chloride, and sulphate solutions, the dependence of the extraction coefficient on the concentration of the amine in the organic phase shows that the anionic protactinium species carry unit charge.[219,223,226,229] These processes can be regarded as anion-exchange processes between two liquid phases.[233]

(*c*) *Extraction of solvates.* Tributyl phosphate extracts protactinium from hydrochloric,[143,226,237] nitric,[219,237] perchloric,[237,238] oxalic,[185,238] or sulphuric acid.[237] In each case the effects of acidity and anion concentration on the extraction have been investigated. For the first two acids, plots of log (extraction coefficient) against log (acid concentration) are nearly linear and parallel to similar plots for zirconium.[237,238] The relation is more complicated for the other acids, in which the protactinium seems to resemble quinquevalent neptunium.[237] The extraction coefficients are usually smaller for the sulphuric acid solutions.

The change in the extraction coefficient when the concentration of the tributyl phosphate is reduced by dilution with an inert solvent, such as kerosene, shows that two molecules of the ester are combined in the extracting complex. Largely from analogy with other tributyl phosphate extractions it has been suggested[219] that the extracting species is a solvate of a neutral molecular species, such as $Pa(OH)_n(NO_3)_{5-n},2TBP$ (TBP = tributyl phosphate). An earlier report[239] had suggested a trisolvate $Pa(NO_3)_5,3TBP$. Presumably n is restricted to low values, perhaps only unity or zero. There is, however, very little direct evidence for such neutral complexes, and tributyl phosphate is certainly capable of extracting ion-pair complexes. It is, perhaps, significant that ^{233}Pa is reported as

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[231] E. Nakamura, *J. Atom. Energy Soc. Japan*, 1961, **3,** 684.

[232] G. W. Leddicotte and F. L. Moore, *J. Amer. Chem. Soc.*, 1952, **74,** 1618.

[233] F. L. Moore, *Analyt. Chem.*, 1957, **29,** 1660.

[234] F. L. Moore, *Analyt. Chem.*, 1958, **30,** 908.

[235] W. E. Keder, J. C. Shepparo, and A. S. Wilson, *J. Inorg. Nuclear Chem.*, 1960, **12,** 327.

[236] F. L. Moore, *Analyt. Chem.*, 1960, **32,** 1075.

[237] T. Ishimori and E. Nakamura, *Bull. Chem. Soc. Japan*, 1959, **32,** 713.

[238] H. Scherff and G. Herrmann, *Z. Elektrokem.*, 1960, **64,** 1022.

[239] G. Carleson, *Svensk kem. Tidskr.*, 1958, **70,** 55.

giving the same extraction coefficient as ^{231}Pa, indicating the dissociation in the organic phase does not take place.[143]

A study of the influence of acidity and anion concentration in an aqueous nitrate phase on the extraction by tributyl phosphate led Sheĭdina and Il'Menkova[240] to suggest that in the pH range 0—1 the protactinium exists as cationic species of mean composition $Pa(OH)_{4\cdot5}^{0\cdot5+}$ and that an important change in the state of the protactinium occurs as one passes from 3N to 5N in nitric acid. From 5N to 14N they consider increasing amounts of neutral species to exist in the aqueous phase. These conclusions, although compatible with most existing information, are not rigorously established.

It has been suggested that these tributyl phosphate solvates are sufficiently strong to reverse the hydrolytic condensation that makes it difficult to obtain reliable data in so many of the other systems,[239] but this observation has been disputed.[219]

Another group of solvents, with similar characteristics, that may extract neutral complexes, are the trialkylphosphine oxides.[203–205]

(*d*) *Extraction of chelate complexes.* Several neutral chelate complexes of protactinium can be extracted with solvents such as benzene or carbon tetrachloride.

(i) β-Diketones. There is evidence for an extractable acetylacetonate but this is formed at such a high pH that hydrolytic condensation rapidly destroys it.[222] Extraction of the trifluorothenoylacetone (TTA) complex by benzene is much more satisfactory. The extraction is quite efficient even from 6N-nitric acid and provides a good separation from many elements (refs. 47, 91, 142, 175, 201, 241, 242). The dependence of the extraction coefficient on the trifluorothenoylacetone concentration is reported[243] as indicating a complex $Pa(TTA)_5$.* The extraction coefficients are less than those for the Pa(IV) complex.

The extraction of this complex has been used to compare the complexing power for protactinium(V) of various ligands in the aqueous phase and to establish the order $ClO_4^- < NO_3^- < Cl^- < SO_4^{2-} < F^-$.[224] Thus this diketone in benzene extracts hardly any protactinium(V) from an aqueous sulphate or fluoride solution.

(ii) Cupferron. Cupferron gives one of the strongest organic complexes of protactinium(V);[135,176] this complex can be extracted by pentyl acetate even from 4N-sulphuric acid.[135] The extraction does not, however, succeed with fluoride solutions. Neocupferron gives a similar complex.[224] Both complexes are of unknown composition.

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* The published work supporting this formulation is not, in fact, compatible with such a complex. Presumably there are some typographical errors in the report.

[240] L. D. Sheĭdina and L. I. Il'Menkova, *Radiokhimiya*, 1961, **3,** 24.

[241] F. L. Moore, W. D. Fairman, J. G. Ganchoff, and J. G. Surak, *Analyt. Chem.*, 1959, **31,** 1148.

[242] A. M. Puskanzer and B. M. Foreman, *J. Inorg. Nuclear Chem.*, 1961, **16,** 323

[243] G. Bouissières and J. Vernois, *Compt. rend.*, 1957, **244,** 2508.

(iii) Alkyl phosphoric esters. Both mono- and di-alkyl esters of phosphoric acid give strong complexes which are extractable into esters, alcohols, and ketones, as are the liquid esters themselves.[185,244–247] The dialkyl esters give especially high extraction coefficients and since both these acid esters are common impurities in tributyl phosphate the triester must be rigorously purified before use in solvent extraction studies.[185,226] The extracted species are clearly strong complexes, and extraction can be carried out successfully even from aqueous phases containing anions known to form complexes with the element, such as sulphate and oxalate,[244] but not in the presence of fluoride. It has also been reported that these acids will form complexes with, and extract, protactinium even if it is present as the condensed hydrolytic species, but this observation has been disputed:[239] it may well be a question of how far the condensation process has proceeded.

A study of the influence of the concentration of the alkyl phosphoric ester and the composition of the aqueous phase on the extraction coefficient has been carried out for solutions of mono- and di-isopentyl phosphoric esters in isopentyl acetate and an aqueous nitrate phase at an ionic strength of 6. The extraction coefficient depends linearly on the second power of the concentration of the ester.[245] It also increases with the acidity of the solution and by assuming the extraction can be represented by $Pa(OH)_3A_3^- + 2HA + H^+ = PaA_5^0 + 3H_2O$, where A is the anion of the partly esterified phosphoric acid, the equilibria in the aqueous phase can be interpreted in terms of the acid dissociation of the species $Pa(H_2O)_3A_3^{2+} \rightarrow PaOH(H_2O)_2A_3^{+} \rightarrow Pa(OH)_2H_2OA_3 \rightarrow Pa(OH)_3A_3^-$. The dissociation constants for the first two steps were evaluated as 100 and 21, values which are compatible with an estimate[246,247] of the first hydrolysis constant of Pa^{5+} aq. of 10^3. However, there is no rigorous proof that the extracted species is PaA_5^0.

