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COMPREHENSIVE INORGANIC CHEMISTRY

IN FIVE VOLUMES

Volume 5

Actinides
Master Index

Volume 1. H, Noble Gases, Group IA, Group IIA, Group IIIB, C and Si

Volume 2. Ge, Sn, Pb, Group VB, Group VIB, Group VIIB

Volume 3. Group IB, Group IIB, Group IIIA, Group IVA, Group VA, Group VIA, Group VIIA, Group VIII

Volume 4. Lanthanides, Transition Metal Compounds

Volume 5. Actinides, Master Index

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PREFACE

THE Editorial Board of Comprehensive Inorganic Chemistry planned the treatise to fill a gap in the literature. There was no work that provided more information than could be found in single volumes but was not so large as to put it out of reach of all but a few central libraries.

The Editorial Board drew up and incorporated in instructions to authors a scheme that would make the best possible use of about five thousand pages. It was envisaged that the treatise would be of service to a wide range of readers many of whom would not be professional chemists. Convenience for all classes of reader was of paramount importance so that if a conflict arose between brevity and ease of use, the latter was preferred. Nevertheless the arrangement of the treatise is so systematic that such conflicts rarely occurred. The convenience of the reader has been further ensured by the adoption of a consistent arrangement of material within the chapters of the elements. The editors have been very gratified to observe that authors have not found the imposed pattern unduly restrictive. It has certainly helped to keep the accounts coherent and to preserve the intended balance between the chapters. The editors are very sensible to the effort that authors have made to collaborate.

The section of the book devoted to the survey of topics, particularly those relating to the transition elements, was a special interest of Sir Ronald Nyholm, whose death after most chapters were in proof saddened many chemists. We hope that those chapters which bear repeated evidence of his intellectual influence will be judged to be one of the many worthy memorials that he left behind him.

A. F. TROTMAN-DICKENSON

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45. THE ACTINIDES

INTRODUCTION

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THE actinide elements, otherwise known as the 5*f* transition series, are the fourteen elements which follow actinium ($Z = 89$) in the Periodic Table. They result from the successive addition of electrons to the empty 5*f* orbitals of the precursor element, and are analogous to the lanthanide, 4*f*, transition series in this respect. In contrast to the lanthanides, in which the normal oxidation state is +3, both in aqueous solution and in solid compounds, the actinides exhibit a variety of oxidation states in the early part of the series, up to and including americium (Table 1). However, the common oxidation state of americium and the remaining elements in aqueous solution is +3, as in the lanthanides, with the sole exception of nobelium ($Z = 102$), for which the dipositive state appears to be extremely stable with respect to oxidation in aqueous solution, apparently a consequence of the filled *f* shell electron configuration ($5f^{14}$) of the No^{2+} ion.

TABLE 1. KNOWN OXIDATION STATES OF THE FIRST SIX ACTINIDE ELEMENTS*

Th	Pa	U	Np	Pu	Am
					2†
	3(?)	3	3	3	*3*
4	4	4	4	*4*	4
	5	5	*5*	5	5
		6	6	6	6
			7	7	
				8(?)	

* The common oxidation state (*aqueous solution*) is italicized.
† Isolated in a CaF_2 matrix and more recently as the diiodide.

The stability of the tripositive ions with respect to oxidation or reduction in the latter part of the actinide series is due to thermodynamic factors, as in the lanthanide series. The requirements for such stability in aqueous solution are, first, that the enthalpy of hydration of the tripositive ion should exceed that of the dipositive ion by an amount numerically greater than the value of the third ionization potential and, second, that the enthalpy of hydration of the tetrapositive ion—a somewhat nebulous concept in view of the high charge and polarizing power of such an ion—should exceed that of the tripositive ion by an amount numerically less than the value of the fourth ionization potential[1].

---

[1] K. W. Bagnall, in *Essays in Chemistry*, Vol. 3, p. 39. Academic Press, Inc., London (1972).

In the earlier part of the actinide series, the high oxidation states which can be attained indicate, at least qualitatively, that the fourth and higher ionization potentials for these elements must be much smaller than those for the corresponding part of the lanthanide series. No experimentally determined ionization potential data are available for the actinides, but the differences between the 4*f* and 5*f* transition series are probably rather similar to those between the 3*d* and 4*d* transition elements. In the case of the 4*d* elements the known ionization potentials are appreciably less than those in the 3*d* series (Table 2) and the radii of ions in the same oxidation state are larger in the 4*d* series than are their counterparts in the 3*d* series. Similarly, the radii of the tripositive actinide ions are about 7% larger than those of the analogous lanthanide ions at the beginning of the actinide series, but this difference in ionic radius decreases with increasing atomic number and the radius of Cf^{3+} is only about 4% greater than that of Dy^{3+} in the lanthanide series. This suggests that the effective nuclear charge to which the 5*f* electrons are exposed is about 14% less than that of the lanthanide analogue at the beginning of the actinide series, falling to 8% less at californium. Since No^{2+} is demonstrably stable to oxidation in aqueous solution, it would seem that for this element the effective nuclear charge may well exceed that experienced by the *f* electrons of ytterbium.

TABLE 2. SOME IONIZATION POTENTIAL DATA FOR 3*d* AND 4*d* TRANSITION ELEMENTS*

Element	Ionization potential (eV)							
	1st	2nd	3rd	4th	5th	6th	7th	8th
Vanadium	6·74	14·65	29·31	48	65·2	128·9	151	174
Niobium	6·77	13·5	28·1	38·3	49·5	103	125	145
Iron	7·90	16·18	30·64	57·1	78	102	128	151
Ruthenium	7·5	16·4	28·6	46·5	63	81	100	119

* Data from F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 2nd ed., pp. 797, 910, Interscience Publishers, New York (1966).

The increase in effective nuclear charge with increasing atomic number across the actinide series, as in the lanthanide series, is due to the rather poor screening of one *f* electron by another as the *f* shell fills up. The consequences of this are that the whole *f* shell contracts as the atomic number increases—the lanthanide and actinide contractions—and the fourth, or higher, ionization potentials must also increase across the series, so causing a decline in the stabilities of the higher oxidation states towards reduction.

Much of the work described in this volume relates to two of the earlier actinide elements, thorium and uranium. The main reasons for this apparent imbalance are simply the availability and the ease of working safely with these two elements. Whereas thorium and uranium are readily available by the ton, protactinium (^{231}Pa, a member of the ^{235}U decay chain), neptunium, plutonium and americium are available in gram quantities, but are expensive, and from curium onwards the quantities available decrease steadily from milligram (curium) to submicrogram (fermium, $Z = 100$) amounts and thereafter the availability is measured in atoms. The intensity of the radioactivity per unit mass, or specific activity, increases in the same direction.

Although all the known isotopes of the actinide elements are radioactive, the half-lives of ^{232}Th, ^{235}U and ^{238}U are sufficiently long for them to be found in nature and there are no major handling problems involved in working with them. This is in marked contrast to the much greater radioactivity hazard arising from the α-activity of protactinium and the synthetic transuranium elements. Because of these hazards, it is necessary to build very expensive laboratories for chemical research on these elements, and the cost involved has restricted fundamental research in this area of the Periodic Table to government supported research establishments, such as Harwell in the U.K., the Argonne and Oak Ridge National Laboratories in the U.S.A. and so on. In establishments such as these the proportion of effort directed to fundamental chemical research is naturally quite small, and a much larger proportion of the research is of an applied nature, directed at the chemistry of reactor systems, particularly to fuel reprocessing and fuel fabrication, and to analytical control. It will be readily apparent from the content of the following sections that much remains to be done in the transuranium, and more particularly in the transplutonium, region of the actinides.

THE ELEMENTS

J. A. Lee and J. A. C. Marples
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1. DISCOVERY

The first of the actinides to be recognized as a new element was uranium detected in a pitchblende specimen from Saxony by M. H. Klaproth in 1789. Berzelius discovered thorium in 1828 and made the first metal preparation by reduction of thorium tetrachloride with potassium, establishing the basic route by which uranium (1861) and the majority of subsequent members of the series have initially been reduced to metal. Actinium was discovered over half a century later in 1899, by Debierne working in the Curie laboratory and independently by Geisel in 1902. The new radioactive species appeared in those processing fractions in which the rare earth elements concentrated and its position as the prototype element of an actinide series corresponding to lanthanum in the rare earth series was early recognized. The metal was not prepared, however, until 1955. Protactinium, the last of the actinide elements occurring naturally in significant quantities (there is 0·34 ppm ^{231}Pa in uranium ores as a decay product of ^{235}U), was discovered by Fajars and Göhring in 1913 in the isotopic form ^{234}Pa; ^{231}Pa was discovered by Hahn and Meitner and independently by Soddy and Cranston three years later.

Although a study of members of the series began almost two centuries ago, the major developments in actinide chemistry have taken place following the discovery of nuclear fission by Hahn and Strassmann[1] in 1939, and the synthesis of neptunium by the irradiation of natural uranium with neutrons, and plutonium by bombardment of uranium with deuterium ions in 1940. The Periodic Table has been extended beyond the actinide series with element 104 (Kurchatovium Ku, Rutherfordium Rf) shown to behave similarly to hafnium[2]. The main sequence of discovery is outlined in Table 1.

Whilst the basis for continuation of fundamental research on these elements, which has entailed the evolution of entirely new experimental techniques to deal on the one hand with the extreme radioactivity and toxicity of these isotopes, and on the other with the small quantities initially available and often short half-lives of the higher isotopes, has been the development of thorium, uranium and plutonium as nuclear fuels, it was not envisaged that higher elements would become technologically significant. There has, however, been a surprising growth of interest in other actinides for new technological developments and over the next few decades Seaborg[3] has predicted that these could become a significant factor in the economics of power production, providing a continuing incentive for further studies.

---

[1] O. Hahn and F. Strassmann, *Naturwiss.* **27** (1939) 11 and 39.

[2] G. T. Seaborg, J. L. Crandall, P. R. Fields, A. Ghiorso, O. L. Keller and R. A. Penneman, *Proc. 4th Int. Conf. on the Peaceful Uses of Atomic Energy*, Geneva, United Nations (1971), A/Conf. 49/P/841.

[3] G. T. Seaborg, *Nucl. Appl. Technol.* **9** (1970) 830.

TABLE 1

Atomic no.	Element	Symbol	Discovery	First discovered isotope	Source/ Synthesis	First metal preparation	Most stable isotope
89	Actinium	Ac	A. Debierne, *Compt. rend.* **129** (1899) 593 F. O. Geisel, *Ber.* **55** (1902) 3608	^{227}Ac	Uranium ore	Reduction of actinium fluoride with lithium vapour J. G. Stites Jr., M. L. Salutsky and B. D. Stone, *J. Amer. Chem. Soc.* **77** (1955) 237	^{227}Ac
90	Thorium	Th	J. J. Berzelius (1828)		Thorium ore	Reduction of thorium tetrachloride with potassium J. J. Berzelius, *Ann. Physik* **16** (1829) 385	^{232}Th
91	Protactinium	Pa	K. Fajars and O. H. Göhring (1913) O. Hahn and L. Meitner (1917) *Naturwiss.* **6** (1918) 324 F. Soddy and J. A. Cranston, *Proc. Roy. Soc. (London)* **A94** (1918) 384	^{234}Pa ^{231}Pa	Uranium ore concentrates	Bombardment of protactinium oxide with 35 keV electrons in a high vacuum or thermal decomposition of protactinium pentachloride on a hot filament A. V. Grosse and M. Agrass, *J. Amer. Chem. Soc.* **56** (1934) 2200	^{231}Pa
92	Uranium	U	M. H. Klaproth (1789)		Pitchblende	Reduction of tetrachloride with potassium B. Peligot (1841) *Ann. Chim. Phys.* **5** (1842) 7, 42	^{238}U
93	Neptunium	Np	E. McMillan and P. Abelson, *Phys. Rev.* **57** (1940) 1185	^{239}Np	Irradiation of natural uranium with neutrons $^{238}\text{U}(n, \gamma) \xrightarrow{\beta^-}$	Reduction of NpF_3 with barium S. Fried and N. Davidson, *J. Amer. Chem. Soc.* **70** (1948) 3539	^{237}Np

TABLE 1 (*cont.*)

Atomic no.	Element	Symbol	Discovery	First discovered isotope	Source/ Synthesis	First metal preparation	Most stable isotope
94	Plutonium	Pu	G. T. Seaborg, E. M. McMillan, J. W. Kennedy and Al. Wahl (1940) *Phys. Rev.* 69 (1946) 366	^{238}Pu	Bombardment of uranium with deuterium ions $^{238}\mathrm{U}(d, 2n) \xrightarrow{\beta^-}$		^{244}Pu
95	Americium	Am	G. T. Seaborg, R. A. James, L. O. Morgan, A. Ghiorso (1944/45) *Phys. Rev.* 78 (1950) 472	^{241}Am	Irradiation of plutonium with neutrons $^{239}\mathrm{Pu}\ (n, \gamma) \xrightarrow{\beta^-}$	E. F. Westman Jr. and L. Eyring, *J. Amer. Chem. Soc.* 73 (1951) 3396 Reduction of trifluoride with barium	^{243}Am
96	Curium	Cm	G. T. Seaborg, R. A. James and A. Ghiorso (1944) Paper 22.2, p. 1554 of *Transuranium Elements*. Nat. Nuclear Energy Ser. Div. IV, Vol. 14B (1949)	^{242}Cm	Bombardment of plutonium with helium ions $^{239}\mathrm{Pu}(\alpha, n)$	Barium reduction of trifluoride. J. C. Wolfmann, W. W. T. Crane and B. B. Cunningham, *J. Amer. Chem. Soc.* 73 (1951) 493	^{247}Cm
97	Berkelium	Bk	S. G. Thompson, A. Ghiorso and G. T. Seaborg (1949) *Phys. Rev.* 80 (1950) 781	^{243}Bk	Bombardment of americium with helium ions $^{241}\mathrm{Am}\ (\alpha, n)$	Lithium reduction of trifluoride. J. R. Peterson, J. A. Fahey and R. D. Baybarz, Plutonium 1970, *Proc. 4th Internat. Conf.* Pt. 1 (1970) 20	^{247}Bk
98	Californium	Cf	S. G. Thompson, K. Street Jr., A. Ghiorso and G. T. Seaborg (1950) *Phys. Rev.* 80 (1950) 790	^{245}Cf	Bombardment of curium with helium ions $^{242}\mathrm{Cm}\ (\alpha, n)$	Lanthanum reduction of oxide and lithium reduction of trifluoride B. B. Cunningham and L. B. Asprey (1971)	^{251}Cf

TABLE 1 (*cont.*)

Atomic no.	Element	Symbol	Discovery	First discovered isotope	Source/ Synthesis	First metal preparation	Most stable isotope
99	Einsteinium	Es	A. Ghiorso, S. G. Thompson, G. H. Higgins, G. T. Seaborg, M. H. Studier and P. R. Fields S. H. Fried, H. Diamond, J. F. Mech, G. L. Pyle, J. R. Huizanga, A. Hirsch, W. M. Manning, C. J. Brown, H. L. Smith and R. W. Spence (1952)	^{253}Es	Irradiation of uranium with neutrons in the first thermonuclear explosion		^{254}Es
100	Fermium	Fm		^{255}Fm	Ditto		^{257}Fm
101	Mendelevium	Md	A. Ghiorso, B. H. Harvey, G. R. Choppin, S. G. Thompson and G. T. Seaborg, *Phys. Rev.* **98** (1955) 1518	^{256}Md	Bombardment of einsteinium with helium ions ^{253}Es (α, n)		^{258}Md
102	Nobelium	No	A. Ghiorso, T. Sikkeland, J. R. Walton and G. T. Seaborg, *Phys. Rev. Letters*, **1** (1958) 17	^{254}No	Bombardment of curium with carbon ions		^{254}No
103	Lawrencium	Lr	A. Ghiorso, T. Sikkeland, A. E. Larsch and R. M. Latimer, *Phys. Rev. Letters*, **6** (1961) 474	^{257}Lr	Bombardment of californium with boron ions $^{249-252}$Cf+ ^{10}B or ^{11}B		^{256}Lr

2. OCCURRENCE, SEPARATION AND PREPARATION OF THE METALS

2.1. Introduction

It is difficult to generalize about the actinide elements under any of these headings. Only two of them, thorium and uranium, occur to any extent in nature, although the former is in fact relatively common. The other elements are made by man via various nuclear transmutation processes, but the scale on which these are carried out, either deliberately or as by-products of some other reaction, varies widely. Plutonium is produced by the ton in reactors in several countries, both for weapons purposes and as nuclear fuel. Neptunium, protactinium and americium are available in gram quantities whilst the other elements are handled in milligram amounts or in the case of the higher actinides built up virtually atom by atom in particle accelerators.

In consequence, of course, the scale of separation techniques also varies widely. Uranium is mined in large quantities for the nuclear power industry and its separation and that of thorium follows fairly normal metallurgical techniques. The purification of these and of the other actinides relies heavily on solvent extraction and ion exchange methods whilst the rarer elements are often separated by chromatographic techniques.

All the actinide elements form very stable compounds, and powerful reducing agents are needed to produce the metal, the action of the alkali or alkaline earth metals on the actinide halides being usually favoured, although the scale of the operation produces wide variations in technique depending on whether the batch is many kilograms of uranium, a few grams of neptunium or a few milligrams of actinium. Electrolysis of aqueous solutions is not feasible because of the reactivity of the metal, but fused salt electrolysis is used for purification of some of the metals. The van Arkel process of thermal dissociation of the iodide has been used to produce gram quantities of very pure thorium and uranium.

The elements are discussed separately in the following sections.

2.2. Actinium

The only isotope of actinium with a half-life long enough ever to permit macroscopic amounts to be studied is ^{227}Ac ($t_{\frac{1}{2}} = ca.$ 22 years) which decays by β^--emission. ^{227}Ac is a member of the decay chain of ^{235}U, but because of its short half-life occurs only in minute quantities in uranium ores (1 ton of pitchblende contains only about 0·15 mg). Furthermore, the presence of rare earths makes the separation difficult. ^{231}Pa decays by α-emission with a half-life of 32,800 years to form ^{227}Ac, but this is also of rather academic interest because of the rarity of protactinium. The only source of milligram quantities of the element is the neutron irradiation of radium:

$$^{226}\mathrm{Ra}(n, \gamma)\ ^{227}\mathrm{Ra} \xrightarrow[41\ \mathrm{min}]{\beta^-} {}^{227}\mathrm{Ac}$$

Actinium may then be separated from its daughter products and from the radium by two alternative processes[4,5]. The actinium can be extracted from an aqueous solution of

---

[4] F. T. Hagemann, *J. Amer. Chem. Soc.* **72** (1950) 768, and *The Chemistry of Actinium*, in *The Actinide Elements*, G. T. Seaborg and J. J. Katz (Eds.), NNES IV, Vol. 14A, p. 14, McGraw-Hill, New York (1954).

[5] S. Peterson, in *The Transuranium Elements*, G. T. Seaborg, J. J. Katz and W. M. Manning (Eds.), NNES II, p. 1393, McGraw-Hill, New York (1949).

controlled pH using a benzene solution of thenoyltrifluoroacetone (TTA), but for separation of cations of different valencies the alternative ion exchange process is a powerful tool. The trivalent actinium and tetravalent thorium are completely absorbed onto Dowex-50 resin from acid solution. The actinium may then be eluted with acid of slightly higher concentration, leaving the thorium still absorbed.

Recently, Baetsle *et al.*[6] have prepared about 18 g of ^{227}Ac as Ac_2O_3 for use as a thermionic power source. Radium carbonate was irradiated to the optimum level, so as to balance production of ^{227}Ac against its conversion to ^{228}Ac and thence to ^{228}Th. The targets were then dissolved in dilute nitric acid and the remaining radium precipitated with 80 % HNO_3, purified and recycled. The thorium and actinium in the filtrate were then separated by anion exchange: the thorium is absorbed from 5 M HNO_3 while the actinium is delayed in the column more than the non-complexing impurity cations. The separated actinium is about 96 % pure.

Only two preparations of metallic actinium have so far been made and in only the second of these was the X-ray pattern of the metal obtained. Stites *et al.*[7] separated the actinium by ion exchange and it was further purified by precipitation as the oxalate which was then ignited to the oxide. The latter was dissolved in hydrochloric acid and the fluoride was precipitated by adding HF. The fluoride was held in a molybdenum microcrucible in a vessel containing excess lithium metal. The latter vaporized on heating by induction in a good vacuum and reduced the fluoride at about 1200°C to form a bead of actinium metal:

$$AcF_3 + 3Li \rightarrow 3LiF + Ac$$

Their three reductions totalled 20 mg. The fluoride was chosen for reduction because it was the easiest halide to prepare in the anhydrous state: lithium was selected as the reductant because the volatility of lithium fluoride drives the reaction to the right.

Because of the small quantities available, the technique used by Farr *et al.*[8] was to carry out the final stages of the preparation of the metal actually in the capillary tube used for the X-ray examination. Actinium oxide was converted to the chloride by reacting the hydroxide with excess ammonium chloride. The powder was transferred to an X-ray capillary on the side of a larger tube. Potassium metal was added to the latter and on heating to 350°C the vapour diffused into the capillary to reduce the chloride. The capillary was then sealed for X-ray examination, with no attempt being made to separate the KCl that was also formed. The metal was contaminated with the hydride and X-ray reflections corresponding to this were also seen. Some doubt must still exist that the four reflections observed were actually due to the metal, although a similar experiment using lanthanum as a stand-in also showed lines of the hydride in addition to those of the metal.

2.3. Thorium[9–12]

The most stable isotope of thorium, ^{232}Th, is an α-emitter with a half-life of $1{\cdot}4 \times 10^{10}$

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[6] L. H. Baetsle, M. J. Brabers, P. Dejonghe, A. C. Demildt, A. de Troyer, A. Droissart and M. Poskin, *Proc. 4th Int. Conf. on the Peaceful Uses of Atomic Energy*, Geneva, United Nations (1971) A/Conf.49/P/287.

[7] J. G. Stites, M. L. Salutsky and B. D. Stone, *J. Amer. Chem. Soc.* 77 (1955) 237.

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

[9] F. L. Cuthbert, *Thorium Production Technology*, Addison-Wesley, Reading, Mass. (1958).

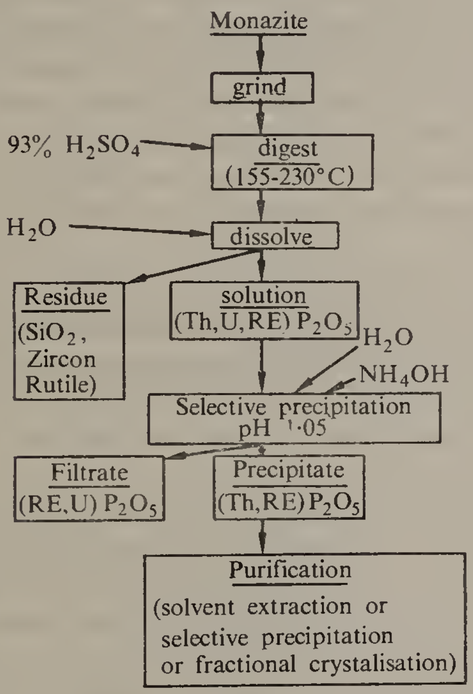
[10] R. G. Bellamy and N. A. Hill, *Extraction and Metallurgy of Uranium, Thorium and Beryllium*, Pergamon Press, Oxford (1963).

[11] N. D. Veigel, E. M. Sherwood and I. E. Campbell, in *The Metal Thorium*, H. A. Wilhelm (Ed.), ASM, Cleveland (1958).

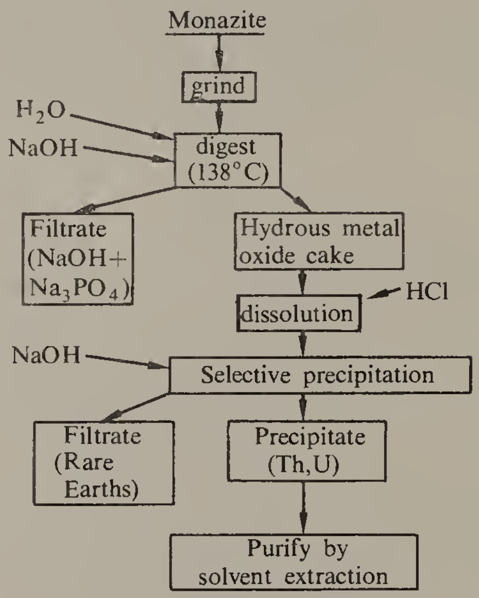
[12] W. L. Silvernail and J. B. McCoy, in *The Encyclopedia of Chemical Technology*, Vol. 20, p. 248, H. F. Mark, J. J. McKetta and D. F. Othmer (Eds.) , Interscience, New York (1969).

years, making it handleable without undue precautions. Although thorium is a fairly common element, only a few tons of the element are produced per year, mainly as a by-product of rare earth element production. Thorium is about the 35th most common element, comprising about 0·001–0·002 % of the earth's crust, i.e. it is roughly three times as common as uranium. Whilst the only commercial sources of the material are the monazite sands, there are some rarer minerals containing larger concentrations of thorium. Among these are thorianite, which contains up to 90 % ThO_2 and which has been worked in Madagascar, and thorite, a silicate which contains up to 62 % thorium, which is found in the Western United States and in New Zealand. Monazite is principally a phosphate of the rare earths which contains between 1 and 10 % thoria. It is a constituent of various granites and other igneous rocks, but in too small a concentration to be useful. However, on weathering, its high density means that it is concentrated naturally in the form of sands, notably in Brazil, India and Ceylon, Australia, South Africa and the United States.

After mining, the monazite sands are first concentrated, initially by sluicing to remove the lighter sands and then magnetically which finally produces monazite of about 95 % purity. This is then "opened" by either acidic or basic digestion[9]. These are shown diagrammatically.



ACID OPENING



ALKALI OPENING

The separation of thorium from the rare earths after the acid process is accomplished either (a) by dissolving both and adding sodium pyrophosphate to precipitate thorium pyrophosphate, (b) by adding ammonia to decrease the acidity and precipitating the thorium as a basic salt or (c) by using a solvent extraction process with a high molecular weight amine or tributyl phosphate dissolved in kerosene. The thorium is extracted into the organic phase in each case.

The total production (*ca.* 1965) in the Western world is probably about 500 tons per annum of ThO_2.

There are several methods[9] for producing the metal, all being complicated by the high melting point (1750°C). The most used process[13] starts with the oxide which is reduced with calcium. The calcium is granulated, mixed with the powdered oxide and loaded into CaO-lined crucibles. The reaction mixture is heated to 1000°C in an argon atmosphere. Insufficient heat is liberated to melt the thorium.

$$ThO_2 + 2Ca \rightarrow Th + 2CaO\ (-\Delta H_{298} = 9{\cdot}8\ \text{kcal})$$

The reaction mass is then leached with water and dilute acid and the thorium metal recovered as a powder which is pressed and sintered.

If an ingot of the metal is required directly it is possible to reduce thorium tetrafluoride with calcium.

$$ThF_4 + 2Ca \rightarrow 2CaF_2 + Th\ (-\Delta H_{298} = 96{\cdot}4\ \text{kcal})$$

This again does not produce enough heat to melt the thorium, but this can be accomplished by adding sulphur or iodine as a booster. In an alternative method zinc chloride is added, the resulting zinc–thorium alloy being heated subsequently to distill off the zinc. A strong drawback to this process is that the thorium is recovered as a very reactive sponge. This is also true of the method developed by Knighton and Steunenberg[14] in which the thorium oxide or fluoride is mixed with a flux of $MgCl_2$, $CaCl_2$ and CaF_2 and held in contact with a Mg–Zn alloy at about 850°C. The magnesium reduces the thorium compound to the metal which dissolves in the zinc; this process is accelerated by stirring. On cooling, the metal ingot can be easily separated from the flux and the zinc and magnesium are then distilled off as before. This latter method is generally applicable to the earlier actinides, but usually results in material contaminated by oxygen.

An alternative method which also produces a sponge[15] is to reduce the tetrachloride at 900°C with magnesium, having added enough excess magnesium to form a Th 20 w/o Mg alloy. This is molten at temperature and is protected by the $MgCl_2$ and an argon atmosphere. The magnesium is later distilled off under vacuum at 920°C, and the thorium sponge remaining is arc-melted and then purified by repeated electron beam melting—the resulting ingot containing 50 ppm C, 80 ppm O and 35 ppm N.

Ductile high-purity metal has been produced by electrolysis of fused salts[9]. $KThF_5$, $ThCl_4$ and ThF_4 dissolved in mixtures of NaCl and KCl at concentrations of about 10 % have all been tried. The build-up of fluoride ions in the bath was found to decrease the conductivity which eventually stopped the process, so most development has been carried out using the tetrachloride. A bath temperature of about 800°C is usual with a graphite-lined crucible (acting also as the anode) and a molybdenum cathode. Yields are about 90 % and current efficiencies about 75 %. After withdrawing the cathode it is found that an equal weight of salts is entrapped with the thorium. The deposit is chipped from the cathode and crushed and the salts removed by washing with water and dilute sulphuric acid. The washing treatment markedly affects the final product, since any hydrated thorium compounds remaining appear as oxide inclusions in the metal.

[13] G. A. Meyerson, *Proc. Int. Conf. on the Peaceful Uses of Atomic Energy*, Geneva, 1955. United Nations, New York, Vol. 8 (1956) P/635, p. 188.

[14] J. B. Knighton and R. K. Steunenberg, USAEC Reports ANL 7057, 7058 and 7059 (1965) and *J. Inorg. and Nucl. Chem.* **27** (1965) 1457.

[15] D. T. Peterson, W. E. Krupp and F. A. Schmidt, *J. Less-Common Metals*, **7** (1964) 288.

Small quantities of very pure metal may be prepared by the van Arkel iodide process[11] in which the non-metallic impurities are removed. Iodine and the impure thorium feed are reacted in a carefully out-gassed vessel to form thorium tetraiodide. This is volatilized at 455–480°C whilst a thorium filament also in the vessel is resistance heated to 900–1700°C. The tetraiodide decomposes:

$$ThI_4 \rightarrow Th + 2I_2$$

depositing the thorium, and the iodine is released to go through the cycle again. The system is not completely self-sustaining and is finally stopped by the formation of some non-volatile lower iodides on the feed material. The product contains about 200 ppm (wt) carbon and less than 100 ppm oxygen and nitrogen.

Scaife and Wylie[16] have used the van Arkel process with a thorium carbide feed. This gave a product containing 40 ppm C, 15 ppm N and 20 ppm O. Considerable purification from metallic impurities was also obtained with the important exception of uranium which was only reduced to one-third of its concentration in the raw material.

Further purification of thorium from interstitial impurities can be obtained by electrotransport[17]. A metal rod is held in an ultra-high vacuum ($\sim 3 \times 10^{-10}$ torr) and heated to 1600°C by a d.c. current of ~ 1900 A/cm^2. The current "sweeps" the impurities to the anode end of the rod, and total impurity contents of better than 50 ppm can be achieved. The same workers also prepared single crystals of α-thorium by cycling the sample a few times through the α/β transformation (1345°C) and then holding the sample for 50 hr just below this temperature.

2.4. Protactinium

There is only a single isotope of protactinium with a half-life over a month, ^{231}Pa, for which $t_{\frac{1}{2}} = 3{\cdot}28 \times 10^4$ years. This is a member of the ^{235}U decay series and protactinium occurs in nature to about the same extent as radium, one ton of uranium containing (at radioactive equilibrium) 340 mg. It is not worth extracting protactinium separately from uranium ores, but fortunately it becomes concentrated in various residues from uranium processing plants. These, of course, differ and so differing methods have been used to extract and purify the protactinium. The earlier ones, which are summarized by Brown and Maddock[18], resulted in the isolation of only a few milligrams of protactinium until the mid-1950s. Maddock and coworkers[19] then studied the distribution of protactinium in the residues from the Springfields (U.K.) uranium plant which was at that time processing a high grade UO_2 ore. They found that much of the protactinium became concentrated in the "ethereal sludge" which separated at the ether extraction stage of the purification. This sludge was retained and 60 tons of it containing over 100 g of protactinium were available. Maddock[19] developed a process for extracting this which was then adapted for larger scale work by Nairn *et al.*[20] who finally produced about 130 g of protactinium. In their method, the sludge was leached with nitric acid and the uranium extracted from the leach liquor with

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[16] D. E. Scaife and A. Wylie, *Proc. 2nd Int. Conf. on the Peaceful Uses of Atomic Energy*, Geneva, 1958, Vol. 4, p. 215.

[17] D. T. Peterson and F. A. Schmidt, *J. Less-Common Metals*, **24** (1971) 223.

[18] D. Brown and A. G. Maddock, *Quarterly Reviews*, Vol. 17, p. 289, Chemical Society, London (1963),

[19] A. Goble, J. Golden, A. G. Maddock and D. T. Toms, *Progress in Nuclear Energy*, Series 3, Vol. II, p. 86, F. R. Bruce, J. M. Fletcher and H. H. Hyman (Eds.), Pergamon, London (1959).

[20] J. S. Nairn, D. A. Collins, H. A. C. McKay and A. G. Maddock, *Proc. 2nd Int. Conf. on the Peaceful Uses of Atomic Energy*, Geneva, 1958, Vol. 16, p. 216.

tributyl phosphate. $AlCl_3$ was added, the resulting precipitate dissolved in NaOH and the protactinium extracted with di-isobutyl ketone. Final purification was by ion exchange from hydrochloric acid solution.

Several workers have produced the metal. Grosse[21] used two methods. Firstly he bombarded the oxide with 35 keV electrons in a high vacuum: this decomposed the oxide leaving the metal. Secondly, he decomposed the pentahalides on a tungsten filament, i.e. by a van Arkel process. In neither case does he appear to have checked by X-rays that he really had produced protactinium metal, and the former method in particular seems rather improbable. The van Arkel process has surprisingly not been tried by subsequent workers.

Sellers *et al.*[22] reduced 0·1 mg of tetrafluoride with barium vapour at 1400°C in a double beryllia crucible system. The fluoride was placed inside the inner crucible which had a loose fitting cover. The outer crucible contained this and the barium reductant (in large excess). The whole was rapidly heated in a good vacuum with a tantalum spiral. The barium vapour diffused into the inner crucible and reduced the fluoride to several globules of protactinium metal which were identified by X-rays[23].

Four other preparative methods have been used. Marples[24] reduced the tetrafluoride with calcium at 1250°C: the temperature was not sufficient to melt the products and the protactinium metal was present as a powder dispersed in the calcium fluoride slag. Some of the metal was arc-melted into a bead weighing 70 mg, but this was rather wasteful and introduced contamination. The zinc magnesium reductant method due to Knighton and Steunenberg[14] (described above under thorium) also works for protactinium[25], but again the purity of the product is not good.

Cunningham at Berkeley has prepared the metal, also from the tetrafluoride, in two ways. Originally[26] he used a barium vapour reductant in an induction heated tantalum double crucible system, the tetrafluoride being contained in a tungsten wire basket: the metal was formed round the tungsten wires. More recently[27] he has used a barium fluoride crucible, carrying out the reduction at 1300°C. The temperature is then increased to 1600°C when the molten protactinium metal separates as a bead held in contact with the melt by surface tension. This method probably produces the highest purity material.

2.5. Uranium

Uranium is the heaviest element to occur in nature in recoverable amounts, the isotopes, all α-emitters, occurring in the following proportions: ^{238}U, 99·28 %, with a half-life of $4{\cdot}5 \times 10^9$ years; ^{235}U, 0·71 %, half-life $7{\cdot}00 \times 10^8$ years; and ^{234}U, 0·005 %, half-life $2{\cdot}35 \times 10^5$ years.

Whilst care must be taken in handling it (particularly in a dusty form), natural uranium does not require the extreme precautions needed for the other actinides except thorium. Enriched uranium, i.e. uranium containing more of the fissile and more α-active ^{235}U, must be handled more carefully.

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[21] A. V. Grosse, *J. Amer. Chem. Soc.* 56 (1934) 2200.

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

[23] W. H. Zachariasen, *Acta Cryst.* 5 (1952) 19.

[24] J. A. C. Marples, *Physico-Chimie du Protactinium*, p. 39, Centre National de le Recherche Scientifique, Paris (1966).

[25] A. Hough and J. A. C. Marples, Unpublished work (1968).

[26] B. B. Cunningham, *Physico-Chimie du Protactinium*, p. 45, C.N.R.S., Paris (1966).

[27] B. B. Cunningham, Private communication to D. Brown (1970).

Uranium occurs widely in nature and the earth's crust averages 4 ppm: copper for comparison is about 40 ppm. Sea water contains 0·002 ppm. Uranium is thought to have crystallized late in the igneous rocks and so occurs unpredictably in the faults of earlier rocks, generally not in recoverable concentrations. It is usually tetravalent in this form but can be oxidized to uranium(VI) which forms soluble compounds. Reprecipitation, often caused by carbonaceous materials, is thus a much more common natural concentration method. Many minerals are known—about 150 are listed by Wilkinson[28], and Chervet gives a fuller description of the principal ones[29]: only a few, however, are of economic importance. These are generally either anhydrous oxides ($UO_2 + UO_3$: pitchblende or uraninite) or hydrated mixed oxides of varying compositions (e.g. carnotite, $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 3H_2O$). Pitchblende is mined principally in Canada (Ontario and North West Territories), in France, in Australia and in South Africa where it is only economically competitive because it is a by-product of the Rand gold mines. The ores in the United States (Wyoming basin and Colorado plateau) are mainly of the sedimentary type[30].

Uranium production in the Western world and estimated resources are outlined in Table 2. A fixed price structure, aimed at encouraging prospecting, coupled with stockpiling for defence needs, led to the high production in the late 1950s. This tailed off in the early 1960s, but recently, spurred by increasing estimates of power requirements, output is recovering.

TABLE 2. MAJOR FREE WORLD PRODUCERS OF URANIUM (short tons of U_3O_8)

	Australia	Congo	Canada	France	S. Africa	U.S.A.	Total
1952[a]	—	2000	500	—	200	1000	3700
1959[a]	1100	2300	15,900	950	6450	16,400	43,300
1966[a]	330	—	3760	1260	3290	9600	19,000
1973 (planned[b])	1150	600	4230	1800	4600	14,600	29,400
Reserves[b]	17,000	8000	178,000	35,000	154,000	192,000	650,000

[a] R. C. Merritt, *The Extractive Metallurgy of Uranium*, p. 3, Colorado School of Mines Research Institute and U.S. Atomic Energy Commission (1971).

[b] L. W. Boxer, W. Haussermann, J. Cameron and J. T. Roberts, *Proc. 4th Int. Conf. on the Peaceful Uses of Atomic Energy*, United Nations, Geneva (1971) 49/P/678.

The reserves are totals thought in 1970 to be available at a cost of below $10/lb U_3O_8. These figures always show a rising trend as discoveries exceed production. 1971 Australian finds are not included but may exceed 100,000 tons. The totals include the relatively small figures for other countries.

Uranium ore normally contains only a few hundred ppm uranium, but the details of the treatment depend on the concentration of and the diluents in the ore itself. A typical flowsheet is shown in Table 3 (adapted from ref. 31) and more details of the processes may be

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[28] W. D. Wilkinson, *Uranium Metallurgy*, Vol. I, *Process Metallurgy*; Vol. II, *Corrosion and Alloys*. Interscience–John Wiley, New York (1962).

[29] J. Chervet, Les minerais d'uranium, in *Nouveau Traité de Chimie Minérale*, Vol. XV (1), pp. 52–94, P. Pascal (Ed.), Masson et Cie, Paris (1960).

[30] R. C. Merritt, *The Extractive Metallurgy of Uranium*. Colorado School of Mines and U.S. Atomic Energy Commission (1971).

[31] R. G. Bellamy and N. A. Hill, *The Extraction and Metallurgy of Uranium, Thorium and Beryllium*, p. 21, Pergamon Press, Oxford (1963).

TABLE 3. EXTRACTION OF URANIUM OXIDE FROM THE ORE

ORE Crushing Ore dressing	Physical concentration (electronic or sedimentation). Roasting
CONCENTRATE	
Wet extraction	Sulphuric acid leaching (95–98 % efficient) or Sodium carbonate leaching (for alkaline–carbonate ores): after this process the next stage can usually be omitted
CRUDE LIQUOR ($\sim$5 g U/l)	
Intermediate purification	Ion exchange (absorb on resin from SO_4^{--} rich soln.: elute with strong HNO_3 or HCl) or Chemical precipitation (with $H_2O_2+NH_4OH$: for conc. leach liquors) or Solvent extraction (as in final purification stage)
INTERMEDIATE LIQUOR ($\sim$15 g/l)	
Precipitation	With ammonia or sodium hydroxide or magnesia
HIGH GRADE CONCENTRATE (50–80 % U_3O_8) Final purification	By solvent extraction from uranyl nitrate solution with 20 % tributyl phosphate or alkyl amines or organophosphorous compounds in kerosene or hexane using a counter-current process. Originally ether was used: the necessary double extraction gave higher purities than the single TBP one
PURE URANYL NITRATE SOLUTION Denitration	Ammonium diuranate precipitation and ignition or Thermal denitration at 300°C
PURE UO_3 OR U_3O_8 (600 ppm total impurities) Reduction	Reduction with hydrogen at 700°C (UO_3 gives a more reactive oxide suitable for metal production)
PURE UO_2 ("Yellow cake")	

found in refs. 28, 30, 32–36. Reference 30 is particularly detailed: refs. 31 and 36 provide a good summary: some recent developments are covered in refs. 32 and 32a.

The main isotopes of uranium, ^{238}U and ^{235}U, can be separated either by the gaseous diffusion of UF_6[37,38] or by using a centrifuge method[39,40].

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[32] International Atomic Energy Agency Symposium, *The Recovery of Uranium*, Sao Paulo, 1970. Proceedings published by the I.A.E.A. (1971).

[32a] S. E. Smith and K. H. Garrett, *The Chemical Engineer*, No. 268 (Dec. 1972) 440.

[33] P. Mouret, P. Vertes and J. Sauteron, Préparation de l'uranium, in *Nouveau Traité de Chimie Minérale*, Vol. XV (1), pp. 95–179, P. Pascal (Ed.), Masson et Cie, Paris (1960).

[34] P. Mouret, Préparation des concentrés a partir des minerais, in *Nouveau Traité de Chimie Minérale*, Vol. XV (4), pp. 12–18, P. Pascal (Ed.), Masson et Cie, Paris (1967).

[35] H. Huet, Préparation de l'uranium métal a partir des concentrés, in *Nouveau Traité de Chimie Minérale*, Vol. XV (4), pp. 19–48, P. Pascal (Ed.), Masson et Cie, Paris (1967).

[36] J. H. Gittus, *Uranium*, Butterworths, London (1963).

[37] C. Boorman, in *Separation of Isotopes*, p. 332, H. London (Ed.), Newnes, London (1961).

[38] J. Shacter, E. Von Halle and R. L. Hoglund, in *Encyclopedia of Chemical Technology*, Vol. 7, pp. 91–175, H. F. Mark, J. J. McKetta and D. F. Othmer (Eds.), Interscience, New York (1965).

[39] W. Groth, in *Separation of Isotopes*, p. 249, H. London (Ed.), Newnes, London (1961).

[40] D. G. Avery, M. Bogaardt, P. Jelinek-Fink and J. V. L. Parry, *Proc. 4th Int. Conf. on the Peaceful Uses of Atomic Energy*, Geneva, United Nations (1971) A/Conf.49/P/493.

UF_4 (for metal production) and UF_6 for the enrichment plants are produced successively from "yellow cake", UO_2[41-43].

Production of uranium metal usually involves reducing the tetrafluoride with either calcium or magnesium[28,36,44,45]. A list of possible uranium compounds and reductants is given in Table 4.

TABLE 4. SOME URANIUM COMPOUNDS AND POSSIBLE REDUCTANTS

Compound	UCl_4	UF_4	U_3O_8	UF_4	UF_4	UO_2	UO_2
Reductant	Na	Ca	Ca	Na	Mg	Ca	Mg
ΔH_{298} (kcal/mol)	−141	−134	−123	−98	−82	−47	−35
M. pt. of slag (°C)	800	1420	2600	980	1260	2600	2500

In this thermochemical method it is essential that enough heat is provided by the reaction to melt the metal and the slag and to hold them molten for long enough to allow the metal particles to coalesce into an ingot. The high melting points of the oxide slags rule out, therefore, the reduction of the oxides. The fluoride is selected in preference to the other halides as it is less hygroscopic. The reductant is either calcium or magnesium rather than a Group I metal because they are much easier to handle on a large scale. For very large-scale reductions (100 kg) magnesium is usually used[31,41,42] because it can be obtained in a pure form more cheaply than calcium. The reaction is carried out in a closed steel vessel lined with MgF_2, often from a previous reduction. The UF_4 and magnesium are mixed and loaded and the vessel is heated to about 700°C and held at that temperature until the charge fires. The ingot separates cleanly from the slag and yields are about 97 %.

For small-scale reductions[28], down to below a gram, calcium is preferred because of the better heat of reaction. Addition of iodine as a "booster" is also beneficial (a) because of the extra heat produced and (b) because the resulting calcium iodide markedly lowers the melting point of the calcium fluoride slag: the CaF_2/CaI_2 system has a eutectic at 668°C and 19 mol. % CaF_2. Calcium fluoride crucibles are very suitable as they are impermeable, resistant to thermal shock and non-hygroscopic and, if made from pure materials, do not run the risk of contaminating the uranium as, say, alumina might do.

Uranium may be prepared from the oxide by reduction with carbon[28]. This avoids the fluorination stage and carbon is available cheaply, but vacuum equipment is necessary to pump away the CO formed and although it is possible to obtain the uranium with a carbon content of only 77 ppm, a critical leaching and remelting procedure is necessary.

Uranium can also be prepared from the oxide by the zinc–magnesium reduction route[14], but the resultant metal is in the form of sponge with the attendant disadvantages.

The van Arkel method of thermal decomposition of the iodide is difficult for uranium due to the low melting point of the latter and to the tendency of the tetra-iodide to decompose to the non-volatile tri-iodide[45].

[41] F. S. Patton, J. M. Googin and W. L. Griffith, *Enriched Uranium Processing*, Pergamon Press, Oxford (1963).

[42] C. D. Harrington and A. D. Ruehle, *Uranium Production Technology*, Van Nostrand, Princeton (1959).

[43] S. H. Smiley and D. C. Brater, *Proc. 2nd Int. Conf. on the Peaceful Uses of Atomic Energy*, Geneva, Vol. 4, p. 384, United Nations (1958).

[44] J. H. Buddery and H. J. Hedger, in *Progress in Nuclear Energy*, Series V, Vol. 1, pp. 3–38, H. M. Finniston and J. P. Howe (Eds.), Pergamon Press, Oxford (1956).

[45] H. Huet and P. Albert, in *Nouveau Traité de Chimie Minérale*, Vol. XV (1), pp. 180–227, P. Pascal (Ed.), Masson et Cie, Paris (1960).

The other process that has been used extensively is fused salt electrolysis[28,44,46]. This is capable of producing a higher purity product than the reduction method. Blumenthal[46] used a quartz or Hastelloy C cell with a molybdenum cathode and uranium anode: the electrolyte was KCl (38 mol. %), LiCl (55 %), and UCl_3 or UF_4 (7 %) kept at a temperature of 400°C and electrolysed at 2 volts. The uranium metal is deposited as fine dendrites which after cooling are thoroughly washed and then melted in UO_2 crucibles in a very good vacuum. The resulting metal contains only 100 ppm total impurities.

Uranium can be further purified by zone melting[28,45,47]: a short molten zone is passed along an otherwise solid bar of the metal by moving a short furnace relative to the bar, which is held in a separate longer furnace. Impurity elements that are more soluble in the liquid than in the solid are carried along with the zone. Those that are less soluble in the liquid are not so much affected, but may diffuse in the reverse direction. Results in practice, however, are not as good as theory might indicate.

2.6. Neptunium

There is only one isotope of neptunium which is both easily prepared and sufficiently stable to be obtainable in massive quantities: this is ^{237}Np with a half-life of $2{\cdot}14 \times 10^6$ years. It is formed by neutron irradiation of uranium[48]:

$$\left.\begin{array}{ll} 30\,\% & {}^{235}U\,(n,\gamma)\,{}^{236}U\,(n,\gamma)\,{}^{237}U \xrightarrow[6\cdot7\,d]{\beta^-} {}^{237}Np \\ 70\,\% & \qquad\qquad {}^{238}U\,(n,2n) \nearrow \end{array}\right\}$$

The percentages are the amounts formed by each route on irradiation of natural uranium

Neptunium thus has to be extracted from irradiated fuel elements as a by-product of the recovery of the uranium and the separation of the larger quantities of plutonium also formed. The two main processes used are solvent extraction and ion exchange or frequently a combination of the two, the details depending on what fuel is being processed, the concentrations of neptunium, plutonium, and uranium and on local preferences. Originally[20] neptunium was extracted from a batch of waste liquor, but since then it has become valuable as the raw material for the production of ^{238}Pu by irradiation and it is often now extracted as part of the normal fuel treatment process (Summary refs. 49–51; Details, refs. 48, 52, 53). An extensive review has recently been published[53a].

The feed material for the original batch process[20] had a concentration of 1 g neptunium in 15 tons of solution. After conditioning to 3 N in HNO_3, the neptunium, Np(IV), was absorbed on an anion exchange resin and then eluted with $0{\cdot}1$ N HNO_3 as Np(V). This gave an increase in concentration of 400×. Repeating the process with slightly different conditions gave a further increase of 200×, leaving a dilute nitric acid solution relatively free

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[46] B. Blumenthal and R. A. Noland, in *Progress in Nuclear Energy*, Series V, Vol. 1, p. 62, H. M. Finniston and J. P. Howe (Eds.), Pergamon Press, Oxford (1956).

[47] P. Lacombe and M. Oxley, in *Nouveau Traité de Chimie Minérale*, P. Pascal (Ed.), Vol. XV (4), pp. 49–76, Masson et Cie, Paris (1967).

[48] Symposium on the Production Technology of ^{237}Np and ^{238}Pu. M. Smutz, Chairman. Denver, 1964. *Ind. Eng. Chem. Proc. Des. Dev.* **3** (1964) 289.

[49] R. D. Baybarz, *Atomic Energy Rev.* **8** (2) (1970) 327.

[50] J. Ulstrup, *Atomic Energy Rev.* **4** (4) (1966) 3.

[51] H. J. Groh and C. S. Schlea, in *Progress in Nuclear Energy*, Series III, Vol. 4, p. 507, C. E. Stevenson, A. T. Gresky and E. A. Mason (Eds.), Pergamon Press, Oxford (1970).

[52] M. Pages, in *Nouveau Traité de Chimie Minérale*, P. Pascal (Ed.), Masson et Cie, Paris. Vol. XV (3), pp. 237–324 (1962) and Vol. XV (5), pp. 1–94 (1970).

[53] W. H. Lewis, *Proc. 2nd Int. Conf. on the Peaceful Uses of Atomic Energy*, Geneva 1958, Vol. 17, p. 236, United Nations (1958) P/537 and *Ind. Eng. Chem. Proc. Des. Dev.* **3** (1964) 289.

[53a] W. W. Schulz and G. E. Benedict, *Neptunium-237: Production and Recovery*. U.S.A.E.C. Report TID 25955 (1972).

of fission products but containing neptunium, plutonium and uranium in roughly equal amounts. The neptunium (conditioned to Np(IV) with HNO_3 and ferrous sulphamate) was then extracted into a solution of thiophenoyltrifluoroacetone (TTA) in benzene and finally recovered as Np(V) with 8 N HNO_3.

In the Savannah River Purex process[49,51,54], nitrite is added to the feed, giving Np(V), U(VI), and Pu(IV). The U(VI) and Pu(IV) are extracted by the tributylphosphate (TBP) dissolved in kerosene leaving Np(V) in the aqueous phase. Addition of ferrous sulphamate, hydrazine and 8 M HNO_3 gives Np(IV) which is absorbed on an anion exchange resin, washed with further strong nitric acid to remove fission products and then eluted with dilute acid. Two further anion exchange cycles increase the decontamination from fission products and remove any residual plutonium. A cation exchange to remove thorium completes the process: Np(V) is not affected while Th(IV) is strongly held.

At Hanford[49,51,55,56] the initial feed is more dilute in nitrate and the Np(VI) follows the uranium and plutonium into the organic (TBP) stream. The plutonium is then extracted into an aqueous ferrous sulphamate solution, leaving U(VI) and Np(VI) in the TBP to be stripped with dilute HNO_3. This is concentrated and the U(VI) is extracted again with TBP leaving Np(VI) to be extracted in its turn in the next column. The TBP used for this is recycled to the previous column where the Np(VI) is forced to return to the aqueous phase. Thus the neptunium accumulates at this stage until it reaches a sufficient concentration when it is withdrawn and purified by ion exchange.

Many other variations of method are possible: in the Savannah River enriched uranium process[57], the initial step is to add ferrous sulphamate to the original nitrate feed. On extracting with TBP the Np(IV) follows the U(VI) into the organic phase leaving Pu(III) in the aqueous stream.

The workers who have described the preparation of the metal are unanimous in starting from either the trifluoride[58] or the tetrafluoride[59-63].

The earlier workers used barium vapour as the reductant, but latterly calcium has been preferred. The technique used is to mix the calcium (in about 30 % excess of the stoichiometric quantity) with the fluoride and load into a crucible of calcium fluoride (preferred), magnesia or calcia. The crucible and the fluoride should be well dried before use. It is beneficial, especially for small-scale reductions, to add about one-third molar quantities of calcium and iodine to boost the reaction (see above: section 2.5). The loaded crucible is then heated in an argon atmosphere to about 600–750°C when the charge "fires". On cooling, good separations and yields of above 95 % are achieved. The residues may readily be reprocessed[63] and the neptunium recovered by an ion exchange route.

No other methods of producing the metal have been reported, but there is no reason why the zinc–magnesium reduction method[14] should not work: this avoids the fluorination step, but yields a sponge which is liable to oxidation.

[54] D. R. Vondy, J. A. Lane and A. T. Gresky, *Ind. Eng. Chem. Proc. Des. Dev.* **3** (1964) 293.

[55] J. P. Duckworth and L. R. Michels, *Ind. Eng. Chem. Proc. Des. Dev.* **3** (1964) 302.