(iv) Other chelate complexes. Protactinium has been extracted from solutions of calcium chloride by acetone in the form of a salicylate complex of unknown composition.[248]

(*e*) *Re-extraction into an aqueous phase.* Protactinium can be re-extracted into an aqueous phase by washing the organic phase with a solution of a strongly complexing anion, *e.g.*, fluoride,[25,249] sulphate,[139] or oxalate.[117,139] In addition, acidic hydrogen peroxide may be used.[119,120]

Ion-exchange Data.—Most of the published information relates rather to the use of ion-exchange to effect separation from other elements (see

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[244] K. Kimura, *J. Atom. Energy Soc. Japan*, 1960, **2**, 585.

[245] V. B. Schevchenko, V. A. Mikhaĭlov, and Y. P. Zaval'skiĭ, *Zhur. neorg. Khim.*, 1958, **3**, 1955.

[246] V. A. Mikhaĭlov, V. B. Schevchenko, and V. A. Kolganov, *Zhur. neorg. Khim.*, 1958, **3**, 1959.

[247] V. A. Mikhaĭlov, *Radiokhimiya*, 1959, **1**, 395.

[248] A. V. Nikolaev, A. G. Kurnakova, and Z. G. Rumyantseva, *Zhur. neorg. Khim.*, 1959, **4**, 1682.

[249] K. A. Kraus and A. Garen, 1948, Report ORNL-65.

section 3) than to identification of the species in solution. In chloride and nitrate solutions the distribution coefficient K_d for anion-exchange increases rapidly above concentrations 4N in acid up to the strongest solution studied.[146,156,219,226] Below 3N-acid the protactinium can be removed from the anion-exchange resin but is concentrated in the resin phase on a cation-exchanger. The reproducibility of studies of the cation-exchange behaviour is poor because of the usual hydrolytic phenomena. These observations confirm the pattern of the solvent-extraction, showing that with increasing acidity and ligand concentration the equilibria move so that, for the species $Pa(H_2O)_m(OH)_nX_p^{(5-n-p)}$, m and n decrease and p tends to increase. In nitric acid the plot of log K_d against log (normality of acid) for cation-exchange shows a minimum and a subsequently rising slope of 1·6.[219] It has been suggested that this is due to a decrease in n before p increases, so that less hydrolysed cationic species are formed. This conclusion, however, involves several simplying assumptions.

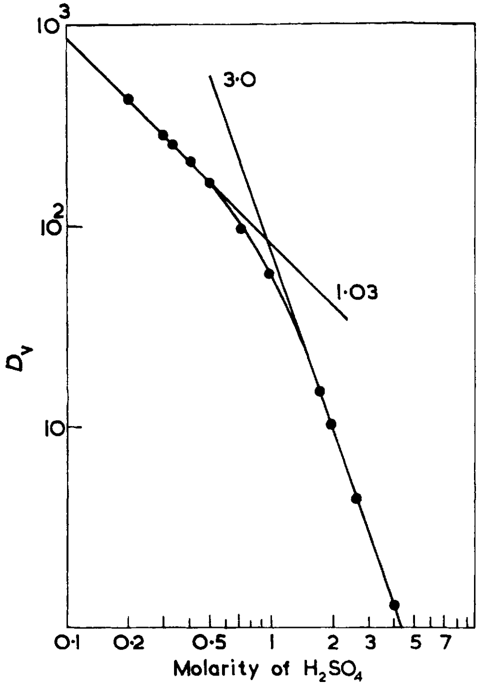

FIG. 6. *Charges on anionic complexes of protactinium*(V) *in sulphuric acid.*

With the more strongly complexing and the chelating ligands such as fluoride, oxalate, and citrate the protactinium forms anionic species at much lower acidities. At high ligand concentrations the co-ordination number of the protactinium may rise to seven or eight. In sulphuric acid, for example, between 1N and 2N, substantially all the protactinium is present as a singly-charged anionic complex which competes with the bisulphate anions for the resin sites as the acid concentration is raised. Thus, a plot of log K_d against log (acid molarity) shows a slope of -1 (Fig. 6). Above 1·5M-sulphuric acid, however, the protactinium is substantially all converted into a triply-charged complex, its co-ordination number increasing to eight, and the slope of the above plot to -3.[223] Similar behaviour has been reported for oxalate solutions,[221] and both observations agree with the conclusions from solvent-extraction.

The behaviour of fluoride solutions has not been investigated in detail and seems rather complicated. In concentrated solutions the fluoroprotactinate complex is readily adsorbed by anion-exchange resins, possibly as the PaF_8^{3-} anion,[119,225] but for more dilute solutions fluorides are reported as removing the element from both cation- and anion-exchange resins. In solutions of very high pH, prepared from alkali melts, protactinium can be removed from solution by the anion-exchange resin Dowex 2, which supplements the ionographic evidence for a protactinate ion, possibly PaO_4^{3-}.[250]

Paper-chromatographic and Ionographic Work.—The solvent-extraction behaviour of protactinium has been investigated by partition chromatography,[226] and various procedures for the separation of protactinium from other elements have been reported (see section 3). From the point of view of the solution chemistry of the element the most interesting discovery was that protactinium moves readily in fluoride solutions when the more alkaline, water-soluble solvents are used. Thus, developing a paper, spotted with a solution of ^{233}Pa, with a solution of composition butyl alcohol 50%, 12M-hydrochloric acid 25%, and 2N-hydrofluoric acid 25%, gave an R_F value of 0·45.[251] Acetone[162,251] and ethyl methyl ketone[160,167] have also been used as organic components of the developing mixture. In these systems it seems likely that 'onium ion-pair complexes of PaF_7^{2-} may be involved. It is significant that butyl alcohol extracts protactinium from an acidic aqueous fluoride solution, to which sufficient salt has been added to permit separation of the two phases.

Ionographic studies have supplemented the transference studies with compartmented cells. In 0·6N-hydrochloric acid–2N-hydrofluoric acid the element is present as an anion and moves rapidly, giving a well-resolved peak.[165] Evidence has been obtained for both cationic and anionic species in hydrochloric acid, but the peaks are poorly resolved and there is continuous production of slow-moving, probably colloidal, species.[252] The most useful result obtained with this technique is the discovery of the protactinate ion.[250,253] Ionography of a solution in N-potassium hydroxide, prepared by dilution of a potassium hydroxide melt containing ^{233}Pa

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[250] Z. Jakovac and M. Lederer, *J. Chromatog.*, 1959, **2**, 411.

[251] A. Grand-Clements, Z. Jakovac, M. Lederer, and E. Pluchet, Proc. Internat. Symp. Microchem., Birmingham, 1958, p. 221.

[252] J. Shankar, K. S. Venkatewarlu, and C. Gopinathen, *J. Inorg. Nuclear Chem.*, 1963, **25**, 57.

tracer, revealed a sharply defined anionic species, probably carrying unit charge and possibly $PaO_2(OH)_2^-$. Addition of barium hydroxide eliminates this species, possibly by precipitation as barium protactinate.[253]

Spectrophotometric Studies.—The simpler complexes of protactinium(V) are colourless, but they display strong absorption bands in the ultraviolet spectrum. These spectra were first studied by Elson and others in the Manhattan project,[25] but although some of the absorption peaks reported have been confirmed it is clear that the materials used were contaminated with absorbing impurities.

(*a*) *Chloride solutions.* The principal feature of the spectrum is an intense absorption band with a maximum quite close to the cut-off in hydrochloric acid solutions, *i.e.*, at about 210 $m\mu$.[113,144,221,254,255] Probably because of the considerable absorption by the acid solution used as control, different authors report slightly different positions for the maximum. It is generally agreed that the peak moves to longer wavelengths as the acidity and chloride concentration in the solution increases;[144,255] for instance, a maximum found at 208 $m\mu$ in M-acid moved to 213 $m\mu$ in 12M-solution. This band has a very high molar extinction coefficient ($> 10^4$), but reproducibility of the coefficient is poor and Beer's law appears not to be obeyed in 8M-hydrochloric acid. The band is very likely due to an electron-transfer, perhaps from the chloride ligand to the protactinium,[113,144] though other investigators have preferred to associate it with $Pa = O$.[255] The appearance of a similar band in sulphuric acid solution (see the next sub-section) may support this choice.[223] It is generally agreed that there are no absorption bands beyond 300 $m\mu$, but the other details of the spectrum are not certainly established. In the less acid solutions the absorption at 210 $m\mu$ decreases with storage of the sample and a strong band appears with a maximum at 260 $m\mu$.[113,144] This band is undoubtedly associated with hydrolysis of the protactinium complex and is always observed as soon as the hydrolytic condensation begins to interfere with the solvent-extraction of the chloro-complex; but it is not certain whether this band can appear while the hydrolysis is still reversible.[113] In addition, there is evidence of another band, appearing at low acidities, with its maximum at about 225 $m\mu$.[113,255]

All these results are analogous to the spectrophotometric properties of solutions of niobium(V) in hydrochloric acid. For the niobium(V) system they have been interpreted in terms of equilibria between species $Nb(OH)_2Cl_4^-$, $Nb(OH)_2Cl_3$, and $Nb(OH)Cl_3^+$. The anionic species has bands with maxima at 210 and 281 $m\mu$, and the cationic species has an absorption maximum at 260 $m\mu$.[256]

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[253] Z. Jakovac and M. Lederer, *J. Chromatog.*, 1958, **1**, 289.

[254] R. Guillaumont, R. Muxart, G. Bouissières, and M. Haissinsky, *Compt. rend.*, 1959, **248**, 3298.

[255] R. Guillaumont, R. Muxart, G. Bouissières, and M. Haissinsky, *J. Chim. phys.*, 1960, **57**, 1019.

[256] J. H. Kamzlemeyer, J. Ryan, and H. Freund, *J. Amer. Chem. Soc.*, 1956, **78**, 3020.

TABLE 6. *Co-deposition of traces of protactinium*(V).
(See especially refs. 22 and 25.)

No.	Macroscopic precipitate	Conditions	Comments	References
1	Hydroxides, basic salts of most metals and other ppts. from alkaline solns.	pH 4·0 Fe and Ti often used as carriers	Hydrol., followed by adsorption on macroscopic ppt.	22, 25, 94, 126, 130, 170, 222, *a*—*d*
2	Acid-insol. sulphides	pH 0—1·0, Hg, Bi, or Sb	Inefficient co-deposition, possibly after hydrol.	25, 132
3	Th chromate	pH 3	Probably hydrolytic adsorption	248
4a	Zr phosphate	Up to 6N in HNO_3	Ppt. sol. in aq. HF	19, 22, 25, 38, 88, 94, 101—106, 174, 178, 189, 190, 222, *e*
b	Th phosphate	,, ,,		
5a	Zr iodate	Up to 8N in HNO_3		22, 25, 94, 106, 186—188, 222, 248
b	Th iodate	,, ,,		
6	Zr arsenite	2·6N-HCl		25
7	Zr phthalate	pH 0		129
8	Zr phenylarsonate	pH 0		22, 129, 222
9	Zr mandelate	5N-HCl		128, 129, 191
10	Zr cupferronate	Up to 4M-H_2SO_4		22, 25, 94, 222, 248, *f*, *g*
11a	Th oxalate	pH 0		19, 116, 221, *e*
b	Cal oxalate	pH 2		248
12a	Zr peroxide			22, 94
b	Th peroxide			22, 25, 248, *h*
13	Zr oxyfluoride	pH 1·0		160
14a	Ba sulphate	3N-H_2SO_4	Variable co-deposition	25, *g*
b	$K_2Th(SO_4)_3$	M-K_2SO_4, M-H_2SO_4	About 80% co-deposited	25, 105, 222

15a	MnO_2	Up to 6N-HNO_3	Soln. chemisorption separates Th and U	38, 92, 133, 134–136, 174–183
b	PbO_2	,, ,,		184
c	SnO_2	,, ,,		184
16a	BaF_2	Up to 3N-HNO_3	Incorporated as $BaPaF_7$	107
b	$BaZrF_6$	,, ,,	,, ,,	91, 107, 170
c	K_2CeF_6	0·1N-HNO_3	Variable, but low, co-deposition	25
d	K_2UF_6	,, ,,	Variable, but low, co-deposition	25
e	LaF_3	Up to 3N-HNO_3	Variable, but low, co-deposition	22, 25, 222
f	ThF_4	,, ,,	Variable, but low, co-deposition	22, 25, 94, 105, 160, 222, 248
17a	Ta salicylate	pH 1·0—3·0	Not hydrol., since Pa extracted by acetone	248, *i*
b	Th salicylate	,, ,,		
18a	Nb tannate	M-Oxalate pH 5·0	Possibly isomorphous incorporation	120, 160
b	Ta tannate	,, ,,		
19a	Niobic acid	HCl or HNO_3 solution	Simple adsorption?	25, 160
b	Tantalic acid	,, ,,	,, ,,	5, 6, 8, 14—16, 32, 43, 44, 96—98, 100, 101, 124—127
20	Salicylidenethylenediamine complexes of Nb(v) and Ta(v)	in CCl_4 soln. of chloride	Isomorphous incorporation on MCl_3R_2	*j*

Additional refs.: (*a*) Tcheng-da-Tchang and Li Houang, *J. Chinese Chem. Soc.*, 1936, **4**, 93. (*b*) M. Bachelet, *Ann. Chim.* (*France*), 1939, **12**, 348. (*c*) A. S. Newton, *Phys. Rev.*, 1949, **75**, 23. (*d*) K. A. Kraus, Proc. Internat. Conf. Peaceful Uses Atom. Energy, Geneva, 1955, Vol. VII, p. 245. (*e*) A. Von Grosse, *J. Russ. Phys. Chem. Soc.*, 1928, **60**, 842, 847. (*f*) M. R. Sales-Grade, *Rev. Quim. Apl.*, 1950, **1**, 184. (*g*) E. F. Tret'yakov, M. P. Anikina, L. L. Gol'din, G. I. Novikova, and N. I. Pirigova, *Zhur. Ekspt. Teor. Fiz.*, 1959, **37**, 917. (*h*) Report ORNL-3061, 1960. (*i*) Gmelin, "Handbuch der Anorganischen Chemie," No. 51, "Protactinium und Isotope," Verlag Chemie, G.m.b.H. Berlin, 1942, p. 61. (*j*) A. V. Lapitskiĭ and Ya-Wu Chuang, *Radiokhimiya*, 1961, **3**, 241.

(*b*) *Sulphate solutions.* The absorption spectra of solutions of protactinium(V) in sulphuric acid were also investigated in the Manhattan project.[25] More detailed studies have shown that the spectra[223,255] are similar to those of the chloride solutions. The strongest absorption has a maximum moving from about 206 mμ in 4M-acid to about 220 mμ in 8·8M-acid. At the higher acidity it may split, to give peaks at 212 and 220 mμ. Solutions in 2·2M-acid do not obey Beer's law as far as the 214 mμ peak is concerned. The solutions are transparent above about 340 mμ. As with the chloride solutions the hydrolytic instability of the weakly acid solutions is revealed by their spectra.[223] For these solutions ($<$2M) a plateau in the absorption appears between ~280 and 300 mμ. On storage of the solutions the absorption in this region becomes steadily more pronounced, as does the 260 mμ absorption of the chloride solutions.