[56] R. E. Isaacson and B. F. Judson, *Ind. Eng. Chem. Proc. Des. Dev.* **3** (1964) 296.

[57] W. L. Poe, A. W. Joyce and R. I. Martens, *Ind. Eng. Chem. Proc. Des. Dev.* **3** (1964) 314.

[58] E. F. Westrum and L. Eyring, *J. Amer. Chem. Soc.* **73** (1951) 3399.

[59] S. Fried and N. Davidson, *J. Amer. Chem. Soc.* **70** (1948) 3539.

[60] A. C. McKay, J. S. Nairn and M. B. Waldron, *Proc. 2nd Int. Conf. on the Peaceful Uses of Atomic Energy*, Geneva, Vol. 28, p. 299, United Nations (1958) P/304.

[61] A. N. Morgan, K. W. R. Johnson and J. A. Leary, USAEC Report LAMS 2756 (1962).

[62] J. A. S. Mowat and W. D. Yuille, *J. Less-Common Metals*, **6** (1964) 295.

[63] D. L. Basso, W. V. Conner and D. A. Burton, USAEC Report RFP 1032 (1967).

2.7. Plutonium[64]

Plutonium is only found in nature in minute quantities: because of the short half-lives of its isotopes, only a little primordial ^{244}Pu remains[64a], although some ^{239}Pu is continuously produced by the natural neutron flux irradiating uranium ores. The amount varies with uranium content and environment. As an example, one sample of pitchblende was found to contain one atom of ^{239}Pu in 3×10^{11} atoms of uranium[65].

There are several plutonium isotopes with half-lives long enough to permit, at any rate in theory, the handling of massive amounts of them. Of these, ^{239}Pu is much the most readily available, being produced in reactors by the irradiation of uranium:

$$^{238}\mathrm{U} + n \rightarrow {}^{239}\mathrm{U} \xrightarrow[23\cdot5\ \mathrm{m}]{\beta^-} {}^{239}\mathrm{Np} \xrightarrow[2\cdot33\ \mathrm{d}]{\beta^-} {}^{239}\mathrm{Pu}$$

The higher isotopes are produced by further neutron capture and thus are more difficult to make, particularly as fission is more likely to occur than capture in some cases and ^{243}Pu is likely to decay by β^--emission before capture can occur. In reactors run primarily for plutonium production (for weapons), the uranium fuel is removed before much of the

TABLE 5. PLUTONIUM ISOTOPES: HALF-LIVES

Isotope	Decay mode	Half-life	Method of formation
^{238}Pu	α	89·6 y	$^{237}\mathrm{Np}\ (n, \gamma)\ ^{238}\mathrm{Np} \xrightarrow{\beta^-}$
^{239}Pu	α	24,400 y[a]	$^{238}\mathrm{U}\ (n, \gamma)\ ^{239}\mathrm{U} \xrightarrow{\beta^-} {}^{239}\mathrm{Np} \xrightarrow{\beta^-}$
^{240}Pu	α	6600 y	$^{239}\mathrm{Pu}\ (n, \gamma)$
^{241}Pu	β^-	13 y	$^{240}\mathrm{Pu}\ (n, \gamma)$ or $^{238}\mathrm{U}\ (\alpha, n)$
^{242}Pu	α	$3{\cdot}8 \times 10^5$ y	$^{241}\mathrm{Pu}\ (n, \gamma)$
^{243}Pu	β^-	5·0 h	$^{242}\mathrm{Pu}\ (n, \gamma)$
^{244}Pu	α	$8{\cdot}3 \times 10^7$ y	$^{243}\mathrm{Pu}\ (n, \gamma)$

[a] F. L. Oetting, *Plutonium 1970 and Other Actinides*, W. N. Miner (Ed.), Met. Soc. AIME, New York (1970), finds 24,065 years by a calorimetric method.

TABLE 6. ISOTOPIC CONTENTS OF PLUTONIUM[66]

Reactor	Burn-up (MWD/tonne)	Percentage of each isotope				
		238	239	240	241	242
Production	600	0	95	4·6	0·4	
Pressurized water	5000	0	91	8·5	1·5	
	25000	0·8	63	24	11	2·7
Boiling water	5000	0	89	10·5	1·3	
	25000	0·3	51	32	13·6	5·6
Fast breeder	3 years exposure Core		61	33	4·7	1·2
	Blanket		96	3·5	0·2	

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[64] O. J. Wick (Ed.), *Plutonium Handbook*, Div. Tech. Inf., U.S. Atomic Energy Commission (1967), 2 volumes.

[64a] D. C. Hoffman, F. O. Lawrence, J. L. Mewherter and F. M. Rourke, *Nature* **234** (1971) 132.

[65] W. A. Myers and M. Lindner, *J. Inorg. Nucl. Chem.* **33** (1971) 3233.

[66] J. A. Leary and L. J. Mullins, in *Encyclopedia of Chemical Technology*, Vol. 15, p. 879, H. F. Mark, J. J. McKetta and D. F. Othmer (Eds.), Interscience, New York (1968).

^{239}Pu is converted to ^{240}Pu. The isotopic content of plutonium recovered from power reactors depends on the type of reactor as well as on the burn-up: typical examples are given in Table 6.

Plutonium is an extremely hazardous material to handle, the danger arising in three ways. Firstly because it is an α-emitter; secondly because of the possibility that a critical assembly may accidentally occur; and thirdly because high burn-up material gives an appreciable γ-flux. The health physics aspects of plutonium are reviewed in the *Plutonium Handbook*[67], but it may be noted that:

1. Despite the maximum permitted body burden being only 0·75 μg, and the maximum permissible concentration in laboratory air being $3 \cdot 2 \times 10^{-14}$ g/l, hundreds of grams of plutonium may be safely handled in glove boxes[68].

2. The criticality hazard[69] (i.e. the chance of an accidental chain reaction occurring) depends markedly on the form of the plutonium. The minimum critical mass of a solid sphere is about 10 kg unreflected or 5·6 kg when fully reflected. However, the minimum amount which can become critical in solution in water is only 509 g when homogeneous and fully reflected. Because of this low figure the ^{239}Pu content of a glove box used for general work is usually restricted to 200 g if there is any possibility of the box being flooded[70].

3. The external dose from plutonium is generally less restrictive than the other hazards. It increases with the content of the higher isotopes and handling times need to be reduced for plutonium from power reactors.

Plutonium is produced as a minor constituent (~200 ppm) of irradiated uranium fuel elements (metal, alloy, oxide or carbide) which also contain quantities of highly radioactive fission products, the whole contained in a can or jacket. The problem is to separate and recover the plutonium and the uranium and thoroughly decontaminate them from fission products. The process must be extremely efficient (a) because of the high value of the plutonium and (b) because of the health hazard caused by any plutonium left in the effluent.

The first stage in the process is to decan the fuel and dissolve the latter, usually in nitric acid. The decanning may be either mechanical or chemical: this preparation of the fuel has been reviewed by Slansky[71].

The separation of the plutonium from this solution is almost exclusively by solvent extraction, of which the general principles have been discussed by Haas[72] and Ulstrup[50] and there is a vast amount of literature on the details of the process. Cleveland[73] provides a good review of this and more details are given in refs. 74–78. Tributylphosphate (TBP) is the usual solvent, but ketones, ethers and amines have also been used.

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[67] R. C. Thompson, in ref. 64, p. 785.

[68] See, for example, *Glove-Boxes and Shielded Cells*, G. N. Walton, A. G. Ashburn, J. K. Dawson, M. B. Waldron and D. J. O'Connor (Eds.), Butterworths, London (1958).

[69] E. D. Clayton and S. R. Bierman, *Actinides Reviews*, **1** (1971).

[70] E. D. Clayton and W. A. Reardon, in ref. 64, p. 875.

[71] C. M. Slansky, in *Chemical Processing of Reactor Fuels*, p. 75, J. F. Flagg (Ed.), Academic Press, New York and London (1961).

[72] W. O. Haas, in *Chemical Processing of Reactor Fuels*, p. 125, J. F. Flagg (Ed.), Academic Press, New York and London (1961).

[73] J. M. Cleveland, in ref. 64, p. 521.

[74] J. M. Cleveland, *The Chemistry of Plutonium*, Gordon & Breach, New York (1970).

[75] T. H. Sidall, in *Chemical Processing of Reactor Fuels*, p. 199, J. F. Flagg (Ed.), Academic Press, New York and London (1961).

[76] P. Faugeras, in *Nouveau Traité de Chimie Minérale*, Vol. XV(3), p. 339, P. Pascal (Ed.), Masson et Cie, Paris (1962).

In the Purex process the extractant is 20% TBP dissolved (usually) in kerosene. Since plutonium is most efficiently extracted as Pu(IV), the aqueous feed is conditioned with nitrite ion by adding either $NaNO_3$ or NO_2 (gas). The plutonium and uranium are then extracted into the organic phase, leaving most of the fission products in the aqueous stream. The plutonium is next "stripped" from the TBP by reducing it to the trivalent state with an aqueous solution of ferrous sulphamate: the uranium remains in the organic phase and is separately stripped by a dilute acid stream in another contactor. A second basically similar cycle follows to achieve sufficient decontamination. The use of ferrous sulphamate as a reductant is not entirely satisfactory as it leads to an increase in the volume of waste and to high final levels of iron as an impurity. Use of U(IV) ion (added as U(IV) nitrate) or hydrogen have been suggested as alternatives. The adjustments of the valencies of the heavy ions, the acidity and the nitrate concentrations are critical in the solvent extraction process since some important fission products are also extractable under certain conditions into the organic phase.

Some variations of the process are possible, e.g. the uranium and plutonium may be stripped together in the first stage and then separated in the second. Again a French process uses trilauryl amine as the extractant in the second stage: TLA is specific for plutonium, leaving the uranium in the aqueous phase[74]. Some British processes use Butex (dibutyl carbitol) in the first stages[74,78a].

To achieve further purification and to concentrate the plutonium, the final stage is usually anion exchange, although some plants use cation exchange. To prepare for the anion exchange, the final stripping is done with dilute acid only—complete extraction is not necessary here as the organic phase is recycled. Total recoveries of plutonium are about 99·8% and decontamination factors of 10^7 are achieved.

Whilst the Purex process is now almost universal, some other processes have been used in the past. The two most important were:

(a) The Redox process[79], in which hexone is the solvent and the aqueous phase is salted with $Al(NO_3)_3$ to drive the plutonium into the organic phase. Hexone is inflammable and somewhat soluble in water and so has fallen from favour.

(b) The bismuth phosphate process[80], which was developed in the course of the Manhattan project. The plutonium is precipitated out of solution with a carrier of $BiPO_4$.

Two other isotopes of plutonium have been separated in gram quantities. ^{238}Pu is produced by neutron irradiation of ^{237}Np and is then separated from the latter by anion exchange[49,77,81,82]. ^{242}Pu is produced by a long irradiation of ^{239}Pu (i.e. three successive neutron captures) as an intermediate stage in the production of ^{244}Cm and the higher actinides (see below, section 2.9).

Plutonium metal is almost universally produced by reducing the tetrafluoride with

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[77] P. Faugeras and E. Poulin, in *Nouveau Traité de Chimie Minérale*, Vol. XV(5), p. 119, P. Pascal (Ed.), Masson et Cie, Paris (1970).

[78] C. E. Stevenson, E. A. Mason and A. T. Gresky, *Progress in Nuclear Energy*, Series III, Process Chemistry, Vol. 4, Chapter 4, p. 213 (1970).

[78a] T. G. Hughes, B. F. Warner, J. R. Catlin, A. S. Davidson and H. Corns, *Fourth International Conference on the Peaceful Uses of Atomic Energy, Geneva* 8 (1971) 367.

[79] J. F. Flagg, in *Chemical Processing of Reactor Fuels*, p. 249, J. F. Flagg (Ed.), Academic Press, New York and London (1961).

[80] G. T. Seaborg, *The Transuranium Elements*, p. 19, Yale University Press, Connecticut (1958).

[81] W. L. Poe, A. W. Joyce and R. I. Martens, *Ind. Eng. Chem. Proc. Des. Dev.* 3 (1964) 314 and G. A. Burney, *ibid.* 3 (1964) 328.

[82] I. L. Jenkins, *Actinides Reviews*, 1 (1969) 183.

calcium[83]. The reasons for this were discussed in section 2.5, and the procedure is similar to that for uranium and neptunium. The equation is:

$$PuF_4 + 2Ca \rightarrow Pu + 2CaF_2 \ (\Delta H_{298} = -150 \text{ kcal/mole})$$

As for uranium and neptunium, the use of iodine as a booster is almost essential for small-scale reactions. Suggested values for the mole ratio of I_2:Pu range from 0·5 for 5 g reductions to 0·3 for 500 g and to zero for over 1 kg. The method may be used down to below a gram. Impurity levels will usually be around 2000 ppm (wt.), but with great care may be reduced to a tenth of this.

Recently, T. Yahata *et al.*[84] have described the calcium reduction of sodium plutonium (IV) fluoride, $NaPuF_5$. This compound has the advantage of an aqueous preparation route. Yields from a 1 g scale reduction were about 80%.

The zinc–magnesium reduction of the oxide is also possible[14], but has not been fully developed.

Electrolysis of molten salts as a preparative technique is also an attractive possibility. Suggested methods[83] involve the electrolysis of $PuCl_3$ in a molten mixture of alkali and alkaline earth halides in an MgO–TiO_2 cell with a tantalum cathode at 800° to 900°C. The biggest drawback is the rapid corrosion of the cell by the evolved chlorine.

Electrolysis has been most successful in the electrorefining of plutonium, either for the recovery of scrap or to produce extremely pure material for experimental work. The kilogram scale process developed by Leary and coworkers at Los Alamos[85] involves the electrolysis of a molten salt bath containing 2 mol. % $PuCl_3$, PuF_3 or PuF_4, 49 % NaCl and 49 % KCl in a magnesia–yttria cell. The plutonium is transferred from the anode (a well-stirred impure central molten pool) to the annular tungsten cathode, whence it drains into a molten annular trough in the cell. With this process the total metallic impurities can be reduced to below 50 ppm: on a smaller scale, 65 ppm can be reached[86]. Whilst plutonium freshly prepared in this way contains little americium, the ^{241}Pu content decays to ^{241}Am and the latter builds in at about 30 ppm per month for each percent of ^{241}Pu present.

2.8. Americium

There are two isotopes of americium with sufficiently long half-lives to make handling of massive quantities practicable, both being α-emitters: ^{241}Am with a half-life of 458 years and ^{243}Am, 7400 years. Both are formed by multiple neutron capture:

$$\begin{tikzcd}
{}^{239}\mathrm{Pu} \arrow[r, "n"] & {}^{240}\mathrm{Pu} \arrow[r, "n"] & {}^{241}\mathrm{Pu} \arrow[r, "n"] \arrow[d, "13{\cdot}2\mathrm{y}"', "\beta^-"] & {}^{242}\mathrm{Pu} \arrow[r, "n"] & {}^{243}\mathrm{Pu} \arrow[d, "5\mathrm{h}"', "\beta^-"] \\
 & & {}^{241}\mathrm{Am} & & {}^{243}\mathrm{Am}
\end{tikzcd}$$

Although the half-life of ^{241}Am is shorter, fewer steps are required for its formation and it is more readily available. During the process, two-thirds of the ^{239}Pu and five-sevenths of the ^{241}Pu are consumed by fission. Although isotopically pure ^{241}Am can be prepared from aged

[83] J. M. Cleveland in ref. 64, p. 553.

[84] T. Yahata, T. Muomura, K. Ouchi, Y. Sasaki, N. Kamegashira and K. Naito, *J. Nucl. Sci. Tech. (Tokyo)* **8** (1971) 682.

[85] L. J. Mullins and J. A. Leary, *Ind. Eng. Chem. Proc. Des. Dev.* **4** (1965) 394.

[86] B. Blumenthal and M. B. Brodsky, in *Plutonium 1960*, p. 171, E. Grison, W. B. H. Lord and R. B. Fowler (Eds.), Cleaver-Hume Press, London (1961).

plutonium, the americium obtained from highly irradiated fuel elements is a mixture of the two isotopes. Some 4 kg of ^{241}Am are recovered annually in the U.S.A.

The separation of the americium from the plutonium and from the fission products (the lanthanides can prove troublesome) has been summarized by several authors[49,50,87,88]. Various methods have been used, including:

(a) *Ion exchange.* Four stages of alternate cation and anion exchange are used, the eluants being ammonium thiocyanate and strong hydrochloric acid.

(b) *Solvent extraction/ion exchange.* An initial extraction with TBP is followed by a cation exchange step, using diethylenetriamine–pentacetic acid (DTPA) as the eluant.

(c) *Solvent extraction alone.* This avoids problems caused by radiation degradation of the resins. The americium is complexed by DTPA and the lanthanides extracted with an organophosphide.

(d) *Precipitation.* This process[50], which is now less used, depends on the fact that the most stable valence state of americium is +3 and very strong oxidizing agents are required to obtain +6. The americium is separated from plutonium by four successive lanthanum fluoride precipitations—the americium but not the plutonium is carried with the lanthanum.

Americium metal is more difficult to prepare than plutonium because of its higher melting point (1176°C) and high vapour pressure which causes considerable losses of material on melting. Four different methods have been used:

(a) *Bomb reduction of the tetrafluoride*[89]. AmO_2 was converted to AmF_4 with fluorine at about 300°C. This was then reduced with calcium in a manner similar to that used for plutonium: 30 % excess calcium was added and iodine and calcium used as a booster, the mole ratio of iodine to americium being between 0·75 and 1. The reaction was on the 20 gram scale, but yields were low (34–64 %), due probably to vaporization of the americium, and some pick-up of magnesium occurred from the MgO crucible. The process has not been optimized: better results might have been obtained with a CaF_2 crucible and less iodine booster.

(b) *Reduction of AmF_3 with barium*[90]. This was carried out in an all tantalum double crucible system, heated by induction to 1300°C. The barium in the lower part of the crucible vaporized and reduced the fluoride suspended in a wire basket above it. The americium metal, with a coating of slag, remained on the wires of the basket, while the excess barium diffused through a hole in the outer crucible. A good vacuum ($\sim 10^{-6}$ mm Hg) is essential: the reduction is complete in 10 sec at 1300°C and 3 min at 1100°C suffices to distil off the barium.

(c) *Reduction of AmO_2 with lanthanum.* This can be accomplished on both the milligram[90] and the gram scale[91,92]. The AmO_2 and a 50 % excess of lanthanum are placed in a tantalum crucible, heated by induction to 1500°C. The AmO_2 is reduced to the metal which diffuses out of the crucible to a tantalum condenser (in the large-scale experiment) or onto a fibre for X-ray examination (in small-scale work). In the former case, the americium is recovered by inverting the condenser over an yttria-coated crucible and casting the metal

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[87] M. Haissinsky and C. Ferradini, in *Nouveau Traité de Chimie Minérale*, Vol. XV(3), p. 865, P. Pascal (Ed.), Masson et Cie, Paris (1962).

[88] C. Ferradini, in *Nouveau Traité de Chimie Minérale*, Vol. XV(5), p. 595, P. Pascal (Ed.), Masson et Cie, Paris (1970).

[89] W. V. Connor, USAEC Report RFP 1188 (1968).

[90] D. B. McWhan, B. B. Cunningham and J. C. Wallmann, *J. Inorg. Nucl. Chem.* **24** (1962) 1025.

[91] J. Johnson and J. A. Leary, USAEC Report LA 2992 (1964).

[92] W. Z. Wade and T. Wolf, *J. Inorg. Nucl. Chem.* **29** (1967) 2577.

into this. The reduction process gave considerable purification: the best metal produced contained only 100 ppm impurities and 600 ppm was achieved routinely. Yields were about 75 %.

(d) *Thorium reduction.* Recently a similar method has been used with thorium as the reductant[93]. AmO_2 powder was mixed with a 50 % excess of thorium metal and pressed into a pellet. The whole was then heated to 1550°C by induction in a tantalum still, the distilled americium being collected on a quartz dome: the yield was low at 50 %. The metal was used to prepare thorium–americium alloys by levitation melting for use as Mossbauer sources.

The zinc–magnesium reduction method does not appear to be suitable for americium which remains in the flux rather than transferring to the metal phase[14]. Also, because of its high vapour pressure, much of the americium would probably be lost in the distillation step.

2.9. Curium, berkelium and californium

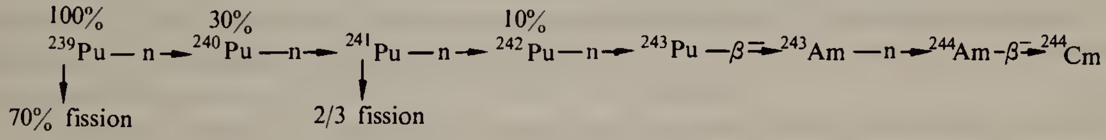
There are two isotopes of curium which are currently available in gram quantities. These are both α-emitters with short half-lives: ^{242}Cm, 162 days, and ^{244}Cm, 18 years. Some higher isotopes have longer half-lives but are not easily prepared by irradiation.

To prepare ^{242}Cm, $^{241}AmO_2/Al$ cermets are irradiated[49]:

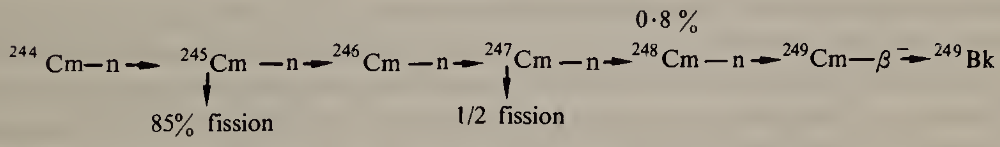
$$^{241}\mathrm{Am}\ (n, \gamma)\ ^{242}\mathrm{Am} \xrightarrow[16\ \mathrm{h}]{\beta^-} {}^{242}\mathrm{Cm}$$

They are then dissolved in HCl and the curium, americium and rare earths extracted into di(2-ethylhexyl)phosphoric acid (HDEHP). Separation of these trivalent elements was originally by anion exchange, but the effects of radiation are more easily controlled in the "Tramex" solvent extraction process. The basis of this is that the actinide elements are much more readily extracted than the rare earths from a strong solution of LiCl into a tertiary amine dissolved in diethyl benzene.

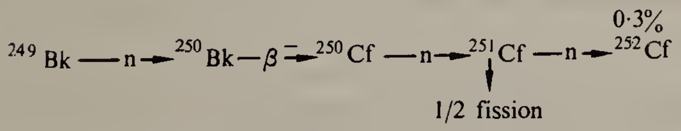
^{244}Cm is one of the elements produced by prolonged irradiation of ^{239}Pu, a process that is also used to make several of the higher actinide isotopes at the U.S.A.E.C. Oak Ridge Laboratory[49,94,95,95a]. Production of ^{244}Cm is hundreds of grams per year.



$$\underset{\substack{\downarrow\\ 70\%\ \text{fission}}}{\overset{100\%}{^{239}\mathrm{Pu}}} \xrightarrow{\ n\ } \overset{30\%}{^{240}\mathrm{Pu}} \xrightarrow{\ n\ } \underset{\substack{\downarrow\\ 2/3\ \text{fission}}}{^{241}\mathrm{Pu}} \xrightarrow{\ n\ } \overset{10\%}{^{242}\mathrm{Pu}} \xrightarrow{\ n\ } {}^{243}\mathrm{Pu} \xrightarrow{\ \beta^-\ } {}^{243}\mathrm{Am} \xrightarrow{\ n\ } {}^{244}\mathrm{Am} \xrightarrow{\ \beta^-\ } {}^{244}\mathrm{Cm}$$



$$^{244}\mathrm{Cm} \xrightarrow{\ n\ } \underset{\substack{\downarrow\\ 85\%\ \text{fission}}}{^{245}\mathrm{Cm}} \xrightarrow{\ n\ } {}^{246}\mathrm{Cm} \xrightarrow{\ n\ } \underset{\substack{\downarrow\\ 1/2\ \text{fission}}}{^{247}\mathrm{Cm}} \xrightarrow{\ n\ } \overset{0{\cdot}8\,\%}{^{248}\mathrm{Cm}} \xrightarrow{\ n\ } {}^{249}\mathrm{Cm} \xrightarrow{\ \beta^-\ } {}^{249}\mathrm{Bk}$$



$$^{249}\mathrm{Bk} \xrightarrow{\ n\ } {}^{250}\mathrm{Bk} \xrightarrow{\ \beta^-\ } {}^{250}\mathrm{Cf} \xrightarrow{\ n\ } \underset{\substack{\downarrow\\ 1/2\ \text{fission}}}{^{251}\mathrm{Cf}} \xrightarrow{\ n\ } \overset{0{\cdot}3\%}{^{252}\mathrm{Cf}}$$

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[93] H. L. Adair, *J. Inorg. Nucl. Chem.* 32 (1970) 1173.

[94] D. E. Ferguson and J. E. Bigelow, *Actinides Reviews*, 1 (1969) 213.

[95] M. Haissinsky, in *Nouveau Traité de Chimie Minérale*, Vol. XV(5), p. 627, P. Pascal (Ed.), Masson et Cie, Paris (1969).

[95a] C. Keller, *Industries Atomiques et Spatiales*, 16 (1972) 5, 19.

The initial stage is the irradiation of some kilograms of ^{239}Pu at a moderate neutron flux in a reactor (Savannah River) which has the capacity to remove the large amount of heat produced. The product (mostly ^{242}Pu with a little americium and curium) is then processed by conventional TBP extraction, refabricated into targets and irradiated again in a high-flux reactor: HFIR, the High Flux Isotope Reactor. The targets are dissolved in nitric acid and the residual plutonium extracted into TBP or HDEHP, leaving the higher actinides in the aqueous phase, which is then used as the feed for the Tramex process. It is possible to separate most of the curium from the higher actinides by stripping it from the organic liquor with 9 M LiCl.

Alternatively, these higher actinides may be separated by anion exchange, the rare earths and americium and curium being eluted successively by LiCl/HCl solutions of differing strengths and the transcurium elements finally stripped with 8 M HCl. The transcurium elements are separated from each other by high pressure ion exchange.

Where only trace amounts are involved, ion exchange is a very powerful tool for the separation of transplutonium elements[50,95]. The sample is dissolved in nitric acid and the metal ions are absorbed on the ion exchange resin. A complexing agent (e.g. α-hydroxy-isobutyrate) is then poured through the column and the ions are successively eluted, generally in order of decreasing atomic number.

Curium metal was originally prepared[96] by the reduction of the trifluoride with barium metal vapour in a tantalum double crucible system (as described under neptunium) and this technique was also used for a more recent preparation[97]. It was found, however, that curium dissolves tantalum and so the bead of CmF_3 was held between two parallel tungsten wires.

For the preparation of larger quantities of metal, it was easier to use the zinc–magnesium reduction method (see above, section 2.3)[98,99]. The reduction was carried out in a tungsten crucible and the reactants then poured into a beryllia crucible for ease of separation. The flux was dissolved in water and the zinc and magnesium distilled off. Curium has a lower vapour pressure than americium, so that this and the preceding method are easier to apply. Neither the yields (75–90 %) nor the impurity level (*ca.* 0·5 % metallic impurities) were very satisfactory, but may improve with further development.

Current production of berkelium in HFIR is about 20 mg per year of the isotope ^{249}Bk which has a half-life of 314 days. ^{247}Bk with a longer half-life (1400 years) is not easily made.

Two 5 μg-scale metal preparations have been reported[100,101]. Both used the same technique, the reduction of the trifluoride with lithium metal in a tantalum crucible system. The fluoride was suspended in a tungsten spiral in a crucible with an effusion hole in the lid. A large excess of lithium was also placed in the crucible and the whole heated by induction in a good vacuum to 1000–1050°C for about 3 min. The metal product was usually easily separated from the tungsten wire. Because of the short β^- half-life, 0·2 % per day of ^{249}Cf "builds-in" to berkelium compounds. However, californium metal is much more volatile than berkelium and distils off during the reduction so that freshly prepared berkelium metal contains almost none.

[96] J. C. Wallmann, W. W. T. Crane and B. B. Cunningham, *J. Amer. Chem. Soc.* 73 (1951) 493.

[97] B. B. Cunningham and J. C. Wallmann, *J. Inorg. Nucl. Chem.* **26** (1964) 271.

[98] I. D. Eubanks and M. C. Thompson, *Inorg. Nucl. Chem. Lett.* **5** (1969) 187.

[99] J. B. Knighton and R. K. Steunenberg, USAEC Reports ANL 7057, 7058 and 7059 (1965), and *J. Inorg. Nucl. Chem.* **27** (1965) 1457.

[100] J. R. Peterson, J. A. Fahey and R. D. Baybarz, *J. Inorg. Nucl. Chem.* **33** (1971) 3345.

[101] D. K. Fujita, University of California, Lawrence Radiation Laboratory Report UCRL 19507 (1969).

Output of ^{252}Cf is currently about 0·2 g per year, with small amounts of ^{249}Cf. Both are α-emitters, the former having a half-life of 2·6 years and the latter 360 years. ^{252}Cf is also spontaneously fissile.

An early attempt[101] to prepare the metal by the same lithium reduction technique used for berkelium failed because of the high volatility of the product, but it has recently been prepared[2] both by this technique and by reduction of the oxide with lanthanum, the method used to prepare americium.

2.10. The elements beyond californium

The work on these elements has recently been reviewed by Seaborg[102], by Flerov and Druin[103] and by Keller[95a].

With increasing atomic number, the nuclei become rapidly less stable and only einsteinium has an isotope with a half-life long enough to offer any hope of conventional chemical studies on other than the tracer scale. Methods of making these elements are as follows[95,104].

1. *Reactor irradiation.* This is really only practicable for einsteinium and fermium, and even for ^{257}Fm the production rate in HFIR is estimated to be 10^{-8} that of ^{252}Cf.[94]

2. *Nuclear explosions.* The extreme neutron fluxes available have led to the detection of elements up to ^{257}Fm in the debris of underground nuclear tests[2].

3. (*α*, *n*) *reactions*, e.g.

$$^{257}_{100}\mathrm{Fm}\ (\alpha, n)\ ^{260}_{102}\mathrm{No}$$

Nobelium is in fact the highest atomic number element that can be made in this way since the target element must be available in reasonable amounts.

4. *Heavy ion reactions.* Here a heavy ion is accelerated in a cyclotron or linear accelerator to collide with a target, usually of one of the early actinides, e.g.

$$^{238}_{92}\mathrm{U}\ (^{22}_{10}\mathrm{Ne}, 5n)\ ^{255}_{102}\mathrm{No}$$

Unfortunately most of the nuclei formed immediately decay by fission because they are produced in a highly excited state: more energy must be used in the bombardment than is needed to form the intermediate nucleus. However, this is the only method that is likely to enable further advances up the Periodic Table to be made.

Identification of the isotopes produced is a difficult problem since the number of atoms formed is very small—maybe only hundreds or even tens. Chemical studies are just possible in some cases even with half-lives measured in seconds[104]. The more usual identification methods, however, are by physical studies[95,104]. (a) The nuclear excitation functions can be calculated and compared with those determined experimentally. (b) The systematics of α-decay. The α-energies of known nuclides follow a pattern which can be extrapolated either empirically or theoretically. (c) The systematics of spontaneous fission. The same extrapolation procedure can be applied to the spontaneous fission energies. (d) X-ray identification. The energy of an emitted X-ray can be predicted by Moseley's law and this has recently been used[2] to confirm the identification of ^{255}No. However, there are some uncertainties in all these methods and disputes as to the interpretation of results have arisen[105].

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[102] G. T. Seaborg, *Ann. Rev. Nucl. Sci.* **18** (1968) 53.

[103] G. N. Flerov and V. A. Druin, *Atomic Energy Rev.* **8** (1970) 255.

[104] G. Herrmann and K. E. Seyb, *Naturwiss.* **56** (1969) 590.

[105] A. Ghiorso, M. Nurmia, J. Harris, K. Eskola and P. Eksola, *Nature*, **229** (1971) 603.

The actinide group is completed with element 103, lawrencium. The higher actinides all appear to be predominantly trivalent except for the penultimate one, nobelium, which completes its *f*-shell by taking one of the valency electrons, leaving the atom divalent, i.e. $5f^{14}, 7s^2$ is lower in energy than $5f^{13}, 7s^2, 6d^1$ (the equivalent rare earth ytterbium behaves in a similar way).

Element 104 (kurchatovium) is expected to be a Group IV transition element. Support for this supposition comes from some elegant experimental work[2,104] which shows that it has a volatile chloride like zirconium and hafnium although the actinides do not.

Whilst elements with atomic numbers just over 100 are becoming less stable to both α-decay and spontaneous fission, calculations suggest that at certain higher numbers, particularly around 110, the atoms should become more stable again, forming the so-called "island of stability". These calculations and the possible physical and chemical properties of these elements are discussed in refs. 2, 95, 102, 104, 106, 107 and 108.

3. CRYSTAL STRUCTURES

The crystal structures are listed in Table 7.

3.1. Actinium

The X-ray pattern of metallic actinium was only observed for one of the two reported preparations[8] and that sample was contaminated with actinium hydride. Further, the X-ray pattern was not very good, only the first four fcc reflections being observed. Thus some uncertainty must remain until the work is repeated, perhaps on a larger scale.

3.2. Thorium

α-Thorium

The lattice parameter of fcc α-thorium varies with purity, in general increasing with impurity content. This effect has been studied by Blumenthal and Sanecki[109] and the value they obtained for their purest material is probably the most reliable (Table 7). The metal contained 86 ppm metallic and 60 ppm non-metallic (interstitial) impurities. Chiotti and White[110] have studied the variation of lattice parameter with temperature from room temperature up to the α/β transformation. Marples[111] has shown that no phase changes or sudden alterations in expansion coefficient occur between 4 and 300K. The expansion coefficient near room temperature is about $11{\cdot}6 \times 10^{-6}/°\mathrm{C}$.

β-Thorium

α-Thorium transforms to the bcc β-thorium at 1380°C. Chiotti and White[110] have measured the variation of lattice parameter with temperature and shown that a small expansion (0·63 %) occurs on transformation. The melting point of thorium is somewhat uncertain and it is affected by impurities, oxidation and reaction with the crucible. Since 1950, published values range from 1690° to 1750°C, but because the value is reduced by carbon contamination the true value may be at the upper end of this range.

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[106] G. N. Flerov, *Atomic Energy* (*USSR*), **28** (1970) 302.
[107] J. R. Nix, *Physics Today*, **25** (1972) No. 4, 30.
[108] O. L. Keller, J. L. Burnett, T. A. Carlson and C. W. Nestor, *J. Phys. Chem* **74** (1970) 1127.
[109] B. Blumenthal and J. E. Sanecki, *J. Nucl. Mater.* **22** (1967) 100.
[110] P. Chiotti and R. W. White, *J. Nucl. Mater.* **23** (1967) 37.
[111] J. A. C. Marples, Unpublished work.

3.3. Protactinium

The various determinations of the lattice parameters of protactinium have given results in remarkably good agreement, but as the sample purities are not known it is difficult to say which is the most reliable. Zachariasen[23, 112] determined the structure as bc tetragonal with $c/a = 0\cdot825$, i.e. a normal bcc structure slightly compressed in the c-direction. Donohue[113] suggested that the structure could be orthorhombic, but this did not fit the data so well[112,114,115]. Marples[114] studied the variation of the lattice parameters with temperature. As the temperature increases, c/a increases towards unity more and more rapidly and it was suggested that the structure would become bcc with a lattice parameter of 3·81 Å above 1170°C. Near room temperature the expansion coefficients were approximately: $\alpha_a = 7 \times 10^{-6}$ and $\alpha_c = 17 \times 10^{-6}/°\mathrm{C}$.

In a recent paper Asprey *et al.*[116] have suggested the existence of a high-temperature form: some of their quenched samples showed a fcc pattern with $a = 5\cdot02$ Å. These reverted to the normal tetragonal form on cold-working. The X-ray density is 12·13 g/cc and the metallic radius 1·78 Å, a value expected if this form of protactinium has one $5f$ electron. A fcc high-temperature form of protactinium is somewhat surprising since the neighbouring actinides thorium, uranium, neptunium, and plutonium all have bcc high-temperature phases and the tetragonal form shows every sign of reverting to bcc at higher temperatures.

The two published values for the melting point[114,115] are in good agreement: 1560° and 1575°C.

3.4. Uranium

α-Uranium

Probably the best values for the lattice parameters are those found by Cooper[117], given in Table 7, for a single crystal containing about 100 ppm total impurities. The structure is a complex one which can be considered as comprising parallel puckered sheets of uranium atoms stacked together. The unit cell contains four atoms with coordinates:

$$(0, y, \tfrac{1}{4})\colon (0, \bar{y}, \tfrac{3}{4})\colon (\tfrac{1}{2}, \tfrac{1}{2} + y, \tfrac{1}{4})\colon (\tfrac{1}{2}, \tfrac{1}{2} - y, \tfrac{3}{4})$$

The atom position parameter is $y = 0\cdot1024 \pm 0\cdot0003$ at 25°C. The space group is *Cmcm*.

The thermal expansion behaviour has been tabulated by Lloyd and Barrett[118]. The expansion coefficients at 25°C are:

$$\alpha_a = 23\cdot9 \times 10^{-6};\ \alpha_b = 0\cdot92 \times 10^{-6};\ \alpha_c = 19\cdot9 \times 10^{-6}/°\mathrm{C}$$

Probably the best determination of the lattice parameters at elevated temperatures is that by Chiotti *et al.*[119] for material containing less than 200 ppm impurities. However, the

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[112] W. H. Zachariasen, *Acta Cryst.* **12** (1959) 698.

[113] J. Donohue, *Acta Cryst.* **12** (1959) 697.

[114] J. A. C. Marples, *Acta Cryst.* **18** (1965) 815.

[115] B. B. Cunningham, *Physico-Chimie du Protactinium*, p. 45, C.N.R.S., Paris (1966).

[116] L. B. Asprey, R. D. Fowler, J. D. G. Lindsay, R. W. White and B. B. Cunningham, *Inorg. Nucl. Chem. Lett.* **7** (1971) 977.

[117] A. Cooper, *Acta Cryst.* **15** (1962) 578.

[118] L. T. Lloyd and C. S. Barrett, *J. Nucl. Mater.* **18** (1966) 55.

[119] P. Chiotti, H. H. Klepfer and R. W. White, *Trans. ASM*, **51** (1959) 772.

TABLE 7. CRYSTAL STRUCTURE DATA FOR THE ACTINIDES

Element	Structure (°C)	Stability range (°C)	Lattice parameters (Å)			β°	Temp.[1] °C	X-ray[2] density	Met.[3] Rad.
			a	*b*	*c*				
Ac	Fcc		5·311				R.T.	10·07	1·88
α-Th	Fcc	< 1380	5·0840[a]				24·5	11·78	1·79
β-Th	Bcc	1380–*c*. 1750*	4·115				1425		
Pa	Tetragonal	See text	3·929		3·241[b]		R.T.	15·37	1·63
α-U	Orthorhombic	< 668	2·8536	5·8698	4·9555[c]		24·6	19·05	1·56
β-U	Tetragonal	668–775	10·759		5·656		720	18·11	
γ-U	Bcc	775–1132*	3·524				805	18·06	1·55
α-Np	Orthorhombic	< 280	6·663	4·723	4·887		20	20·45	1·55
β-Np	Tetragonal	280–577	4·897		3·388		313	19·36	
γ-Np	Bcc	577–640*	3·518[d]				600	18·08	1·54
α-Pu	Monoclinic	< 115	6·183	4·822	10·963	101·79	21	19·86	1·58
β-Pu	Bc Monoclinic	115–185	9·227	10·449	7·824	92·54	93	17·70	1·59
γ-Pu	Orthorhombic	185–310	3·159	5·768	10·162		235	17·13	1·589
δ-Pu	Fcc	310–452	4·637				320	15·92	1·644
δ′-Pu	Tetragonal	452–480	3·326		4·463[e]		450	16·00	1·644
ε-Pu	Bcc	480–640*	3·638				500	16·48	1·594
α-Am	Dhcp	< 1074	3·4681		11·241		20	13·67	1·73
β-Am	Fcc	1074–1175*	4·894				22	13·65	1·73
		See text							
α-Cm[f]	Dhcp		3·496		11·331		20	13·51	1·74
β-Cm[g]	Fcc	–1345*	4·382				R.T.	19·26	1·55
α-Bk[h]	Dhcp	< 930	3·416		11·069		R.T.	14·78	1·70
β-Bk[h]	Fcc	930–960*	4·997				R.T.	13·25	1·77
Cf	Cubic		See text						

equations given by Konobeevsky *et al.*[120] also fit Chiotti's data quite well:

$$a = 2{\cdot}8522\,(1 + 21{\cdot}7 \times 10^{-6}\,T + 2{\cdot}2 \times 10^{-8}\,T^2)$$
$$b = 5{\cdot}8650\,(1 + 8{\cdot}5 \times 10^{-6}\,T - 2{\cdot}8 \times 10^{-8}\,T^2)$$
$$c = 4{\cdot}9536\,(1 + 16{\cdot}7 \times 10^{-6}\,T + 2{\cdot}1 \times 10^{-8}\,T^2)$$

The lattice parameters at low temperatures have been studied by Barrett[121] and by Marples[122]. At 43K a second order change occurs, below which the volume expansion coefficient and the expansion coefficients in the a and b directions become negative. No change in structure occurs, although the atom position parameter y also shows a minimum at 43K. The anomaly is thought to be caused by electron transfer from the valency band to the localized $5f$ band. Two further small changes at 23K and 37K have also been reported[123] from strain gauge measurements on single crystals.

β-Uranium

The structure of β-uranium is complex and the space group is still in doubt. The situation has recently been reviewed by Donohue and Einspahr[124] who conclude that the X-ray intensity data available are not accurate enough to distinguish between the space groups $P4_2/mnm$, $P\bar{4}n2$ and $P4_2nm$. The last of these, however, gives slightly the smallest residual and also gives the largest closest-distance-of-approach of the three groups (2·49, 2·55 and 2·63 Å: the shortest interatomic distance observed in either α- or γ-uranium is 2·76 Å).

The agreement between the three published sets of lattice parameters is good considering the experimental difficulties[119]. The expansion coefficients are:

$$\alpha_a = 21{\cdot}3 \times 10^{-6} \text{ and } \alpha_c = 8{\cdot}8 \times 10^{-6}/°\text{C}$$

γ-Uranium

This phase has the usual bcc structure. The lattice parameters have been determined by

[120] S. T. Konobeevsky, A. S. Zaimovsky, B. M. Levitsky, Y. N. Sokursky, N. T. Chebotarev, Y. V. Bobkov, P. P. Egorov, G. N. Nikolaev and A. A. Ivanov, *Proc. 2nd Int. Conf. on the Peaceful Uses of Atomic Energy*, Geneva, Vol. 6, p. 194, United Nations (1958).

[121] C. S. Barrett, M. H. Mueller and R. L. Hitterman, *Phys. Rev.* **129** (1963) 625.

[122] J. A. C. Marples, *J. Phys. Chem. Solids*, **31** (1970) 2421.

[123] M. O. Steinitz, C. E. Burleson and J. A. Marcus, *J. Appl. Phys.* **41** (1970) 5057.

[124] J. Donohue and H. Einspahr, *Acta Cryst.* **B27** (1971) 1740.

Notes to Table 7:

It is expected that this table will be used in conjunction with the text.

Unless a reference is given (for the more recent data), the entries are taken from the review book by W. B. Pearson, *Handbook of Lattice Spacings and Structures of Metals*, Pergamon Press (Oxford), Vol. 1, 1958, and Vol. 2, 1967.

* Melting point.

[1] R.T. indicates "room temperature" values for the parameters.

[2] The X-ray densities are in g/cc.

[3] The metallic radii in Å are corrected to coordination number 12 and, approximately, to room temperature for the higher temperature phases.

[a] B. Blumenthal and J. E. Sanecki, *J. Nucl. Mater.* **22** (1967) 100.

[b] B. B. Cunningham, in *Physico-Chimie du Protactinium*, p. 45, C.N.R.S., Paris (1966).

[c] A. Cooper, *Acta Cryst.* **15** (1962) 578.

[d] P. G. Mardon, J. H. Pearce and J. A. C. Marples, *J. Less-Common Met.* **3** (1961) 281.

[e] R. O. Elliott and A. C. Larson, in *The Metal Plutonium*, p. 99, A. S. Coffinberry and M. B. Waldron (Eds.), University of Chicago Press (1961).

[f] B. B. Cunningham and J. C. Wallmann, *J. Inorg. Nucl. Chem.* **26** (1964) 271.

[g] P. K. Smith, W. H. Hale and M. C. Thompson, *J. Chem. Phys.* **50** (1969) 5066.

[h] J. R. Peterson, J. A. Fahey and R. D. Baybarz, *J. Inorg. Nucl. Chem.* **33** (1971) 3345.

Chiotti[119]. The expansion coefficient is $22{\cdot}5 \times 10^{-6}/°\mathrm{C}$ and the lattice parameter extrapolated to room temperature is 3·473 Å.

The volume changes at the phase transformations are: α/β +1·12 %; β/γ +0·70 %.

3.5. Neptunium[52]

α-Neptunium

The symmetry is orthorhombic, space group *Pmcn*, with eight atoms per unit cell in positions:

$$4\mathrm{Np(I)}: \pm (\tfrac{1}{4}, y_1, z_1), (\tfrac{1}{4}, \tfrac{1}{2} - y_1, z_1 + \tfrac{1}{2})$$

$$4\mathrm{Np(II)}: \pm (\tfrac{1}{4}, y_2, z_2), (\tfrac{1}{4}, \tfrac{1}{2} - y_2, z_2 + \tfrac{1}{2})$$

with:

$$y_1 = 0{\cdot}208 \pm 0{\cdot}006, \; y_2 = 0{\cdot}842 \pm 0{\cdot}006$$

$$z_1 = 0{\cdot}036 \pm 0{\cdot}006, \; z_2 = 0{\cdot}319 \pm 0{\cdot}006$$

The various published lattice parameters are in good agreement. The expansion coefficients are:

$$\alpha_a = 24 \times 10^{-6}; \; \alpha_b = 25 \times 10^{-6}; \; \alpha_c = 34 \times 10^{-6}/°\mathrm{C}$$

Marples[111] has shown that there are no anomalies in the range 4 to 300K.

β-Neptunium

β-Neptunium possesses tetragonal symmetry, space group $P42_1$ with four atoms per unit cell in positions:

$$2\mathrm{Np(I)} \text{ in } (0, 0, 0) \text{ and } (\tfrac{1}{2}, \tfrac{1}{2}, 0) \text{ and } 2\mathrm{Np(II)} \text{ in } (\tfrac{1}{2}, 0, u) \text{ and } (0, \tfrac{1}{2}, \bar{u})$$

where $u = 0{\cdot}375 \pm 0{\cdot}015$. The expansion coefficients are:

$$\alpha_a = 64 \times 10^{-6}/°\mathrm{C} \text{ and } \alpha_c = \text{zero}$$

γ-Neptunium

Zachariasen found difficulty in determining the lattice parameters of this phase, which he assumed to be bcc, due to a coincidental overlap between its reflections and those of NpO. Mardon *et al.*[125], investigating the neptunium–plutonium phase diagram, found that plutonium in solution altered the parameter enough to remove the overlap and they were able to determine the parameter by extrapolation (Table 7).

3.6. Plutonium[76,77,126]

α-Plutonium

α-Plutonium is monoclinic, space group $P2_1/m$ with sixteen atoms per unit cell. All the atoms lie in reflection planes in positions $\pm(x, \tfrac{1}{4}, z)$ where x and z are given by:

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[125] P. G. Mardon, J. H. Pearce and J. A. C. Marples, *J. Less-Common Metals*, 3 (1961) 281.
[126] W. N. Miner and F. W. Schonfeld, in ref. 64, p. 33.

	x	z		x	z
I	$0{\cdot}345 \pm 0{\cdot}005$	$0{\cdot}162 \pm 0{\cdot}003$	V	$0{\cdot}025 \pm 0{\cdot}005$	$0{\cdot}618 \pm 0{\cdot}003$
II	$0{\cdot}767$	$0{\cdot}168$	VI	$0{\cdot}473$	$0{\cdot}653$
III	$0{\cdot}128$	$0{\cdot}340$	VII	$0{\cdot}328$	$0{\cdot}926$
IV	$0{\cdot}657$	$0{\cdot}457$	VIII	$0{\cdot}869$	$0{\cdot}894$

The expansion coefficients are:

$$\alpha_a = 60 \times 10^{-6};\ \alpha_b = 72 \times 10^{-6};\ \alpha_c = 29 \times 10^{-6}/^{\circ}\mathrm{C}$$

Marples[127] has measured the lattice parameters between 4 and 300K and shown that a change in expansion coefficient occurs at about 70K.

β-Plutonium

β-Plutonium has a complex structure in the space group $I2/m$ with thirty-four atoms per unit cell[128]. The atom positions are:

$$(0, 0, 0) \text{ and } (\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2})$$

plus:

Type	No.	Coordinates	x	y	z
I	2	$(0, 0, 0)$	0	0	0
II	4	$\pm(x, 0, z)$	$0{\cdot}146 \pm 0{\cdot}004$	0	$0{\cdot}387 \pm 0{\cdot}005$
III	4	$\pm(x, 0, z)$	$0{\cdot}337$	0	$0{\cdot}082$
IV	4	$\pm(x, 0, z)$	$0{\cdot}434$	0	$0{\cdot}672$
V	4	$\pm(\tfrac{1}{2}, y, 0)$	$\tfrac{1}{2}$	$0{\cdot}220 \pm 0{\cdot}003$	0
VI	8	$\pm(x, y, z)\colon (x, \bar{y}, z)$	$0{\cdot}145$	$0{\cdot}268 \pm 0{\cdot}002$	$0{\cdot}108$
VII	8	$\pm(x, y, z)\colon (x, \bar{y}, z)$	$0{\cdot}167$	$0{\cdot}150$	$0{\cdot}753$

The expansion coefficients are:[128]

$$\alpha_1 = 94 \times 10^{-6};\ \alpha_2 = 14 \times 10^{-6};\ \alpha_3 = 19 \times 10^{-6};\ \bar{\alpha} = 42 \times 10^{-6}/^{\circ}\mathrm{C}$$

γ-Plutonium

γ-Plutonium has orthorhombic symmetry, space group *Fddd*, with eight atoms per unit cell in positions[129]:

$$(0, 0, 0),\ (0, \tfrac{1}{2}, \tfrac{1}{2}),\ (\tfrac{1}{2}, 0, \tfrac{1}{2}),\ (\tfrac{1}{2}, \tfrac{1}{2}, 0),\ (\tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{4}),\ (\tfrac{1}{4}, \tfrac{3}{4}, \tfrac{3}{4}),\ (\tfrac{3}{4}, \tfrac{1}{4}, \tfrac{3}{4}),\ (\tfrac{3}{4}, \tfrac{3}{4}, \tfrac{1}{4})$$

The expansion coefficients are:

$$\alpha_a = -19{\cdot}7 \times 10^{-6};\ \alpha_b = 39{\cdot}5 \times 10^{-6};\ \alpha_c = 84{\cdot}3 \times 10^{-6};\ \bar{\alpha} = 34{\cdot}7 \times 10^{-6}/^{\circ}\mathrm{C}$$

δ-Plutonium

This phase has a normal fcc metallic structure but is remarkable in having a negative

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[127] J. A. Lee, J. A. C. Marples, K. Mendelssohn and P. W. Sutcliffe, in *Plutonium 1965*, p. 176, A. E. Kay and M. B. Waldron (Eds.), Chapman & Hall, London (1967).

[128] W. H. Zachariasen and F. H. Ellinger, *Acta Cryst.* **16** (1963) 369.

[129] W. H. Zachariasen and F. H. Ellinger, *Acta Cryst.* **8** (1955) 431.

expansion coefficient—about $-9 \times 10^{-6}/°C$[130,131]. It has a greater solubility for other elements than the lower temperature phases and a range in lattice parameters of 0·003 Å is observed depending on purity[131].

Three different explanations of the negative expansion coefficient have been proposed. Zachariasen[132] suggests that there is electron transfer between the valency band and the more localized $5f$ band, thus changing the size of the atom and also the valency. According to this scheme the latter would increase by 0·1 over the δ-range of stability. Varley[133] points out that a negative expansion coefficient is possible if the density of states is both high and steeply sloping at the Fermi surface. Konobeevsky and Chebotarev[134] postulate a superlattice structure with the face-centring atoms of the fcc lattice displaced by a varying amount thus varying the cell size. This was shown not to accord with X-ray line intensity measurements[135].

δ-phase alloys with other metals have positive expansion coefficients above a certain concentration[131].

δ′-Plutonium

This phase is most unusual, being in some ways like a hybrid between δ and ε. Its symmetry is bc tetragonal with c/a greater than unity[130]. The expansion coefficients of high purity material (220 ppm impurities, not including oxygen) are[136]:

$$\alpha_a = 440 \times 10^{-6}/°\text{C};\ \alpha_c = -1060 \times 10^{-6}/°\text{C};\ \bar{\alpha} = -66 \times 10^{-6}/°\text{C}$$

but these vary with purity.

ε-Plutonium

This has a bcc structure. Again the lattice parameters vary somewhat with purity[130,131] as do the expansion coefficients. Values of the latter determined from X-ray measurements are $36{\cdot}5 \times 10^{-6}/°C$[130] and $27 \times 10^{-6}/°C$[131]: the latter is nearer the values determined dilatometrically.

3.7. Americium

α-Americium

Americium is the first of the actinides to have a crystal structure resembling those of the rare earths, the double close packed hexagonal array of α-Am being similar to that of α-La. The space group is $P6_3/mmc$ with four atoms per unit cell at (0,0,0), (0,0,$\frac{1}{2}$), ($\frac{1}{3}$,$\frac{2}{3}$,$\frac{1}{4}$), and ($\frac{2}{3}$,$\frac{1}{3}$,$\frac{3}{4}$). Two different sets of lattice parameters have been reported: (a) The more usual one: $a = 3{\cdot}4681 \pm 0{\cdot}0008$; $c = 11{\cdot}241 \pm 0{\cdot}003$ Å and (b) $a = 3{\cdot}642$; $c = 11{\cdot}76$. McWhan *et al.*[90] suggested that americium can exist with either of two possible radii as cerium does. The former set of parameters has the following temperature variation between −120° and 605°C:

$$a_T = 3{\cdot}4672 \pm 0{\cdot}0002 + (2{\cdot}60 \pm {\cdot}03) \times 10^{-5}T + (0{\cdot}54 \pm {\cdot}02) \times 10^{-8}T^2$$

$$c_T = 11{\cdot}237 \pm 0{\cdot}001 + (6{\cdot}95 \pm {\cdot}40) \times 10^{-5}T + (6{\cdot}8 \pm 0{\cdot}5) \times 10^{-8}T^2$$

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[130] F. H. Ellinger, *Trans. AIME* **206** (1956) 1256.

[131] J. A. C. Marples, *J. Phys. Chem. Solids*, **25** (1964) 521.

[132] W. H. Zachariasen, in *The Metal Plutonium*, p. 99, A. S. Coffinberry and W. N. Miner (Eds.), The University of Chicago Press (1961).

[133] J. H. O. Varley, *Proc. Roy. Soc.* A237 (1956) 413.

[134] S. T. Konobeevsky and N. T. Chebotarev, *Atomnaya Energiya*, **10** (1961) 50.

At 20°C:

$$\alpha_a = (7{\cdot}5 \pm 0{\cdot}2) \times 10^{-6}/^{\circ}\mathrm{C};\ \alpha_c = (6{\cdot}2 \pm 0{\cdot}4) \times 10^{-6}/^{\circ}\mathrm{C}$$

β-Americium

This is probably fcc with $a = 4{\cdot}893$ Å at room temperature. The α/β transition is sluggish, and the fcc phase can be retained to room temperature: its expansion coefficient is $9 \times 10^{-6}/^{\circ}\mathrm{C}$. The phase exhibits complete solid solubility with δ-plutonium[137].

McWhan *et al.*[90] gave the melting point as 994°C and the α/β transition as about 600°C. Neither temperature was confirmed by later workers[92,138] who found the transition temperature to be 1075° ± 4°C and the melting point 1173°C. A recent differential thermal analysis study gave, α/β: 1074°C; melting point: 1175°C[138a].

3.8. Curium

Two forms of curium have been reported, a dhcp structure, similar to americium[97] and a high density fcc form[139]. While both observations were made at room temperature on different batches of material, the latter phase is thought to be stable at high temperatures: this is rather unusual as it has a much higher density. The radii observed for the two phases correspond to valencies of 3 and 4 respectively (see below).

3.9. Berkelium

Berkelium also exhibits a dhcp and fcc form, the latter again being the high-temperature allotrope[100]: here, however, the densities of the two phases are much more comparable than they are for curium. An independent sample prepared by Fujita[101] was also fcc with $a = 4{\cdot}989$ Å. The transformation temperature given by Fahey *et al.*[140] must be somewhat uncertain as it is the temperature at which the appearance of the sample changed during an optical pyrometer determination of its melting point.

3.10. Californium

While Seaborg *et al.*[2] report the preparation of californium metal by Cunningham and Asprey, the only details given are that it exists in two cubic modifications, the lower of which is fcc.

3.11. The valencies and metallic radii of the actinides

Zachariasen[132] derived a relation between the valencies and the radii of the actinide metals. This was deduced by analogy with the transition elements and the rare earths,

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[135] J. A. C. Marples and J. A. Lee, *Atomnaya Energiya*, **12** (1962) 423.

[136] R. O. Elliott and A. C. Larson, in *The Metal Plutonium*, p. 265, A. S. Coffinberry and W. N. Miner (Eds.), The University of Chicago Press (1961).

[137] F. H. Ellinger, K. A. Johnson and V. O. Struebing, *J. Nucl. Mater.* **20** (1966) 83.

[138] D. R. Stephens, H. D. Stromberg and E. M. Lilley, *J. Phys. Chem. Solids*, **29** (1968) 815.

[138a] C. Sari, W. Müller and U. Benedict, *J. Nucl. Mat.* **45** (1972/73) 73.

[139] P. K. Smith, W. H. Hale and M. C. Thompson, *J. Chem. Phys.* **50** (1969) 5066.

[140] J. A. Fahey, J. R. Peterson and R. D. Baybarz, *Inorg. Nucl. Chem. Lett.* **8** (1972) 101.

Table 8. Zachariasen's Metallic Valency versus Radius Relationship[132]

Valency	3	4	5	6	7
Ac	2·02				
Th	1·99	*1·79*			
Pa	1·96	1·77	*1·63*		
U	1·94	1·75	1·61	*1·56*	
Np	1·93	1·74	1·60	*1·55*	*1·52*
Pu	1·92	1·73	*1·59*	1·54	1·51
Am	1·91	*1·73*	1·58	1·53	1·51

using a conversion factor derived by assuming a valency of 4 for thorium. The results are shown in Table 8.

More recently, first Cunningham and Wallmann[97] and later Weigel and Trinkl[141] revised this arrangement using different reference points. The former thought that Zachariasen's predicted valency of 3·8 for curium was not in agreement with its other fundamentally trivalent properties so they used Cm = 3 as their reference. Weigel and Trinkl proposed that radium with a valency of two should be the starting point. (They found radium to be bcc, $a = 5{\cdot}158$ Å, $D_x = 5{\cdot}50$, atom radius: 2·32 Å.) These three schemes are compared in Table 9.

Table 9. The Metallic Valencies of the Elements according to Various Authors

Element	Z.[a]	C. & W.[b]	W. & T.[c]
Ra			(2)
Ac		3·1	3·1
Th	(4)	3·3	3·1
Pa	5·1	3·9	4·0
U	6·0	4·2	4·5
Np	5·8	4·1	4·5
Pu	5·0	3·9	4·0
Am	3·9	3·1	3·2
Cm Dhcp	3·8	(3)	3·1
Fcc[d]	4·8	4·0	4·1
Bk Fcc[e]	3·5	2·8	2·9
Dhcp	3·9	3·2	3·3

[a] W. H. Zachariasen, in *The Metal Plutonium*, p. 99, A. S. Coffinberry and W. N. Miner (Eds.), The Univ. of Chicago Press (1961).

[b] B. B. Cunningham and J. C. Wallmann, *J. Inorg. Nucl. Chem.* **26** (1964) 271.

[c] F. Weigl and A. Trinkl, *Radiochim. Acta*, **10** (1968) 78.

[d] P. K. Smith, W. H. Hale and M. C. Thompson, *J. Chem. Phys.* **50** (1969) 5066.

[e] J. A. Fahey, J. R. Peterson and R. D. Baybarz, *Inorg. Nucl. Chem. Letters*, **8** (1972) 101.

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[141] F. Weigel and A. Trinkl, *Radiochim. Acta*, **10** (1968) 78.

The last two are not very much in disagreement and the authors had more data available than Zachariasen had when his system was originally proposed. The use of curium as a reference involves less of an extrapolation than using radium. The different valencies for each phase of each element have not been included in the table.

3.12. The electronic structure of the actinide metals

One of the most important recent developments has been the emergence of theoretical treatments of the electronic band structure which bear a meaningful relationship to experimental observations. Previously, the approaches available to explain these observations were of three kinds. Useful progress had been made as above by correlating empirical estimates of metallic radii in various structures with a scheme of metallic valencies, but these depend on the assumption that 5*f* electrons do not contribute to bonding. A second, somewhat similar, approach was proposed by Friedel[142] who deduced a pattern of 7*s*, 6*d*, 5*f* and *s–d*, *d–f* hybridized wave function behaviour from the physical characteristics of the actinide elements. This approach, however, only provides a basis for establishing generalized models for interpretation and calculation. The third kind of approach has been to set up suitable theoretical models for calculations of the band structure and Fermi surface following the pattern already proposed for the transition elements and for the lanthanides. Until recently, Wigner-Seitz calculations made for uranium[143] were used as the best available approximation to the probable band structure of the early actinides. It was possible to interpret the properties largely in terms of a broad, hybridized *s–d* or *d–f* band at the Fermi surface and a fairly narrow 5*f* band moving from above to below the Fermi surface, analogous to descriptions of the transition and lanthanide series.

More recently[144], both non-relativistic and relativistic augmented plane wave calculations have been made for the actinides using improved free electron potentials and optimized Slater exchange terms which significantly modify the 5*f* band position and width. The general conclusion from these calculations is that even in the early actinides, the 5*f* electrons play an important part in conduction and bonding, hybridizing with the *s* and *d* levels to give a broad band in the region of the Fermi level. It is suggested by Hill and Kmetko that this substantial *f* contribution is first appreciable in protactinium and persists through to plutonium and americium. The fact that *f* electrons take the place occupied by *d* electrons in the transition series gives rise to differences in melting and bonding behaviour, consistent with the highly directional bonding in many of the allotropes concerned. In order to correlate both melting point data and bond strengths based on interatomic distances with the electron configuration, it has been proposed that only *s*, *p* and *d* electrons contribute to bonding as it affects the melting process but that the hybridized *f* electrons augment the bonding forces which determine interatomic distances. It is also proposed that the appearance of superconductivity and the disappearance of magnetism as the series progresses is consistent with the broadening of the *f*-band.

The theoretical models mentioned above would require a substantial modification to treatments of the actinide elements based on the Zachariasen approach or on a thermodynamic approach adopted by Brewer[145] and others in which the contribution of the 5*f* electrons to bonding is considered to be slight. At present, this possibility is discounted by

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[142] J. Friedel, *J. de Physique et le Radium*, **19** (1958) 573.

[143] E. C. Ridley, *Proc. Roy. Soc.* A**243** (1958) 422 and **247** (1958) 199.

[144] H. H. Hill, in *Plutonium 1970 and Other Actinides*, Vol. I, p. 2, W. N. Miner (Ed.), AIME (1970).

[145] L. Brewer, in *Plutonium 1970 and Other Actinides*, Vol. II, p. 650, W. N. Miner (Ed.), AIME (1970).

the two schools and apparently no attempt has been made to adapt these empirical treatments accordingly.

4. CHEMICAL PROPERTIES OF THE METALS

Information on the chemical properties of the actinide metals is fairly sparse, indeed apart from thorium, uranium and plutonium it is almost non-existent. The reason for this is fairly obvious, most of the rarer actinide metals are sufficiently difficult to prepare that they are rarely if ever used as a stepping stone to some other compound. There are, however, considerable data available on the corrosion, compatibility and dissolution of thorium, uranium and plutonium obtained when the development of metallic reactor fuels was being undertaken.

4.1. Thorium

A recent article by Blumenthal and O'Boyle[146] has reviewed the corrosion and other reactions of the metal. Where no reference is given, the data provided here are taken from this article or from that by Flahaut[147], although some of the references in the latter are to very old work (pre-1920).

Massive thorium is relatively resistant to atmospheric corrosion under normal conditions. In a dry atmosphere a stable blue oxide coating is formed and even normal outdoor exposure merely darkens the surface and forms some superficial nodular growths. Long-term exposure to extremes of temperature and humidity have more effect, but protective coatings are possible. Finely divided thorium is pyrophoric in air.

In oxygen, the reaction follows a parabolic rate law, as long as the oxide formed is adherent, up to 350°C. From 350° to 450°C a linear law is obeyed, but above 450°C oxidation is accelerated, probably due to the high heat of formation of ThO_2.

Nitrogen is much less reactive than oxygen, but follows a similar pattern: parabolic rates at lower temperatures (up to 1370°C) when the process is controlled by diffusion, giving way to a linear rate at higher temperatures when the surface film cracks up. This film is an inner layer of ThN with an outer coating of Th_2N_3.

In air, variable rates are found[148], e.g. at 500°C two reports give weight gains of 8 and 0·4 mg/cm^2/hr. The faster corrosion rate is for material with a high oxygen content. In the more recent work two activation energies are given: 13 kcal/mole from 100° to 200°C and 18 kcal/mole from 400° to 900°C. Corrosion rates in still air are:

Temperature	100	150	200	300	400	500	600	700	800
Weight increase rate (mg/cm^2/hr)	0·0026	0·016	0·10	0·15	0·17	0·36	3·1	4·0	15·1

With hydrogen, the reaction follows a parabolic rate law, yielding the dihydride. The rate is not sensitive to purity and holds until about 20 % of the sample has reacted. The

[146] B. Blumenthal and D. R. O'Boyle, *Nucl. Eng. and Des.* **17** (1971) 281.

[147] J. Flahaut, in *Nouveau Traité de Chimie Minérale*, Vol. IX, p. 1039, P. Pascal (Ed.), Masson et Cie, Paris (1963).

[148] I. B. Roll, in *Nuclear Reactor Fuel Elements*, p. 176, A. R. Kaufmann (Ed.), Interscience–John Wiley, New York (1962).

reaction is fairly rapid: 3 mg/cm^2 are absorbed at a pressure of 120 mm in 1 hr at 480°C and in 15 min at 550°C. The reaction reverses at higher temperatures and this is used to prepare very finely divided (i.e. highly reactive) metal. Both this product and the hydride are pyrophoric in air.

The reaction of thorium with water vapour is a complex one. The main reaction is:

$$Th + 2H_2O = ThO_2 + 2H_2$$

The liberated hydrogen diffuses into the metal and ThH_2 can be seen metallographically. A logarithmic rate law has been observed, the weight gain being given by:

$$w = k \log (1 + 0{\cdot}45t)$$

with t in hours and w in mg/cm^2. At 70 mm partial pressure, typical weight gains in 30 min were: 0·2 mg H_2O/cm^2 at 200°C and 1·0 mg/cm^2 at 400°C, where the activation energy is 6·4 ± 0·7 kcal/mole. Above 400°C the reaction rate decreases again: at 550°C it is lower by almost a factor of 10.

In boiling distilled water at 100°C, thorium exhibits excellent corrosion resistance, but in autoclave tests above 200°C the corrosion increases rapidly as the oxide layer ceases to be protective: at 260°C the specimens lost 317 mg/cm^2/hr, about 30 times the rate at 200°C. Some improvement in corrosion is obtained by alloying with titanium or zirconium.

Thorium is relatively inert to acids and is attacked only very slowly by conc. or dil. HF, dil. HCl, dil. H_2SO_4, conc. H_3PO_4, or conc. $HClO_4$. Conc. H_2SO_4 dissolves it more readily, especially when hot, whilst *aqua regia* reacts rapidly. Conc. (12 N) HCl reacts to form a precipitate identified as ThO(X)H, where X is —OH or Cl[149]. Dilute HNO_3 dissolves thorium slowly, but conc. HNO_3 passivates it. Addition of fluoride ion, however, breaks up the oxide layer and attack by 8–16 N HNO_3 is then very rapid, being increased by about 10^4 times: a similar effect is shown by chloride ions with H_2SO_4[150]. An explosive residue (possibly of finely divided zirconium) is sometimes left if thorium–zirconium alloys are dissolved in HNO_3. Thorium does not react with molten alkali hydroxides, but molten $KHSO_4$ attacks it rapidly.

Thorium has a good resistance to the alkali metals at 600°C but reacts preferentially with any oxygen in the latter. Thorium is soluble in lead, bismuth, tin, antimony, indium, thallium, aluminium and gallium. Compatibility data with most usual canning materials are available. Stainless steel does not react at 600°C, but is attacked at 700°C.

Molten thorium reacts with all the normal oxide crucible materials: beryllia, magnesia and stabilized zirconia are better than the others.

The metal does not react with fluorine at room temperature. It reacts with phosphorus vapour at 450°C to form U_3P_4[151] and with H_2S[152] at low pressures and between 440° and 540°C to form $Th_{7-x}S_{12}$—typically the reaction with 2·5 μ thorium powder is complete in 1 hr at 540°C in 20 torr of H_2S.

The reaction with graphite between 900°C and 1200°C has been studied by Takeuchi *et al.*[153] Below 1200°C only ThC is formed (activation energy 53 kcal/mole), but above 1300°C ThC_2 is produced and the activation energy rises to 120.

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[149] R. S. Newbury and A. W. Searcy, *Inorg. Chem.* **1** (1962) 794, and L. I. Katzin, L. Kaplan and T. Steitz, *Inorg. Chem.* **1** (1962) 963.

[150] L. E. Kindlimann and N. D. Greene, *Corrosion*, **23** (1967) 35.

[151] H. Adachi and S. Imoto, *Nippon Genshiryoku Gakhaishi*, **9** (1967) 381.

[152] S. Toesca, F. LeBoete, J-C. Colson and D. Delafosse, *Comptes Rendus*, **C268** (1969) 1099.

[153] S. Takeuchi, T. Honma and T. Satow, *Trans. Jap. Inst. Met.* **5** (1964) 105.

4.2. Protactinium

The only available information on the chemical properties of protactinium metal is given by Cunningham[26]. He found that it reacted with 6N HCl at first, but that the reaction soon ceased as a protective layer formed. Similar behaviour was observed with hydrofluoric acid.

4.3. Uranium

Reaction with Gases and Water: Corrosion[28,36,154,155,156]

Uranium is much more reactive than thorium. It reacts with air even at room temperature in a massive form: the silvery lustre of freshly polished uranium quickly tarnishes to a golden yellow and after a few days to black. The oxidation is less in air with less than 1 % relative humidity, but increases in moisture above this level have little further effect on the corrosion rate. The oxide film formed is usually adherent and protective at room temperature. Finely divided uranium can be pyrophoric.

On heating massive uranium in air at low pressures, e.g. in a poor vacuum, "UO" forms on the surface above 600°C ("UO" probably contains some carbon and nitrogen). Below 600°C, UO_2 forms, sometimes epitaxially.

Heating massive metal in air at atmospheric pressure gives variable results, but ignition usually occurs at about 600°C to 700°C. Uranium must be machined in a fume hood since there is a radioactivity hazard and the swarf is also easily ignited. Variable results have also been obtained in oxidation studies in air and oxygen at lower temperatures: surface finish, purity, and, especially, water content of the atmosphere are important. Reported weight gains under nominally equivalent conditions can differ by as much as a factor of 40. Typically[28], a weight gain of 1 mg/cm² is reported after 10 hr at 185°C, 3 hr at 220°C, 0·4 hr at 260°C and 0·2 hr at 275°C. Two stages of oxidation have often been found[28,36], both stages fitting the equation:

$$\log K = \log A - E/2{\cdot}303RT$$

with:

Pressure (mm)	First stage		Second stage	
	E (kcal/mole)	A (μg/cm²/min)	E (kcal/mole)	A (μg/cm²/min)
20	$12{\cdot}4 \pm 0{\cdot}9$	$1{\cdot}7 \times 10^5$	$16{\cdot}8 \pm 0{\cdot}7$	$2{\cdot}0 \times 10^8$
50	$12{\cdot}6 \pm 0{\cdot}7$	$2{\cdot}4 \times 10^5$	$18{\cdot}2 \pm 0{\cdot}3$	$1{\cdot}4 \times 10^9$
200	$15{\cdot}0 \pm 0{\cdot}6$	$5{\cdot}3 \times 10^6$	$19{\cdot}9 \pm 0{\cdot}5$	$1{\cdot}0 \times 10^{10}$
800	$18{\cdot}7 \pm 2{\cdot}4$	$3{\cdot}1 \times 10^8$	$20{\cdot}5 \pm 0{\cdot}9$	$2{\cdot}1 \times 10^{10}$

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[154] V. I. Montenyohl, in *The Reactor Handbook*, Vol. I, p. 127, C. R. Tipton (Ed.), Interscience, New York (1960).

[155] R. Darras, in *Nouveau Traité de Chimie Minérale*, Vol. XV(1), p. 557, P. Pascal (Ed.), Masson et Cie, Paris (1960).

[156] J. T. Waber, *Progress in Nuclear Energy*, Series V: Metallurgy and Fuels, Vol. 4, p. 871, Pergamon Press (1961).

Increasing the air velocity increases the oxidation rate, e.g. at 805°C from 20 mg/cm^2/min at an air velocity of 1 cm/min to 70 mg/cm^2/min at 100 m/min. The corrosion rate also depends on the oxygen pressure, P, increasing as P^a where a increases from 0·09 at 125°C to 0·47 at 250°C.

At low temperatures (*c.* 100°C) the product oxide is UO_2: at 500°C it is U_3O_8. A mixture is found at intermediate temperatures. The maximum solubilities of oxygen in uranium are 10 ppm in α, 20 ppm in β, 30 ppm in γ and 50 ppm in the liquid.

At 805°C, uranium is completely oxidized in a time given by the expression:

$$t\,(\text{min}) = 0{\cdot}071\,(w/A) - 43$$

where w is the weight of the sample in milligrams and A is the original surface area in square centimetres.

The effect of moisture[36] on the corrosion rates at 200°C has been studied. Up to a few thousand ppm H_2O in air or oxygen there is little effect, but above this level the rates increase as shown below for air. (The rates in oxygen were not too dissimilar.)

	Oxidation rate (μg/cm^2/min)		
Concentration of water vapour (ppm)	10	1000	30000
1st stage	1	2	12
2nd stage	3	5	20

Comparison of corrosion rates in air and steam is interesting. At low temperatures steam is much more corrosive, but at 600°C the situation is reversed as the corrosion by steam increases much less rapidly with temperature: the activation energy is about 7 kcal/mole for steam compared to 16 kcal/mole for oxygen. As with oxygen, the product oxide is UO_2 below 200°C, but is almost all U_3O_8 above 400°C.

The reaction between uranium and water has been reviewed by Wanklyn and Jones[157]. UO_2 again forms and, at temperatures below 70°C, the oxide film initially has a protective action. Saturating the water with oxygen reduces the corrosion rate at 70°C by about 100 times compared to gas-free water. This explains why corrosion is most rapid at the bottom of a crack where the oxygen is rapidly used up. The activation energy for corrosion by hydrogen-saturated water is about 18 kcal/mole, typical rates of corrosion being 1000 mg/cm^2/hr at 230°C and 0·1 mg/cm^2/hr at 50°C.

Nitrogen does not react with uranium below 300°C and can be used as a protective atmosphere even above this temperature: the uranium will pick up any trace of oxygen in the atmosphere rather than form nitrides. Melting uranium in a nitrogen atmosphere leads to a nitrogen contamination of about 400 ppm. Heating uranium in nitrogen at 350°C to 650°C leads to the formation of $UN_{1\cdot75}$. The solubility of nitrogen in uranium is about 10 ppm at the melting point.

Uranium reacts readily with hydrogen, even below room temperature, when in powder form. The reaction with massive uranium depends on the surface finish, but unless the surface is clean (when reaction occurs immediately) there is an induction period before reaction commences. The reaction rate is highest at about 225°C when the penetration is 0·2 to 0·3 cm/hr, but decreases above this temperature and reaches zero when the dissocia-

[157] J. N. Wanklyn and P. J. Jones, *J. Nucl. Mater.* 6 (1962) 291.

tion pressure of UH_3 equals the external pressure (1 atm at 432°C). The solubility of hydrogen in uranium is 1·8 ppm at the α/β transformation temperature and 28 ppm at the melting point. The reaction of uranium with deuterium has also been studied[158]. The controlling-rate step is molecular diffusion across the UD_3 layer first formed.

Since CO_2 is the coolant in many uranium metal fuelled reactors, the corrosion of uranium in both CO and CO_2 has been studied[28,36,155] and this work has recently[159] been reviewed. In CO the reaction rate increases steadily with temperature[159] between 375° and 650°C with an activation energy of 38 kcal/mole. Above 700°C, the reaction rate increases up to 850°C but then decreases and the rate at 1000°C is two orders of magnitude smaller than it was at 700°C.

In CO_2, there is again little reaction below 350°C, but above this the rate increases, reaching about 35 mg/cm^2/hr at 700°C: the activation energy is about 30 kcal/mole. At 750°C the reaction is so rapid that spontaneous ignition occurs if the metal is finely divided: above 800°C even massive samples ignite. The reaction product in all cases is largely UO_2 mixed with some carbides. Reaction rates are increased by water vapour and the metal can ignite at temperatures as low at 400°C in CO_2 containing 80 ppm water. Oxygen increases the rate even more markedly: at 300°C, CO_2 containing 600 ppm reacts a thousand times faster than does a gas with less than 5 ppm.

Reaction with Acids[160,161]

Aqueous hydrofluoric acid reacts rather slowly with uranium at 80° to 90°C, probably because a protective film of fluoride forms: the presence of an oxidant does not increase the rate of reaction. The reaction with HF gas at 250°C is exothermic, yielding UF_4.

Concentrated hydrochloric acid (12 N) dissolves uranium rapidly, but when dilute (1–2 N) reacts much more slowly. Dilute sulphuric acid, even at boiling point, does not attack uranium much more than water does unless an oxidant is added, e.g. H_2O_2 or HNO_3, or unless electrolytic dissolution is used. Nitric acid only reacts slowly when dilute, but more rapidly when concentrated[162], the rate increasing a thousand-fold between 3 N and 12 N; the addition of nitrite ions also increases the rate. Dilute phosphoric acid reacts slowly, but organic acids do not attack metallic uranium unless a little HCl is added as a catalyst. The electrolytic dissolution of uranium metal fuel elements in nitric acid has also been studied[163]. Dissolution of uranium and its alloys to prepare solutions for analysis has been reviewed by Larsen[164].

Other Reactions

Uranium is not attacked by alkalis unless an oxidant is present, when a peruranate is formed[161].

Uranium is a powerful reducing agent[161] and reduces all the metallic oxides except CaO, BeO and ThO_2: Al_2O_3, Li_2O and MgO are only reduced at very high temperatures. In most instances the reduction leads to alloy formation. Metallic uranium reduces many of

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[158] R. M. Alire, B. A. Mueller, C. L. Peterson and J. R. Mosley, *J. Chem. Phys.* **52** (1970) 37.

[159] R. J. Pearce, I. Whittle and D. A. Hilton, *J. Nucl. Mater.* **33** (1969) 1.

[160] J. J. Katz and G. T. Seaborg, *The Chemistry of the Actinide Elements*, Methuen, London (1957).

[161] J. Elston, in *Nouveau Traité de Chimie Minérale*, Vol. XV(1), p. 557, P. Pascal (Ed.), Masson et Cie, Paris (1960).

[162] J. R. Lacher, J. D. Salzman and J. D. Park, *Ind. Eng. Chem.* **53** (1961) 282.

[163] G. R. Hall and D. H. Logsdail, *Trans. Inst. Chem. Engrs.* **41** (1963) 336.

[164] R. P. Larsen, *Anal. Chem.* **31** (1959) 545.

its quadrivalent compounds to the trivalent ones, e.g.

$$3UF_4 + U \rightarrow 4UF_3$$

The reaction with ammonia has been used to make the nitrides[166] and that with methane or propane to yield the monocarbide[165].

All the halogens react with uranium, the temperature at which the reaction takes place increasing with atomic weight. Fluorine reacts at room temperature with uranium powder, the latter becoming incandescent, but massive metal must be heated to start the reaction: the product is UF_6. Uranium powder must be heated to 150°C before it reacts with chlorine and to about 225°C for bromine and iodine. At 50°C and above uranium dissolves in the liquid interhalogen compounds such as BrF_3 to form the hexafluoride, the reaction being very exothermic. At 1250°C uranium displaces the alkali metals from their fluorides, forming uranium tri- and tetrafluorides[167]. Potassium fluoride reacts more strongly than LiF and NaF: CaF_2 is almost inert.

Sulphur, selenium and tellurium all react with the metal at about 500°C to yield the higher pnictides. These can be reduced to the monocompounds with further uranium. The chalcogens behave in a like manner, e.g. phosphorus reacts with uranium swarf at about 425°C[168]. The reactions of PH_3 and H_2S with finely divided uranium can be used to prepare UP and US respectively[167].

Carbon reacts with uranium above 800°C, but the product is usually inhomogeneous.

Uranium reacts with nitrosyl chloride to form $UCl_4 \cdot 2NOCl$[169].

Molten uranium reacts with most crucible materials, but graphite moulds are[170] satisfactory for large (over 4 in cross-section) castings whilst zirconia and fused magnesia crucibles are best for smaller applications. Calcium fluoride is also satisfactory, but has a relatively low melting point. The reaction rate of molten uranium with stainless steel[171] is very high just above the melting point (0·38 mm/sec at 1150°C), but surprisingly it is somewhat slower at higher temperatures (0·17 mm/sec at 1350°C).

There is a review available on the compatibility of uranium metal with the various nuclear cladding materials: Al, Zr, Mg, Be, steel, metals of Group VIII, W, Mo, V, Nb, and Ta[172].

4.4. Neptunium

There is little information available on the chemical properties of neptunium metal. It does not appear to oxidize as readily as plutonium at room temperature, but the oxide is not as protective as that of uranium.

The reactions with various acids at room temperature have been reported[61]. HCl reacts vigorously at all concentrations, completely dissolving the specimen. Nitric, sulphuric and acetic acids, on the other hand, react either slowly or not at all even after several days' exposure: this behaviour is more like that of plutonium than of uranium.

[165] F. Brown, F. S. Drummond, P. Ellis, P. T. Good and R. Lapage, in *Carbides in Nuclear Energy*, Vol. 2, p. 693, L. E. Russell, B. T. Bradbury, J. D. L. Harrison, H. J. Hedger and P. G. Mardon (Eds.), Macmillan, London (1964).

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[168] J. L. Driscoll and P. E. Evans, *J. Nucl. Mater.* **28** (1968) 311.

[169] C. C. Addison and N. Hodge, *J. Chem. Soc.* (1961) 2490.

[170] F. H. Hueston and R. S. Barclay, *Can. Mining Met. Bull.* **60** (1967) 795.

[171] C. M. Walter and L. R. Kelman, *J. Nucl. Mater.* **6** (1962) 281.

[172] H. E. Roellig, *Kernenergie*, **5** (1962) 641.

Neptunium reacts with hydrogen at 50°C to form the hydride and with graphite at 1200°C to form a mixture of NpC and Np_2C_3 in the ratio 5 to 1[52].

4.5. Plutonium

Plutonium metal is extremely reactive: the potential for the couple $Pu = Pu^{+++} + 3e^-$ is 2·03 volts, which places it between scandium and thorium in the emf series of the elements. It is so susceptible to atmospheric corrosion that storage at ambient temperatures is a difficult problem. The storage behaviour has been reviewed by Stakebake[173] and its corrosion by Waber[174].

The storage of plutonium is complicated by the fact that the self-heat caused by the α-decay ($\sim 2 \times 10^{-3}$ watts per gram for ^{239}Pu) is sufficient to keep the temperature of any but the smallest samples appreciably above ambient; large samples (i.e. over 100 g) can reach 90°C.

The oxidation is markedly affected by the presence of water vapour[173,174]. In one experiment, at 90°C in air, the oxidation rate increased from 0·004 mg/cm^2/hr when the relative humidity was 0·2 % (P_2O_5 dried) to 0·08 mg/cm^2/hr at 2 % humidity. Above this the rate remained roughly constant until about 80 % humidity when it again increased slightly. In another experiment, the weight gain after 1000 hr at 75°C was increased from 0·1 mg/cm^2 when the air was dried over $MgClO_4$ to 100 mg/cm^2 at 50 % relative humidity: in this temperature range the activation energy is 17 kcal/mole. The accelerating effect of water vapour is important up to 200°C, but above this there is little effect.

Even in an inert atmosphere (e.g. argon) plutonium will corrode rapidly if there is any water vapour present: indeed oxygen has an inhibiting effect since corrosion rates are higher in moist argon than in moist air—by a factor of 6 at 30°C and 95 % humidity. Various mechanisms have been proposed for this corrosion by moisture, usually involving the hydride as an intermediary. The corrosion rates are markedly higher for pure plutonium than for plutonium stabilized in the δ-phase by alloying with, say, aluminium or zirconium: a 6·0 at. % gallium alloy was stored in laboratory air at Los Alamos for 8 years without noticeable deterioration.

Plutonium is best stored in continuously circulating dried air[174]: storage at liquid nitrogen temperatures is also effective, but is only practicable for small samples or short periods. Storage in the presence of large amounts of molecular sieve has also been recommended[174], only interference colours being observed on the plutonium surface after 6 weeks under these conditions. Since hydrogen reacts readily with plutonium (see below), hydrogen-containing substances must be rigorously excluded from storage containers because they may be decomposed by radiolysis, liberating free hydrogen.

In dry oxygen, the oxide film growth is usually parabolic at low temperatures indicating a diffusion controlled process. A 200 Å thick oxide layer formed at 30°C in 4 hr on a 1 wt. % gallium alloy whilst at 80°C the layer was over 1000 Å thick after 1 hr. The activation energy was about 30 kcal/mole. In the β-phase (120–200°C) the behaviour was more complex, an initial parabolic rate with an activation energy of 30 kcal/mole being replaced by a linear rate with a lower activation energy: 17 kcal/mole.

Plutonium is pyrophoric under certain conditions[173–175]. Massive pieces, with a surface

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[173] J. L. Stakebake, *J. Nucl. Mater.* **38** (1971) 241.
[174] J. T. Waber, in ref. 64, p. 145.
[175] S. H. Pitts, *Nucl. Safety*, **9** (1968) 112.

area less than ~2 cm^2/g, have an ignition temperature of about 500°C whilst lathe turnings have ignited at 265°C and 140 mesh powder at 135°C. Burning plutonium forms 0·1–0·01 μ diameter particles, typically in 3–15 μ clusters. Ignition occurs less readily in lower oxygen-content atmospheres except for the fine powder where the ignition temperature is not altered significantly until the oxygen content is below 3 %. Other factors affecting the pyrophoricity are surface finish and impurity and alloying content: again δ-stabilized alloys have higher ignition temperatures. The presence of moisture and also of carbon tetrachloride lowers the ignition temperature. Pyrophoric products can be formed on plutonium stored in a closed container for any length of time and may ignite when the can is opened unless this is done in a protective atmosphere.

Some work has been reported[174] on the oxidation of plutonium at higher temperatures. Several teams have found a minimum in the initial parabolic oxidation rates in the δ-phase, e.g. Notley *et al.*[176] report weight gains after 20 min of 9 mg/cm^2 at 320°C, which decreased to 1 mg/cm^2 at 413°C before increasing again to 2·5 mg/cm^2 at 430°C. Recent work[177] has shown that below the minimum the product oxide is α-Pu_2O_3, whilst above this temperature it is largely composed of "PuO": the monoxide is probably only stable in the presence of excess metal or of carbon or nitrogen. Initially some samples display a parabolic rate law, but most follow approximately a linear gain in weight. This second stage has an activation energy of 16 kcal/mole between about 150° and 350°C.

Plutonium reacts fairly slowly with nitrogen: arc-melting in a nitrogen atmosphere converts only 70–80 vol. % of the plutonium to nitride and it was thought that an overpressure of nitrogen would have been necessary for complete conversion[178]. Plutonium powder, containing 4 at. % hydrogen, heated slowly in nitrogen, started reacting[179] at 300°C and the reaction was complete by 540°C.

Plutonium reacts readily with hydrogen to form the dihydride at low temperatures. The reaction reverses at higher temperatures[180], the decomposition pressure reaching 1 mm Hg at ~540°C and 760 mm at ~830°C. The reaction with deuterium is of course similar; the reaction rates have been studied by Bowersox[181]. He found that the rate is proportional to the surface area of the plutonium and to the square root of the deuterium concentration. The activation energy between 120° and 200°C is low: 2·9 kcal/mole.

Plutonium metal also reacts with the halogens and hydrogen halides to form the trihalides, with ammonia (gas) at 1000°C to form nitrides, with carbon monoxide to form carbides and with carbon dioxide to form a mixture of carbides and oxides. Finely divided plutonium reacts with propane to form the sesquicarbide[182] and with phosphorus at 600°C to form the monophosphide[183].

Plutonium dissolves in mercury[184], the solubility increasing from 2·1 g/l at 20°C to

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[176] M. J. F. Notley, J. A. C. Davidson and E. N. Hodkin, U.K. Atomic Energy Authority Report AERE-R 4070 (1962).

[177] K. Terada, R. L. Meisel and M. R. Dringman, *J. Nucl. Mater.* **30** (1969) 340.

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[179] J. A. Leary, W. C. Pritchard, R. L. Nance and M. W. Shupe, in *Plutonium 1965*, p. 639, A. E. Kay and M. B. Waldron (Eds.), Chapman & Hall, London (1967).

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[181] D. F. Bowersox, *Trans. Amer. Nucl. Soc.* **14** (1971) 578.

[182] F. Brown, F. S. Dennard, P. Ellis, P. T. Good, and R. Lapage, in *Carbides in Nuclear Energy*, Vol. 2, p. 693, L. E. Russell (Ed.), Macmillan, London (1964).

[183] J. B. Moser and O. L. Kruger, *J. Less-Common Metals*, **10** (1966) 402.

[184] D. F. Bowersox and J. A. Leary, *J. Inorg. Nucl. Chem.* **9** (1959) 108.

86 g/l at 325°C, the activation energy being 4·33 kcal/mole. This has been suggested[185] as the basis of a purification method: in conjunction with halide slagging, good separations from various transition metals can be achieved. The plutonium is recovered by distilling the mercury at 750°C. The solubility of plutonium in liquid sodium at 700°C is less than 2 ppm[189].

The reactions of plutonium with various acids are given in Table 10.

TABLE 10. THE REACTIONS OF PLUTONIUM METAL WITH ACIDS

Acid	Concentration	Reaction
H_2O	Pure	Slow reaction
HCl, HI, HBr	All concs.	Dissolves readily
$HClO_4$	Conc.	Rapid dissolution
H_2SO_4	Conc.	No reaction
	Dil.	Slow reaction
CH_3COOH	Conc.	No reaction
	Dil.	Slow reaction
HNO_3	All concs.	No reaction
H_3PO_4	85 %	Dissolves
CCl_3COOH	Conc.	Dissolves
NH_2SO_3H	Dil.	Rapid reaction

Plutonium is generally inert to alkalis. Scrap plutonium can be dissolved in nitric acid to which some HF has been added. Wilkinson and Peacegood found[186] that 240 g of plutonium would dissolve in 1 l. of boiling 16 N HNO_3 to which 4 g of HF had been added. The solution rate was about 0·2 g/cm²/hr. Adding hydrazine was also beneficial[187]: Hopkins *et al.* used 1–5 N HNO_3, with hydrazine at 0·1–2·0 N and HF at 0·0001 to 0·01 N. Solution occurred above 50°C. Electrolytic dissolution has been studied by Berry and Miner[188]: they found that the most rapid rates were obtained in 15 N HNO_3 at a high current density. The addition of fluoride ions was helpful, but the rate was not sensitive to concentration between 0·01 and 0·13 M.

Probably the best solvent for plutonium is ~1·7 M sulphamic acid. This must be kept cool (below 40°C) to prevent decomposition, but will then dissolve[190] plutonium with only a little sludge formation. For non-aqueous dissolution[191] a salt melt containing 10–40 wt. % NaCl in $ZnCl_2$ can be used. At 800°C the plutonium reacts with the zinc chloride to yield $PuCl_3$ and zinc: the latter may be separated by filtration through a pyrex frit.

Plutonium may be cleaned by dissolution of the oxide layer in nitric acid or, better, by electropolishing the sample as the anode in an electrolyte of concentrated orthophosphoric acid and ethylene glycol[192].

Plutonium was found to react with sea-water after an induction period, 90 % of a 60 mg sample dissolving in 5 hr. The maximum concentration of plutonium in the water was 67 μg/l[193].

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[192] M. Kolodney, U.S. Patent 3377257 (1968).
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The reaction of burning plutonium with various solvents has been investigated[194] by igniting plutonium coupons and dropping them into the solvent. Carbon tetrachloride reacted most vigorously, but the plutonium was extinguished in 1,1,1-trichloroethane, perchloroethylene, 1,1,2-trichloroethylene, chloroform, methanol and water.

The solubilities of selected solutes in liquid plutonium have been discussed by Bowersox[195]. At 850°C the solubilities are:

Element	C	V	Cr	Zr	Nb	Mo	Tm	Ta	W	Re
Solubility (wt.%)	2·7	2·3	4·4	8·0	2·1	3·1	5·0	0·2	0·017	2·8

The solubility data were used to calculate the partial molar enthalpies of solution over the temperature range 700° to 1000°C.

5. APPLICATIONS

5.1. Introduction

Prior to the development of the nuclear industry, significant application of the actinide elements had been confined to that of thorium in the incandescent gas mantle industry developed in the latter part of the nineteenth century. Present applications depend on the nuclear properties of the elements rather than the chemical properties of the element or compound used. The major use of thorium, uranium and plutonium in the nuclear power industry is well known, but the use of metal fuels is now limited, and ceramic fuels in which the physical properties of the compound play a major role are not considered in this article. The peaceful use of nuclear explosives and the potential applications of the higher actinides as energy and radiation sources which have become apparent and which are foreseen as eventually providing an economic contribution to the reduction of nuclear power costs[2,196] are discussed in sections 5.2 to 5.4.

5.2. Peaceful uses of nuclear explosives

Peaceful application of nuclear explosives became possible with the successful production of thermonuclear devices, which reduced the radiation problem of nuclear explosives to within manageable proportions and offered economic advantages over conventional techniques for large-scale excavations. Proposals put forward by the Lawrence Radiation Laboratory scientists were formalized in the Plowshare programme in June 1957. Potential uses identified were the excavation of canals, harbours and reservoirs, the recovery of valuable minerals from some kinds of mineral deposits, and the creation of underground caves for the storage of fluids. A limitation is imposed by the small number of geometric configurations possible for the cavities with no way of shaping the blast developed[197–199].

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[196] G. T. Seaborg, *Proc. 4th Int. Conf. on Plutonium and Other Actinides*, Santa Fe, New Mexico (1970).

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5.3. Energy sources

The future of transuranium nuclides as energy sources has been extensively discussed[196, 200–204].

The primary use of actinide elements as energy sources is in batteries based on thermoelectric conversion using the Seebeck effect. Though only 5–10 % of the heat is converted to electrical energy, the elimination of moving parts is a major advantage, reducing the space requirements and maintenance. Thermionic devices in which the nuclide provides the heat source for an electron-emitting surface have almost doubled the electrical yield, but the necessary high emission temperatures (~1800°C) limit their use (an actinium source has been used[6]; curium-244, potentially attractive, has the drawback of a high neutron flux from spontaneous fission); photoelectric batteries have a low efficiency, ~0·1 %, and are only practical with β-emitters, α-emission decomposing the phosphor too rapidly. ^{238}Pu has been used as a direct heat source in the water recovery system in the Apollo programme and in swimsuits developed for the Man-in-the-sea programme, and for maintaining the temperature of the experimental package left on the Moon by Apollo 11 during the long lunar night. The principle isotopes used in energy sources and their relevant properties are summarized in Table 11.

Space Applications

Radioisotope thermoelectric generators (RTG) find application where long life and high reliability are required, where long periods of darkness or great distances from the Sun, or orientation or other problems reduce the effectiveness of solar cells. Whilst most of the American SNAP generators (Systems for Nuclear Auxiliary Power) have used fission products (principally ^{90}Sr as $SrTiO_3$) as heat sources, actinide elements have found increasing use. SNAP 11 used 7·5 g ^{242}Cm (20 watts, electrical, W_{el}); SNAP 27 used 3·6 kg ^{238}Pu (56 W_{el}) in the Apollo 12 Lunar Surface Experimental Package. Seaborg[2,196] has predicted that extension of the TRANSIT, Department of Defense navigation satellite programme, PIONEER missions to Jupiter, and "Grand Tour" missions to Jupiter, Saturn and Pluto in 1977 and Jupiter, Uranus and Neptune in 1979 together with missions to Mars, weather satellites and manual orbiting laboratories could lead to a use of 200 kg of ^{238}Pu before the turn of the century.

Medical and Industrial Uses

The first human implantation of a heart pacemaker with a radionuclide battery was made in France in early 1970. To replace chemical batteries, which need changing every 1–2 years, a nuclide battery with a life of about 10 years and an electrical energy output of some 160 W_{el} energy is needed. The power requirement can be met by 200 mg of ^{238}Pu. Absence of γ-emission from the pure isotope minimizes shielding requirements. In practice ^{238}Pu formed by irradiation of ^{237}Np in power reactor fluxes contains ^{236}Pu at the 1 ppm level formed by the reaction

$$^{237}\mathrm{Np}\,(n, 2n)\,^{236}\mathrm{Np} \xrightarrow{\beta^-} {}^{236}\mathrm{Pu}$$

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[200] R. P. Baybarz, *Atomic Energy Review*, **8** (1970) 327.
[201] R. P. Perret and W. Hausserman, *Atompraxis*, **11** (1965) 508.
[202] W. C. Lyon, T. C. Bustard and A. C. Hiebert, *Nucl. Appl.* **4** (1968) 79.
[203] W. Muller, Euratom Report EUR-3893 (1968).
[204] H. J. Born, *Atompraxis*, **15** (1969) 32.

TABLE 11. PRINCIPLE ACTINIDE ISOTOPES USED IN ENERGY SOURCES

Isotope	Half-life	Mode of decay	Specific power (W_{th}/g)	Production	Useful characteristic	Form in which used	Use
^{227}Ac	22 y	α, β, γ	14·6	^{226}Ra (n, γ) ^{227}Ra $\xrightarrow{\beta^-}$	Use limited by heavy shielding requirement	Ac_2O_3	Thermionic RTG
^{228}Th	1·9 y	α, β, γ	170	^{227}Ac (n, γ) ^{228}Ac $\xrightarrow{\beta^-}$		ThO_2	RTG
^{238}Pu	86·4 y	α	0·54	^{237}Np (n, γ) ^{238}Np $\xrightarrow{\beta^-}$	Applications where a constant energy supply is required over a long period. Has the advantage of no emission*	PuO_2 PuN	RTG(SNAP) (Mechanical Heart) (Heart Pacer)
				^{241}Am (n, γ) ^{242}Am $\xrightarrow{\beta^-}$ ^{242}Cm $\xrightarrow{\alpha}$ ^{238}Pu	Isotopically more pure		Direct heat Neutron sources
^{242}Cm	162·5 d	α			High power density ideal for very small high output batteries		RTG(SNAP)
^{244}Cm	17·85 y	α			Applications where a constant energy source over a long period is required		RTG
^{252}Cf	2·646 y	α, SF			Good heat source. Associated shielding problems formidable. High production cost		Neutron source
^{241}Am	458 y	α			Particularly important γ source: 59·6 keV		Neutron source etc.

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* It should be noted, however, that ^{236}Pu produced by ^{237}Np $(n, 2n)$ forms high γ-emitters in its decay chain, chiefly ^{208}Tl. Irradiation of ^{237}Np with purely thermal neutrons minimizes this reaction and yields a virtually ^{236}Pu free product.

and decay products of ^{236}Pu, principally ^{205}Tl, emit hard γ-rays; irradiation of ^{237}Np in thermal fluxes can minimize this effect. Alternatively a more isotopically pure product can be obtained by the decay of ^{242}Cm or ^{242}Am formed by neutron irradiation of ^{241}Am. The neutron dose from (α, n) reactions can be reduced by use of the nitride, or forming the oxide from oxygen depleted in ^{18}O.

^{238}Pu is equally well suited for the power source in a totally implantable artificial heart. The maximum pumping energy required to maintain a human life is 7 W. Present conceptual designs call for a 30 W heat source, equivalent to about 54 g of ^{238}Pu. Implants in humans are unlikely before the end of the decade, but Seaborg suggests some 6000 kg of ^{238}Pu could be used in this way by the turn of the century.

5.4. Radiation sources

Neutron Sources

The principal sources are tabulated in Table 12.

TABLE 12.

Source	Half-life $t_{\frac{1}{2}}$	Type	Mean neutron energy (MeV)	Neutron yield (n/sec) per curie of radionuclide
^{238}Pu–Be	86·4 y	α, n	~4	$2{\cdot}8 \times 10^6$
^{239}Pu–Be	$2{\cdot}4 \times 10^4$ y	α, n	4·5	$2{\cdot}0 \times 10^6$
^{241}Am–Be	433 y	α, n	~4	$2{\cdot}0 \times 10^6$
^{242}Cm–Be	163 d	α, n	~4	4×10^6
^{244}Cm–Be	18·1 y	α, n	~4	3×10^6
^{252}Cf	2·65 y	Self-fissile	2·3	$4{\cdot}4 \times 10^9$

Neutron sources have found a wide use in activation analysis. J. L. Crandal, reviewing the general applications of transplutonium isotopes at the Third International Transplutonium Element Symposium, Argonne, October 1971, listed their use as on-line analysis in flowing process control of taconite iron ores—copper, nickel, cobalt and silver analysis; cement mixes—copper, iron and moisture; steel manufacture—manganese; coal—sulphur and ash. Neutron logging, e.g. of oil wells, is well established: thermalization and pulsed logs can give information on hydrogen content and porosity; activation of chlorine, aluminium, silicon and calcium, information on salt water incursion, shale and clay and strata identification. The use of water-moderated ^{252}Cf as a portable quasi-reactor for activation analysis has been described by Ricci and Handley[205].

The spontaneous fission source ^{252}Cf is of increasing importance and offers economic advantages for sources greater than 10^9n/ sec. Its specific advantages of high neutron yield, low evolution of heat (19 W/g from α-decay; 20 W/g from spontaneous fission) show to advantage in its development as a source for radiotherapy, both as an implantable source for cancer therapy[206–209] to kill diseased tissue and for neutron radiography where it

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[209] J. D. Goldstein, *Proc. 3rd Int. Transplutonium Element Symposium*, Argonne, 1971.

complements X-ray techniques, giving improved delineation of air-filled structures in soft tissues, and reducing interference from bones[210–213]. A further potential medical use would be on-site production of short-lived isotopes for diagnostic applications to reduce radiation damage to healthy tissues.

Gamma and Alpha Sources

^{241}Am is the only nuclide to find significant usage. The 59·6 keV gamma-ray emitted in about 35 % of the alpha-particle decays is useful in industrial gauge and measurement using transmission and back-scattering techniques. In medicine, gamma-ray back-scattering has been used in bone mineralization measurements and gamma-induced X-ray fluorescence for the analysis of iodine in the diagnosis of thyroid disorders. The latter technique is particularly effective for elements in the middle of the atomic series[214]. Gamma-absorption has also been used as a technique for solution analysis[208].

The high absorption of α-particles necessitates using sources bare or covered with very thin foil, limiting their potential application. Transmission (absorption) can be used for thickness gauging thin foils and in smoke detection. Alpha-induced ionization has been used in dew-point hygrometers for moisture detection. Backscattering of α-particles can be used in determining composition. ^{242}Cm was used on the Surveyor V lunar probe in α-source back-scattering measurements and analysis of (α, p) reactions, with the 6·44 MeV α-particles used to calibrate the α-spectrometer.

6. PHYSICAL PROPERTIES

6.1. Introduction

Until recently, general comparisons of the behaviour of the actinide elements have been restricted to comparatively few properties. As early as 1956 Cunningham and Wallmann[160] compared variations in heats of vaporization, melting point and atomic volume across the series with similar changes in the rare earth elements. Subsequent reviews[215–217] covered measurements of the simpler physical properties such as thermal expansion and electrical resistivity, but with an inadequate theoretical understanding of the band structure of these elements it was not possible to make more than generalized statements about these trends. A general summary of physical property data is given in Table 13. Subsequent sections discuss in more detail areas of current interest and where the theoretical band structure calculations outlined in section 3 have made possible more meaningful interpretations.

6.2. Melting points

The high melting point of thorium has been related to the existence of two electrons in the 6*d* shell with an associated high cohesive energy as seen in the transition elements

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[210] M. R. Hawkesworth and J. Walker, *J. Mat. Sci.* 4 (1969) 817.
[211] R. W. Reinig, *Isotop. Radiat. Technol.* 7 (1970) 62.
[212] J. P. Barton, *Isotop. Radiat. Technol.* 7 (1970) 285.
[213] J. L. Crandall, *Isotop. Radiat. Technol.* 7 (1970) 306.
[214] J. R. Rhodes, *Analyst*, **91** (1966) 683.
[215] A. S. Coffinberry and M. B. Waldron, *Progress in Nuclear Energy*, Series V, Vol. 1, p. 354 (1956).
[216] W. B. H. Lord, *Met. Rev.* **8** (1963) 277.
[217] M. B. Waldron, *Contemp. Phys.* **2** (1961) 385.

TABLE 13

	Ac	Th	Pa	U	Np	Pu	Am
Melting point (°K)	1373±50	2023	1840±10	1405	913	912·5	1446
Heat of fusion (kJ mole^{-1})		19·2		12·13	5·19	2·89	14·4
Vapour pressure (log P mm)		−29,400/T +10	(5·1 × 10^{-5} atm at 2200K)	−23,300/T +8·583	−20,600/T +7·98	−17,587/T +7·895	−13,162/T +7·563
Heat of vaporization (kJ mole^{-1})	(293)	575±2 (1857K)		422 (1800K)	394 (1800K)	334 (1100–1800K)	238
Entropy of vaporization (kJ mole^{-1} K^{-1})				0·108	0·098	0·094	
Boiling point (°K)		(5061)		(4200)	(4000)	(3460)	(2880)
Heat of sublimation (kJ mole^{-1}) (L. Brewer, *Plutonium 1970*)		573	527	527–540	439	351	276
Thermal conductivity (W m^{-1} K^{-1})		65		30	10	6	
Electrical resistivity ($\mu\Omega$ cm) (295K)		15·4	19·1	30·8	122	150	
Hall coefficient (V cm A^{-1} G^{-1})		$-11 \cdot 10 \times 10^{-13}$		$3 \cdot 93 \times 10^{-13}$	(32 to 41) × 10^{-13}	2·5 to 3·5 × 10^{-13}	
Characteristic temperature: (°K)							
Resistivity θ^e_D		144	108	121	137		
Elastic constants θ^r_D		164·2		248·2		204	
Thermal capacity θ^s_D		170		222	188	162	

The melting points of berkelium and curium are 1259 ± 25 K and 1623 ± 60 K respectively.

generally: the presence of some f character is responsible for the unusually low melting points in the middle of the series in comparison with metallic valency[218]. Recently Hill and Kmetko[144, 219] have discussed the role of the $5f$ electrons in the melting process and concluded that hybridized f electrons, whilst augmenting the bonding forces which determine interatomic distances, play no role in bonding as it affects melting.

6.3. Transport properties

Resistivity

Electrical resistivity measurements on uranium, neptunium and plutonium up to 1965 have been summarized by Meaden[220]. Measurements on very high purity thorium[221], on protactinium[222] and on single crystals of uranium[223] and plutonium[224] have subsequently been reported.