(*c*) *Perchlorate solutions.* Some results have been reported for solutions in perchloric acid.[25,255] However, only very little protactinium(V) dissolves, and the resulting solutions are very susceptible to hydrolysis, so that the significance of the results is questionable. A weak absorption is found at ~210 mμ in 2·3M-acid and this gradually disappears on storage of the solution. A broad absorption band is found between 220 and 255 mμ, which becomes more pronounced for more concentrated acid solutions. Again it is probable that the absorption changes with time. The solutions are effectively transparent above ~320 mμ.

(*d*) *Other species.* The spectrum of solutions of the trifluorothenoylacetone (TTA) complex in benzene has been investigated.[110,111] A maximum, which obeys Beer's law, is found at 414 mμ.

Anhydrous solutions of protactinium pentachloride in methanol[111] and tetrahydrofuran[111] show no absorption peaks due to the protactinium, the absorption merely increasing from around 300 mμ to the cut-off wavelength of the respective solvents.

Co-deposition of Protactinium.—It has been emphasised that most protactinium(V) derivatives are liable to hydrolysis. It is, therefore, not surprising that analysis has shown that the compounds of the element precipitated from aqueous solution are seldom of sharply defined composition and generally appear to be partially hydrolysed (cf. section 2). For the same reason the co-deposition reactions are more than usually difficult to interpret. Unless they are carried out in a strongly acid or complexing medium they may always be due to simple adsorption of hydrolytic products. In very few cases has it proved possible to demonstrate that isomorphous incorporation is taking place. In some cases, rather strong and specific chemisorption processes seem to be involved. Table 6 summarises the behaviour of protactinium(V), the co-deposition being $>$90% where no contrary indication is made.

Behaviour of Protactinium in Molten Salts and Metals.—A substantial amount of empirical information on the behaviour of protactinium in systems of potential importance as reactor fuels, or in the processing of such fuels by pyrochemical methods, has accumulated in the last few years. Since its chemical significance is often obscure it is presented simply in tabular form (Table 7).

TABLE 7. *Behaviour of protactinium in various systems.*

System	Behaviour of Pa	Refs.
Molten CaF_2–Th or Th/U alloy	Pa concentrates in metallic phase	*a*
$ThBi_2$ solid–liquid Bi	Pa concentrates in solid $ThBi_2$	*b*
Zn–U/Bi alloy	Pa concentrates in Zn phase	*c*
Mg–Th/U alloys	Pa concentrates in uranifirous phase	*d*, *e*
LiCl or LiCl/KCl–U	Pa concentrates in salt phase	*e*, *f*
$AlCl_3$ or $AlCl_3$/KCl–U or U alloy	Pa concentrates in salt phase	*g*

Additional refs.: (*a*) A. G. Buyers and E. E. Motta, 1957, Report NAA-SR-1710; K. R. Hyde, D. J. O'Connor, and J. L. Woodhead, Proc. Australian Atom. Energy Symp., 1958, p. 420; G. E. Brand, E. W. Murbach, and A. G. Buyers, *Nuclear Sci. Eng.*, 1959, **5**, 157; A. G. Buyers, E. E. Motta, and F. D. Rosen, U.S.Pt. 2,918,366. (*b*) J. S. Bruyer, *Nuclear Sci. Eng.*, 1959, **5**, 149. (*c*) O. E. Dwyer, H. E. Howe, and E. R. Avrutik, U.S.Pt. 2,914,399. (*d*) P. Chiotti, P. F. Woerner, and K. L. Malaby, *J. Chem. Eng. Data*, 1960, **5**, 435; P. Chiotti, U.S.P. 2,990,273; Reactor Chem. Ann. Rep., 1961, ORNL-3127. (*e*) Report IS./193, 1960. (*f*) P. Chiotti and S. J. S. Parry, 1961, Report IS./286. (*g*) R. H. Moore and W. L. Lyon, 1959, Report H.W. 59,147

5. Electrochemical Studies

Although there are numerous electrochemical observations on protactinium, their interpretation is generally doubtful. Most of the electrode reactions are irreversible, and in no case has the identity of the electrode deposit been satisfactorily established. The pH of the catholyte rises during electrolysis, so that hydrolysis and condensation become very likely and electrophoretic deposition may ensue; all these factors render the interpretation of the data rather uncertain.

Spontaneous Deposition.—It has been known for a long time that traces of protactinium will be deposited on metal foils from sulphate or fluoride solutions.[38,174] With the more electropositive metals this may well be due to local hydrolytic condensation on the surface of the dissolving metal, in the sulphate solutions. In fluoride solutions, reduction to the fluoride-insoluble protactinium(IV) state may be followed by adsorption on the metal. The peculiarly effective deposition on lead may take place because of special reactions. In fluoride solutions this deposition seems to follow a Langmuir isotherm,[257] and may be due to superficial formation of an insoluble lead fluoroprotactinate, analogous to the known barium fluoroprotactinate, $BaPaF_7$, which is nearly as insoluble as barium

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[257] M. Camarcat, G. Bouissieres, and M. Haissinsky, *J. Chim. phys.*, 1949, **46**, 153.

sulphate. Formation of a similar lead sulphatoprotactinate in the sulphate solution may also occur.

Cathodic Deposition.—Protactinium can be deposited on a variety of metal cathodes. The process is disappointing for the preparation of thin samples for counting since, unlike the other actinide elements, conditions have not yet been discovered which lead to complete deposition. About 95% of a trace quantity can be deposited from weakly acidic ammonium chloride solutions.[258] This process must involve electrophoretic deposition of some hydrolysed, and probably colloidal, material.

Although a brief report has appeared on cathodic deposition from sulphate solutions,[259] more detailed studies have been made of fluoride solution. Earlier work related to the possible application of the process to the purification of the element. Conditions for the separation from zirconium,[171] titanium,[259] and tantalum,[260] were discovered. More fundamental studies were conducted by Mlle. Ferradini.[261–263] Using Hevesy and Paneth's method,[264] she showed that with 10^{-11}M-protactinium in M-sodium fluoride the deposition potential lay between $-1{\cdot}18$ and $-1{\cdot}21$ v when gold, platinum, silver, or copper cathodes were used, but was only 0·89 v on nickel. Changing the protactinium concentration through the range 10^{-11} — 10^{-4}M gave a linear relation between the deposition potential on a gold or platinum cathode and the logarithm of the concentration, of slope 0·011. Haissinsky[265] has interpreted these results in terms of the electrode reaction $PaF_7^{2-} + 5e \rightarrow Pa + 7F^-$, obtaining a standard potential for the reaction of $-1{\cdot}03$ v. With nickel, however, the E–log c plot, although linear, had a negative slope.

An alternative interpretation of these and similar results is that reduction at the cathode to the fluoride-insoluble protactinium(IV) state is followed by electrophoretic deposition.

Because protactinium(V) is found only in complex ions, the Pa(V)/Pa(IV) potential is defined only when the particular complexes are specified. In most cases the protactinium(V) complex is metastable and the potential probably cannot be determined electrochemically. Fluoride solutions may constitute an exception.