Thorium follows most closely normal metallic behaviour, the data fitting the Block–Gruneisen relation over a wide temperature range. However, at the lowest temperatures the ideal resistivity is proportional to T^3 rather than to the T^5 of the free electron model, and at higher temperatures the resistivity increases more rapidly than theory predicts. The characteristic temperature derived from resistivity data is compared to those derived from specific heat and elastic constants in Table 13.

The resistivity–temperature dependence becomes increasingly anomalous through the series, showing an increasing negative curvature at higher temperatures and high absolute values of resistivity (Table 13, Fig. 1). The α-, β- and γ-phases of neptunium all develop small negative temperature coefficients. At plutonium this tendency has developed into well-defined resistivity maxima. No absolute measurements have been reported for elements beyond plutonium, though the concavity towards the temperature axis is still present in americium[225]. Similar behaviour persists in actinide alloy systems, e.g. Pu_6Fe[222], ThPt, UPt and NpPt[226].

As in thorium, the ideal resistivities for α-uranium and α-neptunium are proportional to T^n with n close to 3[227], and a value of $n = 2{\cdot}8$ has been measured for protactinium[222]. For the α- and β-phases of plutonium the measured exponents are even lower, $n = 2{\cdot}3 \rightarrow 2{\cdot}8$ and $n = 1{\cdot}5$[229] respectively, but those values must be treated with some reservation, the strong temperature dependence at the lowest temperatures of measurement, $\sim 3\ \mu\Omega$ cm. deg^{-1} at 1·7K for β-phase plutonium, leading to difficulties in determining the ideal resistivity. Moreover, self-irradiation damage measurements[228, 230] and work on solid solution

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[225] M. B. Brodsky, Unpublished.

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[228] E. King, J. A. Lee, K. Mendelssohn and D. A. Wigley, *Proc. Roy. Soc.* **A284** (1965) 235.

[229] R. O. A. Hall and C. J. Purser, in *Rare Earths and Actinides*, Conf. Digest 3, Durham, Institute of Physics, London (1970).

[230] D. A. Wigley, *Proc. Roy. Soc.* **A284** (1965).

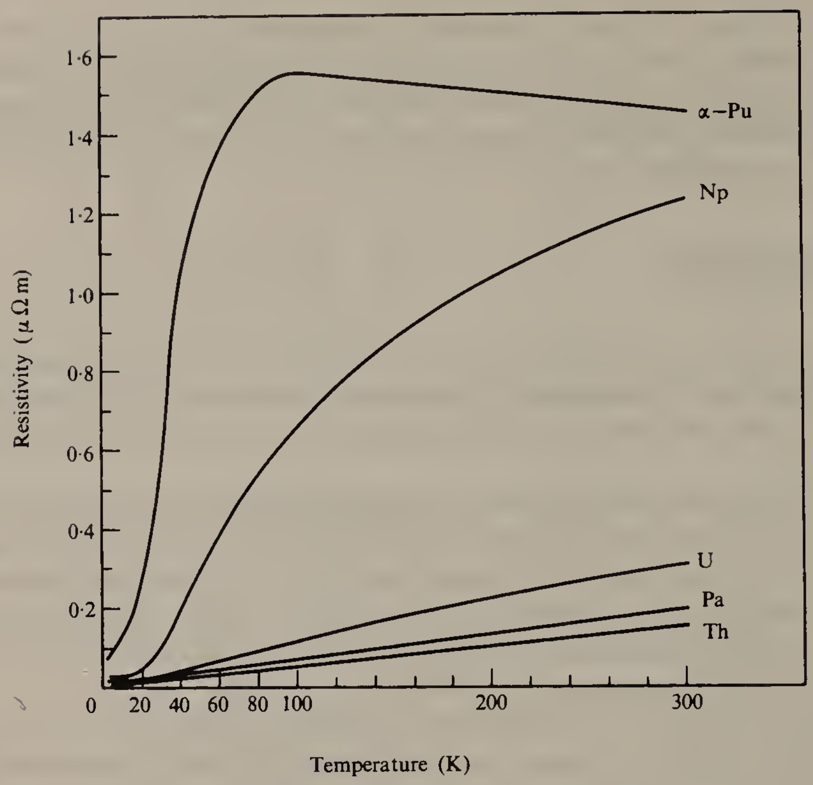

FIG. 1. Electrical resistivity of actinide metals

alloys[231] show that Matthiessen's rule is not obeyed; the resistivity due to impurity scattering is not temperature independent, and a simple subtraction of the residual to derive the ideal resistivity is not valid. Similar uncertainties are involved in any analysis of the temperature dependence above the maxima.

The earlier theoretical treatment of Smoluchowski[232], based on phonon cut-off at low temperatures and interband scattering above the maxima, which predicted a resistivity proportional to exp $(-\theta/T)$ and to $(1-CT^2)$ in these regions respectively, cannot be reconciled with experiment.

The Rocher treatment[233], which suggested a magnetic order–disorder transition at ~60K in α-plutonium with resonance scattering of the conduction electrons from localized bands, leads to a T^2 dependence at the lowest temperatures, However, a predicted T^{-1} dependence immediately above the transition due to local ordering does not fit experiment. Further, it is well established that the 5*f* electrons in plutonium are not localized as assumed in this model, but well hybridized with the *s–d* electrons.

Qualitatively the temperature dependence at low temperatures is in keeping with spin-dependent scattering, and strong support is given by specific heat measurements[234,235] which show small co-operative type contributions at ~60K in plutonium and ~45K in uranium (sections 3.4, 6.5), though the small size of these contributions precludes a simple magnetic ordering. The exact energy involved is difficult to determine: a simple

[231] C. E. Olsen and R. O. Elliot, *Phys. Rev.* A437 (1965) 139.

[232] R. Smoluchowski, *Phys. Rev.* **125** (1962) 1577.

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[234] J. A. Lee, K. Mendelssohn and P. W. Sutcliffe, *Proc. Roy. Soc.* **A317** (1970) 303.

[235] J. A. Lee, K. Mendelssohn and P. W. Sutcliffe, *Phys. Lett.* **30A** (1969) 106.

subtraction from the measured C_p of a graphical interpolation of the basic specific heat[236] curves gives 1·42 cal mol^{-1} and 0·026 cal mol^{-1} K^{-1} for the energy and entropy involved in plutonium; the corresponding figures for uranium are 1·86 cal mol^{-1} and 0·047 cal mol^{-1} K^{-1}. On the other hand, following for plutonium the procedure adopted[237,238] on α-manganese, and choosing a fixed θ_D of 161K, figures of 11·98 cal mol^{-1} and 0·145 cal mol^{-1} K^{-1} are derived for energy and entropy, respectively. These latter figures set an upper limit of $\sim$0·04 μ_B for the average spin on a plutonium atom. Similarly the absence of any significant anomaly in magnetic susceptibility measurements on single crystals[224] sets an upper limit of $\sim$0·01 μ_B on any random moment above $\sim$100K; neutron diffraction has failed to reveal magnetic ordering. Mössbauer effect measurements on α- and γ-phase plutonium[239] capable of detecting moments much less than 0·1 μ_B have also failed to provide evidence for local moments or magnetic order. To resolve this difficulty, Brodsky[240,241] has recently proposed that the primary scattering mechanism is spin-flip scattering from paramagnons in a fairly narrow $5f$ level. A model based on Doniach's[242] theory of spin fluctuations in narrow band intermetallic compounds gives a qualitative description of many of the features observed, predicting a T^2 temperature dependence at low temperatures and a tendency to negative resistivity coefficients above the characteristic spin fluctuation temperature. The measured temperature dependence at low temperatures does not distinguish between the various "magnetic" models and at elevated temperatures a comparison with theory is difficult because of the uncertainties of separating different contributing terms. An introduction to the extensive literature on self-irradiation damage studies, which offer the possibility of establishing the temperature dependencies of these terms, is given in the review by C. S. Griffin[243].

Hall Coefficient and Magneto-resistance

Hall coefficient measurements have been made on thorium, uranium, neptunium, and plutonium[224,244–249]. For α-uranium and the α-, β- and δ-phases of plutonium (Fig. 2) a strong temperature dependence in the electron–phonon small angle scattering region suggests a change in scattering mechanism rather than a change in carriers, and becomes more marked with increasing atomic number. Measurements on single crystals of α-plutonium[224] show fine structure. Behaviour is very sensitive to purity in this range. At higher temperatures the coefficients are more consistent and characterized by a weak temperature dependence. Typical values at 300K are given in Table 13.

Transverse magneto-resistances have been measured in thorium[245,247], α-uranium[245],

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[243] C. S. Griffin, K. Mendelssohn, J. A. Lee and M. J. Mortimer, in *Plutonium 1970 and Other Actinides*, Vol. 2, p. 635, W. N. Miner (Ed.), AIME (1970).

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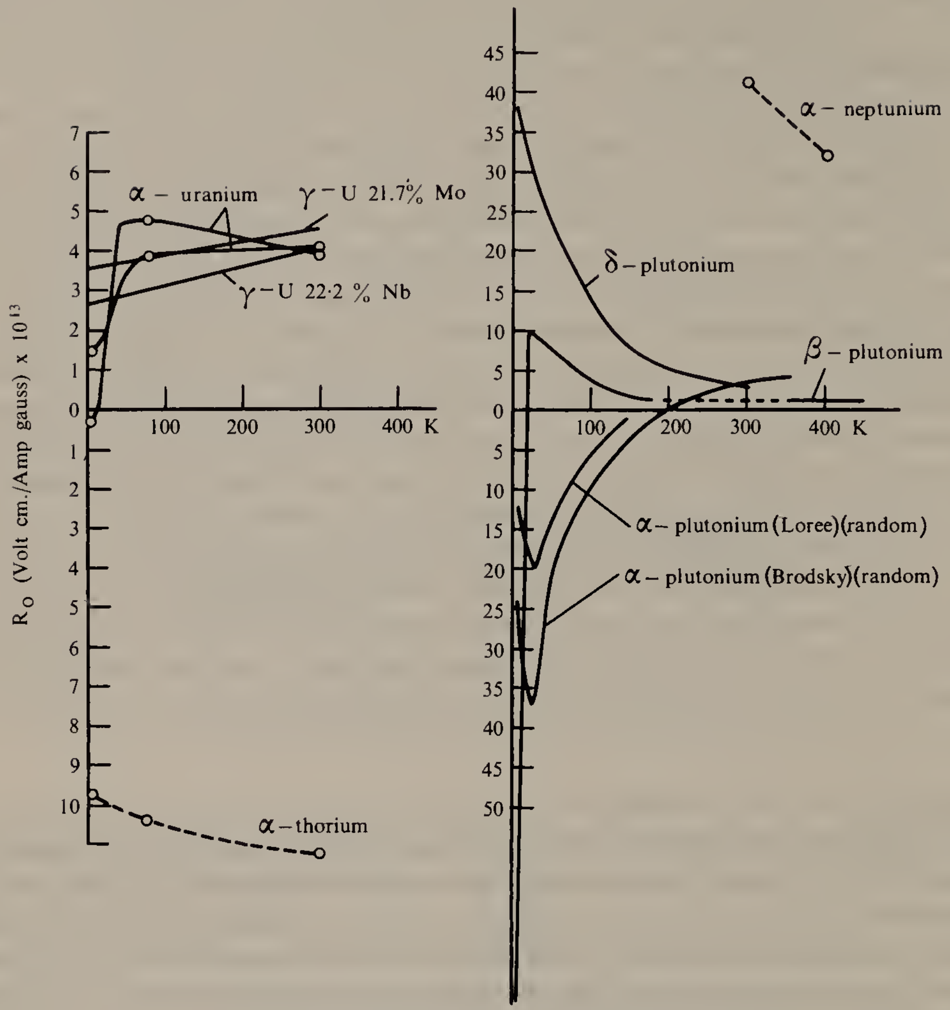

Fig. 2. Hall coefficients of actinide metals.

and in the α- and β-phases of plutonium[250]. For thorium and uranium the magneto-resistance in low fields is proportional to the square of the applied field, as simple theory predicts; at high fields the magneto-resistance is a linear function of the field in uranium. For α- and β-phase plutonium at low temperatures a negative magneto-resistance at low fields provides strong evidence for magnetic ordering; at high fields the magneto-resistance becomes positive and proportional to the square of the field.

With the reservations noted earlier, Brodsky has interpreted the actinide Hall coefficients in terms of a two-band model assuming a general band configuration $5f^{a+x}7s^{2-x}$, where a is two less than the number of electrons outside the radon core, the value of x increasing from zero in thorium to about 0·3 in plutonium. The magneto-resistance data are consistent with this interpretation though these electronic configurations are incompatible with the recent band structure models.

[249] T. R. Loree and H. T. Pinnick, *J. Nucl. Materials*, **38** (1971) 143.
[250] M. B. Brodsky, *Phys. Rev.* **163** (1967) 484.

De Haas–van Alphen Effect

Measurements of the de Haas–van Alphen effect have been limited to thorium[251,252]. The theoretical model of the Fermi surface developed by Gupta and Loucks[253,254] is in qualitative agreement with experiment.

Thermal Conductivity

Thermal conductivity measurements on thorium, uranium and plutonium at low temperatures have recently been reviewed[255]. The conductivities fall by nearly two orders of magnitude from ~68 W m^{-1} K^{-1} at 100K for thorium, through 34 W m^{-1} K^{-1} for uranium to a value of 3·5 W m^{-1} K^{-1} for plutonium at this temperature. The value for plutonium is the lowest reported for any pure metal. For uranium and plutonium a thermal conductivity rising with temperature, rather than falling to a constant value as in most metals, reflects the progression towards a negative temperature dependence of electrical resistivity (Fig. 3).

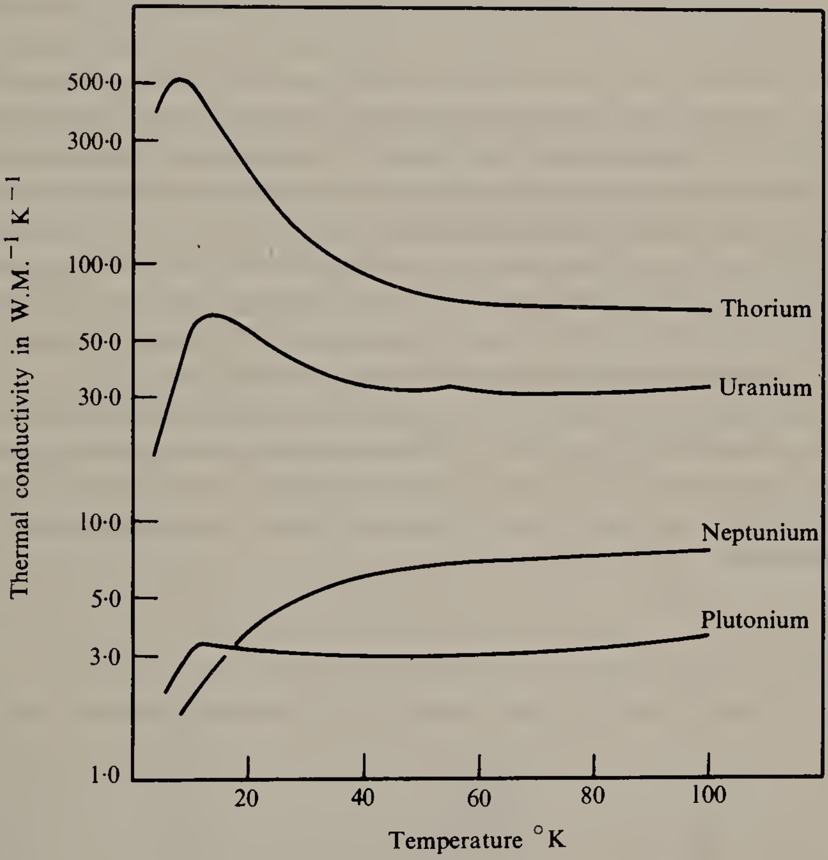

FIG. 3. Thermal conductivity of actinide metals.

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[251] A. C. Thorsen, A. S. Joseph and L. E. Valby, *Phys. Rev.* **162** (1967) 574.

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[254] R. P. Gupta and T. L. Loucks, *Phys. Rev.* **133** (1971) 1834.

[255] R. O. A. Hall and J. A. Lee, in *Plutonium 1970 and Other Actinides*, Vol. 1, p. 35, W. N. Miner (Ed.), AIME (1970).

For normal metals, where the lattice thermal conductivity is small compared with that of the electrons, measured thermal and electrical conductivities can be directly related. The Wiedmann–Franz–Lorenz (W.F.L.) rule holds at low temperatures, where impurity scattering dominates, and at high temperatures where nearly elastic phonon–electron scattering predominates; the Lorenz ratio, $L = \lambda_e \rho T^{-1}$, relating the electronic thermal conductivity, λ_e, to the electrical resistivity, ρ, approaches a constant value, $L_0 = 2{\cdot}45 \times 10^{-8}\ \mathrm{V^2\,K^{-2}}$ in these limits. At intermediate temperatures the W.F.L. rule breaks down and the Lorenz ratio shows a minimum, the inelastic phonon–electron scattering limiting the thermal conductivity more than the electrical resistivity in this region; the effect of impurities is to suppress this minimum.

The validity of applying this type of analysis to the actinide metals is not immediately obvious. Even in thorium this behaviour is followed only qualitatively; for the highest purity samples the "Lorenz ratio", derived by substituting the measured thermal conductivity, i.e. including any lattice term, starts at approximately L_0, drops sharply to the expected minimum at 15K, but then rises to a high value of $3 \times 10^{-8}\ \mathrm{V^2\,K^{-2}}$ at higher temperatures, suggesting some lattice contribution. The higher actinides show more marked deviations; for high purity plutonium the "Lorenz ratio" derived from the measured thermal and electrical conductivities is reported as rising from a value $\sim 3{\cdot}4 \times 10^{-8}\ \mathrm{V^2\,K^{-2}}$ at 8K to a maximum $\sim 8 \times 10^{-8}\ \mathrm{V^2\,K^{-2}}$ at 50K with a still high value $\sim 5{\cdot}7 \times 10^{-8}\ \mathrm{V^2\,K^{-2}}$ at 100K; at room temperature the value is close to the Lorenz number. However, a careful comparison of the effect of self-irradiation damage on the thermal and electrical conductivities in the plutonium case shows that the Lorenz ratio behaves sensibly as for a normal metal; the scattering mechanisms giving rise to the abnormal electrical resistivity–temperature behaviour do not significantly affect its form.

The separated lattice term is significant and of a similar order of magnitude: $\sim 10\ \mathrm{W\,m^{-1}\,K^{-1}}$ at 100K in thorium and uranium and $\sim 3{\cdot}5\ \mathrm{W\,m^{-1}\,K^{-1}}$ in plutonium.

The measured thermal conductivities of neptunium of moderate purity, $\sim 8\ \mathrm{W\,m^{-1}\,K^{-1}}$ [256], and of δ-phase plutonium alloys[257] fit well into this sequence.

Reliable data at elevated temperatures are limited. For the β- and γ-phases of uranium[258] slightly higher conductivities than in the α-phase are measured but with a nearly normal Lorenz number. Wittenberg *et al.*[259] have measured the thermal diffusivity of the δ- and ϵ-phases of plutonium, and the conductivity in the liquid state; the derived thermal conductivities are given in Table 14.

TABLE 14

Phase	Temperature (°C)	Thermal conductivity (cal cm^{-1} sec^{-1} K^{-1})	Electrical resistivity ($\mu\Omega$ cm)	$L \times 10^8$ (V^2 K^{-2})
α	25	0·016	145	3·2
δ	450	0·014	100	0·8
ϵ	550	0·012	110	0·7
liquid	700	0·016	—	—

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[256] R. O. A. Hall, Unpublished work.

[257] J. F. Andrew, *J. Nucl. Materials*, **30** (1969) 343.

[258] G. Erez and U. Even, *J. Appl. Phys.* **37** (1966) 1633.

[259] L. J. Wittenberg, T. K. Engel and G. A. Vaughn, in *Plutonium 1970 and Other Actinides*, Vol. 1, p. 48, W. N. Miner (Ed.), AIME (1970).

The thermal conductivity of liquid plutonium is the smallest value reported for any liquid metal and the ratio of the solid and liquid thermal conductivities is anomalously low, as is the Lorenz ratio for the δ-, ϵ- and liquid phases. No plausible explanation has been suggested for these effects.

Superconductivity

The data up to 1971 have been well reviewed by Hill[260]. Where no specific reference is given, details will be found in that paper.

Thorium. Magnetic susceptibility and specific heat measurements have shown thorium to be a bulk superconductor with $T_c = 1{\cdot}374 \pm 0{\cdot}001$K and a value of $C_{es}(T_c)/\nu T_c = 2{\cdot}42$[261], in good agreement with the 2·43 predicted by the Bardeen–Cooper–Schriefer (B.C.S.) theory; $C_{es}(T_c)$ is the superconducting electronic specific heat at the transition temperature and ν the temperature coefficient of the normal electronic specific heat. The transition temperature, as in most superconductors, is depressed with increase in pressure; $dT_c/dP = -1{\cdot}7 \pm 0{\cdot}2 \times 10^{-5}$ K.bar^{-1}. The critical field deviates in a negative sense from a parabolic law, approximating to the weak coupling case of the B.C.S. theory to within ~0·3 %. The energy gap at $T = 0$ is $3{\cdot}53\ kT_c$ as compared with the B.C.S. prediction of $3{\cdot}52\ kT_c$, and the discontinuity in the specific heat at T_c is $1{\cdot}42\ \nu T_c$ as compared with the $1{\cdot}43\ \nu T_c$ of theory.

Dilute thorium–uranium alloys exhibit normal and superconducting state anomalies due to uranium 5*f* moments similar to those for 3*d* solutes dissolved in noble and simple metal hosts, the uranium impurities showing weakly magnetic behaviour. The alloys, however, show a specific heat jump at the superconducting transition following the B.C.S. law of corresponding states, suggesting the system is essentially non-magnetic at superconducting temperatures[202]. Similar behaviour is shown by curium; gadolinium follows the Abrikosov–Gor'kov theory. The effect of small additions of thorium, protactinium, uranium and americium on the superconducting behaviour of fcc lanthanum is consistent with valencies of 4, 5, 6 and 3, respectively; for neptunium and plutonium the *f* electrons appear to mix with the conduction band of lanthanum and the behaviour is more complex[263].

Protactinium. Matthias'[264] empirical rule for the transition elements predicts that superconductivity is favoured for valencies of 3, 5 and 7. On this basis, protactinium with a valency of 5 might be expected to become superconducting with a transition temperature higher than that for thorium. A broad transition starting at ~1·4K and incomplete by 0·5K was reported for a sample prepared by the Van Arkel process[265], but not confirmed in subsequent work[222] on metal of a similar purity prepared by reduction of the fluoride by zinc–magnesium alloy, removal of the excess alloy by distillation and consolidation of the protactinium sponge by arc melting. A more detailed study[266] suggests an explanation

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[260] H. H. Hill, *Physica*, **55** (1971) 186, and references therein.

[261] J. E. Gordon, H. Montgomery, R. J. Noer, G. R. Pickett and R. Tobon, *Phys. Rev.* **152** (1966) 152.

[262] C. A. Luengo, J. M. Cotignola, J. G. Sereni, A. R. Sweedler, M. B. Maple and J. G. Huber, *Solid State Communications*, **10** (1972) 459, and references therein.

[263] H. H. Hill, J. D. G. Lindsay, R. W. White, L. B. Asprey, V. O. Struebing and B. T. Matthias, *Physica*, **55** (1971) 615.

[264] B. T. Matthias, *Progress in Low Temperature Physics*, J. C. Garter (Ed.), North Holland, Amsterdam (1957).

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[266] R. D. Fowler, L. B. Asprey, J. D. G. Lindsay and R. W. White, Los Alamos Report 72/919. To be published in *Proc. 13th Low Temperature Conf.* Boulder, 1972.

for this discrepancy. A broad superconducting transition below 1·4K is confirmed for samples with the tetragonal structure ($a_0 = 3{\cdot}932$ Å, $c_0 = 3{\cdot}238$ Å) prepared by the Van Arkel process; the transition temperature is depressed with increasing pressure. For samples prepared by arc melting, a fcc phase ($a_0 = 5{\cdot}02$ Å) was found with only traces of the tetragonal phase[116]. No superconducting transition was observed for largely fcc-phase samples. Partial transformation back to the tetragonal α-phase was observed on cycling under pressure, though the superconducting transition temperatures were low, strain inhibiting the transition. The tetragonal phase showed a slight positive pressure dependence of T_c; $dT_c/dP = 0{\cdot}04$ K.bar^{-1}.

Uranium. The two high-temperature phases of uranium, β and γ, can be stabilized down to low temperatures by small solute additions. For β-phase uranium stabilized with 2 wt. % rhodium or platinum, sharp superconducting transitions were observed at 0·96K and 0·87K respectively[267]; the superconducting critical temperature of γ-uranium stabilized with 15 wt. % molybdenum is 2·1K. The γ-uranium alloy shows a small positive pressure dependence $\partial T_c/\partial P \simeq 0{\cdot}9 \times 10^{-5}$ K.bar^{-1}; for β-phase uranium a pressure dependence $\partial T_c/\partial P < (2-3) \times 10^{-5}$ K.bar^{-1}. Measurement of the isotope effect in γ-uranium has shown $T_c \propto M^\alpha$, with $\alpha = -0{\cdot}53 \pm 0{\cdot}02$, very close to the B.C.S. prediction.

The position in pure uranium is more complex and interpretation of results on superconductivity needs careful assessment of the experimental conditions. The well-established second order phase change at 43K from α to α_0 has been discussed in section 3.4. Recently two first order transitions have been observed at 22K and 37K in dilatometric measurements on single crystals and confirmed by specific heat measurements, though these transitions are not evident in polycrystalline material where, presumably, strains suppress the phase changes. An important feature of Crangle's[268] specific heat data is that they show unambiguously that, although in quenched samples some α-phase may be retained[269], the phase present below 43K in polycrystalline samples is the α_0 phase.

Values of T_c determined from either magnetization or resistivity measurements vary from 0·2K, with a sharp transition, for a good single crystal, to 1·5K, with a broad transition, for cold-worked polycrystalline samples. Specific heat measurements have shown these transitions to result from a connected network of superconducting filaments rather than bulk superconductivity. Measurements of the pressure dependence of T_c with either single or polycrystalline samples show the temperature of the transition, as measured by resistivity or magnetization techniques, to rise with pressure up to ~9 kbar, passing through a broad maximum before decreasing. The single crystal data show fine detail[270]; dT_c/dP has a high positive value up to ~6 kbar where it shows a sharp change to approximately zero, changes sharply again at 8 kbar to an intermediate positive value rising to a maximum T_c of ~2·2K near 12 kbar, above which dT_c/dP is negative and remains negative to at least 80 kbar. Specific heat measurements (Ho *et al.*[263]) made at 10 kbar have shown that the superconducting transitions measured at this pressure are representative of bulk superconductivity.

An appreciation of this complex position is important. The isotope effect, measured (by Fowler *et al.*[263]) at 11 kbar to ensure bulk superconductivity, differs radically from the predictions of the ordinary B.C.S. theory, the exponent being large and positive: $T_c \propto$

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[267] B. T. Matthias and T. H. Geballe, *Science*, **151** (1966) 985.

[268] J. Crangle and J. Temporal, To be published in *J. Physics F.*

[269] A. Hough, J. A. C. Marples, M. J. Mortimer and J. A. Lee, *Phys. Lett.* **27A** (1968) 222.

[270] T. F. Smith, Superconductivity in *d*- and *f*-band metals, D. H. Douglass (Ed.), *Proc. AIP Conf.* Vol. 4, p. 293 (1972).

$M^{2\cdot 2}$. This dependence is in good agreement with that deduced from the pressure dependence at the lowest pressure where $dT_c/dP \simeq 10\cdot 5 \times 10^{-2}$ K.bar^{-1}; above 11 kbar, however, as Mortimer[222] has pointed out, a pressure dependence of $dT_c/dP \simeq -2\cdot 5 \times 10^{-2}$ K.bar^{-1} indicates a normal isotope effect with $T_c \propto M^{-0\cdot 48}$. To explain the anomalous isotope effect, which they felt could not be reconciled with the normal electron–phonon pairing mechanism, Fowler *et al.* postulated a coupling through polarization effects involving the f electrons. It has, however, been shown that this mechanism is inadequate, but that the presence of a peak in the f-band density of states $N_f(E)$ either just above the maximum phonon frequency ω_m or just below any peak in the phonon spectral weight function $B(\omega)$ can lead to the observed pressure and isotope dependencies and that a peak in $N_f(E)$ above ω_m is the more reasonable[271].

Both Smith and Mortimer have attempted to correlate the experimental observations in pressure–temperature phase diagrams; Smith's correlation, based on single-crystal data, has postulated phase boundaries running from the 43K, 37K and 22K transitions at zero pressure to terminate at a phase boundary defined by the superconducting transition under pressure, and at 12, 8 and 6 kbar respectively, i.e. he assumes a change from a positive isotope effect to the normal effect within a single superconducting phase field. In Mortimer's simplified diagram based on polycrystal data it has been found necessary to postulate a new pressure-induced phase, α', forming at a triple point with the α- and α_0-phases at $\sim 2\cdot 5$ kbar and 35K: this phase exhibits the positive isotope effect, the α-phase the normal effect at higher pressures. Isotope effect measurements on the plutonium in α-uranium solid solution alloys, in which Marples[272] has shown suppresion of the 43K transition, could help to resolve this difference.

Neptunium and plutonium. Meaden and Shigi (1964) were unable to detect a superconducting transition in neptunium down to 0·41K and in plutonium to 0·5K.

Thermoelectric Power

The thermoelectric power, S, is a sensitive function of the form of the Fermi surface. For simple metals theory predicts $S \propto (1/T)\,(dn/dE)_F$, $(dn/dE)_F$ being the change in density of states at the Fermi surface. The validity of this relationship in the case of the actinides is questionable[273]. The measured values show strong temperature dependencies and are purity sensitive.

G. T. Meaden[274] has made detailed measurements on thorium, uranium, neptunium and plutonium at low temperatures. Unless stated otherwise, references are listed in this paper. His results are summarized in Table 15. In Fig. 4 the data for thorium are for a sample of different purity.

For thorium at elevated temperatures the thermoelectric power remains large and negative[275]. The thermoelectric powers of the β- and γ-phases of uranium[276] remain high and positive (+20 μV K^{-1} for β-uranium at 980K; +22 μV K^{-1} for γ-uranium at 1100K), of neptunium, large and negative (−42 μV K^{-1} for β-neptunium at 700K; −26 μV K^{-1} for γ-neptunium at 875K). For the plutonium phases Lee and Hall (1959) and Costa (1960) have shown the high positive value for α-plutonium to fall with temperature through the

[271] J. W. Garland and F. M. Mueller, *Bull. J. Amer. Phys. Soc.* **13** (1968) 75.
[272] J. A. C. Marples, *J. Phys. Chem.* **31** (1970) 2421.
[273] C. Domenicali, *Phys. Rev.* **117** (1960) 984.
[274] G. T. Meaden, *Proc. Roy. Soc.* **A276** (1963) 553.
[275] J. H. Bodine, Jr., *Phys. Rev.* **102** (1956).
[276] A. Dahl and M. S. Van Dusen, *J. Nat. Bur. Standards*, **39** (1957) 53.

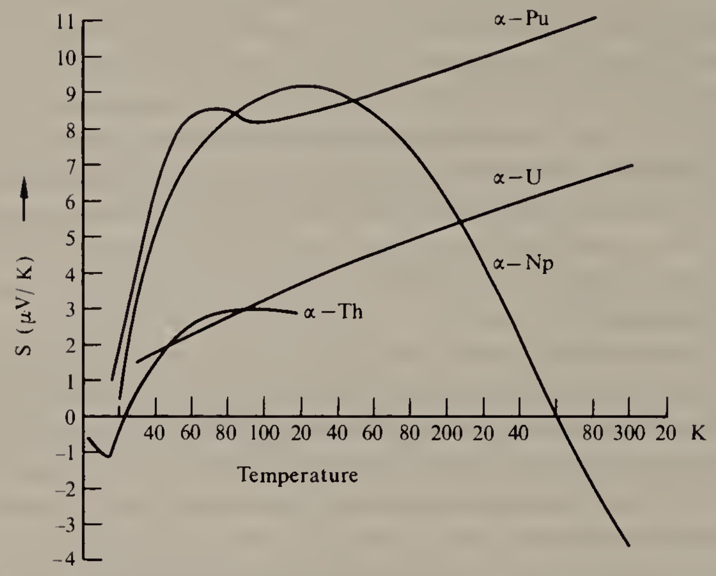

FIG. 4. Absolute thermoelectric power of actinide metals.

higher temperature phases to δ′, rising again to the ϵ-phase (10 μV K^{-1} for β-plutonium at 400K; 4 μV K^{-1} for the γ-phase at 500K; 3 μV K^{-1} for the δ-phase at 600K; 2 μV K^{-1} for the δ′-phase at 720K; 4 μV K^{-1} for the ϵ-phase at 800K).

Measurements at low temperatures have also been reported for δ-plutonium stabilized with various alloying additions by Lee *et al.*[277], by Lallement and Solent[278], and by Brodsky[278] and a theoretical analysis given by Kmetko[278].

TABLE 15[a]

Temperature (K)	Thorium (μV K^{-1})	Uranium (μV K^{-1})	Neptunium (μV K^{-1})	Plutonium (μV K^{-1})
20	−1·5	+1·2	+0·1	+1·0
40	0	+1·8	+5·8	6·0
60	+1·0	+2·3	+7·2	8·1
80	+1·2	+2·9	+8·1	8·4
100	+1·1	+3·2	+8·8	8·1
150	+0·6	+4·2	+9·0	8·6
200	−0·6	+5·2	+5·8	9·6
300	−3·1	+7·1	−3·2	11·4

[a] G. T. Meaden, *Proc. Roy. Soc.* A276 (1963) 553.

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[277] J. A. Lee, R. O. A. Hall, E. King and G. T. Meaden, in *Plutonium 1960*, p. 39, E. Grison, W. B. H. Lord and R. D. Fowler (Eds.), Cleaver-Hume Press, London (1961).

[278] R. Lallement and P. Solente, in *Plutonium 1965*, p. 147, A. E. Kay and M. B. Waldron (Eds.), Chapman & Hall, London (1967); M. B. Brodsky, *ibid.*, p. 210; E. A. Kmetko, *ibid.*, p. 222.

6.4. Magnetic properties

Susceptibility

In comparison with the $3d$ or the $4f$ transition metals the magnetic behaviour of actinides is complex. In the case of the transition metals the spin–orbit coupling is quenched, and the ground state spin can be described by the quantum number S, alone. In the rare earths the spin–orbit coupling is described by the Russell–Saunders scheme, $J = L + S$ with J a good quantum number. The $4f$ electrons are localized; their extent in space, measured relative to the metallic radius, is about half that of the $3d$ transition metal electrons. They contribute little to bonding and are relatively unchanged by alloying or compound formation. The $5f$ electron shells are less concentrated near the nucleus and less well screened by outer filled shells than are the $4f$. While neutron scattering measurements indicate a spin density distribution quite localized in space, the spatial extent is more comparable to that of the $3d$ electrons and, therefore, the $5f$ electrons enter into bonding processes; $5f$–$6d$ and $5f$–$7s$ hybridization is significant. Spin–orbit coupling is less simple than in the lanthanides; from infrared spectroscopy on solutions of trivalent actinides, Carnell and Wybourne[279] conclude that the spin–orbit constant for the actinides would be about 2–3 $\times$ 10^3 cm^{-1}, that is about twice that for lanthanides. Magnetic[280] and spectroscopic[281] studies of ionic compounds show that the crystal-field strengths are $\sim 10^3$ cm^{-1}, an order of magnitude larger than the lanthanides. This combination of strong spin–orbit coupling and crystal–field interactions is best described by an intermediate coupling system rather than the Russell–Saunders scheme: the susceptibility, χ, is often substantially less than expected from (L–S) coupling; the spin, orbital and total angular momentum numbers (S, L and J) are not good quantum numbers.

The experimental data have been reviewed by Brodsky[282] and references are included in that paper unless otherwise noted; the review also covers work on intermetallic compounds including the chalcogenides and pnictides.

The effective total susceptibility measured is essentially due to the hybridized $5f$–$6d$ states: the $7s$ electrons contribute only weakly; Fournier[283] estimates the core diamagnetism as about one tenth of the measured susceptibility and, with a high density of states at the Fermi surface and large effective mass for the electrons, the Landau diamagnetism ($\chi_L \propto 1/m^*$) is also weak. Three types of behaviour may be distinguished

(a) Thorium behaves as a transition metal with pronounced $6d$ character. The $5f$ level lies well above the Fermi level. The susceptibility is large (Table 16), increasing only slightly with temperature, indicating an orbital moment quenched by the crystal field and a flat density of states curve at the Fermi level. Fournier has measured the magnetization up to 10 kOe.

(b) For protactinium, uranium, neptunium and plutonium $5f$–$6d$ hybridization is significant. The density of states deduced from specific heat and magnetic susceptibility, and given in Table 16, is high and the exchange enhancement factor $S = \chi/\chi_\gamma$, calculated from room temperature susceptibilities, large. The broadening of the

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[279] W. T. Carnell and B. G. Wybourne, *J. Chem. Phys.* **40** (1964) 3428.

[280] G. A. Candela, C. A. Hutchinson Jr. and W. B. Lewis, *J. Chem. Phys.* **30** (1959) 246.

[281] R. A. Salter, D. Young and C. M. Gruen, *J. Chem. Phys.* **33** (1960) 1140.

[282] M. B. Brodsky, Magnetism and magnetic materials, H. C. Wolfe (Ed.), *Proc. AIP Conf.* Vol. 5, p. 611 (1971).

[283] Jean-Marc Fournier, *Ann. Phys.* **6** (1971) 159.

TABLE 16

	Structure	Configuration of free atom	Molar susceptibility			Derived density of states at the Fermi surface (states/eV atom)		
			K	χ_n (emu mol^{-1})	Temperature dependence	From specific heat	From susceptibility	Exchange enhancement factor
α-Th	Fcc	$6d^27s^2$	300	93×10^{-6}[a]	Increasing with temperature	1·0	2·2	2·2
α-Pa	Tetragonal	$5f6d^27s^2$	300	270×10^{-6}	Practically temperature independent		4·1	
α-U	Orthorhombic	$5f6d^37s^2$	300	387×10^{-6}	Slight increase with temperature	2·3	5·8	2·5
β-U[b]	Tetragonal		975	480×10^{-6}		4·0	7·2	1·8
γ-U[b]	Bcc		1100	490×10^{-6}		2·8	7·3	2·6
α-Np	Orthorhombic	$5f^46d7s^2$	300	557×10^{-6}		3·0	8·6	2·8
α-Pu	Monoclinic	$5f^67s^2$	300	514×10^{-6}		3·4	8·1	2·4
β-Pu[a]	Bc monoclinic		410	603×10^{-6}				
γ-Pu[c]	Fc orthorhombic		500	573×10^{-6}				
δ-Pu[c]	Fcc		600	562×10^{-6}				
δ′-Pu[c]	Bc tetragonal		720	560×10^{-6}				
ε-Pu[c]	Bcc		750	577×10^{-6}				
Am	Dhcp	$5f^77s^2$	300	675×10^{-6}	Slight temperature dependence		10·3	

[a] J. F. Smith and J. D. Greiner, *Phys. Rev.* **115** (1959) 884; D. J. Lam, M. V. Nevitt, J. W. Ross and A. W. Mitchell, in *Plutonium 1965*, p. 274, A. E. Kay and M. B. Waldron (Eds.), Chapman & Hall (1969).

[b] J. Friedel, *J. Phys. Chem. Solids*, **1** (1956) 175.

[c] Konobeevsky, *Proc. Anal. Sci. USSR on Peaceful Uses of Atomic Energy, Chemical Science Volume*, p. 362, and ref. 215.

f-band by hybridization with the 6*d* electrons suppresses the formation of localized moments[284]. For α-uranium, Fournier has measured the magnetization to 100 kOe.

(c) From americium, the 5*f* electrons become more localized and valencies are close to three for americium, curium and berkelium. Americium still shows no moment; the susceptibility is large and the temperature dependence slight—either Pauli paramagnetism or a Van Vleck paramagnetism corresponding to a $5f^6$ configuration. Localized moments appear at curium, the susceptibility of which follows a Curie–Weiss law from 300 to 145K with an effective moment 7·97–8·1 μ_B, corresponding to a $5f^7$ configuration; between 145K and 77K it shows ferromagnetism with $T_c =$ 131K. Two phases of berkelium are known; a fcc phase and a dhcp for which Coqblin *et al.*[285] deduce valencies of 3 and 3·5 respectively. The susceptibility of both phases follows a Curie–Weiss law with an effective moment 8·2–8·8 μ_B, close to that for a $5f^8$ configuration. Coqblin has developed a theoretical model—attributing the suppression of localized moments from plutonium to curium to *d–f* hybridization. Plutonium is almost magnetic and some properties probably derive from spin fluctuations[282].

Nuclear Magnetic Resonance

NMR measurements have been limited. For neptunium, van Ostenberg and Brodsky[286] were unable to find a resonance. Measurements of the ^{27}Al nmr in a 4 at. % Al stabilized δ-phase plutonium alloy[287] gave a Knight shift of 0·06 at 77K and 0·05 at ~4K independent of frequency from 4 to 12 MHz; the full width at half maximum intensity was 3·6 Oe at 12 MHz at both temperatures. Butterworth[288] failed to find the expected ^{239}Pu resonance in α-plutonium at room temperature. (Optical spectroscopy[289] and electron paramagnetic resonance methods[290] have shown the ^{239}Pu nucleus to have a spin of one-half, giving an estimated nuclear moment of 0·4 ± 0·2 nuclear magnetons.) Fradin and Brodsky[287] looked unsuccessfully for the resonance in the ranges $0{\cdot}61 \leqslant \nu/H \leqslant 0{\cdot}89$ at 8 MHz, and $0{\cdot}31 \leqslant \nu/H \leqslant 0{\cdot}61$ at 4 MHz at liquid helium temperatures.

Mössbauer Measurements

For uranium metal the Mössbauer effect has been measured in ^{234}U, ^{236}U and ^{238}U[291, 292]. Hyperfine field splitting is observed, but essentially no isomer shift. For neptunium the Mössbauer effect, primarily by the decay of ^{241}Am, has been extensively studied[293,294]; the 59·6 keV resonance is very sensitive to hyperfine field effects and isomer shift; no local magnetic field is present in the metal, though a localized moment is seen for neptunium in

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[284] H. H. Hill, in *Plutonium 1970 and Other Actinides*, Vol. 1, p. 2, W. N. Miner (Ed.), AIME (1970).

[285] B. Coqblin, E. Galleani d'Angliano and R. Jullien, in Superconductivity in d- and f-band metals, D. H. Douglass (Ed.), *Proc. AIP Conf.* Vol. 4, p. 154 (1971).

[286] M. B. Brodsky, in *Rare Earths and Actinides*, Conf. Digest 3, Inst. of Physics, London (1971).

[287] F. Y. Fradin and M. B. Brodsky, *Intern. J. Magnetism*, **1** (1970) 89.

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[289] M. Van den Berg and P. F. A. Klinkenberg, *Physica*, **20** (1954) 461.

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[291] J. C. E. Eisenstein and M. H. L. Pryce, *Proc. Roy. Soc.* (*London*) **A229** (1955) 20; ibid. **A238** (1956) 31.

[292] S. L. Ruby, G. M. Kalvius, B. D. Dunlap, G. K. Shenoy, D. Cohen, M. B. Brodsky and D. J. Lam, *Phys. Rev.* **184** (1969) 374.

[293] J. A. Stone and W. L. Pillinger, *Phys. Rev.* **165** (1968) 1319.

[294] B. D. Dunlap, G. M. Kalvius, S. L. Ruby, M. B. Brodsky and D. Cohen, *Phys. Rev.* **171** (1968) 316.

palladium and for neptunium in americium[295]. Blow[296,297] has used ^{57}Fe to make Mössbauer studies of the intermetallic compounds UFe_2, $NpFe_2$, $PuFe_2$; U_6Fe, Pu_6Fe.

6.5. Elastic properties

Single-crystal elastic moduli have been measured adiabatically for thorium[298] and uranium[299]. At ambient temperature and pressure the moduli, in units of 10^{12} dynes cm^{-2}, are: for thorium, $C_{11} = 0{\cdot}753$; $C_{12} = 0{\cdot}489$; $C_{44} = 0{\cdot}478$; $C' = (C_{11} - C_{12})/2 = 0{\cdot}132$; the shear anisotropy ratio $A = C_{44}/C' = 3{\cdot}62$; bulk modulus $K = 0{\cdot}577$: for uranium, $C_{11} = 2{\cdot}148$; $C_{12} = 0{\cdot}458$; $C_{44} = 1{\cdot}244$; $C_{22} = 1{\cdot}986$; $C_{13} = 0{\cdot}216$; $C_{55} = 0{\cdot}753$; $C_{33} = 2{\cdot}671$; $C_{23} = 1{\cdot}078$; $C_{66} = 0{\cdot}754$ and $K = 1{\cdot}112$. The elastic moduli of polycrystalline actinide metals at 300K, adiabatic unless noted, are given in Table 16.

For thorium the temperature dependence of single-crystal moduli have been measured between 80 and 340K, and Young's modulus from 300 to 573K[300]. No anomalies are reported in either dC_{ij}/dT or dE/dT.

For α-uranium at low temperatures, the second order phase transition at 43K is clearly defined in single crystals by an inverse λ-type anomaly in the C_{ij} and by very large anomalies in the linear and volume compressibilities[301,302]. For the two first order transitions at 37 and 22K discussed under section 6.3, anomalous behaviour is also seen; at 35 ± 2K the attenuation and certain C_{ij} change abruptly; hysteresis effects are seen at 22K. In polycrystals the 22K transition is generally inhibited[303]. At elevated temperatures there is a significant softening of the nearest neighbour central force constant as the α–β phase transition is approached, with the shear modulus C_{55} decreasing to less than 25 % of its maximum value.

The only data for the β- and γ-phase of uranium are from the torsion pendulum measurements of Dashkovskiy *et al.*[304] giving dG/dT from room temperature to 1175K: a relatively abrupt increase in the temperature dependence occurs within the α-phase at 670K but only a slight change at the $\alpha \rightleftharpoons \beta$ transition; a step change occurs at the $\beta \rightleftharpoons \gamma$ change, dG/dT becoming zero within the γ-phase.

No single-crystal measurements have been made on plutonium. For α-plutonium, though there is good agreement between different dynamic measurements of E, the reported values of σ and K differ widely, presumably because of the formation of microcracks and voids, common in the phase. A mean value of $0{\cdot}51 \times 10^{12}$ dynes cm^{-2} for K is in good agreement with Bridgeman's isothermal measurement. Taylor's data for δ-phase alloys stabilized with aluminium and cerium indicates that for unalloyed δ-phase plutonium $E \sim 0{\cdot}37 \times 10^{12}$ dynes cm^{-2}; $G \sim 0{\cdot}15 \times 10^{12}$ dynes cm^{-2}. Bouchet's high-temperature data extrapolate to a value $E \sim 0{\cdot}30 \times 10^{12}$ dynes cm^{-2}.

[295] B. D. Dunlap, M. B. Brodsky, G. M. Kalvius and G. K. Shenoy, in *Plutonium 1970 and Other Actinides*, Vol. 1, p. 331, W. N. Miner (Ed.), AIME (1970).

[296] S. Blow, *J. Phys. C: Solid St. Phys.* 3 (1970) 835.

[297] S. Blow, *J. Phys. Chem. Solids*, 30 (1969) 1549.

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TABLE 17

	Young's modulus E (10^{12} dynes cm^{-2})	Shear modulus G (10^{12} dynes cm^{-2})	Bulk modulus K (10^{12} dynes cm^{-2})	Poisson's ratio	Reference
α-Th	0·735	0·287	0·577	0·288	Calculated from data of ref. 298
α-U	2·022	0·841	1·130	0·201	Calculated from data of ref. 299
U–2·5 at.% Mo	1·84				H. L. Laquer, *Nucl. Sci. Eng.* 5 (1959) 197
U–2·0 at.% Nb	1·94	0·785			*Ibid.*
U–7·5 wt.% Nb–2·5 wt.% Zr	0·60	0·213	1·059	0·41	A. E. Abey and E. D. Joslyn, *J. Less-Common Metals*, 27 (1972) 9
α-Np	1·0				J. A. Lee, in *Progress in Nuclear Energy*, Vol. 3, Series V, p. 453, H. M. Finniston and J. P. Howe (Eds.), Pergamon Press, London (1961)
α-Pu	1·00	0·437	0·476	0·15	H. L. Laquer, cited by A. S. Coffinberry and M. B. Waldron in *Progress in Nuclear Energy*, Vol. 1, Series 5, p. 383, H. M. Finniston and J. P. Howe (Eds.) Pergamon Press, London (1956)
	0·88	0·35	0·515	0·18	A. E. Kay and P. F. Lindford, in *Plutonium 1960*, p. 56, E. Grison *et al.* (Eds.), Cleaver Hume, London (1961)
	0·99	0·413	0·550	0·20	J. M. Bouchet, *CEA Report* 3771 (1969)
			0·490		P. W. Bridgman, in *The Physics of High Pressures*, p. 160, Bell & Sons, London (1958)
δ-Pu–1·2 at.% Al	0·39	0·152	0·29	0·28	J. C. Taylor, R. G. Loasby, D. J. Dean and P. F. Lindford, in *Plutonium 1965*, A. E. Kay and M. B. Waldron (Eds.), p. 162, Chapman & Hall, London (1967)
δ-Pu–2 at.% Al	0·40	0·155	0·32	0·29	
δ-Pu–6 at.% Al	0·47	0·18	0·41	0·31	
δ-Pu–up to 20 at.% Ce	0·40	0·17	0·27	0·24	

An estimate of the extent to which band structures and ionic repulsion determine the elastic moduli can be made by calculating the electrostatic contribution and comparing the measured C_{ij} and sound velocities[305]. For thorium, taking a valency of 4, Fisher[306] has calculated $C_{44} = 1{\cdot}05 \times 10^{12}$ dynes cm^{-2} as compared with a measured $0{\cdot}478 \times 10^{12}$ dynes cm^{-2}; the C' calculated was $0{\cdot}117 \times 10^{12}$ dynes cm^{-2} as compared with a measured $0{\cdot}132 \times 10^{12}$ dynes cm^{-2}. It appears that the cohesion in α-thorium is dominated by

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[305] D. Bohm and T. Staver, *Phys. Rev.* **84** (1950) 836.

[306] E. Fisher, Private communication.

Coulomb forces. For α-plutonium and α-uranium, similar calculations evidence quite large contributions from the band structures.

6.6. Phase equilibria and thermodynamics

Pressure–Temperature Phase Diagrams

The pressure–temperature phase diagrams of uranium, neptunium, plutonium, and americium have been studied[307] (Fig. 5).

For uranium, the early work of Bridgeman showed no volume discontinuities up to 10 kbar and no discontinuities in resistivity up to 75 kbar at room temperature. The α–β, β–γ and the direct α–γ phase transition have been studied up to 45 kbar by DTA. The equilibrium α–β–γ triple point occurs at less than 31·5 kbar and greater than 803°C.

The α–β transition of neptunium rises with pressure up to 12 kbar. Stephens extended the phase diagram to 35 kbar and 752°C confirming the rise in the α–β transition temperature and showing a triple point, tetragonal–bcc–liquid, at 32 kbar and 517°C. The compressibility in the α-phase was 0·00136 kbar^{-1}.

Bridgeman has reported high pressure measurements on plutonium made as early as

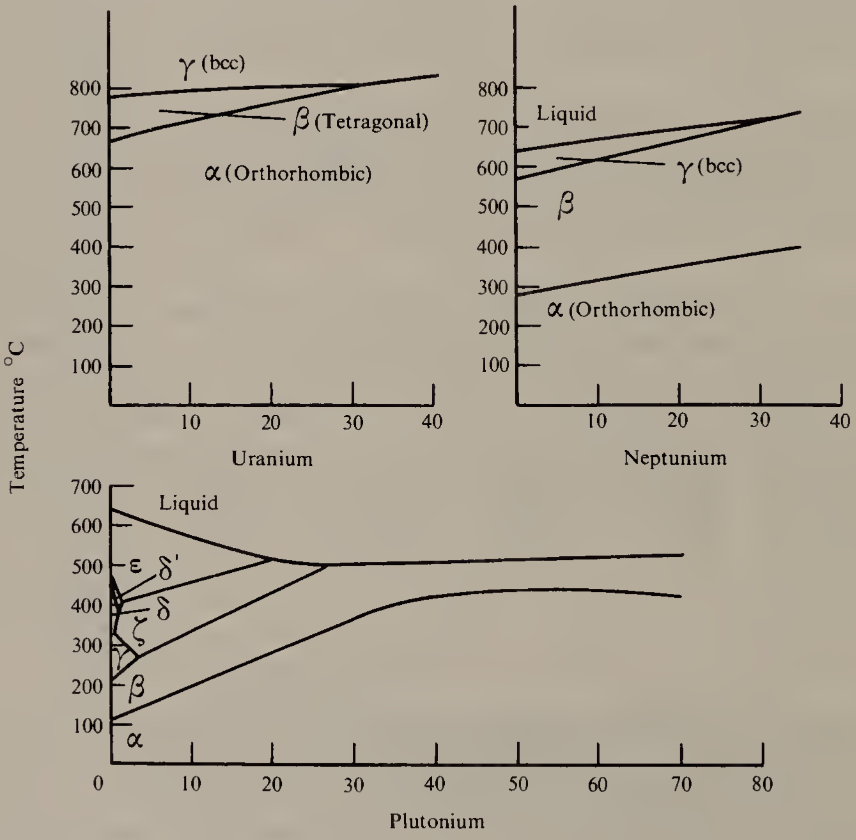

FIG. 5. Pressure–temperature phase diagrams of actinide metals.

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[307] J. A. Lee and M. B. Waldron, *Contemp. Phys.* **13** (1972) 113, and references therein.

1945. The phase diagram is now well established up to 75 kbar. A most interesting feature is the maximum in the α–β phase boundary at ~53 kbar; above this pressure the negative slope implies that the density of the β-phase is greater than that of the α-phase. Morgan has shown that a new phase, ζ, whose structure has not yet been determined, replaces γ as well as δ and δ', first appearing at a triple point with γ and δ at 0·6 kbar and 330°C. Delta (δ) disappears at a triple point with δ' and ζ at about 1·0 kbar and 385°C; δ' at a triple point with ϵ and ζ at ~1·7 kbar and 410°C; γ at a triple point with ζ and β at 3·5 kbar and 270°C; ϵ at a triple point with ζ and liquid at ~518°C and 19·5 kbar. The slope of the melting curve is negative up to the β–ζ–liquid triple point at ~500°C and 27 kbar, reflecting the increase in density on melting. A pressure–temperature phase equilibrium study of the binary alloy system plutonium–gallium provides strong support for the existence of the ζ-phase[308].

Stephens has also reported DTA measurements on the phase diagram of americium at pressures up to 35 kbar. The hcp to fcc transformation suggested by McWhan as occurring between 600° and 700°C was not observed, and McWhan's liquidus at 994°C has been rather related to a solid–solid transition (fcc to bcc?) seen at 1072°C. The melting point (bcc–liquid) is given as 1173°C.

The compressibilities, falling from thorium to a minimum value at uranium then increasing through neptunium and plutonium to americium, lie intermediate between those of the transition metals and the rare earths, though the high value for americium (0·00277 kbar^{-1}) is more typical of rare earths.

Of other properties, only the resistivity has been systematically measured as a function of pressure. With the exception of americium the effect of pressure is to decrease the resistivity as in typical metals. The change in pressure coefficient of resistivity across the series follows the general trend shown by the compressibilities, falling from thorium to maximum negative values at uranium, protactinium, then rising through neptunium and plutonium as the population of the *f*-like states increases, reaching an anomalous positive value for americium directly comparable with that of its rare earth analogue, europium.

Heat Capacity

No measurements have been made on protactinium, nor on actinides later in the series than plutonium.

(a) Low-temperature measurements on thorium, uranium, neptunium and plutonium up to the end of 1970 have been reviewed[309] and references are given in that paper unless otherwise stated. The data reviewed together with measurements from two recent papers[268, 310] are summarized in Table 18.

The marked increase in the molar heat capacity, C_p, with atomic number can almost entirely be accounted for by two factors; an increase in the dilation term $C_p - C_v = \alpha_v^2 K_T T V$, where α_v is the volume expansivity, K_T is the isothermal bulk modulus and V is the molar volume; and an approximately linear increase in the electronic contribution with the atomic number, i.e. in the density of states at the Fermi surface (see also Table 16). The latter is indicative of a gradual population of the 5*f* levels irrespective of the differences in crystal structures, and consequent differences in detail of the band structures.

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[308] C. Roux, P. le Roux and M. Rapin, *J. Nucl. Materials*, **40** (1970) 305.

[309] J. A. Lee, P. W. Sutcliffe, D. J. Martin and K. Mendelssohn, in *Plutonium 1970 and Other Actinides*, Vol. 1, p. 58, W. N. Miner (Ed.), AIME (1970).

[310] T. A. Sandenaw and R. B. Gibney, *J. Chem. Thermodynamics*, 3 (1971) 85.

TABLE 18. SPECIFIC HEAT MEASUREMENTS OF THE ACTINIDES

	Authors	Year of Publ.	Temp. range of C_p measurements (K)	C_p at 298·15 (J/g atom/K)	Electronic coefficient (γ mJ/g atom/K^2)	Debye temp. at 0°K θ^s_D(K)	$S_{298 \cdot 15}$ (J/g atom/K)	$H^\circ_{298 \cdot 15}-H_0^\circ$ (J/g atom)	$-(G_{298 \cdot 15}-H^\circ_0)/T$ (J/g atom K)
α-Th	Griffel and Skochdopole	1953	20–300	27·33	—	—	53·39	6510	31·55
	Smith and Wolcott	1955	1·2–20	—	4·70	170			
	Gordon, Montgomery *et al.*	1966	1–4	—	4·31 (±0·5)	163·3 (±·7)			
α-U	Jones, Gordon and Long	1952	15–300	27·48	—	—	50·33 (±·13)	6385 (+13)	28·91 (±·07)
	Flotow and Lohr	1960	5–350	27·66	—	—	50·21 (±·02)	6364 (±13)	28·84 (±·06)
	Clusius and Piesbergen	1958	10–300	C_p not quoted	~8·8	~170			
	Smith and Wolcott	1955	1·2–20	—	10·9	200			
	Goodman, Hilliaret *et al.*	1961	1–4	—	10·6 (±5)	206 (±5)			
	Flotow and Osborne	1966	1·7–25	—	9·88 (±·05)	222 (±2)			
	Dempesey, Gordon *et al.*	1963	0·15–0·75	—	12·1 (±·3)	—			
	Gordon, Montgomery *et al.*	1966	1–4	—	10·03 (±·02)	207 (±1)			
	Phillips and Ho	1966	1·0–3·0	—	10·3	—			
	Lee, Mendelssohn and Sutcliffe	1969	10–90	—	—	—			
	Crangle and Temporal	1972	2–70	—	9·14–10·00	210–195			
α-Np	Sandenaw	1965	8–320	32·93	~13·8	~190	50·37 (±·3)	6795 (±·46)	22·79 (±·2)
	Lee, Mendelssohn and Sutcliffe	1968, 70	7·5–300	29·63	14·2	187·5	50·46 (±·4)	6619 (±84)	28·29 (±·2)
α-Pu	Sandenaw, Olsen and Gibney	1961	11–420	—	49–86	171–176	62·01 (±1·5)	7468 (±260)	36·96 (±1·5)
	Sandenaw	1962	11–300	31·97	82	200	51·46 (±·5)	6456 (±105)	21·65 (±·3)
	Lee, Mendelssohn and Sutcliffe	1965	12·5–80	—	~12·6	~160			
	Lee, Mendelssohn and Sutcliffe	1968, 70	12·5–300	32·82	~15·9	162	55·69 (±·2)	7171 (±42)	31·64 (±·1)
	Taylor, Loasby, Dean *et al.*	1967	15–300	32·09	~11·9–14·6	165–204	55·15 (±·2)	7058 (±210)	31·48 (±·2)
	Sandenaw	1970, 71	15–373	32·90	44·41	170	56·34	7122	32·44

In contrast, and probably as a result of the differences in crystal structures, no general trend is apparent in the lattice contribution as seen in the Debye temperature, θ_D (Table 13), whereas the lanthanide series does show a gradual progression in θ_D.

It was noted earlier (section 6.3) that in polycrystalline α-plutonium and α-uranium samples, second order transitions were observed at 60K and 43K, respectively, and the difficulties of determining the exact energies associated with these transitions were discussed. For the two first order transitions reported in single crystals of α-uranium at 22K and 37K Crangle has assumed a temperature-dependent θ_D in subtracting the lattice and electronic terms and deduces latent heats of $1 \cdot 38 \pm 0 \cdot 05$ and $2 \cdot 08 \pm 0 \cdot 5$ J mole^{-1} respectively; for comparison, this analysis gives an entropy of 0·398 J mole^{-1} K^{-1} for the 43K transition in a single-crystal sample and 0·406 J mole^{-1} K^{-1} in a polycrystalline.

(b) Heat capacity measurements at elevated temperatures have been limited. Reviews for thorium[311], uranium[311,312] and plutonium[313,314] list the basic references to 1967 and give detailed tables of values. Selected values are tabulated together with data for the allotropic transformations taken from the review by Wittenberg *et al.*[315] in Table 19. Heat capacity measurements have also been reported on δ-phase plutonium alloys stabilized by minor alloying additions.[316] Selected values for heats of vaporization are given in Table 13.

6.7. Isotopes

The known actinide isotopes form too extensive and changing a list for their nuclear properties to be detailed here. References should be made to the standard works[317,318] and more particularly to the continuously amended Data Sheets[319]. Those isotopes most useful industrially were discussed in section 5. The use of actinide elements in Mössbauer spectroscopy is, however, becoming increasingly important and has recently been reviewed[320].

Mössbauer Resonances in the Actinides

In even–even actinide nuclei, where the ground state has zero spin, the first excited, 2^+, state is about 45 keV above the ground state. A suitable $2^+ \rightarrow 0^+$ transition is available in most actinides. These transitions make for good Mössbauer resonances with three reservations: (i) The multiplicity of the transition is E2 and therefore the conversion coefficient α is large (~700 for the 45 keV state in ^{238}U) leading to weak sources since a γ-ray is emitted only once in α decays; the resonance cross-section σ_0 becomes small. (ii) The lifetime of

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[311] R. Auttgren, R. L. Orr, P. D. Anderson and K. K. Kelly, *Selected Values of Thermodynamic Properties of Metals and Alloys*, John Wiley, Supplement (1967).

[312] M. H. Rand and O. Kubaschewski, in *The Thermochemical Properties of Uranium Compounds*, Oliver & Boyd (1963).

[313] M. H. Rand, D. T. Livey, P. Feschotte, H. Nowotny, K. Seifert, R. Ferro, in *Plutonium: Physico-Chemical Properties of Its Compounds and Alloys*, IAEA Publ. 4 (1) 1966.

[314] F. L. Oetting, *Chemical Reviews*, **67** (1967) 261.

[315] L. J. Wittenberg, G. A. Vaughn and R. De Witt, in *Plutonium 1970 and Other Actinides*, Vol. 2, p. 659, W. N. Miner (Ed.), AIME (1970).

[316] J. C. Taylor, P. F. T. Linford and D. J. Dean, *J. Inst. Metals*, **96** (1968) 178.

[317] E. K. Hyde, I. Perlman and G. T. Seaborg, *Nuclear Properties of the Heavy Elements*, Prentice Hall (1964).

[318] C. M. Lederer, J. M. Hollander and I. Perlman, *Table of Isotopes*, John Wiley (1967).

[319] *Nuclear Data Sheets*, Academic Press (N.Y.).

[320] G. M. Kalvius, in *Plutonium 1970 and Other Actinides*, Vol. 1, p. 296, W. N. Miner (Ed.), AIME (1970).

TABLE 19

Phase	Crystal structure	Transition	Transition temperature (K)	C_p (J/G atom/K)	ΔH (J/G atom)	ΔS (J/G atom/K)	ΔV (%)
α-Th	Fcc	$\alpha \rightarrow \beta$	1636 ± 10	27·33 (298·15K)	2736	1·67	0·63
β-Th	Bcc	$\beta \rightarrow$ liquid	2028 ± 10	46·02 (1636K)	16134	7·95	
liquid				46·02 (2028K)			
α-U	Orthorh.	$\alpha \rightarrow \beta$	940	27·57 (298·15K)	2929	3·14	1·1
β-U	Tetrag.	$\beta \rightarrow \gamma$	1048	42·93 (940K)	4791	4·56	0·7
γ-U	Bcc	$\gamma \rightarrow$ liquid	1406	38·28 (1048K)	12134	8·62	2·2
liquid				47·91 (1406K)			
α-Np	Orthorh.	$\alpha \rightarrow \beta$	553	29·63 (298·15K)	5607	10·13	3·3
β-Np	Tetrag.	$\beta \rightarrow \gamma$	848		5272	6·23	3·6
γ-Np	Bcc	$\gamma \rightarrow$ liquid	913		5188	5·69	1·5
α-Pu	Monocl.	$\alpha \rightarrow \beta$	388	32·82 (298·15K)	3360	8·66	10·0
β-Pu	Bc monocl.	$\beta \rightarrow \gamma$	458	34·10 (392K)	636	1·34	3·5
γ-Pu	Fc orthorh.	$\gamma \rightarrow \delta$	583	35·73 (477K)	523	0·88	7·0
δ-Pu	Fcc	$\delta \rightarrow \delta'$	725	37·66 (584K)	42	0·04	−0·5
δ'-Pu	Bc tetrag.	$\delta' \rightarrow \epsilon$	753	46·86 (731K)	1858	2·47	−3·0
ϵ-Pu	Bcc	$\epsilon \rightarrow$ liquid	913	35·15 (753K)	2900	3·18	−2·4
liquid				35·56 (911K)			
α-Am	Dhcp	$\alpha \rightarrow \beta$	1352		5858	4·35	1·1
β-Am	Bcc	$\beta \rightarrow$ liquid	1449		14393	9·92	2·3
liquid							

these states is short ($\tau \sim 0{\cdot}2$ nsec) and resolution therefore limited, though partly offset by a simple hyperfine spectra, the ground state not being split. (iii) The nucleon states do not change in the $2^+ \rightarrow 0^+$ transition and isomer shifts become unobservable.

In the odd isotopes, low-lying transitions are of two kinds: (i) Purely rotational transitions, between states with $I_{gr} = n/2$ and $I_{ex} = (n + 2)/2$, e.g. the 33 keV, $7/2^+$–$5/2^+$ transition in ^{237}Np. Here the multipolarity is Ml giving conversion coefficients of *ca.* 100, but shorter lifetimes than for the $2^+ \rightarrow 0^+$ transitions. The hyperfine spectra are poorly resolved and complex. These have not so far been used. (ii) Transitions where the lowest state of the next higher rotational band is close to the energy of the ground state, e.g. the 59·6 keV γ transition in ^{237}Np. The states have opposite parity and the multipolarity of the γ transition between them is usually El, making the conversion coefficient ~ 1 and the lifetime long (several nsec). The transition is not collective and isomer shifts can be observed. These form good Mössbauer resonances.

The useful resonances are summarized briefly.

Actinium. The only possible resonance is the 27·5 keV transition in ^{227}Ac. The short half-life of 22 years limits its usefulness.

Thorium. The only available resonance is the 49·8 keV, $2^+ \rightarrow 0^+$ transition in ^{232}Th, with poor resolution for reasons noted above. No convenient γ-ray source is known and the Mössbauer effect has been established using Coulomb excitation.

Protactinium. The 84·2 keV $3/2^- \rightarrow 5/2^+$ transition of ^{231}Pu has a multiplicity El and a half-life of 40 nsec, and is therefore ideal for resonance. Limited availability has so far restricted its use.

Uranium. No high resolution resonances are available in the odd uranium isotopes restricting availability to the $2^+ \rightarrow 0^+$ transitions in the even isotopes. The Mössbauer effect has been observed in ^{234}U, ^{236}U and ^{238}U using α-decay sources; resolution is poor and no isomer shifts have been observed, though hyperfine splitting can be studied. The ^{242}Pu source used for the ^{238}U resonance gives low count rates and requires repeated chemical separation, but has the advantage of relative abundance. The resonance in ^{238}U has also been observed by Coulomb excitation.

Neptunium. The 59·6 keV, $5/2^- \rightarrow 5/2^+$, E1, transition in ^{237}Np, $\tau \sim 80$ nsec, has been extensively used; ^{241}Am is the most convenient source. Other resonances in ^{237}Np, e.g. the 33 keV rotational transition, could be used.

Plutonium. No Mössbauer effect measurements have been reported to date. For ^{239}Pu the 57 keV $5/2^+ \rightarrow 1/2^+$ E2 transition (lifetime uncertain) offers a potential resonance, though for preparation of the source ^{239}Np [^{238}U (n,γ) ^{239}U $\xrightarrow{\beta^-}$ ^{239}Np] extremely pure ^{238}U must be used to avoid fission product poisoning. The isotope ^{240}Pu is a potential alternative (source ^{244}Cm).

Americium. ^{243}Am has a 83·9 keV $5/2^+ \rightarrow 5/2^-$ E1 transition with nuclear parameters similar to the 59·6 keV resonance in ^{237}Np, and is potentially as useful; a source, ^{243}Pu, is readily available.

Curium. No high resolution resonance is known.

ANALYTICAL CHEMISTRY

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1. INTRODUCTION

Despite the theoretical analogies drawn between the actinides and the lanthanides, the analytical chemistry of the actinides differs significantly from that of the lanthanides in a number of ways. Firstly, the individual elements are invariably radioactive and they occur in a variety of isotopic compositions. An examination of the nuclear properties of the isotopes of the actinide elements indicates the many analytical possibilities available for the qualitative detection and quantitative determination of these elements. Furthermore, a knowledge of the isotopic composition of the element is essential for use in those analytical methods requiring accurate knowledge of the atomic weight. Secondly, although actinium and thorium exhibit only one valency state in solution with consequent limitations on availability of methods for their determination, the elements Pa, U, Np, Pu and Am exhibit multiple valency states which offer the possibility of determining them by procedures based upon redox reactions and absorption spectrophotometry.

The lower actinide elements up to and including curium are available in significant quantities as a consequence of the use of natural uranium in power-producing nuclear reactors. The analytical chemistry of these elements is therefore highly developed. Beyond curium, however, trace quantities only of the actinide elements are encountered and their analytical chemistry is in consequence restricted to radiochemical determinations.

Although the emission spectra of the actinide elements are characterized by a multiplicity of lines, the identification of a particular actinide in the presence of other members of the series is possible by spectrochemical methods[1]. In general, however, spectrochemical analysis in the actinide series is used mainly for the detection and determination of impurity elements.

2. ACTINIUM

Actinium, the first member of the actinide series, is only encountered in nature in tracer amounts as Ac-227 and Ac-228. Consequently, there is no conventional solution analytical chemistry of the element, and quantitative determination of actinium consists of a radiochemical separation followed by measurement of the radioactivity of the product. In radiochemical procedures actinium behaves predictably as a trivalent element closely resembling lanthanum, and it precipitates from solution as the hydroxide, fluoride, oxalate, carbonate, phosphate, fluosilicate and iodate. Precipitation reactions require the presence of a carrier element such as Th, Ba, La, Bi, Zr, Al, Fe or Y. The choice of carrier is governed by the precipitating anion and the separation required. Further details are given elsewhere[2]. Other separations are based upon ion exchange and solvent extraction techniques, and these have the advantage of not requiring the presence of a carrier element. This type is necessary for separating actinium from rare earths and other trivalent elements. The radiochemical separation processes used need not be quantitative, but an estimate of the overall chemical

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[1] *The Chemistry of the Transuranium Elements*, p. 97. Cornelius Keller, Verlag Chemie GmbH (1971).

[2] I. M. Kolthoff and P. J. Elving, *Treatise on Analytical Chemistry*, Part II, Vol. 6, Interscience Publishers 1964).

yield is necessary in order to apply a correction factor to the radioactivity measured. A convenient method of determining the chemical yield is by means of a tracer. For example, Ac^{228} (β-emitter) may be used as a tracer for Ac^{227} (α,β-emitter). Details of the nuclear properties of the commonly available actinium isotopes 227 and 228 are given in Table 1. Information on other shorter-lived isotopes and appropriate counting procedures is given elsewhere[2].

TABLE 1. COMMONLY AVAILABLE ACTINIUM ISOTOPES

Mass number	Half-life	Mode of decay	Energy
227	21·6 yr	β ~99% α 1·2% γ Many	0·04 MeV 4·94 MeV Weak
228	6·13 hr	β Many γ Many	0·45 to 2·18 MeV 0·057 to 1·035 MeV

3. THORIUM

Introduction

Thorium is the second element in the actinide series and its behaviour in analysis is very similar to cerium which is its counterpart in the lanthanide series. The main difference in behaviour between the two elements is that whereas cerium exhibits both tri- and tetravalencies in solution, thorium is invariably tetravalent. The analytical chemistry of thorium is therefore limited, and it consists mainly of gravimetric, complexometric and spectrophotometric methods of analysis. Solutions of thorium are not as readily hydrolysed as those of zirconium, hafnium and protactinium (V), and thorium forms strong complexes with EDTA and other organic ligands which are employed as the basis of the complexometric and spectrophotometric methods. Natural thorium is predominantly Th^{232} which is an α-emitter of such low specific activity that the direct radiochemical determination of this element is not a sensitive method of analysis.

Gravimetric methods for the determination of thorium

Thorium is readily precipitated from solution as its insoluble hydroxide, oxalate, iodate, fluoride or peroxide, or by organic reagents such as cupferron, benzoic acid, diphenic acid, etc. In this respect the behaviour of thorium is similar to that of titanium, zirconium, hafnium and the rare earths. Gravimetric methods for thorium are usually completed by igniting the precipitate to the oxide, but some precipitates with organic reagents (e.g. benzoic acid and its derivatives) may be filtered, dried at a suitable temperature and weighed directly.

The choice of a suitable precipitant for thorium is governed by the necessity to avoid coprecipitation of the interfering elements mentioned above. In general, no single reagent is completely specific for thorium, and procedures for the gravimetric determination of this element usually describe a sequence of repetitive precipitations involving at least two different reagents. Precipitations are generally performed from hydrochloric or nitric acid solutions, since sulphate ions usually inhibit the completeness of the precipitation. However, control of acidity is an important factor in ensuring an optimum recovery of thorium from solution, and the method of homogeneous precipitation is frequently employed to improve the separation of thorium from interfering elements.

Alkali hydroxide, ammonium hydroxide, hexamine and urea are all suitable for the precipitation of the hydroxide or basic salt of thorium. Certain of these reagents can afford a useful preliminary separation from several elements including the rare earths, but not from uranium, zirconium or titanium. Hexamine and urea give better separations of thorium from interfering elements, and also the precipitates are more filterable than those produced by alkali hydroxides or ammonia. The precipitation of thorium hydroxide is carried out at pH 6, and it is complete under these conditions in the absence of sulphate ions. On increasing the pH, some contamination results from rare earth elements, if present. Thorium hydroxide is converted to the dioxide by ignition above 475°C.

Thorium iodate is precipitated from nitric acid solutions in the acidity range from 1 to 6 N, and this constitutes a useful procedure for the separation of thorium from solutions containing phosphate. The precipitation is more complete at the lower end of the acidity range, but the use of high acidities may be advantageous in achieving a better separation of thorium from interfering elements. Thorium iodate is not usually ignited directly to the oxide, but it may be redissolved in hot 5 M hydrochloric acid and the determination completed by precipitation of the hydroxide.

Thorium can be precipitated from nitric acid solutions as its oxalate either by the direct addition of oxalic acid or by the generation of this reagent by the hydrolysis of methyl oxalate. The solubility of thorium oxalate in dilute mineral acid solutions is not insignificant, and the gravimetric procedures described in the literature[3] are designed to reduce solubility losses to a minimum. The published procedures are, however, apparently contradictory, and they appear to be critically dependent upon the presence of small amounts of rare earths which ensure the recovery of the last traces of thorium from solution. The presence of excess ammonium salts in solution is undesirable as they cause increased solubility of thorium oxalate. This separation procedure is useful in the presence of phosphate, and the thorium oxalate may be ignited to the oxide for weighing.

The precipitation of thorium as its fluoride from acid solution is very similar to that of the oxalate procedure as regards the separation of thorium from interfering elements. Thorium fluoride has been used as a preliminary step for the separation of small amounts of thorium[4] followed by the determination of the element as its peroxynitrate.

A large number of organic reagents have been proposed as precipitants for thorium[5], and in general these reagents are more specific than the inorganic precipitants discussed earlier.

Solution methods for the determination of thorium

Titrimetric

The stable complexes of thorium with reagents of the EDTA type (e.g. $Th^{4+} + Y^{4-} = ThY$, $pK = 23{\cdot}2$, where Y^{4-} is the anion of ethylenediamine tetra-acetic acid), form the

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[3] I. M. Kolthoff and P. J. Elving, *Treatise on Analytical Chemistry*, Part II, Vol. 5, p. 159, Interscience Publishers (1961).

[4] F. S. Grimaldi and C. A. Marsh, AECD–2818 (1947).

[5] I. M. Kolthoff and P. J. Elving, *Treatise on Analytical Chemistry*, Part II, Vol. 5, p. 163, Interscience Publishers (1961).

basis of the most useful volumetric method for the determination of this element. Many EDTA titration procedures are described[6] in which a variety of colorimetric reagents are employed for the detection of the endpoint in the pH range 1·5 to 3·5. The ability to titrate thorium at low pH values is particularly important in avoiding interference from the alkaline earths and other elements which form stable complexes with EDTA at higher pH values. Frequently it is possible to carry out consecutive determinations, in which thorium is titrated in the pH range 1·5 to 3·5 and then other elements are titrated after raising the pH of the solution to a suitable value. The presence of sulphate ions must be avoided in EDTA titrations of thorium because of the relatively strong complexing action of sulphate ions with thorium. Some advantage can be taken of this, however, to enable the determination of thorium to be carried out in the presence of certain interfering elements. A typical example is the determination of thorium in the presence of zirconium[7]. The total Zr + Th is first complexed with a small excess of EDTA in the absence of sulphate ions. The Zr + Th concentration is then determined by the back-titration of the excess EDTA with bismuth at pH 2·5 to 2·7 using xylenol orange as the indicator. An excess of ammonium sulphate is then added to the solution to release the thorium from its EDTA complex, and the pH of the solution is adjusted to between 1·2 and 1·3. The liberated EDTA, which is equivalent to the thorium present, is finally titrated with bismuth to the xylenol orange endpoint.

Spectrophotometric

Thorium forms a 1 : 2 complex with 2-(2-hydroxy-3,6-disulpho-1-naphthylazo) benzene arsonic acid which is suitable for the spectrophotometric determination of this element. The reagent is known under a variety of names including thoron, thoronol, APANS and naphtharson, and its red coloured complex with thorium absorbs strongly at 545 nm. The high sensitivity enables from 5 to 50 μg of thorium to be determined in a volume of 25 ml of solution at pH 0·8. Several elements cause serious interferences however, these include zirconium, titanium, tetravalent actinides, fluoride and phosphate. Meso-tartaric acid can be used to suppress the interference from zirconium, and a comprehensive list of the effects of other metallic elements has been published[8].

The reagent morin (2′,3,4′,5,7-pentahydroxy flavine) forms a complex with thorium at pH 2·0. The maximum absorbance at 410 nm is more than double that for the thoronol complex, and, moreover, the reagent does not absorb significantly at this wavelength. Zirconium causes the most serious interference and the precipitation of thorium as its insoluble fluoride is requently used as a preliminary step in the spectrophotometric determination of thorium with this reagent.

Radiochemical methods for the determination of thorium

The direct determination of thorium by measurement of the alpha activity of Th^{232} and Th^{228} is limited by the low specific activity of 0·48 dpm per μg. A more useful direct method of radiometric determination of thorium is by γ-counting the 2·62 MeV gamma of Tl^{208} which is in radiochemical equilibrium with it.

A very sensitive radiometric technique is that involving neutron irradiation of the Th^{232}

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[6] J. Schwarzenbach and H. Flaschka, *Complexometric Titrations*, Methuen (1957).

[7] G. W. C. Milner and J. W. Edwards, *Anal. Chim. Acta*, **20** (1959) 31.

[8] I. M. Kolthoff and P. J. Elving, *Treatise on Analytical Chemistry*, Part II, Vol. 5, p. 190, Interscience Publishers (1961).

nuclide. This produces Th^{233} which decays to produce a 1·2 MeV gamma with a half-life of 22·1 min. The practical lower limit of determination with a neutron flux of 10^{12} neutrons per cm^2 per sec is about 0·01 μg of thorium.

4. PROTACTINIUM

Introduction

Protactinium is the third member of the actinide series, but it possesses many of the properties of the Group V elements in its chemical reactions. It is a naturally-occurring radioactive element producing an oxide (Pa_2O_5) which is useful for gravimetric analysis. The stable valency in solution is Pa(V), and the existence of Pa(IV) is also possible. However, the lower valency state is readily oxidized to the pentavalent state. The solution chemistry of protactinium is dominated by its hydrolytic behaviour, and stable solutions can only be obtained by complexing the element with fluoride, sulphate or other strongly complexing ligands.

Nuclear and radioactive methods for the determination of protactinium

The known isotopes of protactinium are listed in Table 2. Pa^{231} and Pa^{234} are the only naturally-occurring isotopes. They are the daughter products by α-decay from U^{235} and U^{238}, respectively. The half-life of Pa^{234} is short, and hence, for all purposes other than radiochemical analysis, Pa^{231} is the only protactinium isotope encountered. The only other isotope available in comparable amounts is Pa^{233} which is produced artificially by neutron capture in Th^{232}, followed by β-decay to Pa^{233} which possesses a half-life of 27·4 days. From the analytical point of view Pa^{231} is predominantly an α-emitter with a specific activity sufficiently high (*ca.* 10^5 dpm per μg) to enable nanogram quantities to be detected readily. However, a number of features are important when the quantitative determination of Pa^{231} is attempted by measurement of its α-radiation.

TABLE 2. ISOTOPES OF PROTACTINIUM

Mass number	Half-life	Decay mode	Mass number	Half-life	Decay mode
224	0·6 sec	α	231	32,480 yr	α, γ
225	2·0 sec	α	232	1·31 days	β, γ
226	1·8 min	α	233	27·4 days	β, γ
227	38·3 min	E.C. α	234m	1·18 min	β, γ
228	22 hr	E.C. α	234	6·7 hr	β, γ
229	1·4 days	E.C. α	235	23·7 min	β
230	17 days	E.C. β	236	12·5 min	β
			237	10·5 min	β

As a natural product Pa^{231} is usually associated with members of the U^{238} series, including Po^{210}, Ra^{226} and Th^{230} with high α-activities, and also its own daughter products Ac^{227}, Th^{227} and Ra^{223}. Such interfering nuclides may be removed from solution by co-precipitation on appropriate carriers. For example, from sulphuric–hydrofluoric acid solutions, radium isotopes may be removed on barium sulphate carrier, actinium and thorium isotopes on lanthanum fluoride carrier, and polonium on metallic selenium carrier.

However, the final quantitative recovery of Pa^{231} is not easy, and an estimate of the chemical yield may be necessary. This is conveniently carried out by adding a known amount of Pa^{233} to the sample solution and measuring the chemical yield at the end of the separation by means of its β- or γ-radiation. Radiochemical purity may be further confirmed by α-spectrometry, and, in fact, this technique may be used for the determination of Pa^{231} in some naturally-occurring materials without separation. Pa^{231} can also be determined by means of its γ-radiation with energies at 27, 95 and 300 KeV. However, in samples of natural materials this technique suffers interference from the impurity isotopes Ac^{227} (280 keV) and Ra^{226} (320 keV), and radiochemical purification is necessary. Although γ-spectrometry is convenient to carry out experimentally, the determination of Pa^{231} by means of its γ-radiation is less sensitive than by measuring its α-radiation.

The determination of the activity of Pa^{233} in neutron-irradiated natural thorium (Th^{232}) can be carried out by measuring its β- or γ-activity. Radiochemical purification is necessary, and a number of procedures have been described[9]. The chemical yield of the separation may be determined by adding a known amount of the α-emitter (Pa^{231}) to the sample and measuring the final yield in the purified sample by α-counting. Difficulties arise in the measurement of the weak β-energies of Pa^{233} due to self-absorption, and measurement of the 300 keV γ-radiation is recommended. If Pa^{231} has been used to determine the chemical yield, a correction for its γ-activity may be necessary.

Gravimetric methods for the determination of protactinium

The gravimetric determination of protactinium is not likely to be required very often for two reasons. Firstly, it is rare that weighable amounts of this element are available, and secondly, the handling of dry compounds of high specific α-active materials can only be undertaken with extreme care in specially-designed laboratories to avoid ingestion hazards. Nevertheless, it may occasionally be necessary to determine milligram quantities of protactinium by precipitation from solution with an inorganic or organic precipitant, followed by ignition to the oxide Pa_2O_5. The most commonly used precipitants for pentavalent protactinium are hydroxide, peroxide, iodate, phenylarsonic acid, and cupferron. The precipitates are ignited in air at 600–1000°C followed by weighing as Pa_2O_5. The phenylarsonate precipitate may be dried at 120–180°C and weighed as $H_3PaO_2\ (C_6H_5AsO_3)_2$. This may be of considerable advantage when only milligram amounts of protactinium are available.

Some selectivity in the precipitation of protactinium in the presence of interfering elements may be obtained by a suitable choice of precipitant. Many metallic elements co-precipitate with protactinium hydroxide, but hydroxide precipitation is useful for separating protactinium from fluoride ions which tend to deposit as the sparingly soluble sodium fluoride. The selectivity of ammonium hydroxide as a precipitant can be considerably improved, however, in the presence of EDTA. Under conditions described by Vernois[10] it is possible to precipitate protactinium hydroxide selectively in the presence of Cu, Mg, Ca, Sr, Ba, Zn, Co, Ni, Cd, Mn, Pb, Fe, Al, Cr, La, Ce, Th, Mo, W and V. The precipitation of protactinium with sodium or potassium hydroxide may be achieved in the presence of Al, Ga, Zn, Mo, W, V, Be and As. Alkali metal ions are, however, co-precipitated, and they

[9] E. S. Pal'shin, B. F. Myasoedov and W. V. Davydov, *Analytical Chemistry of Protactinium*, Translation, Ann Arbor, Humphrey Science Publishers (1970).

[10] J. Vernois, P. Conte and R. Muscart, *Bull. Soc. Chim. France* 403 (1963).

must be removed by washing before igniting the precipitate to Pa_2O_5. In some cases freshly-precipitated protactinium hydroxide redissolves in mineral acid, but it becomes more difficult to dissolve on ageing. The composition of vacuum-dried protactinium hydroxide is variable with up to three molecules of water per atom of protactinium. Thermal decomposition yields a monohydrate which is stable up to 280°C, but for gravimetric analysis complete dehydration at 1000°C is recommended.

Protactinium peroxide can be precipitated from dilute mineral acid solutions with the exception of those containing fluoride ions. Precipitation is more effective with increasing peroxide concentration and decreasing acidity. Protactinium peroxide is precipitated without interference from Cr, Mg, Ni, Co and Mn, but elements such as Zr, La, Th and U interfere. The composition of the precipitate is variable, and it must be ignited to the oxide for gravimetric analysis.

Protactinium iodate is precipitated from acidic solutions with iodic acid or a soluble iodate. When precipitated from dilute sulphuric acid solutions, protactinium can be separated from U(VI), trivalent rare earths, Fe, Mn, Cr, Co and Ni. Th, Zr and Nb cause interference. The composition of the precipitate has not been established, and the determination is completed by ignition to the oxide.

Protactinium is precipitated from neutral and dilute mineral acid solutions by phenylarsonic acid. The phenylarsonate precipitate is readily compacted and filtered, and on drying between 120° and 180°C it can be weighed as $H_3PaO_2(C_6H_5AsO_3)$. Alternatively, it may be ignited to Pa_2O_5 at 1000°C. Interference occurs from fluoride, phosphate, Zr, Nb and Ta, but the precipitation may be carried out, without interference, in the presence of Cu, Ni, Co, Cr, La, Fe, Mn, Ti, Th and U.

The quantitative precipitation of protactinium with cupferron has been reported[11], but few details are available. The precipitate may be ignited to Pa_2O_5 for gravimetric analysis.

Solution methods for the determination of protactinium

The stable valency in aqueous solutions is Pa(V), but Pa^{5+} ions do not occur in significant amounts due to the extreme tendency of protactinium to hydrolyse. Consequently it is difficult to predict or reproduce the behaviour of Pa(V) in solution. This tendency for the element to precipitate is so marked that stable solutions of Pa(V) can only be obtained in strongly complexing conditions, such as in the presence of fluoride, sulphate or oxalate ions, or in concentrated acid solutions. Protactinium(V) can be reduced to the tetravalent state in solution by suitable powerful reducing agents, such as zinc amalgam, chromous, titanous or vanadous ions. Quantitative reduction is not achieved unless precautions are observed including the use of an inert atmosphere to prevent atmospheric oxidation of the reductant and the Pa(IV), a high acidity to prevent hydrolysis of the Pa(V), and sufficient reaction time because of the irreversible nature of the reduction process. Protactinium(IV) is less easily hydrolysed than Pa(V), and its hydrolytic behaviour is similar to that of Zr or Hf. However, it is more readily hydrolysed than other tetravalent actinide elements such as Th^{4+}, U^{4+}, Np^{4+} and Pu^{4+}. The analytical chemistry of protactinium in solution is difficult and it must be considered with the above behaviour in mind.

Redox titrations

The quantitative electrolytic reduction of Pa(V) in 8 N HCl has been reported by

[11] A. G. Maddock and G. L. Miles, *J. Chem. Soc.* Supplement No. 2 (1949) 248.

Musikas[12]. An amalgamated silver cathode was used for the passage of a current of 100 mA for 5 hr. After reduction, solutions containing about 4 mg of protactinium were titrated with ferric chloride to a potentiometric or amperometric endpoint. The relative error for this determination was ±3%. The reduction and titration could also be carried out in 1·0 to 1·8 N sulphuric acid solutions.

The polarographic behaviour of protactinium in chloride and sulphate media has been investigated by the same author. In sulphate solutions cathodic steps were observed between −0·45 and −0·97 V vs. the SCE, whereas an anodic step occurred at −0·12 V vs. the SCE. This behaviour indicates the irreversible behaviour of the Pa(V)/Pa(IV) couple. In chloride solutions cathodic steps were not observed at potentials lower than that for the reduction of H^+ ions, but a single anodic step occurred for the oxidation of Pa(IV). Polarographic steps have been reported for protactinium in oxalate and fluoride media. For example, in 3·84 M NH_4F solutions at pH 7·2 a reversible step has been observed by Miranda and Maddock[13] for 2×10^{-4} M concentrations of protactinium. The $E_{\frac{1}{2}}$ value was −1·29 V vs. the S.C.E. and the reduction took place according to the expression

$$PaF_8{}^{3-} + e \rightarrow PaF_8{}^{4-}$$

Spectrophotometric methods for the determination of protactinium

Studies of the absorption spectra of protactinium in mineral acid solutions have been the subject of much experimental work. Both Pa(V) and Pa(IV) absorb in the ultraviolet in the region of 250 nm, but the use of spectrophotometric methods in analysis is fraught with difficulty due to the hydrolysis of the protactinium. Protactinium (V) absorbs strongly in the range 210 to 225 nm in hydrochloric acid solutions, but the peak moves towards longer wavelengths with increasing H^+ and Cl^- concentrations. A molar absorptivity of 6×10^3 has been reported[14] for solutions of anhydrous protactinium pentachloride in 11 M HCl at a wavelength of 225 nm. Beer's Law is also obeyed over the concentration range 10^{-4} to 10^{-5} M. A minor absorption band at 260–270 nm has also been observed[15]. The behaviour of Pa(V) in sulphuric acid solutions is very similar to the above, but with higher molar absorptivity[16] (e.g. a value of $7 \cdot 7 \times 10^3$ for 0·5 to 1·5 M H_2SO_4 solutions). The absorption spectra of Pa(IV) in hydrochloric or sulphuric acid solutions are characterized by a shift of the absorption maximum to the region of 290 nm and by the occurrence of lower molar absorption ($\sim 1 \times 10^3$)[17]. Protactinium (IV) is unstable in aqueous solutions, and it is rapidly oxidized to the pentavalent state. It is possible to follow this oxidation process by measuring the respective absorption peaks.

Difficulties associated with the spectrophotometric determination of protactinium by taking measurements in the ultraviolet region can be avoided by using organic instead of inorganic ligands. Protactinium forms suitable organic complexes with Arsenazo III and thenoyltrifluoroacetone, and these complexes have the advantage of being formed in strongly acid solutions and of absorbing in the visible region. Details of the complex formed by

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[12] C. Musikas, Centre d'Etudes Nucleaires de Fontenay-aux-Roses, Report CEA–R 3023 (1966).

[13] C. F. Miranda and A. G. Maddock, *J. Inorg. and Nuclear Chem.* **24** (1962) 1623.

[14] A. M. Pissot, R. Muxart and C. F. Miranda, *Bull. Soc. Chim. France*, 1757 (1966).

[15] D. Brown, A. J. Smith and R. G. Wilkins, *J. Chem. Soc.* 1463 (1959).

[16] B. F. Myasoedov, K. Miranda and R. Muxant, *Z. anal. Chem.* **21** (1966) 1064.

[17] D. Brown and A. G. Maddock, *The Analytical Chemistry of Protactinium. Progress in Nuclear Energy*, Series 9, Vol. 8, Part 1, Pergamon (1967).

Pa(V) with Arsenazo III have been reported by Pal'shin *et al.*[18] This complex absorbs at 620 nm with a molar absorptivity of $2 \cdot 2 \times 10^4$, and it is applicable to the determination of concentrations of protactinium in the range 0·3 to 3·0 μg per ml. The complex is formed in hydrochloric or sulphuric acid solutions and the absorbancy is insensitive to any change in acidity in the range 6 to 10 N. Selectivity in the determination can be ensured by extracting the complex into isoamyl alcohol from 7 N H_2SO_4 solutions. The complexing action of the sulphuric acid prevents interference from Al, Bi(III), Cr(III), Fe(III), La, Mn(II), Mo(VI), Nb, Ni, Sn(IV) and Ti(IV). Traces of Th, U(IV), U(VI), Zr and Hf, which extract with the Pa–Arsenazo III complex, can be removed by washing the organic phase with 0·5 M oxalic acid in 7 N sulphuric acid.

5. URANIUM

Uranium is the fourth element in the actinide series and the analytical chemistry of this element shows the characteristic differences between the earlier actinides and the earlier lanthanides. In solution, four valency states are possible for uranium, namely 3, 4, 5 and 6. The most stable valency is the highest which occurs in solution as the cation UO_2^{2+}. The hexavalent state is readily reduced to UO_2^+ and then further to the U^{4+} species; the change from UO_2^{2+} to U^{4+} forms the basis of redox determinations. The pentavalent state (UO_2^+) is not normally stable in aqueous solution since it rapidly undergoes disproportionation. The tetravalent state (U^{4+}) is stable, however, in the absence of air or other oxidizing agents, but it is slowly oxidized by atmospheric oxygen. The trivalent state (U^{3+}) is produced in solution by the action of powerful reducing agents, but it is rapidly oxidized by the solvent. The tri-, tetra- and hexavalent states in solution are respectively red, green and yellow in colour with characteristic sharp absorption peaks, and each species can be determined spectrophotometrically.

The analytical chemistry of uranium is fairly extensive, and it includes gravimetric, coulometric, polarographic, spectrophotometric, redox titrations and other methods.

Gravimetric methods for the determination of uranium

Hexavalent uranium is precipitated from solution with ammonium hydroxide, and this gives a good separation of uranium from several elements. Carbonate-free ammonia is essential for complete precipitation because of the strong complexing of uranyl ions by carbonate ions. This complexing of uranyl ions may be used for the isolation of tetravalent uranium which is not complexed by carbonate ions and thus precipitated with ammonia. The gravimetric determination is completed by igniting the precipitate to U_3O_8. However, the conditions for this ignition process are critical for satisfactory results to be obtained. Temperature control, atmospheric pressure and time of ignition are all important factors, and close adherence to published procedures is recommended[19]. The optimum conditions involve igniting the precipitate at 875±25°C for a period of about 16 hr at 760 mm pressure.

Uranium(VI) may be precipitated as its peroxide from acid solutions over the pH range 0·5 to 3·5. Complexing anions should be absent for complete precipitation to be obtained. Also thorium, zirconium and hafnium should not be present because they are co-precipitated

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[18] E. S. Pal'shin, B. F. Myasoedov and P. M. Palei, *Z. anal. Chem.* **17** (1962) 471.

[19] I. M. Kolthoff and P. J. Elving, *Treatise on Analytical Chemistry*, Part II, Vol. 9, p. 74, Interscience Publishers (1962).

with the uranium. The peroxide is ignited to U_3O_8 for completion of the determination gravimetrically. Uranium(IV) may be precipitated as its oxalate from acidic solutions, and the precipitate may be weighed either as the anhydrous oxalate after drying at 126–188°C, or as U_3O_8 after ignition. This procedure is suitable for the separation of tetravalent uranium from uranyl ions.

A number of organic reagents have been proposed as precipitants for uranium, and the full extent of their use has been discussed elsewhere[20]. The reagents include cupferron 8-hydroxyquinoline, α-quinaldic acid, β-isotoxine, salicylhydroxamic acid, phenylglycine-*o*-carboxylic acid, arsanilic acid and cacodylic acid. None of these reagents is highly specific for uranium, and a preliminary separation is usually necessary. Some specificity may be obtained by the use of suitable masking agents such as EDTA. In general the gravimetric determination of uranium with organic precipitants is completed by ignition to U_3O_8.

Solution methods for the determination of uranium

Redox methods

The formal oxidation-reduction potentials of uranium ions in volts versus NHE in 1 M $HClO_4$ solutions are as follows:

$$\mathrm{U} \xrightarrow{-1{\cdot}80\mathrm{V}} \mathrm{U}^{3+} \xrightarrow{-0{\cdot}63\mathrm{V}} \underbrace{\mathrm{U}^{4+} \xrightarrow{+0{\cdot}58\mathrm{V}} \mathrm{UO}_2{}^{+} \xrightarrow{+0{\cdot}063\mathrm{V}} \mathrm{UO}_2{}^{2+}}_{+0{\cdot}32\mathrm{V}}$$

The U(V) state is only stable in dilute acid solutions and in the presence of organic complexing agents. Redox methods are therefore essentially based upon the $U^{4+}/UO_2{}^{2+}$ couple, and they are complicated by the irreversibility of this couple. The hexavalent state is the normally stable state in solution and hence many determinations are based upon the reduction of uranyl ions to U^{4+} followed by oxidation with standard solutions of Fe^{3+}, Ce^{4+} or $K_2Cr_2O_7$. Alternatively, uranyl ion concentrations may be determined reductimetrically using Cr^{2+} or Ti^{3+} as titrants, or by the direct controlled-potential coulometric reduction at a stirred mercury-pool electrode. Another approach is to reduce the uranyl ions to the trivalent state in a Jones reductor[21]. The reduced uranium is collected in a solution containing an excess of ferric ions which results in the production of an equivalent of ferrous ions. The ferrous ions are then titrated with potassium dichromate.

Titrimetric methods based upon the preliminary reduction of $UO_2{}^{2+}$ to U^{4+}

In this type of procedure the uranium is reduced either by a strong reducing agent such as chromous or titanous ions, or by a lead reductor. A disadvantage is the reduction to a mixture of the U(III) and U(IV) states, and hence the need to carry out a preliminary selective oxidation of any U(III) to the U(IV) state before titrating to the U(VI) state. The oxidation of U(III) is usually accomplished by aerating the solution, but this step can be subjected to catalytic interference from small amounts of transition elements which promote further air

[20] *Ibid.*, p. 78.

[21] J. H. Kennedy, *Anal. Chem.* **32** (1960) 150.

oxidation to U(VI). A more widely-accepted method of reduction involves the use of the lead column reductor because it produces only tetravalent uranium. This procedure is rapid and it is best carried out in hydrochloric acid solutions. However, sulphate ions can be tolerated provided that sufficient hydrochloric acid is added to the sample solution. Methods of reduction based upon the dissolution of aluminium, copper, magnesium or zinc metal in the sample solution do not offer any advantage over the column reduction procedure and they are inconveniently slow.

After reduction the tetravalent uranium may be titrated directly either with potassium dichromate or ceric sulphate to an endpoint given by a redox indicator of the ferroin type[22]. Potassium dichromate has an advantage of being a primary standard, whereas ceric sulphate must be standardized against arsenious oxide or ferrous iron. Recent improvements in this procedure have been aimed at greater accuracy for the addition of the titrant and at improved precision for the detection of the endpoint by the use of electrometric techniques. In a standard NBS method[23] a weighed excess of potassium dichromate is added to the U(IV) solution, and the amount of oxidant in excess is back titrated with a standard ferrous solution to a potentiometric endpoint using a Pt/SCE electrode system. A precision of 0·01% can be obtained with this procedure. An alternative approach involves the addition of excess ferric ions to the U(IV) solution. The equivalent amount of ferrous ions generated can be titrated with standard potassium dichromate. The use of ceric sulphate as an alternative titrant to dichromate offers the advantage of sharper endpoints whether visual or electrometric. A precision of about 0·01% can be obtained on using an electrometric endpoint.

Coulometrically-generated titrants

The problem of choosing a suitable primary standard for the oxidimetric titration of uranium can be avoided by the application of coulometrically-generated titrants based on the use of the Faraday as an independent physical standard. The technique is known as constant-current coulometry, and several coulometric procedures have been developed for the determination of uranium. The most direct procedure is that reported by Lingane[24] in which U(IV) is titrated with electrogenerated titanous to an amperometric (Pt/Pt) endpoint. An alternative procedure involves the reduction of the uranium to U(IV), then reaction with ferric iron and subsequent titration of the ferrous with electrogenerated ceric ions. This procedure has been developed by Goode[25] to give a precision of about 0·004% (standard deviation) at the 40 mg level of uranium and an accuracy of better than 0·01%.

A further variation on the use of electrogenerated titrants for the determination of uranium has been described by Malinowski[26]. The uranium is reduced by refluxing a hydrochloric acid solution in the presence of metallic aluminium. Phosphoric acid and ferric chloride solution are then added, followed by a weighed excess of potassium dichromate to oxidize the ferrous iron produced. The small amount of potassium dichromate in excess is finally determined by titrating with electrogenerated ferrous ions to a potentiometric endpoint.

[22] W. Davies and W. Gray, UKAEA Report TRG–716 (D) (1964).

[23] C. J. Rodden, private communication.

[24] J. J. Lingane, *Anal. Chim. Acta*, **18** (1958) 240.

[25] G. C. Goode, *Anal. Chim. Acta*, **37** (1967) 445.

[26] J. Malinowski, *Talanta*, **14** (1967) 263.

Controlled-potential coulometric determination of uranium

The determination of uranium by the direct reduction of uranyl ions at a stirred mercury cathode was first demonstrated by Booman[27]. The reduction is performed at a controlled potential of —0·325 volts versus the SCE in molar sulphuric acid solutions. The reduction to U(IV) proceeds via the disproportionation of U(V), and the process is complete in about 15 min in a suitably-designed cell. At the 1–10 mg level of uranium, an accuracy and precision of about 0·1% is readily attainable. For laboratories equipped with controlled-potential coulometers, this technique has great practical convenience for the determination of uranium and, moreover, it has the advantage of absolute standardization based upon electrical calibration and Faraday's laws. The irreversible nature of the U(VI)/U(IV) couple ensures that reoxidation of U^{4+} ions is not possible at the mercury electrode in M H_2SO_4 before oxidation of the mercury takes place.

In sodium tripolyphosphate solutions at pH 7·5 to 9·5 the reduction of uranyl ions is accomplished at —1·35 volts versus the SCE[28]. The reduction is still irreversible, but reoxidation of the U^{4+} ions is just possible at the mercury electrode controlled at +0·1 volts versus the SCE. Uranium is less strongly complexed in 3 M orthophosphoric acid solutions, and the reoxidation of U(IV) to U(VI) is possible at a platinum electrode controlled at about +1·4 volts versus the Ag/AgCl electrode[29]. Similar complexing effects can be obtained for uranium in aqueous sodium fluoride solutions, and it is possible to carry out an analysis by reducing U(VI) to U(IV) at a mercury pool controlled at a potential of —1·0 volts versus the SCE. The conditions of a neutral or slightly acidic solution of 0·75 M sodium fluoride are critical, and the determination can be complicated by the corrosion of the cell components by fluorine. The technique is limited to the determination of 6 mg amounts of uranium because of the insolubility of U(IV) ions in fluoride solutions[30].

The polarographic determination of uranium

Numerous polarographic methods have been published for the determination of uranium[31]. However, the polarography of this element is complicated by the sequence of cathodic reductions possible from VI to V, V to IV, IV to III, and III to the metal. The U(V) to U(IV) change is dependent upon acidity, and U(V) undergoes disproportionation. In addition to the cathodic steps, suitable anodic steps have been reported for the III–IV and the IV–V changes.

In mineral acid solutions such as 0·5 M H_2SO_4, hexavalent uranium is reduced at the dropping mercury electrode with a half-wave potential value of about —0·2 volts versus the SCE. The rate of disproportionation of U(V) is rapid in this medium, and the net composite step observed is for the reduction of U(VI) to U(IV). The behaviour is similar in phosphoric acid solutions, and also in hydrochloric or perchloric acid solutions at molarities greater than 6 M.

The addition of complexing agents to the supporting electrolytes and the use of higher pH solutions has the effect of moving the half-wave potential for the step caused by the

[27] G. L. Booman, *Anal. Chem.* **29** (1957) 219.

[28] H. E. Zittel and L. B. Dunlop, *Anal. Chem.* **35** (1963) 125.

[29] C. M. Boyd and O. Menis, *Anal. Chem.* **33** (1961) 1016.

[30] W. R. Mountcastle, L. B. Dunlop and P. F. Thomason, *Anal. Chem.* **37** (1965) 337.

[31] I. M. Kolthoff and P. J. Elving, *Treatise on Analytical Chemistry*, Part II, Vol. 9, p. 115, Interscience Publishers (1962).

reduction of uranyl ions in a negative direction. This behaviour is employed to avoid some interferences in the determination of uranium in the presence of other elements which undergo reduction at the dropping mercury electrode.

Spectrophotometric methods for the determination of uranium

Uranium (VI), (IV) and (III) solutions give characteristic absorption spectra which can be used for the determination of the valency states in solution. However, the spectrophotometric methods for the determination of total uranium are invariably based on the highest valency state which is the most stable valency. In mineral acid solutions U(VI) absorbs in the region of 450 nm with molar absorptivities of about 30. Despite this low sensitivity the technique has been used fairly extensively for the analysis of solutions containing at least 1 mg per ml of uranium.

Sulphuric acid is the most useful mineral acid medium for the determination of uranium because of the occurrence of absorption peaks for this element at 412, 422 and 430 nm[32]. Close control of the acidity at 4·0 M is required, and removal of nitric and hydrochloric acid is essential. The determination may be carried out differentially with a precision and accuracy of $<0{\cdot}05\%$. However, a disadvantage of the differential technique is the high concentration of uranium (40 mg per ml) required for each analysis. Similar considerations apply to the determination of uranium in perchloric acid solution[33].

Numerous chromogenic reagents have been proposed for the spectrophotometric determination of uranium, but the main disadvantages of many of the proposed reagents include a lack of specificity and sensitivity. The coloured complex formed by uranium with thiocyanate ions was one of the first to be used. This complex has a molar absorptivity of 3850 at a wavelength of 375 nm, but it suffers considerable interference from transition elements and complexing anions[34]. Some increase in sensitivity and freedom from anionic interference can be obtained by the use of solutions of a lower dielectric constant, such as aqueous acetone mixtures[35].