A few observations have been reported on the behaviour of traces of protactinium during the electrolysis of thorium melts.[266]

Anodic Deposition.—Anodic deposition of protactinium is possible from

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[258] R. F. Mitchell, *Analyt. Chem.*, 1960, **32,** 326.
[259] E. Zavizziano and M. Haissinsky, *Compt. rend.*, 1938, **206,** 1102.
[260] G. Bouissières, *J. Phys. Rad.*, 1941, **2,** 72.
[261] J. Danon and C. Ferradini, *Compt. rend.*, 1952, **234,** 1361.
[262] C. Ferradini, *J. Chim. phys.*, 1953, **50,** 589.
[263] C. Ferradini, *J. Chim. phys.*, 1956, **53,** 714.
[264] F. Paneth and G. Hevesy, *Ber. Akad. Wiss.*, *Wien*, 1913, **122,** 1049; 1914, **123,** 1618.
[265] M. Haissinsky, Comité Internal. Therm. et Cinét. Élect. C. R. Réunion, 1951, p.222.
[266] W. N. Hansen, 1960, Report NAA-SR-4885.

sulphate[267] or carbonate[268] solution on lead, nickel, platinum, or gold anodes. It is well known that protactinium is chemisorbed on, and co-deposited with, lead dioxide and such behaviour may account for the results with lead anodes. With the more inert electrodes the deposition may well involve the formation of the complex sparingly-soluble peroxide (see section 3). However, the deposit has not quite the same properties as the macroscopically precipitated peroxide; *e.g.*, it appears to be removed from the electrode by sodium hydroxide solution.[269] Although deposits up to $1\cdot3 \times 10^{-2}$ mg./cm.^{2} of electrode have been prepared, deposition is more efficient with smaller deposits and at trace concentrations of protactinium in the solution. The nature of the deposit has not been established conclusively.

Polarographic Studies.—The polarographic behaviour of protactinium was first investigated by Elson,[25] using oxalate solutions. Two waves with half-wave potentials at $-1\cdot74$ and $-1\cdot92$ v against a standard calomel electrode (S.C.E.) were observed in solution at pH 2·5. More recently, a detailed study of the polarographic behaviour of the element in fluoride, sulphate, oxalate, and citrate solutions has been reported.[270] Persistent maxima in the citrate solutions make interpretation difficult. For oxalate solutions Elson's wave at $-1\cdot74$ v was confirmed, but a similar wave was found with solutions of other complex oxalates and it is possible that this irreversible wave results from reduction of the co-ordinated oxalate group.

With sulphate and fluoride solutions, two waves can be identified. The first wave in the fluoride media (3·84M-NH_4F, pH 7·2) appears at $-1\cdot29$ v against the S.C.E. Its height is proportional to the protactinium concentration and at low concentration it approaches reversible behaviour corresponding to a one-electron reduction. The half-wave potential moves to less negative values as the fluoride concentration of the solution is increased. It is probably due to the electrode reaction, $PaF_8^{3-} + e \rightarrow PaF_8^{4-}$. A second irreversible reduction wave is found at more negative potentials, but its height becomes independent of the protactinium concentration above $7\cdot10^{-4}$M. It does not appear to be a catalytic hydrogen wave, but it is consistent with the reduction of a sparingly soluble protactinium tetrafluoride to a less soluble trifluoride. However, it might also be due to reduction to the metal, provided the metal does not form an amalgam.

Sulphate solutions show more complex behaviour. Experiments have to be carried out in more acid solutions and the analogue of the second fluoride wave is barely distinguishable from the hydrogen wave. The first wave is found at $-0\cdot97$ v in 3M-ammonium sulphate that is 10^{-2}M

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[267] M. Haissinsky, *Nature*, 1945, **156**, 423.
[268] M. Haissinsky, *J. Chim. phys.*, 1946, **43**, 66.
[269] C. Ferradini and M. Haissinsky, *J. Chim. phys.*, 1956, **53**, 722.
[270] A. G. Maddock and C. Miranda, *J. Inorg. Nuclear Chem.*, 1963, **24**, 1623.

in sulphuric acid. It is shifted to more negative values with increasing pH or sulphate concentration.

It seems that polarographic reduction of the more stable protactinium(V) complexes to protactinium(IV) is generally possible. In not too acid solution a further reduction step may be observed, but whether this should be attributed to another one-electron step or to reduction to the metal is uncertain.

6. Protactinium(V): Crystal Chemistry

After the work of Von Grosse,[20,21] almost twenty years elapsed before further reports on the preparation and properties of protactinium compounds became available. However, much has been done in the last decade. The compounds now known, along with some lower oxides, are listed with relevant crystal data in Table 8.

TABLE 8. *Compounds of Protactinium*(V)

Compound	Colour	Symmetry	Lattice parameters *a*	*b*	*c*	Ref.
PaF_5	White	Tetragonal	11·53	—	5·19	278
$PaCl_5$	Pale yellow	Monoclinic	10·25	12·31	8·82	271
$PaBr_5$	Orange-red	Orthorhombic	7·25	12·12	9·13	272
PaI_5	Black	Orthorhombic	7·22	21·2	6·85	272
Pa_2O_5	White	Cubic	5·455	—	—	26
Pa_2O_5	White	Orthorhombic	6·92	4·02	4·18	26
$PaO_{2\cdot3}$	Black	Tetragonal	3·835	—	5·573	26
$PaO_{2\cdot3}$	Black	Cubic	5·476	—	—	26

Halides.—Protactinium(V) chloride, bromide, and iodide were first obtained by Von Grosse.[20b] The pentoxide was heated with carbonyl chloride at 550°, and protactinium pentachloride sublimed as almost colourless needles, m.p. 301° *in vacuo*. Treatment of the pentachloride with the other alkali halides yielded what was thought to be the corresponding pentahalides. However, no analytical or *X*-ray diffraction data were given for these compounds.

Sellers *et al.*[26] treated the pentoxide with carbon tetrachloride at 300° and isolated a white product, volatile *in vacuo* at 150°. Owing to difficulty experienced in interpreting the *X*-ray diffraction pattern, the product was not definitely identified as protactinium pentachloride although this was inferred as probable since reaction with hydrogen yielded the tetrachloride. More recent investigations have produced definite analytical[224] and crystal-chemical values[271] for this product. Flegenheimer[224] examined several methods for preparing milligram quantities of the pentachloride, the most successful being reaction of the pentoxide at 300 — 400° with gaseous chlorine saturated with carbon tetrachloride. The pale greenish-

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[271] D. Brown and A. J. Smith, unpublished work.

[272] R. D'Eye, A. Fox, A. G. Maddock, and D. J. Toms, unpublished work.

yellow crystals, m.p. 306°, sublimed at 160° *in vacuo* and, when ground, gave an almost white powder. Analysis, carried out after dissolving the product in anhydrous methyl alcohol, confirmed a formula $PaCl_5$. A recent single-crystal study[271] has shown the material to be monoclinic with $a = 10{\cdot}25$ Å, $b = 12{\cdot}31$ Å, $c = 8{\cdot}82$ Å, and $\beta = 111{\cdot}8°$, confirming the view that it differs from niobium and tantalum pentachloride.[273] It will be of interest to compare these values with those for uranium pentachloride when the latter are available. Protactinium pentachloride is also readily soluble in anhydrous tetrahydrofuran and gives a deep yellow solution on complex-formation with trifluorothenoylacetone in benzene.[111] A recent investigation has shown that it is possible to obtain very good yields of the pentachloride by treating the freshly precipitated hydroxide with thionyl chloride at room temperature.[274] Niobium and tantalum undergo similar reactions, but the latter element gives only a 50% yield.

Unidentified volatile bromides and iodides have been obtained by the action of various halogenating agents on protactinium pentoxide or pentachloride, and on the metal,[26] but the reaction between aluminium tribromide and protactinium pentoxide yields the orange-red pentabromide, m.p. 317°, which is stable to 400° and sublimes readily *in vacuo* at 250°.[272] Almost black, needle-like crystals of the pentaiodide can be prepared in the same way. This sublimes above 300° and when further heated releases iodine and affords a brown residue which sublimes slowly at 490°. This compound is probably a lower iodide or an oxyiodide of protactinium(v).

X-Ray powder data indicate that both the pentabromide and the pentaiodide are orthorhombic (Table 8).[272] However, they are not isostructural with the niobium and tantalum compounds.[275,276] Unfortunately no data are available for a comparison with the corresponding uranium halides.

Preliminary investigation of the protactinium(v) fluoride system indicated that a white product, volatile *in vacuo* at 350°, resulted from the reaction between silver fluoride and protactinium pentachloride.[277] Similarly[26] a white volatile product has been obtained by the action of bromine trifluoride or pentafluoride on protactinium pentoxide at 600°. No analyses are available on either product. Very recently, however, Stein[278] has isolated the pentafluoride, PaF_5, and an oxyfluoride, Pa_2OF_8. The pentafluoride, which is surprisingly much less volatile than its vanadium, niobium, and tantalum homologues, results from the reaction between protactinium tetrafluoride and purified fluorine at 700°. It is a white solid, volatile *in vacuo* above 500°, and is isostructural with the

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[273] A. Zalkin and E. Sands, *Acta Cryst.*, 1958, **11**, 615.
[274] K. W. Bagnall and D. Brown, unpublished work.
[275] R. E. Rolsten, *J. Amer. Chem. Soc.*, 1958, **80**, 2952; *J. Phys. Chem.*, 1958, **62**, 126.
[276] L. F. Dahl and D. L. Wampler, *J. Amer. Chem. Soc.*, 1959, **81**, 3150 (footnote).
[277] A. G. Maddock and S. Mohanti, unpublished work.
[278] L. Stein, 1961, personal communication.

β-form of uranium pentafluoride (Table 8). When the tetrafluoride is heated with fluorine containing oxygen as impurity the product is the oxyfluoride, Pa_2OF_8. This is a white solid, isomorphous with U_2F_9 (body-centred cubic) with cell parameter $a_0 = 8{\cdot}4065$ Å. It is also obtained when protactinium pentoxide is heated with fluorine or with a mixture of hydrogen fluoride and oxygen. The oxyfluoride partly decomposes at 800°, yielding the pentafluoride and other unidentified solids.

All the pentahalides are extremely sensitive to moisture, possibly being converted into oxyhalides, and consequently great care is necessary during their preparation and subsequent handling.

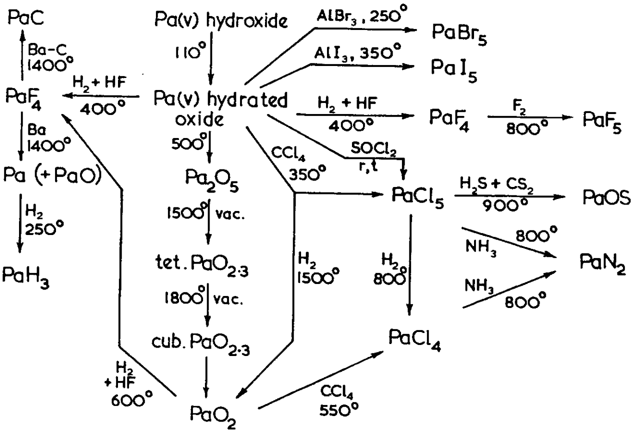

FIG. 7. *Preparation of protactinium compounds.*

Oxides.—The present state of the oxide chemistry poses several interesting problems. Two forms of the pentoxide have been observed.[26] Heating the hydrated oxide, obtained from ammoniacal solution, leads to a cubic phase at 500°, whereas an orthorhombic form, isostructural with niobium and uranium pentoxides, is reported to have been observed during attempts to prepare the pentafluoride. Recently Kirby[77] claimed to have identified both these phases in an oxide prepared by heating hydrolysis products at 670° in air. However, Roberts and Walter's results[279] suggest that the two forms are actually the same tetragonal phase ($a = 5{\cdot}433$, $c = 5{\cdot}488$), no evidence for a pentoxide other than a tetragonal one having been obtained by these authors.

Decomposition of the pentoxide by heating *in vacuo* leads to the formation of the black sub-oxide $PaO_{2\cdot 3}$ which exists as a tetragonal phase between 1000° and 1500° and a cubic one at 1800°.[26]

It is apparent that further *X*-ray diffraction studies and analytical work are necessary to elucidate this confused state of affairs.

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[279] L. J. Roberts and A. Walter, 1962, personal communication.

7. Lower Valencies

Solution Chemistry.—To date, the chemistry of protactinium(IV) has been little studied. The first indications are, however, that it will be more tractable in solution than the higher-valency state, provided sufficient precautions are taken to avoid atmospheric oxidation. The potential of the couple Pa(IV) = Pa(V) + e^- has been estimated at + 0·1 v by Fried and Hindman,[280] but a more recent publication[281] gives + 0·25 ± 0·03 v as the potential in 6M-hydrochloric acid (though the meaning of these statements is obscure).

The earliest attempts to reduce protactinium(V) are reported by Elson,[25] who presented electrolytic and polarographic results. The spectrum of "reduced" solutions in sulphuric and perchloric acid showed evidence of new peaks at 245—260 mμ and 285—290 mμ in the former solvent and at 250 mμ in the latter.

Haissinsky and Bouissières[24] showed that, after prolonged contact with zinc amalgam, more than 50% of the protactinium could be carried on lanthanum trifluoride as opposed to 5% before treatment. A later publication[282] described how milligram quantities were reduced in sulphuric, hydrochloric, and hydrofluoric acid. The reductions, carried out under a hydrogen blanket, were estimated as 80% complete and the new species was precipitated as a fluoride. Reduction by titanous and chromous chloride was said to be less efficient. The fluoride precipitate was soluble in dilute hydrofluoric acid only after re-oxidation had taken place, but it has since been shown to be very soluble in ammonium fluoride solutions.[283] Carrier experiments with zirconium(IV) in carbonate and hypophosphate media indicated that the product was probably protactinium(IV); this was later verified[284] by ceric titrations and it was shown that the reduced species was oxidised rapidly in air (40% in 30 minutes). Other insoluble compounds were obtained on addition of aqueous sodium hydroxide, ammonia, sodium iodate, phosphate, hypophosphate, and phenylarsonate, and potassium sulphate to sulphuric acid solutions containing 0·5 mg. of protactinium(IV) per ml. The protactinium remained in solution on addition of ammonium carbonate, citric acid, or tartaric acid. The resulting complexes in the last two cases were stable to ammoniacal solution, but the citrate was destroyed by sodium hydroxide. Attempts by Welch[221] to verify the reduction by zinc amalgam, using ion-exchange techniques, were inconclusive.

The solvent-extraction behaviour[243] and ion-exchange chromatography[285] have been briefly investigated. Protactinium(IV) produced by chromous chloride reduction was not extracted from 6M-hydrochloric

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[280] S. Fried and J. C. Hindman, *J. Amer. Chem. Soc.*, 1954, **76**, 4863.
[281] M. Haissinsky and E. Pluchet, *J. Chim. phys.*, 1962, **59**, 608.
[282] G. Bouissières and M. Haissinsky, *J.*, 1949, S 256.
[283] M. Haissinsky, R. Muxart, and H. Arapaki, *Bull. Soc. chim. France*, 1961, **28**, 2248.
[284] M. Haissinsky and G. Bouissières, *Bull. Soc. chim. France*, 1951, **18**, 146.
[285] E. Pluchet and R. Muxart, *Bull. Soc. chim. France*, 1961, **28**, 372.

acid by tributyl phosphate or isobutyl methyl ketone, but chelation with trifluorothenoylacetone (TTA) was observed, and the species Pa(TTA)$_4$ and Pa(TTA)$_5$ were claimed for protactinium-(IV) and -(V), respectively (see p. 321, footnote). Like thorium(IV), but unlike uranium(IV), protactinium(IV) is not adsorbed on anion-exchange resin from solutions 6—12M in hydrochloric acid, but any protactinium(V) present, possibly owing to re-oxidation or incomplete reduction, is adsorbed and can be eluted in the usual way.