Dibenzoylmethane is a more sensitive reagent for hexavalent uranium since it has an absorptivity of about 20,000 at 400–450 nm. However, the reagent is lacking in specificity, and the formation of the complex is usually preceded by the extraction of the uranium as its tetrapropylammonium trinitrate complex with methyl isobutyl ketone[36].

The more modern reagents such as Arsenazo III and PAN, offer slightly increased sensitivity, but no improvement in specificity. Rhodamine B forms a complex with hexavalent uranium with a molar absorptivity of 102,700 at 555 nm. The complex is extractable into organic medium and is suitable for the determination of uranium at the microgram level[37].

The fluorimetric determination of uranium

The emission of a yellow-green fluorescence by uranium in a sodium fluoride flux is specific for the presence of uranium. This unique property forms the basis of an attractive and widely-used method for the determination of very small amounts of this element. The

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[32] A. Bacon and G. W. C. Milner, AERE C/R 1637 (1955) and AERE C/R 1813 (1956).

[33] T. W. Steele, *Analyst*, **83** (1958) 988.

[34] I. M. Kolthoff and P. J. Elving, *Treatise on Analytical Chemistry*, Part II, Vol. 9, p. 97, Interscience Publishers (1962).

[35] C. E. Crouthamel and C. E. Johnson, *Anal. Chem.* **24** (1952) 1780.

[36] W. J. Maeck, G. L. Booman, M. C. Elliatt and J. S. Rein, *Anal. Chem.* **31** (1959) 1130.

[37] H. H. Ph. Moeken and W. A. H. Van Heste, *Anal. Chim. Acta*, **37** (1967) 480.

method has a high sensitivity with a limit of detection of approximately 10^{-10} g of uranium. The wavelength of the exciting radiation is 365 nm, and the emission occurs at a wavelength of about 555 nm. The use of primary and secondary filters ensures the specificity of the fluorescence measurement. The main disadvantages of this technique are the difficulty of achieving reproducible results and the "quenching" effect of impurity elements on the uranium fluorescence. The former disadvantage is usually controlled by careful attention to practical details, and the latter by employing a standard addition of uranium to the sodium fluoride flux.

The composition of the sodium fluoride flux has received considerable attention in published procedures. The inclusion of sodium carbonate in the flux reduces the temperature of fusion, and this enables the cooled melt to be removed readily from the platinum tray for measurement in a constant-reflectance source holder. Unfortunately, the use of this flux increases quenching effects and lowers the sensitivity for uranium. A pure sodium fluoride flux avoids these disadvantages, but it produces sources which are difficult to remove from the fusion tray. With this flux, therefore, it is usual to carry out the fusion and emission measurement in the same platinum tray. The source obtained can also be remelted following the addition of a standard amount of uranium. With the standard addition technique, the results obtained for uranium are, *a priori*, accurate and a reproducibility of better than ±10% is typical. Improved precision has been claimed on giving close attention to such variables as flux composition, time and temperature of fusion and the surface condition of the source holders.

Radiochemical methods for the determination of uranium

Although all uranium isotopes are radioactive, the determination of total uranium by measuring its natural radioactivity is a relatively unattractive method of analysis because of the low specific activity of the principal isotopes. The β,γ-activity of the daughter products is useful in semi-quantitative analysis, but the α-activity of the U-238 and U-235 isotopes is of limited value only. The γ-activity is usually that from the daughter products Pb-214 and Bi-214. For samples enriched with respect to U-235, γ-spectrometry can be employed for the determination of the U-235 content by measuring the photopeak at 0·184 MeV.

A more sensitive method of analysis is based on the neutron activation of the fissionable U-235 isotope. The method involves neutron irradiation followed by measurement of either the gross activity or the activity due to a particular fission product. Ba-140, Mo-99 and Zr-95 are fission products that have been used for this purpose, and the sensitivity of the Ba-140 method is approximately 10^{-8} g of total uranium in the sample. This type of method is very suitable for the analysis of samples containing naturally-occurring uranium because the distribution of the uranium isotopes is well known. Samples containing uranium that has been enriched with respect to the U-235 isotope will also need to be analysed for uranium isotopic composition by mass spectrometry (see later).

Another approach to the determination of uranium involves the measurement of the delayed neutrons emitted by some of the fission products. A reported method[38] involves a 4-min irradiation in a thermal flux of 10^{13} neutrons per cm^2, followed by a 3-min counting period arranged to commence 15 sec after the removal of the sample from the thermal flux. The sensitivity of this method is 3×10^{-9} g of U-235.

[38] M. W. Echo and E. A. Turk, USAEC TID 7531 Pt. 1 (1957) 153.

Isotope-dilution methods for the determination of uranium

The ready availability of uranium which has been enriched to $>90\%$ with respect to the U-235 isotope poses a continuing problem in analytical laboratories handling uranium samples. A knowledge of the isotopic composition is required to enable the weight of uranium to be calculated from the moles of uranium determined. With the exception of uranium hexafluoride samples, the determination of the isotopic composition of uranium is normally obtained by surface ionization mass spectrometry. The method is very sensitive since only a few micrograms of uranium are needed; the removal of organic and inorganic impurities from the sample is desirable, but the separation need not be quantitative. The separation of the uranium from other actinides is not necessary.

The above techniques of determining the isotopic composition can be adapted to the measurement of the mass of uranium by using the isotope dilution method of analysis. This involves the addition of a known quantity of a selected uranium isotope to the sample, establishment of isotopic equilibrium and determination of the change in isotopic composition. For natural uranium samples or those enriched in the U-235 isotope, U-233 is the usual choice of selected isotope. This method of analysis gives both a concentration result and also an isotopic assay result[39].

6. NEPTUNIUM

Although the chemistry of neptunium is similar to that of its nearest actinides, there are some differences in behaviour. Neptunium ions can exist in solution in several valency states, from III to VII. Np^3 ions are prepared by the action of powerful reducing agents in the presence of an inert atmosphere. Although these ions are more stable than U^{3+} ions, they find little use in the determination of this element. The tetravalent ions are more useful in analysis, and neptunium can be readily conditioned to this state with reducing agents such as ferrous iron, ascorbic acid, hydrazine, hydroxylamine, etc. Pentavalent neptunium occurs in solution as $NpO_2{}^+$ ions which differ from $PuO_2{}^+$ and $UO_2{}^+$ ions in being fairly stable. In fact, the pentavalent state is the most stable state of neptunium. $NpO_2{}^{2+}$ ions are similar to $UO_2{}^{2+}$ ions and they are more stable in solution than $PuO_2{}^{2+}$ ions. Heptavalent neptunium has been identified spectrophotometrically in strong alkaline solution as $NpO_5{}^{3-}$ ions, but owing to its instability in acid solution the valence state is of limited interest analytically[40]. The existence of these valency states means that coulometric, potentiometric and polarographic methods predominate amongst those available for the determination of neptunium. Other available methods include spectrophotometry, radiochemistry, gravimetry, etc.

Gravimetric methods for the determination of neptunium

Gravimetric methods are of limited usefulness for the determination of neptunium, since only the dioxide has had its stoichiometry proved as a suitable weighing form. Some control of the composition of the atmosphere is necessary during ignition to produce a stoichiometric oxide; for example ignition in an atmosphere of carbon monoxide is necessary to obtain an oxide with an O/Np ratio close to a value of 2·00[41].

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[39] R. K. Webster, A. A. Smales, D. F. Dance and L. J. Slee, *Anal. Chim. Acta*, **23** (1960) 101.

[40] V. I. Spits, N. N. Krot, M. P. Mefodeva, V. Shilah and A. D. Gel'man, *Doklady Akad. Nauk SSSR* **181** (1968) 128.

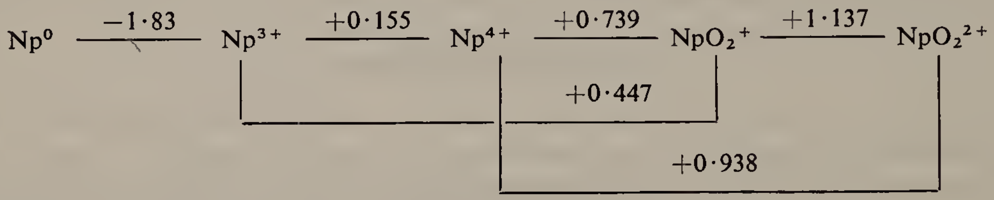
[41] L. E. J. Roberts and A. J. Walter, AERE–R 3624 (1963).

Neptunium(IV) may be precipitated as its hydroxide from alkaline or ammoniacal solutions, and, after filtration, the precipitate may be calcined at 800°C to the dioxide. More selectivity can be achieved by precipitating Np(IV) as its insoluble peroxide or oxalate from nitric acid or hydrochloric acid solutions. However, it must be recognized that losses of neptunium are greater in these precipitations than in the hydroxide precipitation. Neptunium(IV) also forms insoluble compounds from acidic solutions with other precipitants, including fluoride, phosphate, iodate, phenylarsonate, benzene sulphinate, etc., and some of these precipitates could possibly be used for the gravimetric determination of neptunium after further investigation. In general, it may be assumed that Np(IV) can be precipitated in the same way as Pu(IV) and U(IV).

Neptunium (VI) may be precipitated as its hydroxide and as its phenylarsonate in the pH range 2–3.

Solution methods for the determination of neptunium

The oxidation potentials for neptunium ions in 1 M $HClO_4$ in volts versus the NHE at 25°C are as follows:



The Np^{3+}/Np^{4+} and the $NpO_2{}^+/NpO_2{}^{2+}$ couples are reversible and they are potentially suitable for redox methods of analysis. However, since Np^{3+} ions are not stable in solutions in the presence of air, the $NpO_2{}^+/NpO_2{}^{2+}$ couple finds the most application in analysis.

Redox methods

There are a number of possible valency changes available for redox determinations, but the transition from Np^{4+} to the higher valency states is not reversible at normal electrodes. The $NpO_2{}^+/NpO_2{}^{2+}$ couple is reversible and it has a standard potential of +1·137 volts versus NHE in 1 M acid (except H_2SO_4). For a redox titration the oxidant must have a standard potential greater than +1·49 volts, and the reductant a potential less than +0·79 volts in order to achieve a coefficient of variation of 0·1 %. Ferrous iron fulfils the requirement for the reductant and ceric ions in nitric acid for the oxidant. The alternative use of these reagents gives the possibility of check titrations being carried out on a single sample[42]. However, for this to work the only common anions permitted are nitrate and perchlorate. The titration with ferrous has a coefficient of variation of 0·13 %, whereas the value is 0·3 % for the ceric titration. These values apply to the use of weight burettes for the addition of titrant and a platinum–calomel electrode for the endpoint detection.

Controlled-potential coulometric determination of neptunium

The coulometric method for neptunium is based on the reversible behaviour of the $NpO_2{}^+/NpO_2{}^{2+}$ couple at a platinum working electrode. In 1 M H_2SO_4 this couple has an

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[42] J. H. Moss, AERE C/R 3214 (1960).

E_0' value of $+0{\cdot}84$ volts vs. SCE. The general procedure is first to oxidize the neptunium to the VI state with an excess of ceric ions, and then reduce it electrochemically to the V state. On using a voltage of $+0{\cdot}64$ volts vs. SCE for the reduction, interference from iron and plutonium is avoided and any ceric ions are reduced to the cerous state. The Np(V) is finally reoxidized to Np(VI) electrolytically at a voltage of $+1{\cdot}0$ volts vs. SCE, and the integrated current in this step is used to determine the neptunium concentration.

The neptunium couple can be titrated quantitatively in HNO_3, $HClO_4$ and H_2SO_4 solutions, but the latter acid is preferred for several reasons. For instance, the residual current is lower, the titration-blank is less and more reproducible results are obtained. By this method 1 mg amounts of neptunium can be determined to better than $\pm 0{\cdot}5$ μg (1 σ), and 20 μg to better than $\pm 0{\cdot}2$ μg.[43]

The polarographic determination of neptunium

The reversible Np^{4+}/Np^{3+} couple is suitable for determinations involving the use of the dropping mercury electrode. In 1 N hydrochloric acid the standard potential of this couple is $-0{\cdot}10$ volts vs. SCE, and a satisfactory one-electron step is readily obtained. However, Jenkins, Slee and Phillips[44] preferred to use a more complexing supporting electrolyte for the determination of the neptunium content of plutonium metal so as to avoid interferences. The reduction potential for the Np–EDTA complex is about 700 mV more negative than that for the Np^{4+} ions, and the step is moved away from that resulting from the oxidation of chloride ions which can cause difficulties in the HCl supporting electrolyte. The neptunium step at $-0{\cdot}8$ volts vs. the mercury pool anode is separated from the following steps: Cd ($-1{\cdot}4$ V), Pb ($-1{\cdot}2$ V), Cu ($-0{\cdot}5$ V), U ($-0{\cdot}3$ V) and Fe(III) ($-0{\cdot}2$ V). With a square wave polarograph it is possible to analyse solutions containing as little as $0{\cdot}5$ μg per ml of neptunium. Also the precision for the determination of the neptunium content of plutonium metal is $\pm 2\%$ for 500 ppm and $\pm 10\%$ for 25 ppm.

Spectrophotometric methods for the determination of neptunium

Sharp absorption bands are given by the different oxidation states of neptunium, and all the analytically useful bands are summarized in Kolthoff and Elving[45]. The most sensitive bands for Np(III) are in the ultraviolet region at $233{\cdot}5$ and 267 nm, whilst those for Np(IV) and Np(V) are at 964 and 983 nm respectively. There are no bands for Np(VI) in the visible region, but a prominent peak occurs at a wavelength of 1230 nm and this is suitable for the determination of Np(VI) in 1–2 M HNO_3 solutions. Unfortunately, methods based on the above absorption bands generally suffer from a lack of sensitivity, and the nature of the anion can also have some influence. This has resulted in the study of spectrophotometric methods based on the coloured compounds formed by neptunium with suitable organic reagents.

Several organic reagents have been studied for the spectrophotometric determination of neptunium[6], and Arsenazo III appears to be the most sensitive of those investigated so far. Arsenazo III forms a green coloured complex in HCl and HNO_3 solutions. Maximum

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[43] R. W. Stromatt, Hanford Atomic Products Operation, Report HW 59447 (1959); *Talanta*, 6 (1960) 197.

[44] J. Slee, G. Phillips and E. N. Jenkins, *Analyst*, 84 (1959) 596.

[45] I. M. Kolthoff and P. J. Elving, *Treatise on Analytical Chemistry*, Part II, Vol. 9, p. 294, Interscience Publishers (1962).

absorbance readings can be obtained at 665 nm on producing the complex in 6·1 M HCl solutions containing ferrous ammonium sulphate and ascorbic acid to reduce neptunium to the tetravalent state. In the presence of both reducing agents the maximum colour formation takes place immediately. According to Bryan and Waterbury[46], the optimum conditions for the colour development are 6·1 M HCl, ferrous ion and ascorbic acid as reductants, and 5 mg of Arsenazo III per 25 ml of solution. They recommend these conditions for the determination of the neptunium content of plutonium samples.

Neptunium (IV) forms a coloured complex with thorin which is suitable for analytical determinations. In a method reported by Britt[47], the neptunium is reduced with ferrous sulphamate and the final acidity is adjusted to 0·4 M in HNO_3. The thorin–neptunium complex is allowed to develop for 30 min before absorbance measurements are taken at 540 nm. The method is applicable to solutions containing microgram amounts of neptunium per ml, and it has been adapted for use with the Technicon "Auto Analyzer".

A coloured complex formed by Np(IV) with xylenol orange in solutions of pH 2 is convenient for the direct determination of neptunium in the presence of an excess of uranium.

Radioactive methods for the determination of neptunium

The isotope of mass 237 is the only isotope of neptunium emitting α-radiation. It has a specific activity of $1 \cdot 56 \times 10^3$ disintegrations per μg per min and a half-life of $2 \cdot 4 \times 10^6$ years. It is possible to determine Np-237 in amounts of 0·1 μg or more by counting the α-activity emitted, and this constitutes one of the most sensitive methods for the determination of this element. Before applying this method, however, it is generally necessary to separate the neptunium from Pu, U, Am, Cm and fission products. Fortunately, ion exchange and solvent extraction methods are now available for this separation. If α-pulse analysis is used, the occurrence of peaks at 4·781 and 4·762 MeV can be used for the identification of the presence of Np-237.

The isotope of mass 239 is a β-emitter, as well as a weak γ-emitter. It has a specific activity of $5 \cdot 237 \times 10^{11}$ disintegrations per μg per min and a half-life of 2·33 days. It is possible to detect 50×10^{-11} μg by β-counting on the basis of a counter geometry of 30% and a count rate of 100 counts per minute. The γ-activity can be measured with a scintillation counter or a pulse-height analyser. The occurrence of major peaks at 0·228 and 0·278 MeV in the γ spectrum can be employed for the identification of Np-239.

7. PLUTONIUM

Introduction

More research work has been carried out on the analytical chemistry of plutonium during the past two decades than on any other element. This is partly due to the involved chemical properties of plutonium, and partly as a consequence of the application of plutonium in the development of nuclear energy. Plutonium exhibits several valency states from 3 to 6 in dilute mineral acid solutions and the heptavalent state is attainable in alkaline solution. In dilute acid solution there is no principal valency state, and, owing to disproportionation, it is possible for all four valency states to co-exist in the same solution.

[46] R. G. Bryan and G. R. Waterbury, Los Alamos Scientific Laboratory, Report LA 4061 (1969).

[47] R. D. Britt, *Anal. Chem.* 33 (1961) 969.

The stabilization of a selected valency can be achieved by the addition to the solution of either a complexing agent or an excess of "holding" reductant or oxidant. Each of the four valency states gives characteristic absorption spectra in solution which form the basis of absorptiometric methods of analysis. It is important, however, to avoid the occurrence of the hydrolysis of plutonium which can result in the irreversible precipitation of polymeric species from solution.

Redox methods of analysis are based either on the Pu(III)/Pu(IV) change or the Pu(VI)/Pu(IV) change, and complexometric titrations of the Pu(III) and Pu(IV) valency states are also available. Plutonium may be determined gravimetrically by ignition to the dioxide under carefully controlled conditions. The high specific activity of the commonly-available isotopes of plutonium (namely 238, 239, 240 and 241) provides a sensitive means of analytical detection. However, this radioactivity creates a serious health hazard during the handling of this element.

Gravimetric methods for the determination of plutonium

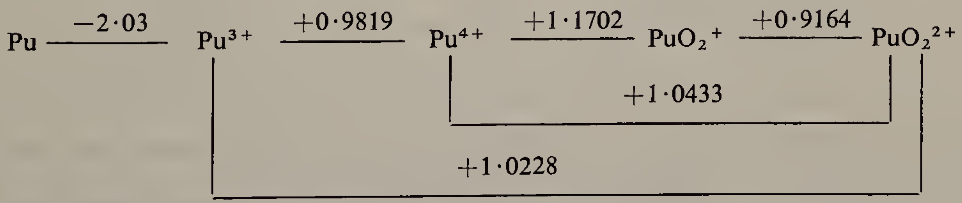
Plutonium is readily precipitated from solution as its insoluble peroxide, hydroxide or oxalate, and also as insoluble organic compounds formed with precipitants such as cupferron, 8-hydroxy-quinoline, phenylarsonic acid, etc. It is generally necessary to condition the valency state of the plutonium before carrying out the precipitation, and the subsequent filtration and handling of the precipitate must be carried out in enclosed glove boxes. Finally, it is usual to complete the determination by igniting the precipitate to the dioxide, but this is not a straightforward procedure.

Ignition in air to a constant weight at a controlled temperature in the range of 850°C and upwards is a practical procedure, but the final composition of the dioxide is influenced by the composition of the starting precipitate[48]. Also conflicting claims have been made regarding the temperature required for ignition to the stoichiometric dioxide. It is now generally accepted that control of the composition of the atmosphere is as important as control of the temperature of ignition. For instance, removal of the last traces of excess oxygen can only be achieved by igniting the precipitate in an atmosphere of carbon monoxide. It is for reasons such as the above that the gravimetric method is seldom employed for the determination of plutonium.

Solution methods for the determination of plutonium

Redox methods

The oxidation potentials for plutonium ions in 1 M $HClO_4$ in volts versus the NHE are as follows:



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[48] J. L. Drummond and G. A. Welch, *J. Chem. Soc.* (1957) 4781.

Redox methods for the volumetric determination of plutonium are based either on the Pu(III)/Pu(IV) couple or the Pu(VI)/Pu(IV) couple. Titrations are usually carried out in dilute sulphuric acid solutions because sulphate ions stabilize the tetravalent state of plutonium. In its lowest valency state plutonium behaves in a manner similar to iron, and so it can be determined by the same redox titration procedures. For example, a typical method involves the reduction of plutonium to the trivalent state in a Jones reductor followed by titration with ceric sulphate to a visual or spectrophotometric endpoint[49].

Complexometric methods

Plutonium(III) and Pu(IV) form very stable 1 : 1 complexes with EDTA which have been utilized in complexometric titrations. Plutonium should not be present in solution in the hexavalent state. The Pu(III) complex is formed at pH 2·5–3·5, but the direct titration with EDTA is unsatisfactory[50]. A back-titration procedure was found to be satisfactory giving results to within 1 % on ~10 mg amounts of plutonium. This involved the addition of EDTA in a slight excess, followed by the titration of this excess with ferric iron using salicylic acid as indicator. An improved endpoint has been obtained by back titrating with thorium nitrate with alizarin S as indicator. Plutonium(IV) may be titrated in a similar manner, but at the higher pH range of 4–5. The higher stability of the Pu(IV)–EDTA complex enables the titration to be carried out in the presence of sulphate ions.

Spectrophotometric methods for the determination of plutonium

The absorption spectra of the plutonium valency states in dilute mineral acid solution are characterized by sharp absorption peaks, and some of the analytically important peaks are listed in Table 3. The absorption peaks are sufficiently resolved to enable the determination of any one plutonium valency state to be carried out in the presence of the others. This feature is very important because of the possibility of all four valency states coexisting in the same solution. Procedures have been described in which absorption measurements are made at four wavelengths selected for each valency and the resulting equations are solved mathematically for the concentration of each valency state[51].

TABLE 3. ABSORPTION PEAKS FOR PLUTONIUM VALENCY-STATES

Oxidation state	Wavelength nm	Molar absorptivity
Pu(III) (0·1 M $HClO_4$)	603	35·40
	560	36·10
Pu(IV) (0·5 M HCl)	700	10·88
	470	49·60
Pu(V) (0·5 M HCl)	569	17·10
Pu(VI) (0·1 M HCl)	953	19·90
	833	~300·00

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[49] C. W. Koch, N.N.E.S. Series, Div. IV, *The Transuranium Elements*, Vol. 14-B (1949) 1337.

[50] G. W. C. Milner and J. L. Woodhead, *Analyst*, **81** (1956) 427.

[51] I. K. Shvetsov and A. M. Yorobyev, *Proceedings International Conference on Peaceful Uses of Atomic Energy*, paper 674, Geneva (1955).

The determination of total plutonium in solution can, in principle, be carried out by measuring the absorbancy at any one of the peaks listed in Table 3. This presupposes that the plutonium can be quantitatively adjusted to the required valency and then stabilized in that state. The most convenient valency for plutonium is the trivalent state which can be stabilized in 1 M hydrochloric acid solutions by the addition of an excess of a reductant such as hydroxylamine hydrochloride. Plutonium concentrations in the range from 1 to 4 mg per ml can be determined by this method with a precision of 1–2% when using cells of 1 cm path length. The wavelength used for absorbancy measurements is 603 nm. Improved precision and accuracy can be attained by employing differential spectrophotometric measurements of the Pu(III) state, but this technique requires higher plutonium concentrations, for example 8–13 mg per ml for 1 cm cells and 2–3 mg per ml for 4 cm cells. Absorbancy measurements on samples are made at a wavelength of 565 nm relative to accurately known standard plutonium solutions. This wavelength was selected in preference to that for the peak at 603 nm because of a lower temperature coefficient and a smaller dependence on variation in chloride concentration. A precision of 0·05% (coefficient of variation) can be obtained for the determination of plutonium by the differential technique[52]. A major disadvantage of this type of spectrophotometric method arises from the relatively low molar extinction coefficients and hence the need to have reasonable quantities (10–50 mg) of plutonium available.

Considerably greater sensitivity can be obtained by forming highly-coloured organic complexes with plutonium[53]. The most suitable organic reagents include thoron [1(*o*-arsonophenylazo)-2-naphthol-3,6-disulphonic acid], Arsenazo I [1(*o*-arsonophenylazo)-2,3-naphthol-5,8-disulphonic acid], and Arsenazo III [1,4(*o*-arsonophenylazo)-2,3-naphthol-5,8-disulphonic acid]. Coloured complexes are formed with plutonium in the tetravalent state, and the relevant details of these reagents and of their analogues are summarized in Table 4. A disadvantage to the use of this approach in analysis arises from the need to adjust the plutonium quantitatively to the tetravalent state which is an intermediate valency state. Considerable care is required to control this adjustment and the recommended procedures

TABLE 4. ORGANIC REAGENTS FOR THE SPECTROPHOTOMETRIC DETERMINATION OF PLUTONIUM

Reagent	Pu(IV) complex peak maximum nm	Molar absorptivity	Optimum solution conditions
Thoron I	545	9000	pH 1·5–2·0 HNO_3 Sulphate interferes.
Thoron II	555	10,000	2 M HCl. Sulphate does not interfere at ratios <25·1 w.r.t. Pu.
Chlorophos-thoron	515	17,300	pH 1·5–4·0
Arsenazo I	595	22,000	pH 2–5
Arsenazo II	610	11,800	pH 2–4
Arsenazo III	670	67,000	1 M HNO_3
		136,000	4–7 M HNO_3
Chlorophosphonazo I	580	24,360	pH 1·5–4
Chlorophosphonazo III	680	125,000	2–4 M HNO_3

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[52] G. Phillips, *Analyst* **83** (1958) 75.

[53] M. S. Milyukova, N. I. Guser, I. G. Sentyurin and I. S. Skylarenko, *Analytical Chemistry of Plutonium*, p. 125, Israel Program for Scientific Translation, Jerusalem (1967).

usually involve a preliminary reduction of plutonium to the trivalent state followed by reoxidation to the tetravalent state.

Electrochemical methods for the determination of plutonium

Electrochemical methods, including potentiometric, amperometric and coulometric titrations, have been fully investigated for the determination of plutonium, and they are widely applied. The attractive features of these methods include high accuracy and precision for the determination of milligram amounts of plutonium and also the possibility of automation.

Potentiometric methods

The potentiometric titrations for plutonium are identical in principle with the classical redox volumetric methods discussed earlier. They differ only in the quantity of sample employed and in the technique of endpoint detection. In methods based upon the Pu(III)/Pu(IV) couple, various preliminary reductants have been used and these include Ti(III)[54], Cr(II)[55], liquid zinc amalgam[56] and metallic silver[57]. The trivalent plutonium is then titrated to the tetravalent state in sulphuric acid solutions with either ceric sulphate or potassium dichromate. The endpoint may be detected by means of either a platinum indicating electrode + SCE or a bimetallic gold–platinum electrode system. The choice of sulphuric acid for the titration medium ensures that the plutonium is not oxidized to a valency higher than the tetravalent state. This is due to a shift in the formal reduction potential of the Pu(III)/Pu(IV) couple from +0·98 volts vs. the NHE in M $HClO_4$ to +0·75 volts in the H_2SO_4. The precision attainable by these procedures varies from 0·05 to 0·20% (coefficient of variation) for the determination of 1–10 mg amounts of plutonium. A major disadvantage of methods based on the Pu(III)/Pu(IV) couple occurs from the interference of iron which has a formal reduction potential of +0·77 volts vs. the NHE in molar sulphuric acid.

Difficulties from the interference of iron can be avoided by changing to potentiometric methods of analysis based upon the Pu(VI)/Pu(IV) couple. In these methods the plutonium is oxidized to the hexavalent state either by fuming with perchloric acid[58] or by reaction with argentic oxide[59]. The Pu(VI) is then reduced to the tetravalent state by the addition of a slight excess of a standard ferrous solution, and the amount of this reagent in excess is titrated with Ce(IV) in molar sulphuric acid to a potentiometric endpoint. This indirect procedure is adopted to avoid difficulties in endpoint detection caused by the sluggish nature of reactions involving the hexavalent oxygenated cation PuO_2^{2+}. The titration may be carried out automatically, and a precision of less than 0·05% (coefficient of variation) can be achieved.

Amperometric methods

The amperometric titration for plutonium[60] is based upon the Pu(VI)/Pu(IV) couple. The plutonium is oxidized to the hexavalent state with argentic oxide, and it is then titrated

[54] C. F. Metz, *Anal. Chem.* **29** (1957) 1748.
[55] A. J. Fudge, A. J. Wood and M. F. Banham, AERE-R 3264 (1960).
[56] H. E. Boaz, USAEC Report LA 507 (1946).
[57] F. Barker and R. H. Dickson, UKAEA Report IGOM/W–040 (1957).
[58] G. R. Waterbury and C. F. Metz, *Anal. Chem.* **31** (1959) 444.
[59] G. W. C. Milner, A. J. Wood and G. E. Cassie, UKAEA Report AERE–R 4975 (1965).
[60] C. A. Seils, R. P. Larsen and R. J. Meyer, USAEC Report T.I.O. 7606 (1960) paper 21.

with standard ferrous solution following the destruction of excess oxidant. A rotating platinum electrode at +0·6 volts vs. the mercurous sulphate electrode is used for the detection of the endpoint, and the current output of this system is at a constant low level on approaching the endpoint. After the endpoint, the indicator current is proportional to the concentration of excess reductant. This technique of endpoint detection is extremely sensitive, and a precision of 0·05% (coefficient of variation) can be achieved by this procedure for the determination of 10 mg amounts of plutonium.

Coulometric methods

Coulometric methods include controlled-potential and constant current coulometry, and both of these techniques have been used for the determination of plutonium. The attractive features of coulometric methods of analysis include the following:

(a) absolute standardization based upon internationally accepted physical standards;
(b) high accuracy and precision for the determination of milligram amounts of material with the minimum of manipulation.

In consequence, coulometry is a very suitable technique for application to the analysis of radioactive solutions of plutonium.

Controlled-potential coulometry

Pu(III)/Pu(IV) Couple

The determination of total plutonium by controlled-potential coulometry is based upon the reversible Pu(III)/Pu(IV) couple by using either reduction of Pu(IV) or oxidation of Pu(III). In the absence of hexavalent plutonium, the determination can be carried out in any suitable mineral acid solution on using the E_0' value appropriate to the particular medium. If hexavalent plutonium is present, however, total plutonium can only be determined in dilute sulphuric acid media, since this is the only one suitable for the complete electrolytic reduction of Pu(VI) to lower valency states. The analytical procedure is fairly straightforward on using a suitable electronic controlled-potential coulometer. For example, a reduction is carried out at a platinum gauze electrode controlled at +0·30 volts vs. the SCE to reduce the plutonium completely to the trivalent state in 1 M H_2SO_4. This is then followed by an electrolytic oxidation at +0·70 volts vs. the SCE to oxidize the plutonium to the tetravalent state. No endpoint detection system is required since the course of titration is followed by observing the electrolysis current; this decays exponentially to a low and constant background value on completion of the determination. An important advantage of this procedure is the specificity achieved by controlling the potential, and this permits the determination of plutonium to be carried out in the presence of all elements with the exception of those reacting at the electrode within the selected potential range. Iron is the major interfering element in this category, since it has an E_0' value of +0·42 volts vs. the SCE. A precision of $\leqslant$ 0·25% (coefficient of variation) is attainable by this technique for the determination of plutonium at the milligram level[61].

[61] G. Phillips and G. W. C. Milner, *Proc. SAC Conference*, Nottingham (1965) 240. W. Heffer & Sons Ltd., Cambridge.

Pu(VI)/Pu(IV) Couple

The interference from iron in the coulometric determination of plutonium can be avoided by means of a secondary controlled-potential procedure based upon the Pu(VI)/Pu(IV) couple[62]. In this procedure the plutonium is oxidized chemically to Pu(VI) either by fuming with perchloric acid or by reacting with argentic oxide. An electrolytic reduction is then carried out at a potential which reduces any ferric iron in the sample to the ferrous state. The ferrous ions react rapidly with the PuO_2^{2+} ions to reduce them to Pu(IV) which undergo further reduction to Pu(III) at the platinum electrode. The electrolysis is continued until the plutonium is reduced completely to Pu(III) and the iron to Fe(II), and the total current required for this step is obtained by integration. An electrolytic oxidation step is then performed to reoxidize the plutonium to Pu(IV) and the iron to Fe(III), and the current in this step is also integrated. The difference between the two integrals is the equivalent of the current required to produce the quantitative reduction of Pu(VI) to Pu(IV) from which the plutonium content of the sample can be calculated.

Valency states of plutonium

A combination of the above controlled-potential procedures for plutonium may be used as a means of analysing for the various plutonium valency states in solution[62]. This is accomplished by carrying out four controlled-potential coulometric steps on a 1 M $HClO_4$ solution of the sample sequentially as follows:

(1) The base electrolyte (1 M $HClO_4$) containing added iron is reduced at +0·50 volts vs. the SCE and then reoxidized at +0·90 volts. This step enables the quantity of iron to be determined

$$\mathrm{Fe(II)} \rightarrow \mathrm{Fe(III)}$$

(2) An aliquot of the plutonium solution is added to the electrolysis cell, and an oxidation at +0·90 volts vs. the SCE is carried out.
This converts the plutonium to the tetravalent state

$$\mathrm{Pu(III)} \rightarrow \mathrm{Pu(IV)}$$

(3) The reduction step at +0·50 volts vs. the SCE is next repeated and this achieves the following reactions:

$$\mathrm{Pu(VI)} \rightarrow \mathrm{Pu(III)}$$
$$\mathrm{Pu(IV)} \rightarrow \mathrm{Pu(III)}$$
$$\mathrm{Fe(III)} \rightarrow \mathrm{Fe(II)}$$

(4) An oxidation of +0·90 volts vs. the SCE completes the sequence of operations to give the following oxidations:

$$\mathrm{Pu(III)} \rightarrow \mathrm{Pu(IV)}$$
$$\mathrm{Fe(II)} \rightarrow \mathrm{Fe(III)}$$

Plutonium(III) is calculated from the integrated current for step (2) whilst Pu(VI) is obtained from the difference between the integrated currents for steps (3) and (4). The total plutonium is determined from the difference between the integrated currents for steps (4) and (1). The amount of Pu(IV) can then be calculated by subtracting the sum of Pu(III) + Pu(VI) from the total plutonium.

[62] W. D. Shults, *Talanta* **10** (1963) 833.

Constant-Current Coulometry

The determination of plutonium by constant-current coulometry is less-widely used than the controlled-potential method. A preliminary chemical adjustment of the plutonium to a single valency state is essential in this method, and this technique therefore offers little advantage over the more precise potentiometric titration methods. Carson[63] has described a method which is based on the titration of Pu(VI) with electrogenerated Fe(II) to a potentiometric endpoint. The chemical pretreatment to Pu(VI) is effected with potassium permanganate by heating the sample solution to 75°C. During this process the permanganate is reduced to manganese dioxide which is then destroyed by heating with excess formaldehyde. The method is reported to be applicable to the determination of plutonium in the range from 3 μg to 10 mg with a precision varying from ±5% at the lower level to ±1% at the milligram level.

The radiometric determination of plutonium

The determination of plutonium by means of α-activity is a very convenient and widely used analytical method. The isotopic composition of plutonium normally encountered, i.e. that produced by neutron capture on U^{238}, can, however, vary widely and significantly alter the specific activity of the material being analysed. The isotopes of importance and the relevant data are listed in Table 5.

TABLE 5. ISOTOPES OF PLUTONIUM

Isotope	Half-life	Specific activity (dis/m/μg)	Mode of decay	Energy MeV
Pu^{238}	86·4 yr	$3{\cdot}88 \times 10^7$	α	5·495 5·452
Pu^{239}	24,360 yr	$1{\cdot}36 \times 10^5$	α	5·147 5·134 5·096
Pu^{240}	6,580 yr	$5{\cdot}00 \times 10^5$	α	5·162 5·118
Pu^{241}	13 yr	$2{\cdot}57 \times 10^8$	α (4×10^{-3}%) β (99%)	
Pu^{242}	$3{\cdot}79 \times 10^5$ yr	$8{\cdot}65 \times 10^3$	α	4·898 4·858

Plutonium-239 is the predominant isotope, but lesser amounts of Pu-238, Pu-240, Pu-241 and Pu-242 are invariably present in commercial plutonium. In addition, Am-241 ($t_{\frac{1}{2}}$ 458 yr, α-energy 5·486, 5·443 MeV) is present as a daughter product of Pu-241. A knowledge of the isotopic composition of the plutonium being analysed is then of vital importance in the radiometric determination of plutonium. Alpha-spectrometric examination of a sample of the plutonium gives information relating to the Pu-238 and Pu-242 isotopes, but does not resolve the Pu-239 and Pu-240 energies. Unless chemically separated, the Am-241 content of the plutonium will be detected with the Pu-238 isotopes. The ratio of the Pu-239 to Pu-240 isotopes can only be determined by mass spectrometry. In order to

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[63] W. N. Carson, *Anal. Chem.* **29** (1957) 1417.

calculate the specific activity of a sample of plutonium, two ratios are required, viz. Pu-239: Pu-240 (mass) and Pu-239 + Pu-240: All other isotopes (α). Given this information plutonium may be determined with a precision and accuracy of $\leqslant 1\%$ on about 10^{-1} to 10^{-2} μg with an ultimate sensitivity of about 10^{-5} to 10^{-6} μg.

8. AMERICIUM

Introduction

Americium is invariably associated with plutonium by virtue of the β-decay of the Pu^{241} isotope to Am^{241}, and the amount of americium present is dependent on the isotopic composition of the plutonium and the elapsed time since the chemical purification of the plutonium. The chemical properties of americium are similar to those of plutonium. For example, both elements have III, IV, V and VI valency states in solution. However, the trivalent state is the most stable valency for americium, whereas the corresponding valency for plutonium is the tetravalent state. This slight shift in stability, together with the practical fact that only milligram amounts of americium are available, has resulted in an incompletely-developed knowledge of the analytical chemistry of americium. Nevertheless, gravimetric, coulometric, spectrophotometric and radiometric methods are available at present, and further developments may be anticipated as increasing quantities of americium, particularly the less-radioactive Am^{243} isotope, become available.

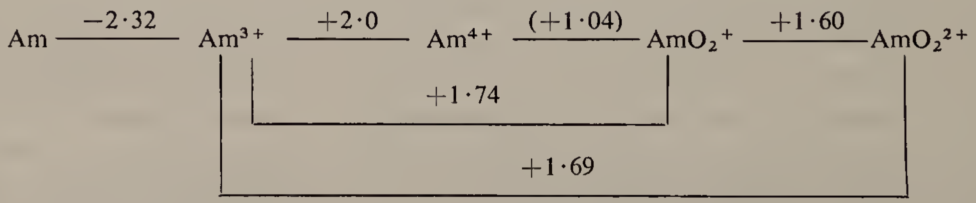
The gravimetric determination of americium

Americium may be precipitated quantitatively from solution either as the hydroxide, $Am(OH)_3$, or as the oxalate, $Am_2(C_2O_4)_3$. Conditions for minimum solubility of the oxalate in solution are critical and occur at 0·1 M HNO_3 + 0·1 M $(COOH)_2$[64]. Ignition to the dioxide may be carried out above 450°C, but loss of oxygen occurs above 1000°C.

Solution methods for the determination of americium

Redox methods

The oxidation potentials of americium in 1 M $HClO_4$ solution in volts vs. the NHE are as follows:



Americium may be oxidized to the hexavalent state electrochemically or with a strong oxidizing agent such as argentic oxide. Solutions of Am^{241} in the hexavalent state tend to undergo autoreduction due to radiolytic decomposition of the solvent. In spite of this,

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[64] A. G. Burney and J. A. Porter, *Inorg. Nucl. Chem. Letters*, **3** (1967) 79.

Koehly[65] has developed a controlled-potential procedure for the determination of americium based upon the reduction of AmO_2^{2+} to AmO_2^{+} at a potential of $+1\cdot3$ volts vs. the NHE.

Spectrophotometric methods

In common with those of the earlier actinides, solutions of americium exhibit absorption spectra characteristic of the valency state present. The trivalent, pentavalent and hexavalent states show extremely sharp peaks which are suitable for the determination of any one valency state in the presence of the others. Specific peaks occur at 812 nm for Am^{3+}, 719 nm for AmO_2^{+} and 996 nm for AmO^{2+} with molar absorptivities of approximately 50, 60 and 100, respectively[66]. Due to the sharpness of the peaks, the exact values of the extinction coefficients are dependent upon the resolution of the spectrophotometer employed. An increased sensitivity for the determination of Am^{3+} can be obtained by complexing with Arsenazo-III at pH 3–3·5, since this complex has a molar absorptivity of about 82,000 at 650 nm[67].

The radiometric determination of americium

The two major isotopes of americium and their relevant nuclear data are listed in Table 6.

TABLE 6. ISOTOPES OF AMERICIUM

Isotope	Half-life	Specific activity (dis/m/μg)	Mode of decay	Energy MeV
Am^{241}	433 yr	$7\cdot67\times10^{6}$	α	5·486 5·443
			γ	0·0596
Am^{243}	7370 yr	$4\cdot49\times10^{5}$	α	5·276 5·234

Am^{241} can be determined by either α- or γ-measurement with a sensitivity of less than 10^{-12} g. Alpha-spectrometry is frequently employed to detect Am^{241} in the presence of other actinides with the exception of Pu^{238} (5·495, 5·452 MeV) when a chemical separation is necessary. The specific activity of Am^{243} is lower than that of Am^{241} by a factor of about 17, but Am^{243} may be determined by α-counting at the level of 10^{-10} g.

9. CURIUM, BERKELIUM, CALIFORNIUM, EINSTEINIUM, FERMIUM, MENDELEVIUM, NOBELIUM, LAWRENCIUM

The elements from curium to lawrencium, completing the actinide series, have only been available in limited quantities. In consequence, there is no formal analytical chemistry of these elements, and the existing knowledge consists of nuclear and radiochemical data together with preliminary chemical properties.

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[65] G. Koehly, *Anal. Chim. Acta*, 33 (1965) 418.

[66] Cr. Ferradini, *Chim. Anal.* 45 (1963) 647.

[67] F. Myasoedov, M. S. Milyukova and L. V. Ryzhova, *Radiochem. Radioanal. Letters*, 5 (1970) 19.

Information on the absorption spectra of Cm(III), Cm(IV), Bk(III), Bk(IV), Cf(III) and Es(III) is available and is of obvious analytical interest. Preliminary information on the stability of curium complexes with thiocyanate ions, lactic acid, α-hydroxyisobutyric acid and EDTA has been obtained. A complexometric titration of curium with EDTA can be anticipated. The redox potentials of the Cm(III)/Cm(IV) and Bk(III)/Bk(IV) couples have not been accurately determined, but they are unlikely to lead to readily-performed redox titrations.

Detailed information on the nuclear properties of these elements has been assembled together with radiochemical means of detection and identification[68].

[68] *The Chemistry of the Transuranic Elements*, pp. 529 *et seq.*, Cornelius Keller, Verlag Chemie GmbH (1971).

COMPOUNDS

ALLOYS

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1. INTRODUCTION

The progressive increase in $5f$ character in the electronic structure of the actinide elements with increasing atomic number and the associated decrease in $6d$ character leads to a series of elements with very variable alloying behaviour. Since the $5f$ shell is relatively unshielded as compared to the $4f$ shell, the differences in alloying behaviour between adjacent members of the series are much more marked for the actinides than for the lanthanides. This difference would be expected to be less noticeable for the elements beyond americium where the relationship with the lanthanides is becoming more obvious, but data for the alloying behaviour of the heavier actinides do not exist. Even for the earlier members, the data are largely restricted to the three elements of prime technological importance, thorium, uranium and plutonium.

In systems where intermetallic compounds exist, the available information is restricted in general to the melting point, crystal structure, density and in some cases thermodynamic functions and transformation temperatures. The absence of data on many other physico-chemical properties in part reflects the fact that such compounds are in general unlikely to find use in nuclear reactors, where more refractory compounds such as oxides, nitrides and carbides are the main contenders for use as fuel materials.

Although the different actinide elements frequently form quite different compounds with a given alloying element, there are a number of systems in which isomorphous compounds form, particularly with uranium and plutonium where the atomic size difference between the actinide and the alloying element may be similar; the large size of the thorium atom frequently results in quite different compounds and structures from those of the corresponding uranium and plutonium systems. Thus, Laves phases of the AB_2 type are common in transition metal systems with uranium and plutonium.

For convenience in the following sections, the compounds are considered on the basis of the Groups of the Periodic Table. Although a number of ternary alloy systems have been studied, very few ternary intermetallic compounds have been detected, most of the phases involved being based upon binary compounds.

Where thermodynamic data are available for the free energy/heat of formation, the various sources have given values in different units. In the current presentation, these may be assumed to be in kcal/mole based on the formula weight in grams unless otherwise stated.

Melting point data are available for many of the compounds and the nature of the solid to liquid transformation is indicated in the following tables by (P) after the appropriate temperature if the compound melts peritectically. The absence of such a symbol indicates that the melting is congruent.

2. GROUP I

Group IA

The alkali metals are completely immiscible in both the liquid and solid states with thorium, uranium and plutonium. An early report of a compound Na_4Th, decomposing by a peritectoid reaction at 121°C, was not confirmed by later work[1].

Group IB

Copper

A large number of compounds have been reported in the systems Cu–Th and Cu–Pu. Many of the thorium compounds reported by early workers have not been confirmed by more recent investigators, the quoted compositions probably being incorrect because of contamination. In the plutonium system, there is uncertainty as to whether Pu_4Cu_{17} and $PuCu_4$ are distinct phases or a single phase. The compound Pu_2Cu_{11} reported by Rhinehammer[2] is now believed to be $PuCu_6$.

The crystal structures of the well-established compounds in the actinide systems are given in Table 1. None of the compounds are isomorphous except for $ThCu_6$ and $PuCu_6$ which have the $CeCu_6$ structure.

TABLE 1. CRYSTAL STRUCTURES AND MELTING POINTS OF ACTINIDE–COPPER COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)			X-ray density (g/cm³)	Melting point (°C)
		a	*b*	*c*		
Th_2Cu	BC Tetragonal[a] $CuAl_2$ type	7·28		5·75	11·50	1007[c]
$ThCu_2$	Hexagonal[b] AlB_2 type	4·387		3·472	10·31	1015[c]
$ThCu_{3\cdot6}$[c]	Unknown					1052
$ThCu_6$[c]	Orthorhombic $CeCu_6$ type	8·110	5·082	10·105	9·78	1055
UCu_5	FCC[d] $MgCu_2$ type	7·033–7·038			10·60	1052(P)[a]
$PuCu_2$	BC Orthorhombic[e] $CeCu_2$ type	4·32	6·69	7·38		865[f]
$PuCu_4$	Orthorhombic[e]	4·37	8·37	9·23		906(P)[f]
Pu_4Cu_{17}	Unknown					954[f]
$PuCu_6$*	Orthorhombic[g] $CeCu_6$ type	10·059	8·500	5·025	10·12	926(P)[f]

* Reference h, whilst agreeing the isomorphism with $CeCu_6$, quotes parameters of 10·06, 8·16 and 5·44Å.

[a] N. C. Baenziger, R. E. Rundle and A. I. Snow, *Acta Cryst.* 9 (1956) 93.

[b] A. Brown, *Acta Cryst.* **14** (1961) 860.

[c] R. J. Schiltz Jr., E. R. Stevens and O. N. Carlson, *J. Less Common Metals* **25** (1971) 175.

[d] F. A. Rough and A. A. Bauer, *Constitutional Diagram of Uranium and Thorium Alloys*, p. 19. Addison-Wesley, Reading, Mass. (1958).

[e] F. Lataillade, F. Pons and M. Rapin, *J. Nucl. Mater.* **40** (1971) 284.

[f] T. B. Rhinehammer, D. E. Etter and L. V. Jones, *Plutonium 1960*, p. 289. Cleaver-Hume Press Ltd., London (1961).

[g] V. I. Kutaitsev, N. T. Chebotarev, I. G. Lebedev, M. A. Andrianov, V. N. Konev and T. S. Menshikova, *Plutonium 1965*, p. 429. Institute of Metals, London (1967).

[h] L. J. Wittenberg and G. R. Grove, U.S. Report MLM-1244.

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[1] M. Hansen, *Constitution of Binary Alloys*, p. 1008. McGraw Hill, New York (1958).

[2] T. B. Rhinehammer, D. E. Etter and L. V. Jones, *Plutonium 1960* p. 289. Cleaver-Hume Press Ltd., London (1961).

Although UCu_5 is stoichiometric when prepared by conventional melting routes, a range of existence from $UCu_{4 \cdot 75}$ to $UCu_{5 \cdot 25}$ has been reported when it forms under pressure in diffusion couples[3].

The free energy of formation of $ThCu_6$ (previously labelled $ThCu_4$) at 973K is —21·9 kcal/mole, the corresponding heat of formation being —14·7 kcal/mole[4].

Silver

In the binary systems with silver, three compounds have been established in the thorium system and two compounds in the plutonium system, whilst no compounds occur with uranium[5]. The thorium–silver phases initially reported were Th_3Ag_5 and $ThAg_3$, but more recent work indicates that there is a third compound, Th_2Ag, and that Th_3Ag_5 is actually $ThAg_2$. The compounds Th_2Ag and $ThAg_2$ are isomorphous with the corresponding compounds with copper and gold.

In the plutonium–silver system, only one compound, $PuAg_3$, was believed to exist until the recent work of Wood *et al.*[6] who showed that this compound has a composition of $PuAg_{3 \cdot 6}$, and that in addition a second compound, $PuAg_2$, exists.

TABLE 2. CRYSTAL STRUCTURES AND MELTING POINTS OF ACTINIDE–SILVER COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)		X-ray density (g/cm³)	Melting point (°C)
		a	*c*		
Th_2Ag	BC Tetragonal[a] $CuAl_2$ type	7·56	5·84	11·38	
$ThAg_2$	Hexagonal[b] AlB_2 type	4·837	3·353	10·95	~1035[a]
$ThAg_3$	Unknown				~1120[a]
$PuAg_2$	Unknown				817(P)[c]
$PuAg_{3 \cdot 6}$	Hexagonal[c] $GdAg_{3 \cdot 6}$ type	12·727	9·392	11·16	977[c]

[a] F. A. Rough and A. A. Bauer, *Constitutional Diagrams of Uranium and Thorium Alloys*, p. 141. Addison-Wesley, Reading, Mass. (1958).

[b] A. Brown, *Acta Cryst.* **14** (1961) 860.

[c] D. H. Wood, E. M. Cramer and P. L. Wallace, *Plutonium 1970 and Other Actinides, Nuclear Metallurgy*, Vol. 17, p. 707. Met. Soc. AIME, New York (1970).

A superconducting transition has been detected in Th_2Ag with a value of T_c of 2·26K[7].

Gold

The actinide–gold systems exhibit considerable variability. The thorium system contains three compounds and is directly comparable to the thorium–silver system whilst two

[3] Y. Adda, M. Beyeler, A. Kirianenko and B. Pernot, *Proc. 4th International Symposium on the Reactivity of Solids*, p. 512. Elsevier Publishing Co., Amsterdam (1960).

[4] N. J. Magnani, W. H. Skelton and J. F. Smith, *Symposium on Reprocessing of Nuclear Fuels, Nuclear Metallurgy*, Vol. 15, p. 727. Met. Soc. AIME, New York (1969).

[5] F. A. Rough and A. A. Bauer, *Constitutional Diagrams of Uranium and Thorium Alloys*, p. 68. Addison-Wesley, Reading, Mass. (1958).

[6] D. H. Wood, E. M. Cramer and P. L. Wallace, *Plutonium 1970 and Other Actinides, Nuclear Metallurgy*, Vol. 17, p. 707. Met. Soc. AIME, New York (1970).

[7] B. T. Matthias, V. B. Compton and E. Corenzwit, *Phys. Chem. Solids* **19** (1961) 130.

compounds exist in the uranium system. The plutonium–gold system is complex and as many as eight intermetallic phases have been reported. The major points of disagreement are indicated in Table 3.

The isostructural nature of $PuAu_3$ and $PuAg_{3\cdot6}$ coupled with the reported composition of 77 at. % gold by Hocheid *et al.*[8] may indicate that $PuAu_3$ should be considered to be $PuAu_{3\cdot6}$.

An estimate of the free energy of formation of $ThAu_3$ at 298K gives a value of greater than −24 kcal/mole whilst a similar estimate for UAu_3 lies in the range −23·6 to −50 kcal/mole[9]. Although the compound UAu has not been reported in the solid state, the gaseous molecule UAu has the extremely high dissociation energy of 75 ± 7 kcal/mole[10].

TABLE 3. CRYSTAL STRUCTURES AND MELTING POINTS OF ACTINIDE–GOLD COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)		X-ray density (g/cm³)	Melting point (°C)
		a	*c*		
Th_2Au	BC Tetragonal[a] $CuAl_2$ type	7·42	5·95	13·41	
$ThAu_2$	Hexagonal[b] AlB_2 type	4·740	3·402	15·72	∼1450[a]
$ThAu_3$	Unknown				∼1460[a]
U_2Au_3	Unknown				1216(P)[a]
UAu_3	Unknown				>1450[a]
η-Pu–Au (35 at. % Au)	Unknown				170[c] (Peritectoid decomposition)
PuAu	Unknown				>1190[c] 1140(P)[c]
θ (58 at. % Au)	Unknown				>1100[c]
$PuAu_2$	Unknown				1130[c] 1170(P)[c]
κ(70 at. % Au)	Unknown				1073(P)[c]
$PuAu_3$	Hexagonal[c]	12·710	9·210	17·11	1250[c]
$PuAu_4$	Unknown				860(P)[c]
$PuAu_5$	Unknown				820(P)[c]

[a] F. A. Rough and A. A. Bauer, *Constitutional Diagrams of Uranium and Thorium Alloys*, pp. 119 and 25. Addison-Wesley, Reading, Mass. (1958).

[b] A. Brown, *Acta Cryst.* **14** (1961) 860.