The first reliable data on the absorption spectrum of protactinium(IV) in solution were those of Fried and Hindman,[280] who examined a sample of the tetrachloride dissolved in oxygen-free M-hydrochloric acid (Table 9). More recently, the reduction with zinc amalgam was coupled with spectrophotometric studies,[111,144,254,255] the extent of reduction being estimated from the residual absorption, due to protactinium(V), below 220 mμ. The reduction progressed more favourably in hydrochloric acid solutions with increased acidity; for example, Guillaumont *et al.*[255] observed 60% reduction in 2M-, 85% in 5M-, and 87% in >5M-solution; Brown *et al.*[144] observed complete reduction only for solutions >7M in hydrochloric acid. The incomplete reduction at lower acidities is believed to be due to the rapid hydrolysis associated with 10^{-4}M-protactinium(V) solutions; more than 70% of the element in 4×10^{-4}M-protactinium(V)–4M-hydrochloric acid settles as a solid in 12 hours.[144] Reductions in sulphuric acid were more satisfactory, presumably owing to greater stability of the protactinium(V) sulphate complexes.[111]

The spectrum of 7M-chloride solution resembles that obtained from the tetrachloride in M-hydrochloric acid;[280] the positions of the peak given by chloride and sulphate solutions are little affected by changes of acidity and anion concentration.[255] Spectra of protactinium(IV) are shown in Fig. 8 and further results are listed in Table 9. Protactinium(V) hydroxide is too insoluble in perchloric acid to allow an accurate measurement of the protactinium(IV) spectrum. A sample of tetrachloride was therefore dissolved in oxygen-free 1·5M-perchloric acid,[111] the resulting spectrum being almost identical with that observed for an M-hydrochloric acid solution.[280] The close similarity in peak positions (Table 9) and molar extinction coefficients suggests that the same species exist in these solutions; the possible complexes range from $Pa(H_2O)_x^{4+}$ to $PaCl_4$. However, the identification of species from spectral data must not be over-emphasised.[286,287]

Like other actinide tetrafluorides, $PaF_4,x\,H_2O$ has been found to be soluble in ammonium fluoride solution.[283] Although the solutions are susceptible to atmospheric oxidation the absorption spectrum in 15M-ammonium fluoride has been measured and peaks at 352·5 and

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[286] H. R. Hoekstra and J. J. Katz, Nat. Nuclear Energy Series, Div. IV, Vol. XIV*A*, McGraw-Hill, New York, 1954, p. 130.

[287] J. C. Hindman, Nat. Nuclear Energy Series, Div. IV, Vol. XIV*A*, McGraw-Hill, New York, 1954, p. 301.

250 mμ have been observed. The absence of a third peak is probably due to the presence of a trace of quinquevalent protactinium.

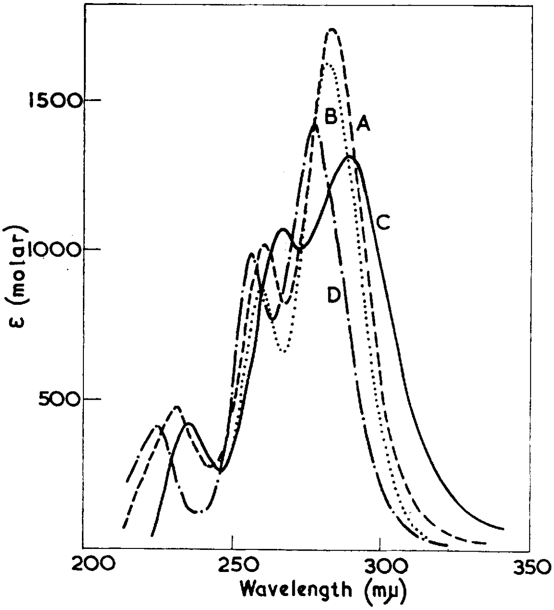

FIG. 8. *Spectra of protactinium*(IV) *in aqueous solutions.*
(A) 7·0M-Cl^- (1·7M-H^+) (B) 8·0M-Br^- (5·6M-H^+).
(C) 3·0M-SO_4^{2-} (4·4M-H^+). (D) 1·5M-$HClO_4$.

TABLE 9.[111] *Spectral characteristics of protactinium*(IV) *solutions.*

Solution	Peaks (mμ)
1·0M-HCl*	224, 255, 276
1·5M-$HClO_4$	225, 256, 277
1·7M-H^+, 7M-Cl^-	229, 260, 282
5·6M-H^+, 8M-Br^-	† 260, 282
4·4M-H^+, 3M-SO_4^{2-}	235, 267, 289
15M-NH_4F‡	— 250, 352·5

* Ref. 280. † Absorption by bromide ion prevented measurements below 245 mμ.
‡ Ref. 283.

Previous observations on the stability of protactinium(IV) in aqueous solutions had indicated rapid oxidation by oxygen[280] and slow oxidation in sealed cells.[144,255,280] Guillaumont *et al.*[255] observed increased resistance to aerial oxidation with increasing acid concentrations: in 1—4M-sulphuric acid the oxidation was complete in 168 hours whereas in 6·6M-acid it was only 68% complete in the same time. A similar effect was noted for hydrochloric acid solutions but in 1·5M-perchloric acid[288] oxidation was

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[288] D. Brown, Thesis, Sheffield, 1960.

rapid and within 24 hours the protactinium(V) produced had hydrolysed, forming a white solid.

The spectra shown in Fig. 8 are similar to those of cerium(III) which has one 4*f*-electron, and Fried and Hindman[280] suggested that possibly protactinium(IV) has one 5*f*-electron. Further, it is interesting that Jørgensen[289] has estimated the energy difference between 5*f*- and 6*d*-shells for protactinium as equivalent to a band at least +43 kilokaisens. This figure is close to the bands observed for protactinium(IV) in aqueous solution and it seems feasible that protactinium(IV) has a $5f^1$-configuration.

Crystal Chemistry.—In addition to the previously mentioned tetrafluoride hydrate and other compounds observed by Haissinsky and Bouissières,[282,284] several compounds have been characterised on the microgram scale by *X*-ray diffraction analysis.[26,290] Table 10 lists knowledge of the known compounds together with that of the metal, monoxide, and hydride.

TABLE 10. *Some compounds of protactinium.*

Compound	Colour	Symmetry	Structure-type	Lattice parameters		
				a	*b*	*c*
PaF_4	Reddish-brown	Monoclinic	ZrF_4; UF_4	—	—	—
$PaCl_4$	Greenish-yellow	Tetragonal	UCl_4	8·377		7·482
PaO_2	Black	Cubic	UO_2	5·505		—
PaOS	Pale yellow	Tetragonal	UOS	3·843		6·694
Pa	—	Tetragonal	—	3·925		3·238
PaH_3	Black	Cubic	UH_3	6·648		—
PaO	—	Cubic	UO; NpO	4·961		—

The tetrafluoride is obtained by hydrofluorination of the dioxide or hydrated pentoxide.[26] It is a non-volatile compound which is attacked by moisture to form the dioxide; it is insoluble in hydrochloric–hydrofluoric acid, nitric acid, and hydrofluoric acid–ammonium fluoride solutions.[278] It provides a suitable starting material for preparation of the metal.[26]

The dioxide, PaO_2, was first observed in an attempted reduction of the pentachloride[290] with zinc powder. It is prepared more conveniently by reducing the pentoxide at 1500° with hydrogen[26] or with carbon.[279] The black product is insoluble in hydrochloric, nitric, and sulphuric acid and dissolves only slowly in hydrofluoric acid, probably after oxidation.