[c] F. H. Ellinger, W. N. Miner, D. R. O'Boyle and F. W. Schofield, U.S. Report LA-3870.

3. GROUP II

Group IIA

The metals calcium, strontium and barium do not form compounds with actinide elements, being immiscible in both the liquid and solid states[11,12].

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[8] B. Hocheid, A. Tanon, S. Bedere, J. Despres, S. Hay and F. Miard, *Plutonium 1965*, p. 321. Institute of Metals, London (1967).

[9] P. R. Wengert, University Microfilms Inc. 70–6258. Ann Arbor, Michigan.

[10] K. A. Gingerich and G. D. Blue, *J. Chem. Phys.* **47** (1967) 5447.

[11] F. A. Rough and A. A. Bauer, *Constitutional Diagrams of Uranium and Thorium Alloys*, p. 12. Addison-Wesley, Reading, Mass. (1959).

[12] O. J. Wick, *Plutonium Handbook*, Vol. 1, p. 197. Gordon & Breach, New York (1967).

Group IIB

Beryllium

A compound of formula MBe_{13}, with the cubic $NaZn_{13}$ structure, is common to all actinide–beryllium systems so far examined. The lattice parameter values, melting points and magnetic susceptibilities are given in Table 4. The susceptibility follows a Curie–Weiss law, the values of the Curie and Weiss constants being 4350 and 70, respectively, for UBe_{13} and 900 and 80, respectively, for $PuBe_{13}$[13]. The uranium compound does not go either ferromagnetic or superconducting at temperatures down to 1·4K[14].

TABLE 4. LATTICE PARAMETERS, MELTING POINTS AND MAGNETIC SUSCEPTIBILITIES OF ACTINIDE–BERYLLIUM COMPOUNDS

Composition	Lattice parameter (Å)	X-ray density (g/cm³)	Melting point (°C)	Magnetic susceptibility (×10⁶ emu/g)
$ThBe_{13}$	10·395[a]	4·10[e]	1930[f]	
UBe_{13}	10·272[a]	4·373[a]	2020[a]	12·0(298K)[g]
$NpBe_{13}$	10·256(Np-rich)[b] 10·266(Be-rich)	4·38	>1400[b]	
$PuBe_{13}$	10·278(Pu-rich)[c] 10·282(Be-rich)	4·35[c]	1950[c]	2·4(298K)[g]
$AmBe_{13}$	10·283[d]	4·41		

[a] F. A. Rough and A. A. Bauer, *Constitutional Diagrams of Uranium and Thorium Alloys*, pp. 109 and 7. Addison-Wesley, Reading, Mass. (1959).
[b] O. J. C. Runnalls, *Acta Cryst.* 7 (1954) 222.
[c] O. J. Wick, *Plutonium Handbook*, p. 198. Gordon & Breach, New York (1967).
[d] R. Caillat and J. Elston, *Nouveau Traité de Chimie Minérale*, Vol. XV, p. 931. Masson et Cie, Paris (1961).
[e] M. S. Farkas, A. A. Bauer and R. F. Dickerson, U.S. Report BMI 1473.
[f] R. P. Elliott, *Constitution of Binary Alloys*, First Supplement, p. 171. McGraw-Hill, New York (1965).
[g] S. T. Konobeevsky, A. S. Zaimovsky, B. M. Levitsky, Y. N. Sokursky, N. T. Chebotarev, Y. V. Bobkov, P. P. Egorov, G. N. Nicholaev and A. A. Ivanov, *Proc. 2nd ICPUAE*, Vol. 6, p. 194. United Nations, Geneva (1958).

The heat of formation of UBe_{13} at 298K is −39·3 kcal/mole and that of $PuBe_{13}$ is −35·7 kcal/mole[13]. The specific heat of UBe_{13} as determined from heat content measurements[14] is given in cal/g-K by:

$$C_p = 0{\cdot}7755 - 9{\cdot}652 \times 10^{-4}\,T - 2{\cdot}926 \times 10^{4}T^{-2} \text{ (298–373K)}$$

An interesting application of actinide–beryllium compounds makes use of the α–n reaction to provide a neutron source. Both plutonium and americium have been extensively used for this purpose, $AmBe_{13}$ having the high yield of $3{\cdot}75 \times 10^6$ n/g-sec[15].

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[13] S. T. Konobeevsky, A. S. Zaimovsky, B. M. Levitsky, Y. N. Sokursky, N. T. Chebotarev, Y. V. Bobkov, P. P. Egorov, G. N. Nicholaev and A. A. Ivanov, *Proc. 2nd ICPUAE*, Vol. 6, p. 194. United Nations, Geneva (1958).
[14] N. M. Wolcott and R. L. Falge Jnr., *Phys. Rev.* **171** (1968) 591.
[15] G. Bracket and C. Vasseur, French Report CEA-R3875.

Magnesium

Thorium forms two compounds with magnesium, $ThMg_2$ and a phase originally considered to be $ThMg_5$, but now thought to be Th_6Mg_{23}. The former is a Laves phase which undergoes a transformation from hexagonal to cubic at about 700°C. No compounds exist in the uranium system whilst $PuMg_2$ and $PuMg_{2+x}$ occur with plutonium.

TABLE 5. CRYSTAL STRUCTURES AND MELTING POINTS OF ACTINIDE–MAGNESIUM COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)		X-ray density (g/cm^3)	Melting point (°C)
		a	*c*		
$ThMg_2$ (high temperature form)	Cubic[a] $MgCu_2$ type	8·570		5·92	Transforms at ~ 700
$ThMg_2$ (low temperature form)	Hexagonal[a] $MgNi_2$ type	6·086	19·64		772(P)
Th_6Mg_{23}	Cubic[a] Th_6Mn_{23} type	12·27*		4·23	550–570 (peritectoid)
$PuMg_2$	Cubic[b] CaF_2 type	7·34		4·83	200–250 (peritectoid)
$PuMg_{2+x}$	Hexagonal[b]	13·8	9·7		425–450 (peritectoid)

* A value of 14·24 KX has also been reported.[c]

[a] F. A. Shunk, *Constitution of Binary Alloys*, Second Supplement, p. 498. McGraw Hill, New York (1969).

[b] O. J. Wick, *Plutonium Handbook*, Vol. 1, p. 210. Gordon & Breach, New York (1967).

[c] D. T. Peterson and C. V. Sundaram, U.S. Report 1S-700.

The free energy of formation of $ThMg_2$[16] is given by:

$$\Delta G^\circ = -14\cdot3 \pm 3\cdot1 + (15\cdot2 \pm 4\cdot3) \times 10^{-3}T \text{ (692–812K)}$$

The vapour pressure, over the same temperature range, follows the relationship

$$\log_{10}P_{\text{mm}} = 10\cdot3 \pm 0\cdot3 - \frac{9130 \pm 210}{T}$$

Zinc

A large number of compounds have been observed in actinide–zinc systems and, in particular, phases originally denoted as MZn_9, which were later modified to M_2Zn_{17}. In the case of uranium and plutonium, this phase is known to exist over a range extending up to about MZn_{12} and in the uranium system three distinct structures have been observed, two of which appear to relate to high- and low-temperature modifications of U_2Zn_{17} and the third to UZn_{12}[17]. The transition temperature for U_2Zn_{17} is given as 550°C. The exact relationship between the structures is undefined since the low-temperature rhombohedral form shows no variation in lattice parameter with composition, whilst the variations for the hexagonal form suggest it exists over a wide range of composition. The hexagonal structure of UZn_{12} appears to involve mainly a trebling of the *c*-axis of the hexagonal U_2Zn_{17} structure. The hexagonal structure reported for Pu_2Zn_{17} is isomorphous with the UZn_{12} structure[18], suggesting that the true Pu_2Zn_{17} may have not yet been detected.

[16] D. B. Novotny and J. F. Smith, *J. Inst. Metals*, **92** (1963) 122.

[17] R. P. Elliott, *Constitution of Binary Alloys*. First Supplement, p. 856. McGraw Hill, New York (1965).

[18] O. J. Wick, *Plutonium Handbook*, Vol. 1, p. 225. Gordon & Breach, New York (1967).

Owing to the low boiling point of zinc, the most zinc-rich compounds can decompose before melting at atmospheric pressure. The quoted melting points in Table 6 relate to sealed capsules in which the pressures may be up to 5 atm.

TABLE 6. CRYSTAL STRUCTURES AND MELTING POINTS OF ACTINIDE-ZINC COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)		X-ray density (g/cm^3)	Melting point (°C)
		a	*c*		
Th_2Zn[a]	BC Tetragonal $CuAl_2$ type	7·95	5·64	9·87	1055
$ThZn_2$[a]	Hexagonal AlB_2 type	4·497	3·718	9·25	1105
$ThZn_4$[a]	BC Tetragonal $BaAl_4$ type	4·273	10·359	8·67	1095
Th_2Zn_{17}[a]	Rhombohedral	9·03	13·20	8·42	1015
U_2Zn_{17} Low temperature	Rhombohedral[b]	8·978	13·160	8·61	
U_2Zn_{17}[b] High temperature	Hexagonal Th_2Ni_{17} type	8·980 (U-rich) 8·948 (Zn-rich)	8·785 8·915		945[e] (decomposition at 1 atm)
UZn_{12}[a]	Hexagonal $SmZn_{12}$ type	8·99	26·35	8·29	
$PuZn_2$[c]	Cubic $MgCu_2$ type	7·760 (Pu-rich) 7·747 (Zn-rich)		10·50	935
Pu_2Zn_9[c]	Hexagonal	28·96	14·14		912
$PuZn_{7\cdot 7}$	BC Tetragonal[d]	8·85	21·18	8·71	880(P)[c]
Pu_2Zn_{17}[c] (probably $PuZn_{12}$)	Hexagonal UZn_{12} type	8·994	26·60	8·50	810(P)

[a] R. P. Elliott, *Constitution of Binary Alloys*, First Supplement, pp. 849 and 856. McGraw Hill, New York (1965).

[b] R. C. Vogel and M. Levenson, U.S. Report ANL-7020.

[c] O. J. Wick, *Plutonium Handbook*, p. 225. Gordon & Breach, New York (1967).

[d] Q. Johnson, D. H. Wood and G. S. Smith, *Acta Cryst.* **B24** (1968) 480.

[e] F. A. Rough and A. A. Bauer, *Constitutional Diagrams of Uranium and Thorium Alloys*, p. 83. Addison-Wesley, Reading, Mass. (1958).

For all three binary systems, data on the free energy of formation of the compounds have been reviewed by Johnson[19], who gives the following relationships, in kcal/mole:

Th_2Zn $\Delta G^\circ = -14{\cdot}0 - 14{\cdot}4 \times 10^{-3}T + 5{\cdot}83 \times 10^{-3}T\log T$ (693–1181K)
$ThZn_2$ $\Delta G^\circ = -23{\cdot}8 - 29{\cdot}2 \times 10^{-3}T + 11{\cdot}7 \times 10^{-3}T\log T$ (693–1181K)
$ThZn_4$ $\Delta G^\circ = -36{\cdot}3 - 60{\cdot}6 \times 10^{-3}T + 23{\cdot}3 \times 10^{-3}T\log T$ (693–1181K)
Th_2Zn_{17} $\Delta G^\circ = -106{\cdot}9 - 26{\cdot}3 \times 10^{-3}T + 99 \times 10^{-3}T\log T$ (693–1181K)
U_2Zn_{17} $\Delta G^\circ = -101{\cdot}6 + 68{\cdot}6 \times 10^{-3}T$ (693–1113K)
UZn_{12} $\Delta G^\circ = -54{\cdot}15 + 38{\cdot}22 \times 10^{-3}T$ (693–973K)
$PuZn_{12}$ $\Delta G^\circ = -66{\cdot}36 + 25{\cdot}35 \times 10^{-3}T + 11{\cdot}66 \times 10^{-6}T^2$ (700–950K)

The vapour pressure of U_2Zn_{17} has been determined over a limited temperature range[20] and is given by:

$$\log_{10}P_{\mathrm{mm}} = 9{\cdot}290 - 7724 \times T^{-1} \quad (693\text{–}777\mathrm{K})$$

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[19] I. Johnson, *Compounds of Interest in Nuclear Reactor Technology, Nuclear Metallurgy* Vol. 10, p. 171. AIME Met. Soc., New York (1964).

[20] S. Lawroski, R. C. Vogel and V. H. Munnecke, U.S. Report ANL-6287.

Cadmium

The structures and melting points of compounds in the systems with thorium, uranium, neptunium and plutonium are given in Table 7. Thermodynamic relationships for the isomorphous MCd_{11} and MCd_6 phases have been given, in kcal/mole, as:

UCd_{11} $\Delta G^\circ = -27{\cdot}2 + 36{\cdot}2 \times 10^{-3}T(673\text{–}746\text{K})$[19]
$NpCd_{11}$ $\Delta G^\circ = -44{\cdot}7 + 43{\cdot}3 \times 10^{-3}T(653\text{–}758\text{K})$[21]
$PuCd_{11}$ $\Delta G^\circ = -48{\cdot}44 + 39{\cdot}76 \times 10^{-3}T(623\text{–}676\text{K})$[19]
$NpCd_6$ $\Delta G^\circ = -28{\cdot}4 + 21{\cdot}7 \times 10^{-3}T(758\text{–}818\text{K})$[21]
$PuCd_6$ $\Delta G^\circ = -40{\cdot}02 + 27{\cdot}33 \times 10^{-3}T(676\text{–}843\text{K})$[19]

The decomposition pressure of UCd_{11} is given by:

$$\log_{10}P_{\text{mm}} = 9{\cdot}060 - 6105 \times T^{-1}\ (578\text{–}651\text{K})$$[22]

The magnetic susceptibility of $ThCd_{11}$ is reported to be essentially temperature-independent[23], the value at 295K being $0{\cdot}40 \times 10^{-6}$ emu/g. The susceptibility of the corresponding uranium compound obeys the Curie–Weiss Law over the temperature range 2–300K[24], the constants being 1·798 emu/g deg-mole and 41·5K. The results are consistent with a valency of 4 for thorium or uranium in the MCd_{11} phase.

TABLE 7. CRYSTAL STRUCTURES AND MELTING POINTS OF ACTINIDE–CADMIUM COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)		X-ray density (g/cm³)	Melting point (°C)
		a	*c*		
$ThCd_2$	Hexagonal[a] AlB_2 type	5·005	3·516	9·95	
$ThCd_5$	Hexagonal[b] $EuMg_5$ type	9·812	10·102	9·39	
$ThCd_{11}$	Cubic[c] $BaHg_{11}$ type	9·274		9·17	
UCd_{11}	Cubic[d] $BaHg_{11}$ type	9·289		9·16	473(P)[d]
$NpCd_6$	Cubic[e] $CeCd_6$ type	15·614		9·54	485(P)[e]
$NpCd_{11}$	Cubic[e] $BaHg_{11}$ type	9·288		9·16	>626[e]
$PuCd_2$	Unknown				945[g]
$PuCd_4$	Unknown				800(P)[g]
$PuCd_6$	Cubic[f] $CeCd_6$ type	15·59		9·61	730(P)[g]
$PuCd_{11}$	Cubic[f] $BaHg_{11}$ type	9·282		9·22	410(P)[g]

[a] A. Brown, *Acta Cryst.* **14** (1961) 860.
[b] M. L. Fornasini, *J. Less Common Metals*, **25** (1971) 329.
[c] S. Lawroski, R. C. Vogel, M. Levenson and V. H. Munnecke, U.S. Report ANL-6766.
[d] A. E. Martin, I. Johnson and H. M. Feder, *Trans. Met. Soc. AIME* **221** (1961) 789.
[e] M. Krumpelt, I. Johnson and J. J. Heiberger, *J. Less Common Metals*, **18** (1969) 35.
[f] I. Johnson, M. G. Chasanov and R. M. Yorco, *Trans. Met. Soc. AIME* **233** (1965) 1408.
[g] D. E. Etter, D. B. Martin, D. L. Roesch, C. R. Hudgens and P. A. Tucker, *Trans. Met. Soc. AIME* **233** (1965) 2011.

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[21] M. Krumpelt and J. J. Heiberger, U.S. Report ANL–7575.
[22] E. Veleckis, H. M. Feder and I. Johnson, *J. Phys. Chem.* **66** (1962) 362.
[23] F. Cafasso and D. Gruen, U.S. Report ANL–6648.
[24] S. Lawroski, R. C. Vogel, M. Levenson and V. H. Munnecke, U.S. Report ANL–6766.

Mercury

Amalgams are formed in general by the actinides, but data on specific compounds are restricted to the thorium, uranium and plutonium systems.

TABLE 8. CRYSTAL STRUCTURES AND DECOMPOSITION TEMPERATURES OF ACTINIDE–MERCURY COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)		X-ray density (g/cm^3)	Decomposition* temperature(°C)
		a	*c*		
ThHg[a]	FCC	4·80		12·99	>1000 Eutectoid reaction at 400–600
$ThHg_2$[b]	Hexagonal Related to AlB_2 type	4·82	7·43	13·96	
$ThHg_3$[a]	Hexagonal $MgCd_3$ type	3·361	4·905	14·43	>1000
UHg_2[a]	Hexagonal AlB_2 type	4·985	3·225	15·29	436(P)
UHg_3[a]	Hexagonal $MgCd_3$ type	3·325	4·885	14·91	417(P)
UHg_4[a]	Pseudo BCC†	3·63		14·5	383(P)
$PuHg_3$[c]	Hexagonal $MgCd_3$ type?				
Pu_5Hg_{21}[d]	Cubic γ-Brass type	21·78		13·9	

* Figures relate to small enclosed systems.

† By analogy with Pu_5Hg_{21}, the formula should probably be adjusted and the cell size multiplied by a factor of 6.

[a] R. P. Elliott, *Constitution of Binary Alloys*, First Supplement, pp. 539 and 560. McGraw Hill, New York (1965).

[b] P. Ettmayer, *Monatsh. Chem.* **96** (1965) 443.

[c] O. J. Wick, *Plutonium Handbook*, Vol. 1, p. 211. Gordon & Breach, New York (1967).

[d] A. F. Berndt, *J. Less Common Metals*, **11** (1966) 216.

The free energies of formation of the thorium and uranium compounds have been determined by Jangg and Steppan[25] who quote, in kcal/mole,

$$\begin{array}{ll}
\mathrm{ThHg} & \Delta G^\circ = -63 \pm 5 + (61 \pm 5) \times 10^{-3}T\,(813\text{–}893\mathrm{K}) \\
\mathrm{ThHg_2} & \Delta G^\circ = -98 \pm 5 + (96 \pm 5) \times 10^{-3}T\,(713\text{–}773\mathrm{K}) \\
\mathrm{ThHg_3} & \Delta G^\circ = -118 \pm 5 + (117 \pm 5) \times 10^{-3}T\,(623\text{–}743\mathrm{K}) \\
\mathrm{UHg_2} & \Delta G^\circ = -13{\cdot}3 \pm 0{\cdot}5 + (9{\cdot}9 \pm 0{\cdot}5) \times 10^{-3}T\,(583\text{–}683\mathrm{K}) \\
\mathrm{UHg_3} & \Delta G^\circ = -16{\cdot}0 \pm 0{\cdot}5 + (12{\cdot}2 \pm 0{\cdot}5) \times 10^{-3}T\,(553\text{–}683\mathrm{K}) \\
\mathrm{UHg_4} & \Delta G^\circ = -19{\cdot}5 \pm 0{\cdot}8 + (16{\cdot}8 \pm 0{\cdot}8) \times 10^{-3}T\,(543\text{–}633\mathrm{K})
\end{array}$$

These values do not agree with earlier estimates and measurements given in the review by Johnson[19].

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[25] G. Jangg and F. Steppan, *Z. Metallkunde*, **56** (1965) 172.

4. GROUP III

Group IIIA

Scandium

No compounds have been reported in the Th–Sc and U–Sc systems; the former system exhibits extensive solid solubility of scandium in α-thorium and complete solid solubility at high temperatures between β-thorium and β-scandium[26]. The U–Sc system is characterized by a large liquid immiscibility gap[27]. The Pu–Sc system contains a single intermediate phase, ζ, which exists over the composition range 43·4 at. % Sc[28] and has the double hexagonal structure (lanthanum-type), with parameters of:

$$a = 3{\cdot}310\text{–}3{\cdot}307\text{Å}, \quad c = 10{\cdot}715\text{–}10{\cdot}718\text{Å}^{29}$$

The phase decomposes by a peritectoid reaction at 760°C.

Yttrium

The actinide–yttrium systems are generally comparable to the corresponding scandium systems. Thus extensive mutual solubility exists between α-thorium and α-yttrium[30], complete solid solubility between β-thorium and β-yttrium, an extensive miscibility gap exists in the U–Y system[31] and extensive solubility of plutonium in α-yttrium[31] is observed. No analogue of ζ-Pu–Sc has been reported.

However, recent studies on the Th–Y system[32] have suggested that annealing at relatively low temperatures (600–700°C) produces a sequence of structures paralleling intra-rare earth alloys such as the Ce–Gd system. Thus at 75 at. % Y a rhombohedral (samarium-type) structure has been observed whilst at 70 at. % Y a double hexagonal structure exists with parameters of:

$$a = 3{\cdot}615\text{Å}, \quad c = 11{\cdot}637\text{Å}$$

Lanthanum

See Rare Earths.

Group IIIB

Aluminium

Extensive compound formation occurs with aluminium, and phases of the type MAl_2, MAl_3 and MAl_4 are common to the uranium, neptunium and plutonium systems. Phases richer in the actinide metal than MAl_2 have been reported for plutonium and also for thorium, although in the latter case the compositions and structures of the compounds are quite distinct from those with the other actinides.

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[26] T. A. Badaeva and R. I. Kuznetsova, *Izv. Akad. Nauk. SSSR Metali* No. 5 (1969) 156.

[27] R. P. Elliott, *Constitution of Binary Alloys*. First Supplement, p. 811. McGraw Hill, New York (1965)

[28] V. I. Kutaitsev, N. T. Chebotarev, I. G. Lebedev, M. A. Andrianov, V. N. Konev and T. S. Menshikova, *Plutonium 1965*, p. 420. Chapman & Hall, London (1965).

[29] A. Ballagny, R. Boucher and C. Carrard, *Plutonium 1970 and Other Actinides, Nuclear Metallurgy*, Vol. 17, p. 699. Met. Soc. AIME, New York (1970).

[30] R. P. Elliott, *Constitution of Binary Alloys*. First Supplement, p. 847. McGraw Hill, New York (1965).

[31] F. A. Shunk, *Constitution of Binary Alloys*. Second Supplement, pp. 706 and 635. McGraw Hill, New York (1969).

[32] E. E. Havinga, J. H. N. van Vucht and K. H. J. Buschow, *Philips Research Reports* **24** (Oct. 1969) 407.

TABLE 9. CRYSTAL STRUCTURES AND MELTING POINTS OF THORIUM–ALUMINIUM AND URANIUM–ALUMINIUM COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)			X-ray density (g/cm^3)	Melting point (°C)
		a	*b*	*c*		
Th_2Al[a]	Tetragonal $CuAl_2$ type	7·616		5·861	9·60	1307
Th_3Al_2[a]	Tetragonal U_3Si_2 type	8·127		4·222	8·93	1301
ThAl	Orthorhombic CrB type[b]	11·45	4·42	4·19	8·50	1318(P)[a]
Th_2Al_3[a]	Tetragonal (high temperature phase)	9·870		7·837		1394 Eutectoid 1100
$ThAl_2$[a]	Hexagonal AlB_2 type	4·388		4·162	6·84	~1600
$ThAl_3$	Hexagonal Ni_3Sn type[b]	6·499		4·626	6·14	1120(P)[a]
Th_2Al_7	Orthorhombic[c]	11·479	5·874	5·530	5·80	
UAl_2	FCC $MgCu_2$ type[d]	7·766			8·28	1590[b]
UAl_3	Cubic Cu_3Au type[a]	4·254			6·88	1350(P)[b]
UAl_4	BC Orthorhombic[a]	4·384	6·241	13·670	6·11	730(P)[b]

[a] R. P. Elliott, *Constitution of Binary Alloys.* First Supplement, pp. 58 and 61. McGraw Hill, New York (1965).

[b] M. Hansen, *Constitution of Binary Alloys*, p. 138. McGraw Hill, New York (1958).

[c] A. J. Frueh and J. Sygusch, *Z. Kristallogr.* **127** (1968) 139.

[d] F. A. Shunk, *Constitution of Binary Alloys.* Second Supplement, p. 46. McGraw Hill, New York (1969).

A transformation at a temperature just below the Al–MAl_4 eutectic temperature has been observed in the case of neptunium[33] and of plutonium[34]; Runnalls has suggested that this involves clustering of vacancies, no significant change being noticed in the lattice parameters. The same author has also studied in detail the structure of $PuAl_3$ and shown that four allotropic modifications exist between ambient temperature and the melting point. In plutonium-rich alloys, Ellinger[35] has noted that on prolonged storage (10 years) the tetragonal Pu_3Al becomes cubic with a parameter of 4·500Å whilst the parameter of $PuAl_2$ expands from 7·838 to 7·874Å; these effects are due to self-irradiation damage.

Ferromagnetism has been observed in $NpAl_2$; the paramagnetic moment is 2·30 μ_B[36]. Konobeevsky[13] has reported values of $8{\cdot}43 \times 10^{-6}$, $4{\cdot}85 \times 10^{-6}$ and $6{\cdot}14 \times 10^{-6}$ emu/g for the mass susceptibility (χ_g) of UAl_2, UAl_3 and UAl_4, respectively. These results are consistent with a valency of 4 for uranium in the aluminides. The temperature variation of the mass susceptibility obeys the Curie–Weiss Law up to 800°C for UAl_2 and UAl_3 and up to 650°C for UAl_4, with Curie temperatures of 160, 700 and 320K, respectively, and corresponding constants of 3820, 4580 and 3760. The superconducting transition temperature for Th_3Al_2 has been determined to be 2·6K[37].

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[33] R. E. Myrick and R. L. Folger, *Ind. and Eng. Chem., Process Design and Development* **3** (1964) 309.

[34] O. J. C. Runnalls, *Plutonium 1965*, p. 341. Chapman & Hall, London (1965).

[35] F. A. Shunk, *Constitution of Binary Alloys.* Second Supplement, p. 37. McGraw Hill, New York (1969).

[36] B. D. Dunlap, M. B. Brodsky, G. M. Kalvius, G. K. Shenoy and D. J. Lam, *J. Appl. Phys.* **40** (1969) 1495.

[37] E. E. Havinga, M. H. Van Maaren and H. Damsma, *Phys. Lett.* **29A** (1969) 109.

TABLE 10. CRYSTAL STRUCTURES AND MELTING POINTS OF NEPTUNIUM–ALUMINIUM AND PLUTONIUM–ALUMINIUM COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)			X-ray density (g/cm^3)	Melting point (°C)
		a	*b*	*c*		
$NpAl_2$[a]	FCC $MgCu_2$ type	7·785			8·19	
$NpAl_3$[a]	Cubic Cu_3Au type	4·262			6·82	< 1375 (P?)
$NpAl_4$[a]	BC Orthorhombic UAl_4 type	4·42	6·26	13·71	6·04	< 1150(P)
Pu_3Al	Tetragonal[b] $SrPb_3$ type	4·499		4·536	13·45	Peritectoid 560[c]
PuAl[c]	BCC Distorted CsCl type	10·769*			10·25	Peritectoid 590 Eutectoid 193
$PuAl_2$[c]	FCC $MgCu_2$ type	7·838 (Pu-rich) 7·848 (Al-rich)			8·10	1540
$PuAl_3$[d]	Rhombohedral ($9H_\alpha$)	7·901 $\alpha =$ 45·81°				Transforms at 915
	Rhombohedral ($9H_\beta$)	7·879 $\alpha =$ 45·94°				Transforms at 1027
	Hexagonal (6H)	6·083		14·410		Transforms at 1210
	Cubic	4·262			6·88	> 1400(P)
$PuAl_4$	BC Orthorhombic[b] UAl_4 type	4·387	6·262	13·714	6·12	926(P)[c]

* Runnalls[e] has reported a parameter of 7·833Å and a density of 8·095 g/cm^3.

[a] M. Hansen, *Constitution of Binary Alloys*, p. 122. McGraw Hill, New York (1958).

[b] R. P. Elliott, *Constitution of Binary Alloys*. First Supplement, p. 50. McGraw Hill, New York (1965).

[c] F. A. Shunk, *Constitution of Binary Alloys*. Second Supplement, p. 37. McGraw Hill, New York (1969).

[d] A. C. Larson, D. T. Cromer and R. B. Roof, Jr., *Acta Cryst.* **19** (1965) 281.

[e] O. J. C. Runnalls, *Plutonium 1965*, p. 341. Chapman & Hall, London (1965).

Thermodynamic data on the formation of thorium–aluminium compounds is very sparse; Johnson[19], using an equation devised by Rayleigh, has computed a value of ΔG°_{1323} for $ThAl_3$ of −31 kcal/mole.

For uranium, Chiotti and Kateley[38] have combined EMF measurements in the temperature range 673–1113K with calorimetric data for 298K to establish the following relationships, in kcal/mole,

$$\begin{array}{ll} UAl_2 & \Delta G^\circ = -22\cdot79 - 2\cdot33 \times 10^{-3} T \ln T + 18\cdot37 \times 10^{-3} T \\ UAl_3 & \Delta G^\circ = -26\cdot29 - 1\cdot31 \times 10^{-3} T \ln T + 10\cdot60 \times 10^{-3} T \\ UAl_4 & \Delta G^\circ = -32\cdot04 - 7\cdot52 \times 10^{-3} T \ln T + 59\cdot07 \times 10^{-3} T \end{array}$$

Akachinskii and Kopytin[39] have established values by aqueous calorimetry for the heats

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[38] P. Chiotti and J. A. Kateley, *J. Nucl. Mater.* **32** (1969) 135.

[39] V. V. Akachinskii and L. M. Kopytin, *Thermodynamics of Nuclear Materials*, p. 309. IAEA, Vienna 1962).

of formation (ΔH°_{298}) of the compounds $PuAl_2$, $PuAl_3$ and $PuAl_4$ of $-34{\cdot}0 \pm 0{\cdot}8$, $-43{\cdot}2 \pm 0{\cdot}8$ and $-43{\cdot}2 \pm 0{\cdot}8$ kcal/mole, respectively. They also estimated a value of -17 ± 5 kcal/mole for either PuAl or Pu_3Al.

Gallium

Little information is available on the thorium–gallium system. There is probably more than one compound, but only $ThGa_2$ is well established. Three compounds exist in the uranium–gallium system, whilst the plutonium–gallium system contains nine intermediate phases. The UGa_2 phase has been reported with both the AlB_2 structure and with the α-$ThSi_2$ structure, i.e. isomorphous either with $ThGa_2$ or with $PuGa_2$.

TABLE 11. CRYSTAL STRUCTURES AND MELTING POINTS OF ACTINIDE–GALLIUM COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)			X-ray density (g/cm³)	Melting point (°C)
		a	*b*	*c*		
$ThGa_2$[a]	BC Tetragonal α-$ThSi_2$ type	4·243		14·690	9·33	
UGa[a]	Orthorhombic	9·40	7·60	9·42		Congruent?
UGa_2	Hexagonal[a] AlB_2 type *OR*	4·21		4·01	10·18	Peritectoid?
	BC Tetragonal[b] α-$ThSi_2$ type	4·238		14·664	9·51	
UGa_3[c]	Cubic Cu_3Au type	$4{\cdot}247_5$			9·69	~1300
ηPu–Ga[b] (58–82 at. % Pu)	Unknown (high temperature phase)					928(P) Eutectoid 645
Pu_3Ga[b]	Tetragonal $SrPb_3$ type	4·469		4·527	14·45	Transformation at 363
	Cubic Cu_3Au type	4·507			14·27	Peritectoid 677
Pu_5Ga_3[b]	BC Tetragonal W_5Si_3 type	11·735		5·511	12·29	767(P)
PuGa[b]	BC Tetragonal	6·640		8·066	11·53	979(P)
Pu_2Ga_3[b]	Unknown					Peritectoid ~700
$PuGa_2$[b]	Hexagonal	4·248 (Ga-rich)		4·114	9·76	1264
	AlB_2 type	4·258 (Pu-rich)		4·138		
$PuGa_3$	Hexagonal[b] Ni_3Sn type	6·300		4·514	9·59	Transforms at 922
	Rhombohedral[e]	6·178		28·031	9·63	1105(P)
$PuGa_4$[d]	Orthorhombic UAl_4 type	4·380	6·290	13·673	9·13	420(P)
$PuGa_6$[d]	Tetragonal	5·942		7·617	8·11	321(P)

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[a] R. P. Elliott, *Constitution of Binary Alloys.* First Supplement, p. 459. McGraw Hill, New York (1965).

[b] F. A. Shunk, *Constitution of Binary Alloys.* Second Supplement, pp. 362 and 369. McGraw Hill, New York (1969).

[c] M. Hansen, *Constitution of Binary Alloys*, p. 761. McGraw Hill, New York (1958).

[d] C. C. Land and F. H. Ellinger, *J. Nucl. Mater.* **16** (1965) 87.

[e] A. C. Larson, D. T. Cromer and R. B. Roof, Jr., *Acta Cryst.* **18** (1964) 294.

The free energy of formation of UGa_3 was determined by Johnson and Feder[19] using a high-temperature galvanic cell as:

$$UGa_3 \quad \Delta G^\circ = -41{\cdot}42 + 14{\cdot}51 \times 10^{-3}T \text{ (643–973K, kcal/mole)}$$

More recently Alcock[40] has established relationships for all three uranium compounds using vaporization measurements, but indicates that Johnson and Feder's results are probably more accurate for UGa_3.

$$\left.\begin{array}{ll} UGa & \Delta G^\circ = -9{\cdot}80 + 2{\cdot}05 \times 10^{-3}T \\ UGa_2 & \Delta G^\circ = -20{\cdot}05 + 7{\cdot}45 \times 10^{-3}T \\ UGa_3 & \Delta G^\circ = -27{\cdot}40 + 12{\cdot}15 \times 10^{-3}T \end{array}\right\}\text{(kcal/mole)}$$

Heats of formation of plutonium–gallium compounds as reported by Akachinskii and Kopytin[41] are given in Table 12.

TABLE 12. HEATS OF FORMATION OF PLUTONIUM–GALLIUM COMPOUNDS (kcal/mole)

Measured		Estimated	
Composition	H°_{298}	Composition	H°_{298}
β-Pu_3Ga	$-39{\cdot}5 \pm 2{\cdot}0$	Pu_5Ga_3	-100 ± 10
$PuGa_2$	$-45{\cdot}4 \pm 2{\cdot}5$	$PuGa$	-28 ± 3
$PuGa_6$	$-56{\cdot}5 \pm 3{\cdot}1$	$PuGa_3$	-56 ± 6
		$PuGa_4$	-56 ± 6

The magnetic susceptibility of UGa_3 is temperature-independent according to Ansorge and Menovsky[42] who also report that the susceptibility of UGa_2 obeys the Curie–Weiss Law with a Curie temperature of 126K.

Indium

The systems with indium have not been fully determined. Isomorphous compounds of the type MIn_3 have been observed in actinide systems and in the plutonium systems the same structure, Cu_3Au type, also occurs at the inverse composition, Pu_3In (see Table 13).

The free energy of formation of UIn_3 has been determined by Alcock[40] and by Johnson[19]. The results are in good agreement, Johnson's relationship being:

$$UIn_3 \quad \Delta G^\circ = -26{\cdot}70 + 13{\cdot}70 \times 10^{-3}T \text{ (626–949K, kcal/mole)}$$

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[40] C. B. Alcock, J. B. Cornish and P. Grieveson, *Thermodynamics with emphasis on Nuclear Materials*, p. 211. IAEA, Vienna (1966).

[41] V. V. Akachinskii and L. M. Kopytin, *Thermodynamics of Nuclear Materials with emphasis on Solution Systems*, p. 789. IAEA, Vienna (1967).

[42] V. Ansorge and A. Menovsky, *Phys. Status Solidi*, **30** (1968) K31.

TABLE 13. CRYSTAL STRUCTURES AND MELTING POINTS OF ACTINIDE–INDIUM COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)		X-ray density (g/cm³)	Melting point (°C)
		a	c		
Th_2In[a]	Tetragonal $CuAl_2$ type	7·787	6·113	10·37	1170
$ThIn_2$[a]	Cubic	7·050			
$ThIn_3$[b]	Cubic Cu_3Au type	4·695		9·25	
UIn_3[b]	Cubic Cu_3Au type	4·597		9·95	
Pu_3In[c]	Cubic Cu_3Au type	4·705 (Pu-rich) 4·722 (In-rich)		13·34 12·96	962(P)*
η-Pu–In[c]	Unknown (high temperature phase)				1119(P) Eutectoid 863
PuIn[c]	Tetragonal AuCu type	4·811	4·538	11·19	1145
Pu_3In_5[c]	Unknown				1080(P)
$PuIn_3$[c]	Cubic Cu_3Au type	$4{\cdot}609_6$		9·90	1225

* Hocheid[6] has given a value of 678°C for the peritectic temperature.

[a] R. P. Elliott, *Constitution of Binary Alloys*. First Supplement, p. 554. McGraw Hill, New York (1965).

[b] R. Ferro, *Acta Cryst.* **11** (1958) 737.

[c] F. H. Ellinger, C. C. Land and K. A. Johnson, *Trans. Met. Soc. AIME* **233** (1965) 1252.

Thallium

Compounds of formula MTl_3 exist which are generally isomorphous with the cubic MIn_3 phases, the exception being $PuTl_3$ which has a hexagonal structure. As with indium, the Cu_3Au structure is also found in the most plutonium-rich compound, Pu_3Tl.

TABLE 14. CRYSTAL STRUCTURES OF ACTINIDE–THALLIUM COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)		X-ray density (g/cm³)
		a	c	
$ThTl_3$[a]	Cubic Cu_3Au type	4·748		13·11
UTl_3[a]	Cubic Cu_3Au type	4·684		13·75
Pu_3Tl[b]	Cubic Cu_3Au type	4·723		14·5
$PuTl_3$[b]	Hexagonal Mg type	3·458	5·519	12·4

[a] R. Ferro, *Acta Cryst.* **11** (1958) 737.

[b] A. A. Bochvar, S. T. Konobeevsky, V. I. Kutaitsev, T. S. Menshikova and N. T. Chebotarev, *Proc. 2nd ICPUAE*, Vol. 6, p. 186. United Nations, Geneva (1958).

The free energy of formation of UTl_3 in kcal/mole, is given as:

$$UTl_3 \; \Delta G^\circ = -13{\cdot}3_8 + 12{\cdot}0 \times 10^{-3}T\,(653\text{–}943\mathrm{K})$$[19].

5. GROUP IV

Group IVA

Titanium

The only compound reported in actinide–titanium systems is U$_2$Ti. The compound exists over a narrow homogeneity range close to the stoichiometric composition and decomposes congruently on heating at 898°C to a solid solution of β-titanium in γ-uranium[43]. The structure type is either AlB$_2$ or Ni$_2$In with a hexagonal unit cell of:[43, 44]

$$a = 4{\cdot}828\text{Å}, \quad c = 2{\cdot}847\text{Å} \quad \text{X-ray density } 15{\cdot}14 \text{ g/cm}^3$$

The thorium system is of the simple eutectic type whilst the plutonium system exhibits limited terminal solid solubilities and peritectic decomposition of ϵ-plutonium.

Zirconium

The thorium–zirconium system involves complete solid solubility between the high temperature bcc modifications, β-Th and β-Zr, with a eutectoid decomposition at 650°C; no compounds are formed. The uranium and plutonium systems show compound formation at low temperatures, the phases forming being UZr$_2$, PuZr$_2$, 'Pu$_6$Zr' and 'Pu$_{19}$Zr'. Two different structures have been proposed for Pu$_6$Zr and as the measured density lies between the calculated X-ray densities it has not yet been possible to decide between them.

TABLE 15. CRYSTAL STRUCTURES AND DECOMPOSITION TEMPERATURES OF ACTINIDE–ZIRCONIUM COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)			X-ray density (g/cm^3)	Decomposition temperature (°C)
		a	*b*	*c*		
UZr$_2$[a]	Hexagonal ω-phase or Ni$_2$Sn[b]	5·03		3·08	10·3	617 Peritectoid
'Pu$_{19}$Zr'	BC Tetragonal[c]	18·19		7·851		~280[d] Peritectoid
'Pu$_6$Zr'	Orthorhombic[e]	10·39	10·44	11·18	16·7	345[d]
12–29 at. % Zr	Tetragonal[f]	10·893		14·889	15·86	Congruent at 20 at. % Zr
PuZr$_2$[d]	Hexagonal Disordered AlB$_2$ type	5·055		3·123	10·13	380 Peritectoid

[a] R. P. Elliott, *Constitution of Binary Alloys.* First Supplement, pp. 858 and 764. McGraw Hill, New York (1965).

[b] E. S. Makarov, *Soviet Physics Cryst.* 3 (1958) 3.

[c] W. H. Zachariasen and F. H. Ellinger, U.S. Report LA-4367 (1970).

[d] O. J. Wick, *Plutonium Handbook*, p. 227. Gordon & Breach, New York (1967).

[e] A. A. Bochvar, S. T. Konobeevsky, V. I. Kutaitsev, T. S. Menshikova and N. T. Chebotarev, *Proc. 2nd ICPUAE*, Vol. 6, p. 184. United Nations, Geneva (1958).

[f] A. F. Berndt, *J. Less Common Metals*, **12** (1967) 82.

The paramagnetic susceptibility of 'Pu$_6$Zr' has been given by Konobeevsky[13] as 700 × 10^{-6} emu/g-atom at 20°C.

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[43] M. Hansen, *Constitution of Binary Alloys*, p. 1238. McGraw Hill, New York (1958).

[44] E. S. Makarov, *Soviet Physics Cryst.* 3 (1958) 3.

Hafnium

No compounds exist in the thorium or uranium systems, but plutonium forms two intermetallic phases with hafnium, θ and ζ, which appear to be the analogues of 'Pu_6Zr' and '$Pu_{19}Zr$' although occurring at even higher plutonium contents than do the zirconium compounds.

TABLE 16. LATTICE PARAMETERS AND DECOMPOSITION TEMPERATURES OF PLUTONIUM–HAFNIUM COMPOUNDS

Composition	Symmetry	Lattice parameters (Å)			Measured density (g/cm³)	Decomposition temperature (°C)
		a	*b*	*c*		
ζ ~3 at. % Hf	BC Tetragonal[a]	18·19		7·851	17·5[b]	270*[b] Peritectoid
θ 5–7 at. % Hf	Orthorhombic[c]	10·415	10·428	11·245	17·7	340 Peritectoid

* May be unstable below 50°C.

[a] W. H. Zachariasen and F. H. Ellinger, U.S. Report LA-4367 (1970).

[b] F. H. Ellinger and C. C. Land, *J. Nucl. Mater.* **28** (1968) 291.

[c] V. I. Kutaitsev, N. T. Chebotarev, I. G. Lebedev, M. A. Andrianov, V. N. Konev and T. S. Menshikova, *Plutonium 1965*, p. 420. Chapman & Hall, London (1965).

Group IVB

Germanium

Extensive compound formation occurs in actinide–germanium systems. The thorium system is particularly complex and at the present time two sets of data exist which agree on some compounds but not on others. Unfortunately neither author employed chemical analysis to establish the composition of any individual compound; Shunk[45] has suggested which compounds probably correspond, largely on the basis of the crystal structures, and his proposals are given in Table 17.

The free energies of formation of the thorium-based compounds have been determined by Alcock, Cornish and Grieveson[40] from vapour pressure measurements and the results are given as (in kcal/mole):

Th_3Ge $\Delta G^\circ = -26{\cdot}00 + 0{\cdot}80 \times 10^{-3}T$

Th_3Ge_2 $\Delta G^\circ = -47{\cdot}50 + 1{\cdot}20 \times 10^{-3}T$

$ThGe$ $\Delta G^\circ = -19{\cdot}40 + 0{\cdot}70 \times 10^{-3}T$

Th_3Ge_5 $\Delta G^\circ = -76{\cdot}00 + 3{\cdot}60 \times 10^{-3}T$

$ThGe_2$ $\Delta G^\circ = -27{\cdot}70 + 1{\cdot}14 \times 10^{-3}T$

$ThGe_3$ $\Delta G^\circ = -33{\cdot}60 + 2{\cdot}44 \times 10^{-3}T$

($Th_{0\cdot9}Ge_2$?)

For the uranium and plutonium systems, the phases established by reaction of the elements are given in Table 18. In addition, Alcock and Grieveson[46] have shown by vapour pressure measurements that UGe and U_3Ge_5 exist, although the latter is probably identifiable with the previously reported U_3Ge_4 phase. The free energy data derived from their measurements at 1000–1200°C are, in kcal/mole:

U_5Ge_3 $\Delta G^\circ = -56{\cdot}3 + 0{\cdot}68 \times 10^{-3}T$

UGe $\Delta G^\circ = -14{\cdot}7 + 0{\cdot}52 \times 10^{-3}T$

U_3Ge_5 $\Delta G^\circ = -57{\cdot}6 + 2{\cdot}32 \times 10^{-3}T$

UGe_2 $\Delta G^\circ = -21{\cdot}0 + 0{\cdot}93 \times 10^{-3}T$

UGe_3 $\Delta G^\circ = -25{\cdot}6 + 1{\cdot}38 \times 10^{-3}T$

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[45] F. A. Shunk, *Constitution of Binary Alloys*, Second Supplement, p. 397. McGraw Hill, New York (1969).

[46] C. B. Alcock and P. Grieveson, *J. Inst. Metals*, **90** (1962) 304.

TABLE 17. CRYSTAL STRUCTURES AND MELTING POINTS OF THORIUM–GERMANIUM COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)			X-ray density (g/cm^3)	Melting point (°C)
		a	*b*	*c*		
Th_3Ge[a]	Unknown					1350–1400 Peritectoid
Th_2Ge[b]	Tetragonal $CuAl_2$ type	7·414		6·081	10·67	
Th_3Ge_2	Tetragonal[a] *D5a* type	7·951		4·194	10·54	~1800
	Tetragonal[b] U_3Si_2 type	7·976		4·165		
ThGe[a,b]	FCC NaCl type	6·041 $6·049_6$	 (Ge-rich)		9·17	~1800
Th_2Ge_3[a]	Orthorhombic Distorted AlB_2 type	6·989	8·432	8·136	9·45	~1700(P)
Th_3Ge_5[b]	Hexagonal Distorted AlB_2 type	4·065		4·202		
Th_3Ge_5[a]	Orthorhombic Distorted C_c type	5·913	5·889	14·219	9·34	1650(P)
α-$ThGe_2$[b]	Tetragonal α-$ThSi_2$ type	4·133 4·179	(Ge-rich)	14·202 14·233		
$ThGe_2$[a]*	Orthorhombic $ZrSi_2$ type	4·223	16·911	4·052	8·66	~600 Peritectoid
$Th_{0.9}Ge_2$	Orthorhombic[a]	16·642	4·023	4·160	8·44	1600(P)
	Orthorhombic[b] Cu_2Sb type	16·645	4·027	4·090		

* Not found by ref. b.

[a] A. Brown and J. J. Norreys, *J. Less Common Metals*, **5** (1963) 302.

[b] P. Stecher, F. Benesovsky and H. Nowotny, *Monatsh. Chem.* **94** (1963) 549.

For UGe_3, Alcock, Cornish and Grieveson[40] have computed a value of —12·1 kcal/mole for the heat of formation from solid uranium and liquid germanium. The heat of vaporization of UGe_3 is given as —85 kcal/mole. No thermodynamic data have been published for plutonium–germanium compounds.

The phases UGe_2 and $PuGe_2$ are ferromagnetic[47] with magnetic moments of at least 0·80 and 0·144 Bohr magnetons, respectively, at 4K, and Curie temperatures of 52·0 and 34·5K. Electrical resistivity measurements on UGe_2 indicated that the ferromagnetism arose from an interaction between the conduction electrons and the local spin; the resistivity at 300K was ~2420 $\mu\Omega$-cm.

Tin

The phase diagrams for the systems with thorium, uranium and plutonium have not been fully established and it is conceivable that further compounds exist beyond those already reported (see Table 19). Indirect evidence for this can be drawn for the plutonium–tin system where the two phases Pu_3Sn and $PuSn_3$ both possess the Cu_3Au structure as do the Pu_3M and PuM_3 phases in the systems with the neighbouring elements indium and lead.

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[47] C. E. Olsen, *J. Appl. Phys.* **31** (1960) 340S.

However, both of the latter systems contain a number of compounds between the two Cu_3Au type phases.

Table 18. Crystal Structures and Melting Points of Uranium–Germanium and Plutonium–Germanium Compounds

Composition	Crystal structure	Lattice parameters (Å)			X-ray density (g/cm^3)	Melting point (°C)
		a	*b*	*c*		
'U_7Ge'[a]	Unknown					Peritectoid 1035
U_5Ge_3[a]	Hexagonal Mn_5Si_3 type	8·58		5·79	12·66	1670
U_3Ge_4[a] (U_3Ge_5?)	Orthorhombic	5·87	9·88	8·98		~1440(P)
UGe_2[a]	Orthorhombic $ZrSi_2$ type	4·12	15·10	3·98	10·3	~1450
UGe_3[a]	Cubic Cu_3Au type	4·205			10·18	~1475
Pu_3Ge[b]	Unknown					
Pu_3Ge_2[b]	Unknown					
Pu_2Ge_3[b]	Hexagonal Defect AlB_2 type	3·975		4·198	10·1	
$PuGe_2$[b]	Tetragonal α-$ThSi_2$ type	4·102		13·81	10·98	
$PuGe_3$[b]	Cubic Cu_3Au type	4·223			10·07	

[a] R. P. Elliott, *Constitution of Binary Alloys*, First Supplement, p. 494. McGraw Hill, New York (1965).
[b] O. J. Wick, *Plutonium Handbook*, p. 207. Gordon & Breach, New York (1967).

Thermodynamic data for the uranium–tin compounds have been reviewed by Johnson[19] who has combined his own data from EMF measurements with the effusion data of Alcock and Grieveson[46] to allow for uncertainties introduced by a possible eutectic reaction in uranium-rich alloys.

Table 19. Crystal Structures and Melting Points of Actinide–Tin Compounds

Composition	Crystal structure	Lattice parameter (Å)	X-ray density (g/cm^3)	Melting point (°C)
$ThSn_3$[a]	Cubic Cu_3Au type	4·718	9·30	
U_3Sn_2[b] 36–45 at. % Sn	Unknown			1500
U_3Sn_5[b] 60–64 at. % Sn	Unknown			1380(P)
USn_3[c]	Cubic Cu_3Au type	4·626	9·96	1350(P)
Pu_3Sn[b]	Cubic Cu_3Au type	4·680	13·54	
$PuSn_3$[b]	Cubic Cu_3Au type	4·630	9·96	1198

[a] R. P. Elliott, *Constitution of Binary Alloys*, First Supplement, p. 829. McGraw Hill, New York (1965).
[b] F. A. Shunk, *Constitution of Binary Alloys*, Second Supplement, pp. 691 and 633. McGraw Hill, New York (1969).
[c] M. Hansen, *Constitution of Binary Alloys*, p. 1215. McGraw Hill, New York (1958).

$$\left.\begin{array}{ll} U_3Sn_2 & \Delta G^\circ = -74{\cdot}40 + 19{\cdot}20 \times 10^{-3}T \\ U_3Sn_5 & \Delta G^\circ = -99{\cdot}41 + 30{\cdot}12 \times 10^{-3}T \\ USn_3 & \Delta G^\circ = -41{\cdot}03 + 14{\cdot}3 \times 10^{-3}T \end{array}\right\}\text{(kcal/mole)}$$

Alcock, Cornish and Grieveson have more recently determined the heat of formation of USn_3, starting from solid uranium and liquid tin, to be $-7{\cdot}0$ kcal/mole. The heat of vaporization of USn_3 is given by them as -72 kcal/mole.

Ivanov[48] has determined the dissociation pressure of USn_3 as:

$$USn_3 \qquad \log P_{mm} = 9{\cdot}067 - \frac{17223}{T}\ (1298\text{–}1568\text{K})$$

For the plutonium system, the only thermodynamic datum published is a value for ΔH°_{298} of $-52{\cdot}5 \pm 0{\cdot}9$ kcal/mole[41].

The magnetic susceptibility of USn_3 has been shown not to obey the Curie–Weiss Law; the value at 298K is $4{\cdot}1 \times 10^{-3}$ emu/mole[49].

Lead

As with the other Group IVB elements, a considerable number of compounds are formed between the actinide elements and lead. The actinide-rich compounds, as in the case of tin, tend to be highly pyrophoric and this has made identification of such phases difficult.

TABLE 20. CRYSTAL STRUCTURES AND MELTING POINTS OF ACTINIDE–LEAD COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)		X-ray density (g/cm³)	Melting point (°C)
		a	*c*		
ThPb[a]	FC Tetragonal	4·545	5·644	12·51	> 1200
$ThPb_2$[a]	Unknown				
$ThPb_3$	Cubic[a] Cu_3Au type	4·856		12·31	865(P)[b]
UPb	FC Tetragonal[a]	4·579	5·259	13·27	Syntectic 1280[c]
UPb_3	Cubic[a] Cu_3Au type	$4{\cdot}791_5$		12·93	1220[c]
Pu_3Pb[d]	Cubic Cu_3Au type	4·737		14·56	896(P)
Pu_5Pb_3[d]	Tetragonal W_5Si_3 type	12·310	6·084	13·07	~1350(P)
Pu_5Pb_4[d]	Hexagonal Ti_5Ga_4 type	9·523	6·482	13·31	1385
Pu_4Pb_5[d]	Hexagonal	16·52	6·440		1185(P)
α-$PuPb_2$[d]	Tetragonal Ga_2Hf type	4·621	31·29	12·99	Transformation at 1105
β-$PuPb_2$[d]	Unknown Possibly $ThSi_2$ type				1128(P)
$PuPb_3$[d]	Cubic Cu_3Au type	4·8084 (Pu-rich) 4·8071 (Pb-rich)		12·86	~1150

[a] R. P. Elliott, *Constitution of Binary Alloys*, First Supplement, pp. 725 and 726. McGraw Hill, New York (1965).