The tetrachloride can be prepared from the dioxide by treatment with carbon tetrachloride at 500° or more simply by reduction of the penta-

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[289] C. K. Jørgenson, *Mol. Phys.*, 1959, **2**, 96.

[290] R. Elson, S. Fried, P. A. Sellers, and W. H. Zachariasen, *J. Amer. Chem. Soc.*, 1950, **72**, 5791.

chloride with hydrogen at 800°. It sublimes *in vacuo* at 400° and is readily soluble in oxygen-free solutions of hydrochloric[280] and perchloric acid.[111,288] The pentachloride is also reduced at 900° by a hydrogen sulphide–carbon disulphide mixture. The resulting oxide sulphide, PaOS, is isostructural with the oxide sulphides of other actinide elements.[26]

In addition to these compounds, a non-volatile nitride can be obtained by the action of gaseous ammonia on the penta- and tetra-chloride, and reduction of the tetrafluoride in a carbon crucible by barium vapour yielded what was believed to be a carbide.

Recently, the electronic configuration of octahedrally co-ordinated protactinium(IV) has been investigated by optical spectroscopy[291,292] and paramagnetic resonance absorption.[293,294] Dicæsium hexachlorozirconate was used as a matrix, and the protactinium was incorporated by treating the dioxide with the matrix at 850° and subliming the resulting mixture *in vacuo*. The mixed crystals were stable to moisture, and oxidation of the protactinium(IV) was not observed. On the basis of crystal-field considerations, the spectral data in the visible and near-infrared region, and the paramagnetic resonance spectrum, are shown to be more compatible with a $5f^1$- than with a $6d^1$-system. Similar information on uranium(IV) compounds suggests the presence of two $5f$-electrons.[295]

From the available information it is clear that the dioxides and tetrafluorides of the elements thorium to americium, and the tetrachlorides and oxide sulphides of thorium to neptunium form isostructural series. On the basis of such crystal-chemical data Zachariasen[296] postulates that protactinium is a member of a "thoride" series of elements with a characteristic valency of 4. The covalent radii of these elements in the quadrivalent state are shown in Table 11.

The duality of the nature of the elements of atomic number 92 onwards has been noted by Makarov[297] who mentions the crystal-chemical simi-

TABLE 11. *Covalent single-bond radii* (Å) *of actinides.*[296]

	Valency state	
Element	+4	+5
Thorium	1·67	—
Protactinium	1·64	1·52
Uranium	1·62	1·50
Neptunium	1·60	1·49
Plutonium	1·58	1·48
Americium	1·57	1·47

[291] J. D. Axe, 1960, Report UCRL-9293.

[292] J. D. Axe, H. J. Stapleton, and R. Kyi, *J. Chem. Phys.*, 1960, **32,** 1216.

[293] Ru-Tao Kyi, 1960, Report UCRL-9109.

[294] J. D. Axe, H. J. Stapleton, and C. D. Jefferies, *Phys. Rev.*, 1960, **121,** 1630.

[295] R. A. Satten, D. Young, and D. M. Gruen, *J. Chem. Phys.*, 1960, **33,** 1140.

[296] W. H. Zachariasen, Nat. Nuclear Energy Series, Div. IV, Vol. XIV*A*, McGraw-Hill, New York, 1954, p. 769.

[297] E. S. Makarov, "Crystal Chemistry of Simple Compounds," (translated from Russian), Consultants Bureau, Inc., New York, 1959.

larities with their transition homologues. However, a recent publication by Frère,[298] providing information on the niobium and tantalum tetrachlorides, indicates little resemblance between these two compounds, which are monoclinic (a=12·29, b=11·71, c=6·79; β = 94°·36′), and protactinium tetrachloride.

Metallic Protactinium.—Von Grosse[20b] obtained samples of metallic protactinium by decomposition of the pentahalides on a tungsten filament, and by the more unusual procedure of bombarding the pentoxide with 35 kv electrons. He reported it to be shiny, grey-white, and stable to oxidation. Zachariasen and his co-workers[26,299] reduced the tetrafluoride with barium vapour at 1400° and obtained shiny, malleable globules of the metal. *X*-Ray analysis indicated that it was body-centred tetragonal (Table 10), with a calculated radius of 1·63 Å for a co-ordination number of 12. The calculated density is 15·37 g./c.c. The preparations were coated with a thin film of what was believed to be protactinium monoxide, PaO. The interpretation of the *X*-ray data has recently been challenged by Donohue[300] who considered that a possible, but not necessarily more likely, alternative structure is orthorhombic. This is, however, refuted by Zachariasen.[301] The variation in metallic radius of the elements thorium (1·80 Å), protactinium (1·63 Å), and uranium (1·54 Å) is analogous to that in the triad zirconium, niobium, and molybdenum rather than to the changes in the 4*f*-series of elements. It therefore appears likely that there are no 5*f*-electrons present in metallic protactinium. The melting point, based on the method of preparation by barium vapour, is less than 1600° and the entropy at 295°K, as estimated from actinide trends, is 11 cal. mol.$^{-1}$ deg.$^{-1}$.[302] The metal reacts readily with hydrogen, forming the black hydride, PaH_3, which is isostructural with UH_3.[26] An estimate of the vapour pressure of protactinium at 2200°K leads to the value $5{\cdot}1 \times 10^{-5}$ atm.[303]

8. Protactinium in Relation to the Periodic Classification

A few years ago this subject was a favourite polemic but the question is now largely resolved.

The magnetic properties of cæsium hexachloroprotactinate, Cs_2PaCl_6, show clearly that the protactinium(IV) species in this compound has one 5*f*-electron. This is, indeed, in keeping with the chemical, spectrochemical, and crystallographic results for the simple protactinium(IV) derivatives. These compounds are closely related to the corresponding thorium(IV) and uranium(IV) compounds and noticeably different from niobium(IV)

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[298] P. Frère, *Ann. Chim. (France)*, 1962, **7**, 85.

[299] W. H. Zachariasen, *Acta Cryst.*, 1952, **5**, 19.

[300] J. Donohue, *Acta Cryst.*, 1958, **12**, 697.

[301] W. H. Zachariasen, *Acta Cryst.*, 1958, **12**, 698.

[302] B. B. Cunningham, Proc. U.N. Internat. Conf. Peaceful Uses of Atom. Energy, Geneva, 1955, Vol. VII, p. 225.

[303] E. W. Murbach, 1957, Report NAA-SR-1988.

and tantalum(IV). For instance, the halides of the last species disproportionate much more readily when heated, to give the tri- and quinque-valent halides, than do the protactinium(IV) halides.

It seems probable that the isolated neutral protactinium atom has at least one 5*f*-electron, and in these lower oxidation states protactinium is properly regarded as an actinide element, although the 5*f*- and 6*d*-orbitals are undoubtedly very close.

In the quinquevalent state, where only one electronic configuration is reasonable, there is sharp differentiation from the succeeding elements, uranium, neptunium, and plutonium. In this oxidation state, in solution, there is a remarkably close analogy between protactinium(V), niobium(V), and tantalum(V). It is unlikely that a PaO_2^+ aq. ion exists and, even if it does, it is completely different in properties from UO_2^+ aq., NpO_2^+ aq., etc. The reasons for this sharp change are not yet apparent. It may be that these oxy-cations need an admixture of *f*-orbitals not yet feasible at protactinium.

We thank Dr. K. W. Bagnall for helpful criticism of the manuscript.