[b] W. Gans, O. Knacke, F. Mueller and H. Witte, *Z. Metallkunde*, **57** (1966) 46.

[c] M. Hansen, *Constitution of Binary Alloys*, p. 1116. McGraw Hill, New York (1958).

[d] D. H. Wood, E. M. Cramer, P. L. Wallace and W. J. Ramsey, *J. Nucl. Mater.* **32** (1969) 193.

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[48] V. E. Ivanov, A. A. Kruglykh, V. S. Pavlov, G. P. Kovtum and V. M. Amonenko, *Thermodynamics of Nuclear Materials*, p. 735. IAEA, Vienna (1962).

[49] V. Udaya Shankar Rao and R. Vyayaraghavan, *J. Phys. Chem. Solids*, **29** (1968) 123.

Gans[50] has demonstrated the existence of a further thorium compound, $ThPb_4$, which decomposes peritectically at 770°C, and has given the following values for the free energy of formation of the thorium–lead phases, in kcal/mole:

$$\left.\begin{array}{ll} \mathrm{ThPb} & \Delta G^\circ = -19{\cdot}3 + 5{\cdot}9 \times 10^{-3}T \\ \mathrm{ThPb_2} & \Delta G^\circ = -33{\cdot}2 + 14{\cdot}2 \times 10^{-3}T \\ \mathrm{ThPb_3} & \Delta G^\circ = -45{\cdot}0 + 24{\cdot}6 \times 10^{-3}T \\ \mathrm{ThPb_4} & \Delta G^\circ = -54{\cdot}4 + 33{\cdot}2 \times 10^{-3}T \end{array}\right\} \text{(873–1273K)}$$

Johnson[19] has reported good agreement for the free energy of formation of UPb and UPb_3 from his own work and from that of Alcock and Grieveson[46]. For solid uranium reacting with liquid lead one obtains from effusion measurements, in kcal/mole:

$$\begin{array}{ll} \mathrm{UPb} & \Delta G^\circ = -10{\cdot}2 + 2{\cdot}5 \times 10^{-3}T \\ \mathrm{UPb_3} & \Delta G^\circ = -20{\cdot}9 + 9{\cdot}4 \times 10^{-3}T \end{array}$$

Alcock and Grieveson[46] also determined the heat of formation of UPb_3 using a simple aqueous solution calorimeter and found a value of $-16{\cdot}0 \pm 2{\cdot}0$ kcal/mole. For the heat of vaporization of UPb_3 a value of —44 kcal/mole has been reported[46].

The free energy of formation of $PuPb_3$ has been estimated as —23 kcal/mole at 700°C[19].

6. GROUP VA

No compounds have been observed in the systems between thorium, uranium, or plutonium and any of the elements vanadium, niobium or tantalum. The systems are mainly of the simple eutectic type, with the exception of the U–Nb system which exhibits completely solid solubility in the high temperature bcc field above 975°C with a miscibility gap below that temperature, and the U–Ta system which involves peritectic decomposition of the γ-U phase.

7. GROUP VIA

The binary systems between thorium, uranium or plutonium and chromium, molybdenum or tungsten are all of the simple eutectic type or involve peritectic decomposition of the γ-U phase. The only well-established compound is the γ' phase, U_2Mo in the U–Mo system. This has the tetragonal $MoSi_2$ structure and is chemically ordered at all temperatures up to its congruent transformation to γ-U at 600°C[51]. The lattice parameters are:

U_2Mo $a = 3{\cdot}427$ Å, $c = 9{\cdot}854$ Å X-ray density 16·42 g/cm³ [51]

The γ' phase exists over a small composition range close to 32 at. % molybdenum.

8. GROUP VIIA

Manganese

A limited number of actinide–manganese compounds form, in particular Laves phases of the MMn_2 type.

The magnetic susceptibilities of U_6Mn, UMn_2 and $PuMn_2$ are $\sim 2 \times 10^{-6}$, $\sim 6 \times 10^{-6}$ and $7{\cdot}8 \times 10^{-6}$ emu/g, respectively[13]. A λ-type anomaly has been detected in UMn_2 at 260K, the

[50] W. Gans, O. Knacke, F. Mueller and H. Witte, *Z. Metallkunde*, **57** (1966) 46.
[51] A. E. Dwight, *J. Nucl. Mater.* **2** (1960) 81.

TABLE 21. CRYSTAL STRUCTURES AND MELTING POINTS OF ACTINIDE–MANGANESE COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)		X-ray density (g/cm^3)	Melting point (°C)
		a	*c*		
ThMn$_2$[a]	Hexagonal MgZn$_2$ type	5·476	8·931	12·94	
Th$_6$Mn$_{23}$[b]	FCC	12·533		8·98	
ThMn$_{12}$[b]	BC Tetragonal	8·74	4·95	7·83	
U$_6$Mn[a]	BC Tetragonal	10·29	5·24	17·8	726(P)
UMn$_2$	FCC[c] MgCu$_2$ type	7·146 —7·174		12·57	1120[a]
PuMn$_2$[d]	FCC MgCu$_2$ type	7·290 (Pu-rich) 7·26 (Mn-rich)		12·0	1050

[a] R. P. Elliott, *Constitution of Binary Alloys*, First Supplement, p. 615. McGraw Hill, New York (1965).
[b] M. Hansen, *Constitution of Binary Alloys*, p. 957. McGraw Hill, New York (1958).
[c] F. A. Shunk, *Constitution of Binary Alloys*, Second Supplement, p. 511. McGraw Hill, New York (1969).
[d] O. J. Wick, *Plutonium Handbook*, p. 240. Gordon & Breach, New York (1967).

low temperature form being anti-ferromagnetic[52]. The superconducting transition temperature of U$_6$Mn has been determined as 2·32K[53].

Electrical resistivity measurements on UMn$_2$ have indicated a Neel temperature of 245K as against the above value of 260K from magnetic measurements. The resistivity falls steeply with decreasing temperature below 245K whilst at 300K the value is 85 micro-ohm cm and rises linearly at 4·5×10^{-2} micro-ohm cm/degree. These results indicate a spin disorder component of 64 micro-ohm cm[54]. A much lower resistivity has been reported by Ondracek and Petzow[55] but their results appear to be anomalous since they give a value for the compound which is lower than that of either of the constituents.

Technetium

Little information is available on the plutonium–technetium system, nor have systematic studies been made of the systems with thorium or uranium.

TABLE 22. CRYSTAL STRUCTURES OF ACTINIDE–TECHNETIUM COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)				X-ray density (g/cm^3)
		a	*b*	*c*	*β*	
ThTc$_2$[a]	Hexagonal MgZn$_2$ type	5·394		9·222		12·29
U$_2$Tc[b]	Monoclinic U$_2$Ru type	13·407	3·271	5·213	96°23′	16·81
UTc$_2$[a]	Unknown*					
PuTc$_2$[c]	Unknown					

* UTc$_2$ is not isomorphous with ThTc$_2$ and moreover is not any type of Laves phase.
[a] J. B. Darby, Jr., A. F. Berndt and J. W. Downey, *J. Less Common Metals*, 9 (1965) 466.
[b] A. F. Berndt and A. E. Dwight, *Trans. Met. Soc. AIME* **233** (1965) 2075.
[c] H. R. Haines, Private communication.

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[52] S. T. Lin and A. B. Kaufmann, *Phys. Rev.* **108** (1957) 1171.
[53] B. S. Chandrasekhar and J. K. Hulm, *Phys. and Chem. Solids*, 7 (1958) 259.
[54] Y. Hamaguchi, N. Kunitomi, S. Kumura and M. Sakamoto, *J. Phys. Soc. Japan*, **17** (1962) 398.
[55] G. Ondracek and G. Petzow, *Z. Metallkunde*, **56** (1965) 498.

The superconducting transition temperature of $ThTc_2$ has been determined to be 5·3K[56].

Rhenium

Only limited studies have been made of actinide–rhenium systems. A hexagonal Laves phase, MRe_2, is common to such systems and there is evidence of phases of higher actinide content. The $ThRe_2$ phase is superconducting below 5·0K[56].

TABLE 23. CRYSTAL STRUCTURES AND MELTING POINTS OF ACTINIDE–RHENIUM COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)			X-ray density (g/cm³)	Melting point (°C)
		a	*b*	*c*		
$ThRe_2$[a]	Hexagonal $MgZn_2$ type	5·492		9·097	16·90	~2500(P)
U_2Re[b]	Unknown					~750 Peritectoid
URe_2[a]	Orthorhombic	5·600	9·178	8·463		Transforms at 180
	Hexagonal $MgZn_2$ type	5·433		8·561 (213°C)	18·53	2200
$PuRe_2$[c]	Hexagonal $MgZn_2$ type	5·396		8·729	18·45	

[a] R. P. Elliott, *Constitution of Binary Alloys*, First Supplement, p. 772. McGraw Hill, New York (1965).
[b] R. J. Jackson and W. L. Larsen, *J. Nucl. Mater.* **21** (1967) 277.
[c] O. J. Wick, *Plutonium Handbook*, p. 218. Gordon & Breach, New York (1967).

9. GROUP VIII

First Long Period

Iron

A number of compounds are formed between the actinides and iron. Isomorphous compounds of formula MFe_2 or M_6Fe exist or in some cases are assumed to exist, e.g. '$NpFe_2$' and 'Np_6Fe' have been prepared although their crystal structure has not been verified. The isomorphism of the MFe_2 series extends to the systems with cobalt and nickel and to many of the corresponding actinide compounds with the platinum metals. This is also true of the Th_7Fe_3 structure.

The free energy of formation of Th_2Fe_{17} has been determined and that of $ThFe_5$ estimated by Magnani, Skelton and Smith[4], who report, in kcal/g-atom,

$$Th_2Fe_{17} \quad \Delta G^\circ = -2{\cdot}99 \pm 0{\cdot}22 + (1{\cdot}21 \pm 0{\cdot}23) \times 10^{-3}T(973K)$$

$$ThFe_5 \quad \Delta G^\circ = -5{\cdot}3 + 2{\cdot}5 \times 10^{-3}T(973K)$$

In his review of thermodynamic data, Johnson[19] quotes values of −7·7 and 3·9 ± 1·2 (estimated) kcal/mole for the heats of formation of UFe_2 and U_6Fe respectively, whilst for $PuFe_2$ and Pu_6Fe the corresponding values are −6·5 ± 0·4 and −3·3 ± 1·0 kcal/mole.

[56] A. L. Giorgi and E. G. Szklarz, *J. Less Common Metals*, **22** (1970) 266.

TABLE 24. CRYSTAL STRUCTURES AND MELTING POINTS OF ACTINIDE–IRON COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)		X-ray density (g/cm³)	Melting point (°C)
		a	*c*		
Th_7Fe_3	Hexagonal[a]	9·823	6·211	11·47	962(P)[b]
$ThFe_3$	Rhombohedral[c] $PuNi_3$ type	5·18	25·2	10·2	1200(P)[b]
$ThFe_5$	Hexagonal[d] $CaZn_5$ type	5·13	4·02	9·3	1212(P)[b]
Th_2Fe_{17}	Rhombohedral[c] Th_2Zn_{17} type	8·565	12·469	8·89	1462[b]
U_6Fe	BC Tetragonal[f] U_6Mn type	10·289	5·232	17·79	805(P)[a]
UFe_2	Cubic[a] $MgCu_2$ type	7·061 –7·065		13·21	1233[d]
Pu_6Fe[g]	BC Tetragonal U_6Mn type	10·405	5·349	17·10	428(P)
α-$PuFe_2$[g]	Cubic $MgCu_2$ type	7·189		12·50	
β-$PuFe_2$[a]	Hexagonal $MgNi_2$ type	5·64	18·37		Exists at intermediate temperatures
γ-$PuFe_2$	Cubic[a]	7·15			1240[g] Eutectoid at 1020

[a] F. A. Shunk, *Constitution of Binary Alloys*, Second Supplement, pp. 351, 352 and 343. McGraw Hill, New York (1969).

[b] J. R. Murray, *J. Less Common Metals*, **10** (1966) 432.

[c] J. F. Smith and D. B. Hansen, *Acta Cryst.* **19** (1965) 1019.

[d] M. Hansen, *Constitution of Binary Alloys*, pp. 723 and 728. McGraw Hill, New York (1958).

[e] Q. Johnson, G. S. Smith and D. H. Wood, *Acta Cryst.* **25B** (1969) 464.

[f] R. P. Elliott, *Constitution of Binary Alloys*, First Supplement, p. 440. McGraw Hill, New York (1965).

[g] O. J. Wick, *Plutonium Handbook*, Vol. 1, p. 209. Gordon & Breach, New York (1965).

Ferromagnetic behaviour has been detected in the UFe_2 phase, the Curie temperature being 172K and the Bohr magneton number 1·02 per UFe_2 molecule[57]. Both the uranium and the iron atoms have magnetic moments, and a polarized neutron diffraction study at 84K has indicated that the form factor for the uranium moment is of the $5f^3$ type[58]. An analysis of the variation of electrical resistivity with temperature for UFe_2 has established that out of the 125 $\mu\Omega$-cm total resistivity at 300K, some 60 $\mu\Omega$-cm is associated with the spin–disorder component[54]. The resistivity above room temperature increases by 5×10^{-2} $\mu\Omega$-cm per degree.

Superconducting behaviour in uranium compounds is only found when the alloying element is magnetic, if one allows manganese to be counted by virtue of its antiferromagnetism[53]. The superconducting transition temperature for U_6Fe is 3·9K. For Th_7Fe_3 the corresponding temperature is 1·86K[59].

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[57] S. T. Lin and R. E. Ogilvie, *J. Appl. Phys.* 34 (1963) 1372.

[58] M. Yessik, *J. Appl. Phys.* 40 (1969) 1133.

[59] B. T. Matthias, T. H. Geballe and V. B. Compton, *Rev. Modern Phys.* 35 (1963) 1.

Cobalt

Extensive compound formation occurs in the actinide–cobalt systems. As well as the phases detailed in Table 25, the compounds UCo_4 and U_2Co_{11} have been reported as melting congruently at 1120° and 1130°C respectively[60]. Nothing is known about their structures.

TABLE 25. CRYSTAL STRUCTURES AND MELTING POINTS OF ACTINIDE–COBALT COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)			X-ray density (g/cm³)	Melting point (°C)
		a	*b*	*c*		
Th_7Co_3[a]	Hexagonal Th_7Fe_3 type	9·842		6·207	11·48	1188
ThCo[a]	Orthorhombic CrB type	3·776	10·877	4·153	11·33	1137
$ThCo_3$[a]	Hexagonal	5·038		24·64*	11·28	1125(P)
$ThCo_5$[a]	Hexagonal	5·005 (Th-rich)		3·990	10·13	1437
83·5–87·5 at. % Co	$CaZn_5$ type	4·956 (Co-rich)		4·029		
Th_2Co_{17}	Rhombohedral[b] Th_2Zn_{17} type	8·438		12·254	9·66	1462[a]
U_6Co	BC Tetragonal[c] U_6Mn type	10·36		5·21	17·66	826(P)[d]
UCo	BCC[c]	6·356			15·37	805(P)[d]
UCo_2	Cubic[c] $MgCu_2$ type	6·992			13·83	1170[d]
UCo_3	Rhombohedral[e] $PuNi_3$ type	4·849		24·317	12·52	Peritectoid[c] ~830
Pu_6Co[f]	BC Tetragonal U_6Mn type	10·46		5·33	17·0	Peritectoid 397
Pu_3Co[f]	Orthorhombic Al_2CuMg type	3·501† 3·477	11·03 10·99	9·23 9·20	14·46	449(P)
Pu_2Co[f]	Hexagonal Fe_2P type	7·803† 7·732		3·606 3·654	14·07	605(P)
$PuCo_2$[f]	Cubic $MgCu_2$ type	7·081† –7·095			13·35	1300
$PuCo_3$[f]	Rhombohedral $PuNi_3$ type	5·003		24·42	11·74	1235(P)
Pu_2Co_{17}[f]	Hexagonal Th_2Ni_{17} type	8·327		8·107	10·10	1210(P)

* The true *c* parameter is probably eight times this value.

† Pu-rich parameters.

[a] J. R. Murray, *J. Less Common Metals*, **10** (1966) 432.

[b] Q. Johnson, G. S. Smith and D. H. Wood, *Acta Cryst.* **25B** (1969) 464.

[c] F. A. Rough and A. A. Bauer, *Constitutional Diagrams of Uranium and Thorium Alloys*, p. 17. Addison-Wesley, Reading, Mass. (1959).

[d] M. Hansen, *Constitution of Binary Alloys*, p. 515. McGraw Hill, New York (1958).

[e] A. E. Dwight, *Acta Cryst.* **24B** (1968) 1395.

[f] O. J. Wick, *Plutonium Handbook*, Vol. 1, p. 201. Gordon & Breach, New York (1967).

The free energy of formation of the phases Th_2Co_{17} and $ThCo_5$ has been reported[4] as:

$$Th_2Co_{17} \quad \Delta G^\circ = -3{\cdot}94 \pm 0{\cdot}20 + (0{\cdot}79 \pm 0{\cdot}21) \times 10^{-3}T \text{(973K, kcal/g-atom)}$$

$$ThCo_5 \quad \Delta G^\circ = -7{\cdot}14 \pm 0{\cdot}32 + (2{\cdot}12 \pm 0{\cdot}29) \times 10^{-3}T \text{(973K, kcal/g-atom)}$$

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[60] F. A. Rough and A. A. Bauer, *Constitutional Diagrams of Uranium and Thorium Alloys*, p. 17. Addison-Wesley, Reading, Mass. (1959).

Konobeevsky and his co-workers[13] have determined the magnetic susceptibility of a number of the compounds with plutonium and uranium and their results are summarized in Table 26.

TABLE 26. PARAMAGNETIC MASS SUSCEPTIBILITIES OF SOME URANIUM–COBALT AND PLUTONIUM–COBALT COMPOUNDS AT 298K

Compound	χ_g (10^{-6} emu/g)	Compound	χ_g (10^{-6} emu/g)
U_6Co	~2	Pu_6Co	2·3
UCo	2·3	Pu_3Co	2·5
UCo_2	3·2	Pu_2Co	2·4
		$PuCo_2$	10·5

The susceptibility of the Pu_6Co and Pu_3Co phases is essentially temperature-independent. A recent examination of the UCo_2 phase[61] has confirmed that it is a temperature-independent paramagnetic material with no evidence for a ferromagnetic transition as in UFe_2. The $ThCo_5$ phase is of the $SmCo_5$ type with a Curie temperature of 630K and a magnetic moment of 4·8 Bohr magnetons[62].

The compounds UCo and U_6Co are superconductors with critical temperatures of 1·7 and 2·3K, respectively[53], whilst Th_7Co_3 has a transition temperature of 1·83K[59].

Nickel

The compounds between the actinides and nickel exhibit many analogies with the corresponding cobalt systems but a number of differences also exist, particularly in the U–Ni system and in the Pu–Ni system where no phase exists corresponding to Pu_6Co. The U–Ni system contains four phases of unknown structure[63], all of which melt peritectically, these being U_7Ni_9 (785°C), U_5Ni_7 (820°C), 'X' at about 77 at. % Ni (1260°C) and 'Y' at 78–79 at. % Ni (1290°C). Confirmatory evidence for the existence of these four phases comes from the work of Angerman[64] who observed a total of seven intermediate phases in a U–Ni diffusion couple.

The thermodynamic functions for the formation of the five Th–Ni compounds, at 973K in kcal/g-atom, as established by Skelton, Magnani and Smith[65] using EMF measurements, are:

$$
\begin{aligned}
&Th_7Ni_3 && \Delta G^\circ = -6{\cdot}59 \pm 0{\cdot}47 + (0{\cdot}34 \pm 0{\cdot}31) \times 10^{-3}T \\
&ThNi && \Delta G^\circ = -10{\cdot}82 \pm 0{\cdot}76 + (0{\cdot}57 \pm 0{\cdot}3) \times 10^{-3}T \\
&ThNi_2 && \Delta G^\circ = -10{\cdot}68 \pm 0{\cdot}68 + (0{\cdot}77 \pm 0{\cdot}70) \times 10^{-3}T \\
&ThNi_5 && \Delta G^\circ = -10{\cdot}35 \pm 0{\cdot}18 + (0{\cdot}69 \pm 0{\cdot}18) \times 10^{-3}T \\
&Th_2Ni_{17} && \Delta G^\circ = -5{\cdot}93 \pm 0{\cdot}15 + (0{\cdot}44 \pm 0{\cdot}15) \times 10^{-3}T
\end{aligned}
$$

These results are consistent to ±15% with values obtained by an approximating procedure as proposed by the authors using the $ThNi_5$ or Th_2Ni_{17} data as a starting point and based on the average coordination number of the Th and Ni atoms in each compound.

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[61] V. I. Chechernikov, V. A. Pletyushkin, T. M. Shavishvili and V. K. Slovyanskikh, *Zh. Eksp. Teor. Fiz.* **58** (1970) 86.

[62] W. A. J. J. Velge and K. H. J. Buschow, *J. Appl. Phys.* 39 (1968) 1717.

[63] M. Hansen, *Constitution of Binary Alloys*, p. 1054. McGraw Hill, New York (1958).

[64] C. L. Angerman, *Trans. ASM* 54 (1961) 260.

[65] W. H. Skelton, N. J. Magnani and J. F. Smith, *Met. Trans.* **1** (1970) 1833.

TABLE 27. CRYSTAL STRUCTURES AND MELTING POINTS OF ACTINIDE–NICKEL COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)			X-ray density (g/cm^3)	Melting point (°C)
		a	*b*	*c*		
Th_7Ni_3	Hexagonal[a] Th_7Fe_3 type	9·885		6·225	11·35	1050(P)[b]
ThNi[b]	Orthorhombic	14·51	4·31	5·73	10·8	1200
$ThNi_2$	Hexagonal[a] AlB_2 type	3·960		3·844	11·11	1100(P)[b]
$ThNi_5$[b]	Hexagonal $CaZn_5$ type	4·97		4·01	10·2	1530
Th_2Ni_{17}[b]	Hexagonal	8·37		8·14	9·8	1350(P)
U_6Ni[c]	BC Tetragonal U_6Mn type	10·37		5·31	17·6	790 (P)
UNi_2[c]	Hexagonal $MgZn_2$ type	4·966		8·252	13·46	985(P)
UNi_5[c]	Cubic $AuBe_5$ type	6·783			11·31	1305
PuNi[d]	Orthorhombic TlI type	3·59	10·21	4·22	12·0	800(P)
$PuNi_2$[d]	Cubic $MgCu_2$ type	7·141 (Pu-rich) 7·16 (Ni-rich)			13·00	1210(P)
$PuNi_3$[d]	Rhombohedral	5·00		24·35	11·8	1230(P)
$PuNi_4$[d]	Monoclinic	4·87 $\beta = 100{\cdot}0°$	8·46	10·27	11·3	1260(P)
$PuNi_5$[d]	Hexagonal $CaZn_5$ type	4·872 (Pu-rich) 4·861 (Ni-rich)		3·980 3·982	10·81	1300
Pu_2Ni_{17}[d]	Hexagonal Th_2Ni_{17} type	8·30		8·00	10·3	1235(P)

[a] R. P. Elliott, *Constitution of Binary Alloys*, First Supplement, p. 676. McGraw Hill, New York (1965).
[b] M. Hansen, *Constitution of Binary Alloys*, p. 1048. McGraw Hill, New York (1958).
[c] F. A. Rough and A. A. Bauer, *Constitutional Diagrams of Uranium and Thorium Alloys*, p. 44. Addison-Wesley, Reading, Mass. (1959).
[d] O. J. Wick, *Plutonium Handbook*, Vol. 1, p. 214. Gordon & Breach, New York (1967).

Paramagnetic susceptibilities for the compounds with uranium and plutonium as determined by Russian workers[13] are given in Table 28.

TABLE 28. PARAMAGNETIC MASS SUSCEPTIBILITIES OF SOME URANIUM–NICKEL AND PLUTONIUM–NICKEL COMPOUNDS AT 298°K

Compound	χ_g (10^{-6} emu/g)	Compound	χ_g (10^{-6} emu/g)	Compound	χ_g (10^{-6} emu/g)
U_6Ni	2	PuNi	2·4	$PuNi_4$	3·6
U_7Ni_9	2·2	$PuNi_2$	1·9	$PuNi_5$	4·8
UNi_2	2·6	$PuNi_3$	2·7	Pu_2Ni_{17}	15·4

The susceptibility of the $PuNi_2$ phase is essentially temperature-independent and a similar observation has been made of the behaviour of the compound $ThNi_5$[61].

The U_6Ni phase was originally reported as not being superconducting above 1·04K[53], but more recent work has shown that there is a superconducting transition at 0·41K[66].

Second and Third Long Periods

Very extensive compound formation occurs between the actinides and the platinum metals. The recent work of Keller and Erdmann[67,68,69] has extended the range of actinides covered from protactinium to curium, although the coupled reduction technique employed by them in which the actinide oxide is reduced with hydrogen in the presence of the platinum metal is only applicable to compounds relatively rich in the platinum metal, typically beyond the AB_2 composition (B being the platinum metal). The technique has not yet been successful with either ruthenium or osmium, which systems may require higher reduction temperatures.

Ruthenium

The crystallographic data summarized in Table 29 exhibit a number of features common to most of the platinum metal systems with actinide elements, e.g. a Th_7M_3 phase isomorphous with Th_7Fe_3, a Laves phase of the $MgCu_2$ type at the MRu_2 composition, and a Cu_3Au type structure at the MRu_3 composition. Some disagreement exists as to whether U_2Ru_3 and U_3Ru_5 both exist in the U–Ru system.

The Pu–Ru system includes a phase $Pu_{19}Ru$ which would suggest an analogy to the $Pu_{19}Zr$ and ζ-PuHf phases but the structure has not been reported as being isomorphous with that of the Group IV compounds.

Little information is available on the thermodynamics of formation of the ruthenium compounds. Holleck and Kleykamp[70] have reported that the free energy of formation of URu_3 is given by:

$$URu_3 \quad \Delta G^\circ = -53{\cdot}8 + 8{\cdot}4 \times 10^{-3}T\,(100\text{–}1140\text{K, kcal/mole})$$

EMF measurements have yielded the following data for the formation of $PuRu_2$ from liquid plutonium and solid ruthenium[71]:

$$PuRu_2 \quad \Delta G^\circ = -26{\cdot}8 + 6{\cdot}9 \times 10^{-3}T\,(935\text{–}1069\text{K, kcal/mole})$$

The $ThRu_2$ phase undergoes a superconducting transition at 3·56K[59].

Rhodium

For many of the reported actinide–rhodium compounds no information exists beyond their melting points. These include Th_3Rh_4, 1487(P); Th_3Rh_5, 1450(P); $ThRh_5$, >1500[72]; U_4Rh_3, 1155(P); U_3Rh_4, 1450(P); U_3Rh_5, 1550(P)[73]; Pu_2Rh, 940(P); Pu_5Rh_3, 980(P); Pu_5Rh_4, 1180(P); PuRh, 1300 and Pu_3Rh_4, 1310(P)[28]. In the U–Ru system, Park[73] reports that U_4Rh_3 undergoes a solid state transition at 720°C. He has not observed the phase

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[66] H. H. Hill and B. T. Matthias, *Phys. Rev.* **168** (1968) 464.

[67] C. Keller and B. Erdmann, Paper to the Third International Transplutonium Element Symposium, Argonne National Laboratory, U.S.A., October, 1971.

[68] B. Erdmann and C. Keller, *Inorg. Nucl. Chem. Letters*, **7** (1971) 675.

[69] B. Erdmann, German Report KFK-1444 (1971).

[70] H. Holleck and H. Kleykamp, *J. Nucl. Mater.* **35** (1970) 158.

[71] G. M. Campbell, L. J. Mullins and J. A. Leary, *Thermodynamics of Nuclear Materials, 1967*, p. 75. IAEA, Vienna (1968).

[72] J. R. Thomson, *J. Less Common Metals*, **5** (1963) 437.

[73] J. J. Park, *J. Res. Nat. Bur. Stand.* **72A** (1968) 11.

TABLE 29. CRYSTAL STRUCTURES AND MELTING POINTS OF ACTINIDE–RUTHENIUM COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)			X-ray density (g/cm³)	Melting point (°C)
		a	*b*	*c*		
Th_7Ru_3[a]	Hexagonal Th_7Fe_3 type	9·969		6·302	11·82	1412
Th_3Ru_2[a]	Unknown					1425
ThRu[a]	Orthorhombic CrB type	3·878	11·29	4·071	12·44	1462
$ThRu_2$[a]	Cubic $MgCu_2$ type	7·657			12·89	> 1550
U_2Ru	Monoclinic[b]	13·106 = 96°9·6′	3·343	5·202	16·92	937(P)[c]
'URu'[c]	Unknown					1158 Transition at 759
U_3Ru_4[c]	Unknown					1163(P)
U_2Ru_3[d]	FCC	12·895			14·48	Peritectoid 1025
U_3Ru_5[c]	Unknown					1182(P)
URu_3	Cubic Cu_3Au type	3·988			14·22	1850(P)[e]
$Pu_{19}Ru$[f]	Unknown					Peritectoid 323
Pu_3Ru	Orthorhombic[g]	6·216	6·924	8·093	15·60	599(P)[f]
Pu_5Ru_3	Tetragonal[g]	8·092		10·023	15·17	1025(P)[h]
PuRu	Cubic[f] CsCl type	3·363			14·87	1250(P)[h]
$PuRu_2$	Cubic $MgCu_2$ type	7·476			14·06	> 1500[h]

[a] F. A. Shunk, *Constitution of Binary Alloys*, Second Supplement. McGraw Hill, New York (1969).

[b] A. F. Berndt, *Acta Cryst.* **14** (1961) 1301.

[c] J. J. Park, *J. Res. Nat. Bur. Stand.* **72A** (1968) 1.

[d] A. E. Dwight, U.S. Report ANL-6330.

[e] T. J. Heal and G. I. Williams, *Acta Cryst.* **8** (1955) 494.

[f] O. J. Wick, *Plutonium Handbook*, Vol. 1, p. 219. Gordon & Breach, New York (1967).

[g] A. F. Berndt, *Advances in X-ray Analysis*, 6 (1963) 18.

[h] V. I. Kutaitsev, N. T. Chebotarev, I. G. Lebedev, M. A. Andrianov, V. N. Konev and T. S. Menshikova, *Plutonium 1965*, p. 425. Chapman & Hall, London (1967).

U_2Rh although Berndt and Dwight[74] have determined the structure of the isomorphous phases U_2Ru, U_2Rh and U_2Ir.

The only thermodynamic data available on the rhodium compounds are estimates of ΔG_{298} of $\leqslant -24$ kcal/mole for the $ThRh_2$ and $\leqslant -23\cdot6$ kcal/mole for URh_3[9]. The magnetic behaviour of U_4Rh_3 has been examined by Matthias and co-workers[75] who found it to be a weak ferromagnet with a very low saturation magnetization. A parallel can be drawn to the behaviour of the $U_{0\cdot54}Pt_{0\cdot46}$ phase.

The Th_7Rh_3 phase is superconducting with a transition temperature of 2·15K[59].

Palladium

Whilst many of the palladium–actinide compounds are isomorphous with the corresponding phases in other platinum metal–actinide systems, some marked differences occur.

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[74] A. F. Berndt and A. E. Dwight, *Trans. Met. Soc. AIME* **233** (1965) 2075.

[75] B. T. Matthias, C. W. Chu, E. Corenzwit and D. Wohlenben, *Proc. Nat. Acad. Sci.* 64 (1969) 459.

TABLE 30. CRYSTAL STRUCTURES AND MELTING POINTS OF ACTINIDE–RHODIUM COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)			X-ray density (g/cm^3)	Melting point (°C)
		a	*b*	*c*		
Th_7Rh_3[a]	Hexagonal Th_7Fe_3 type	10·031		6·287	11·72	1362
ThRh[a]	Orthorhombic CrB type	3·866	11·24	4·220	12·13	1500
$ThRh_2$[a]	Unknown					Transforms at 1250
	Hexagonal Ni_2In type	4·629		5·849	13·40	1500
$ThRh_3$[a]	Cubic Cu_3Au type	4·148			12·58	1500
$PaRh_3$[b]	Cubic Cu_3Au type	4·037			13·62	
U_2Rh	Monoclinic[c] U_2Ru type	13·122	3·421 β = 96°26′	5·159	16·71	755[d] Peritectoid
URh_3[d]	Cubic Cu_3Au type	3·992			14·27	1700
$NpRh_3$[b]	Cubic Cu_3Au type	4·034			13·80	
$PuRh_2$[e]	Cubic $MgCu_2$ type	7·488			14·07	1340(P)
$PuRh_3$[e]	Cubic Cu_3Au type	4·009 –4·040			13·95	~1650
$AmRh_2$[b]	Cubic $MgCu_2$ type	7·548			13·80	
$AmRh_3$[b]	Cubic Cu_3Au type	4·098			13·26	
$CmRh_3$[b]	Cubic Cu_3Au type	4·106			13·26	

[a] J. R. Thomson, *J. Less Common Metals*, **5** (1963) 437.
[b] B. Erdmann, German Report KFK-1444 (1971).
[c] A. F. Berndt and A. E. Dwight, *Trans. Met. Soc. AIME* **233** (1965) 2075.
[d] J. J. Park, *J. Res. Nat. Bur. Stand.* **72A** (1968) 11.
[e] V. I. Kutaitsev, N. T. Chebotarev, I. G. Lebedev, M. A. Andrianov, V. N. Konev and T. S. Menshikova, *Plutonium 1965*, p. 426. Chapman & Hall, London (1965).

Thus the most thorium-rich phase is Th_2Pd rather than the analogue of Th_7Rh_3 and, although the cubic Cu_3Au structure occurs in all the palladium–actinide systems, in the case of thorium and uranium it is associated with the composition MPd_4. It is assumed that a fraction of the actinide metal sites in the lattice are occupied by palladium.

The compounds frequently occur at closely spaced compositions and some may exist only at high temperatures. No structural information is available on Th_3Pd_4, 1325(P); $ThPd_x$, (81–83 at. % Pd)[76]; UPd, 1047(P) decomposing eutectoidally at 970; U_5Pd_6, 1110(P), decomposing eutectoidally at 980[77]; UPd_5, (81·2–83·7 at. % Pd) 1440(P); U_2Pd_{11}, transforming congruently to α-Pd_{ss} at 1030, and U_2Pd_{17} (88·2 at. % Pd) which also transforms congruently to α-Pd_{ss} at 800[76]. The close similarity of the composition range of UPd_5 and $ThPd_x$ suggests that the latter may be designated as $ThPd_5$.

[76] F. A. Shunk, *Constitution of Binary Alloys*, Second Supplement, pp. 611 and 613. McGraw Hill, New York (1969).
[77] M. Hansen, *Constitution of Binary Alloys*, p. 1128. McGraw Hill, New York (1958).

TABLE 31. CRYSTAL STRUCTURES AND MELTING POINTS OF ACTINIDE–PALLADIUM COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)			X-ray density (g/cm³)	Melting point (°C)
		a	*b*	*c*		
Th_2Pd[a]	Tetragonal $CuAl_2$ type	7·308		5·960	11·91	1162
ThPd[a]	Orthorhombic CrB type	7·249	4·571	5·856	11·60	1412
Th_3Pd_5[a]	Hexagonal	7·149		3·899	11·83	1387(P)
$ThPd_3$ 22·5–25 at. %Th	Hexagonal $TiNi_3$ type	5·858 5·846	(Th-rich) (Pd-rich)	9·814 9·643	12·29	>1500
$ThPd_4$[a] 19–21·5 at. % Th	Cubic Cu_3Au type	4·110			12·62	
UPd_3[b]	Hexagonal $TiNi_3$ type	5·769		9·640	13·34	~1640
UPd_4[a]	Cubic Cu_3Au type	4·068			13·12	~1525(P)
$NpPd_3$[c]	Cubic Cu_3Au type	4·069			13·73	
PuPd (Pu_5Pd_4)	Orthorhombic[d] CrB type	7·028	4·751	5·658	12·16*	970(P)[e]
Pu_3Pd_4[e]	Rhombohedral	13·304		5·783	12·82	~1190
$PuPd_3$[e] 21–25 at. % Pu	Cubic Cu_3Au type	4·077 –4·119			13·41	1500
$AmPd_3$	Cubic Cu_3Au type	4·138[c] 4·158[f]			13·15	
$CmPd_3$	Cubic[f] Cu_3Au type	4·147			13·14	

* For $Pu_{4\cdot 4}Pd_{3\cdot 6}$ (i.e. Pu_5Pd_4) the corresponding density would be 12·67 g/cm³.

[a] F. A. Shunk, *Constitution of Binary Alloys*, Second Supplement, pp. 611 and 613. McGraw Hill, New York (1969).

[b] M. Hansen, *Constitution of Binary Alloys*, p. 1128. McGraw Hill, New York (1958).

[c] B. Erdmann and C. Keller, *Inorg. Nucl. Chem. Letters*, 7 (1971) 675.

[d] A. Beznosikova, E. S. Smotritskaya and N. T. Chebotarev, *Soviet Atomic Energy*, **25** (1968) 1242.

[e] V. I. Kutaitsev, N. T. Chebotarev, I. G. Lebedev, M. A. Andrianov, V. N. Konev and T. Menshikova, *Plutonium 1965*, p. 427. Chapman & Hall, London (1965).

[f] B. Erdmann, German Report KFK-1444 (1971).

In the Pu–Pd system, the most plutonium-rich phase was originally quoted as Pu_5Pd_4 whilst PuPd was considered to be a high-temperature phase[78]. More recent work has shown that Pu_5Pd_4 is isomorphous with ThPd and it should probably be considered to be PuPd, with the high-temperature phase being slightly more palladium-rich than originally believed[79]. The latter melts peritectically at 1150°C and decomposes eutectoidally at 950°C[78].

The lattice parameters of $AmPd_3$ and $CmPd_3$ increase markedly with time due to self-irradiation damage[69]. The low lattice parameter of 4·138Å for $AmPd_3$ appears to be the more likely initial value as judged by interpolating between the lattice parameters of the series (Np–Pu–Am–Cm) Pd_3.

The magnetic properties of Th–Pd alloys are complex and in the range 60–87 at. % Pd the alloys are diamagnetic[80]. Bates and Leach[81] found that the susceptibility of UPd_3

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[78] V. I. Kutaitsev, N. T. Chebotarev, I. G. Lebedev, M. A. Andrianov, V. N. Konev and T. S. Menshikova, *Plutonium 1965*, p. 427. Chapman & Hall, London (1965).

[79] A. Beznosikova, E. S. Smotritskaya and N. T. Chebotarev, *Soviet Atomic Energy*, **25** (1968) 1242.

[80] L. F. Bates and P. B. Unstead, *Proc. International Conference on Magnetism*, p. 188. Institute of Physics and the Physical Society, London (1965).

[81] L. F. Bates and S. J. Leach, *Proc. Phys. Soc.* **B69** (1956) 997.

obeys the Curie–Weiss law over the temperature range 77–293K with an effective atomic moment of 3·14 μ_B. The magnetic behaviour of Pu–Pd alloys has been examined by Chebotarev and co-workers[82] and by Keller and Erdmann[67,69]; the Russian investigators established values for the mass susceptibility at 298K of certain of the Pu–Pd compounds either directly or by extrapolation of the data for two-phase alloys. The values for $PuPd_3$, Pu_3Pd_4 and PuPd were 1·47, 2·1 and 2·05.10^{-6} emu/g, indicating that palladium makes only a small contribution to the susceptibility, presumably due to its 4*d*-shell being filled and the magnetic contribution being associated therefore with its *s*-electrons. Keller and Erdmann have shown that the susceptibility of $PuPd_3$ obeys the Curie–Weiss law down to low temperatures with a θ value of −108K and an effective moment at 298K of 0·907 μ_B. At 20·5K a magnetic transition occurs, probably to an antiferromagnetic state. The same authors have also noted that $AmPd_3$ behaves quite differently, the susceptibility being strongly dependent on field strength. On extrapolating to infinite magnetic field strength it is found that the susceptibility of $AmPd_3$ obeys the Curie–Weiss law to at least 10K.

The electrical resistivity of the two most palladium-rich compounds in the U–Pd system has been measured by Pells[83] who gives values of 400 $\mu\Omega$-cm and 64 $\mu\Omega$-cm for U_2Pd_{11} and U_2Pd_{17} respectively at 293K.

Osmium

The actinide–osmium systems have received somewhat less attention than other actinide–platinum metal systems and in particular it seems possible that further compounds exist in the Th–Os system beyond the three already reported. No structural information is available on $ThOs_x$ (40 at. % Os), >1500[84]; U_3Os_5, 1030; U_5Os_4, 1280(P)[85]; ζ-Pu–Os (3–5 at. % Os),

TABLE 32. CRYSTAL STRUCTURES AND MELTING POINTS OF ACTINIDE–OSMIUM COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)			X-ray density (g/cm³)	Melting point (°C)
		a	*b*	*c*		
Th_7Os_3[a]	Hexagonal Th_7Fe_3 type	10·031		6·296	13·29	>1500
$ThOs_2$[a]	Cubic $MgCu_2$ type	7·715			17·72	>1500(P)
U_2Os_3	Monoclinic[b] U_2Ru type	13·366	3·335 $\beta = 96°41'$	5·167	19·35	920(P)[c]
UOs_2[c]	Cubic $MgCu_2$ type	7·508 −7·514			19·41	2280
$PuOs_2$[d]	Hexagonal $MgZn_2$ type	5·337		8·682	19·21	>1500

[a] F. A. Shunk, *Constitution of Binary Alloys*, Second Supplement, p. 595. McGraw Hill, New York (1969).

[b] A. F. Berndt and A. E. Dwight, *Trans. Met. Soc. AIME* **233** (1965) 2075.

[c] A. G. Knapton, *J. Nucl. Mater.* 9 (1963) 309.

[d] M. Hansen, *Constitution of Binary Alloys*, p. 1081. McGraw Hill, New York (1958).

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[82] N. T. Chebotarev, Yu N. Sokurskii, M. A. Andrianov and A. A. Ivanov, *Soviet Atomic Energy*, **25** (1968) 1244.

[83] G. P. Pells, *J. Inst. Met.* **92** (1963) 416.

[84] F. A. Shunk, *Constitution of Binary Alloys*, Second Supplement, p. 595. McGraw Hill, New York (1969).

[85] A. G. Knapton, *J. Nucl. Mater.* 9 (1963) 309.

434 peritectoid; η-Pu–Os, 300 peritectoid[86]; θ-Pu–Os (22 at. % Os), transforms to θ′ at 620–625; θ′-Pu–Os (26 at. % Os), 680(P), and Pu_5Os_3[87]. The plutonium-rich end of the Pu–Os system has been studied by Bochvar and co-workers[87] and by Ellinger and Land[86]; the former only found the one phase in this region, η, existing over the range 4–8 at. % Os, but the more detailed studies of Ellinger and Land had shown that η has little composition range, probably corresponding to $Pu_{19}Os$ and with an X-ray diffraction pattern similar to that of the phase $Pu_{19}Ru$ (structure unknown). A second phase, ζ, decomposes by a eutectoid reaction at 195°C and exists in the range 3–5 at. % Os.

Matthias, Geballe and Compton[59] in a review of superconducting behaviour give a transition temperature of 1·51K for Th_7Os_3 and note that $ThOs_2$ does not go superconducting down to 1·02K nor UOs_2 to 0·37K.

Iridium

Owing to the high melting points of the actinide–iridium compounds, generally greater

TABLE 33. CRYSTAL STRUCTURES AND MELTING POINTS OF ACTINIDE–IRIDIUM COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)			X-ray density (g/cm³)	Melting point (°C)
		a	*b*	*c*		
Th_7Ir_3[a]	Hexagonal Th_7Fe_3 type	10·076		6·296	13·01	>1500
$ThIr$[a]	Orthorhombic CrB type	3·894	11·13	4·266	15·74	>1500
$ThIr_2$[a]	Cubic $MgCu_2$ type	7·661₅			18·73	>1500
$ThIr_5$[a]	Hexagonal $CaCu_5$ type	5·315		4·288	18·95	>1500
$PaIr_3$[b]	Cubic Cu_3Au type	4·047			20·08	
U_2Ir[c]	Monoclinic U_2Ru type	13·210	3·457 β = 96°34′	5·095	19·20	Peritectoid 775
UIr_2	Cubic[d] $MgCu_2$ type	7·509			19·58	>1850(P)[e]
UIr_3	Cubic[d] Cu_3Au type	4·023			20·62	>1950[e]
$NpIr_2$[b]	Cubic $MgCu_2$ type	7·483			19·57	
$PuIr_2$[f]	Cubic $MgCu_2$ type	7·512 −7·528			19·59	
$AmIr_2$[b]	Cubic $MgCu_2$ type	7·550			19·18	
$CmIr_2$[b]	Cubic $MgCu_2$ type	7·561			19·19	

[a] F. A. Shunk, *Constitution of Binary Alloys*, Second Supplement, p. 465. McGraw Hill, New York (1969).

[b] B. Erdmann, German Report KFK-1444 (1971).

[c] A. F. Berndt and A. E. Dwight, *Trans. Met. Soc. AIME*, **233** (1965) 2075.

[d] R. P. Elliott, *Constitution of Binary Alloys*, First Supplement, p. 565. McGraw Hill, New York (1965).

[e] J. J. Park, *J. Res. Nat. Bur. Stand.* **72A** (1968) 19.

[f] V. I. Kutaitsev, N. T. Chebotarev, I. G. Lebedev, M. A. Andrianov, V. N. Konev and T. S. Menshikova, *Plutonium 1965*, p. 428. Chapman & Hall, London (1965).

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[86] F. H. Ellinger and C. C. Land, *Plutonium 1970 and Other Actinides*, p. 679. Met. Soc. AIME, New York (1970).

[87] A. A. Bochvar, S. T. Konobeevsky, V. I. Kutaitsev, T. S. Menshikova and N. T. Chebotarev, *Proc. 2nd ICPUAE*, Vol. 6, p. 198. United Nations, Geneva (1958).

than 1500°C, little detailed information is available on the melting behaviour. The observed structures continue the trend shown in the lighter platinum metals with the Cu_3Au structure at the MIr_3 composition, the $MgCu_2$ type at MIr_2, the CrB at MIr and the Th_7Fe_3 type at Th_7Ir_3. The $ThIr_3$ phase is not of the Cu_3Au type, its structure being unknown; other compounds of unknown structure are $ThIr_x$ (40 at. % Ir), 1500(P), eutectoid 1450[88]; U_3Ir, 945(P), eutectoid 758; U_3Ir_2, 1121(P), allotropic transformation at 898; UIr, 1470[89]; Pu_3Ir[90]; Pu_5Ir_3, probably isostructural with Pu_5Rh_3 and Pu_5Os_3, and Pu_5Ir_4, probably isostructural with Pu_5Rh_4[91], neither of these structures having as yet been elucidated.

Wengert[9] has estimated values for ΔG_{298} for $ThIr_2$ and UIr_3 of $\leqslant -24$ and $\leqslant -23{\cdot}6$ kcal/mole, respectively. The Th_7Ir_3 phase has a superconducting transition temperature of 1·52K whilst the corresponding temperature for $ThIr_2$ is 6·5K; the compound UIr_2 is not superconducting down to 0·35K[59].

Platinum

The actinide–platinum compounds are in many cases isomorphous with the corresponding iridium compounds but, in addition, a new series of compounds of formula MPt_5 exists. These phases have either the cubic $AuBe_5$ structure or the orthorhombic $SmPt_5$ structure. In addition, Keller and Erdmann[67] have observed that a sequential change in structure occurs in the MPt_3 series; the structure of $ThPt_3$ is unknown, $PaPt_3$ and UPt_3 have the hexagonal Ni_3Sn structure, $NpPt_3$ is of the hexagonal Ni_3Ti structure and $PuPt_3$ is of the cubic Cu_3Au type. No MPt_3 phase exists in the systems with americium or curium.

No structural information is available on Th_3Pt_4, >1500; $ThPt_2$ >1500(P); $ThPt_3$, >1500; $ThPt_4$, >1500(P)[88], and Pu_5Pt_3 (possibly Pu_2Pt[92]), 1130(P). The NpPt phase has been prepared by Hill and Elliott[93] who have indexed its X-ray diffraction pattern on the basis of isomorphism with the orthorhombic compounds ThPt, UPt and PuPt but do not quote any lattice parameters.

The UPt phase has been found to have a composition of $U_{0{\cdot}54}Pt_{0{\cdot}46}$ and to be ferromagnetic below 29·8K[75]; the magnetic moment is 0·8 Bohr magnetons per uranium atom. The electrical resistivity of the isomorphous ThPt, NpPt and UPt phases has been measured down to low temperatures by Hill and Elliott[93] who observed sharp decreases in resistivity at ~20K for NpPt and ~50K for PuPt. No sudden change was observed for ThPt, but the resistivity is much lower at all temperatures for ThPt than for the other phases. The authors assume by analogy with UPt that magnetic ordering is occurring in NpPt and PuPt at low temperatures, although it is not clear whether the ordered state is ferromagnetic or antiferromagnetic. The shape of the resistivity–temperature curve shows great similarity to that for α-plutonium in which magnetic ordering has long been suspected but never proved. The room temperature resistivities of the phases are given as ~25, ~125, 190 (estimated) and ~75 $\mu\Omega$-cm for the phases ThPt, UPt, NpPt and PuPt respectively. A separate determination of the resistivity of UPt[94] has established a room temperature value of 170 $\mu\Omega$-cm

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[88] J. R. Thomson, *J. Less Common Metals*, 6 (1964) 3.

[89] J. J. Park, *J. Res. Nat. Bur. Stand.* 72A (1968) 19.

[90] O. J. Wick, *Plutonium Handbook*, p. 209. Gordon & Breach, New York (1967).

[91] V. I. Kutaitsev, N. T. Chebotarev, I. G. Lebedev, M. A. Andrianov, V. N. Konev and T. S. Menshikova, *Plutonium 1965*, p. 428. Chapman & Hall, London (1965).

[92] F. A. Shunk, *Constitution of Binary Alloys*, Second Supplement, p. 622. McGraw Hill, New York (1969).

[93] H. H. Hill and R. O. Elliott, *Phys. Lett.* 35A (1971) 75.

[94] A. C. Lawson, *Phys. Lett.* 33A (1970) 231.

and shown that the resistivity obeys the expected T^2 law below the Curie temperature and has a large spin disorder component at higher temperatures; the resistivity falls linearly with increasing temperature at temperatures greater than twice the Curie temperature.

TABLE 34. CRYSTAL STRUCTURES AND MELTING POINTS OF ACTINIDE–PLATINUM COMPOUNDS

Composition	Crystal structure	Lattice parameters (Å)			X-ray density (g/cm^3)	Melting point (°C)
		a	*b*	*c*		
Th_7Pt_3[a]	Hexagonal Th_7Fe_3 type	10·126		6·346	13·03	1362(P)
ThPt[a]	Orthorhombic CrB type	3·900	11·09	4·454	14·73	> 1500
Th_3Pt_5[a]	Hexagonal Th_3Pd_5 type	7·162		3·908	16·00	> 1500
$ThPt_5$	Orthorhombic[b] $SmPt_5$ type	5·364	9·157	26·60	18·42	> 1500(P)[a]
$PaPt_3$[b]	Hexagonal Ni_3Sn type	5·704		4·957	19·42	
$PaPt_5$[b]	Cubic $AuBe_5$ type	7·413			19·68	
UPt	Orthorhombic[c] CrB type	3·721	10·772	4·410	16·28	Peritectoid[d] 961
UPt_2[d]	Orthorhombic	5·60	9·68	4·12	18·7	1370(P)*
UPt_3	Hexagonal[e] Ni_3Sn type	5·764		4·899	19·40	1700[d]
UPt_5	Cubic[c] $AuBe_5$ type	7·421			19·74	1460(P)[d]
$NpPt_3$[b]	Hexagonal Ni_3Ti type	5·822		9·575	19·44	
$NpPt_5$[b]	Orthorhombic $SmPt_5$ type	5·225	9·134	24·73	18·46	
PuPt[c]	Orthorhombic CrB type	3·816	10·694	4·428	15·95	1250(P)
$PuPt_2$[c]	Cubic $MgCu_2$ type	7·631 –7·653			18·69	∼1475(P)
$PuPt_3$[c]	Cubic Cu_3Au type	4·107			19·75	∼1800
$PuPt_5$	Orthorhombic[b] $SmPt_5$ type	5·314	9·100	26·51	18·90	1700[c]
$AmPt_2$[b]	Cubic $MgCu_2$ type	7·615			19·00	
$AmPt_5$[b]	Orthorhombic $SmPt_5$ type	5·319	9·090	26·42	18·99	
$CmPt_2$[b]	Cubic $MgCu_2$ type	7·625			19·01	
$CmPt_5$[b]	Orthorhombic $SmPt_5$ type	5·329	9·108	26·38	18·99	

* Park and Buzzard give a value of 1220 for the peritectic temperature.[f]

[a] J. R. Thomson, *J. Less Common Metals*, 6 (1964) 3.

[b] B. Erdmann, German Report KFK-1444 (1971).

[c] V. I. Kutaitsev, N. T. Chebotarev, I. G. Lebedev, M. A. Andrianov, V. N. Konev and T. S. Menshikova, *Plutonium 1965*, p. 428. Chapman & Hall, London (1965).

[d] R. P. Elliott, *Constitution of Binary Alloys*, First Supplement, p. 752. McGraw Hill, New York (1965).

[e] T. J. Heal and G. I. Williams, *Acta Cryst.* 8 (1955) 494.

[f] J. J. Park and R. W. Buzzard, U.S. Report USAEC TID-7502, Pt. 1 (1960) 191.

10. RARE EARTHS

Compound formation in a strict sense does not occur between the actinide and rare earth elements. The elements europium and ytterbium, which are often abnormal in alloying behaviour as compared to other rare earths by virtue of being divalent rather than trivalent, form liquid immiscible systems with thorium, uranium and plutonium. For the other rare earths, complete solid solubility occurs at high temperatures in the thorium systems between the bcc modifications of thorium and of the rare earths, liquid immiscibility occurs in the uranium systems whilst the behaviour of the plutonium systems differs between those involving the light rare earths and those involving the heavy rare earths. For the elements up to samarium, extensive solubility occurs in δ-plutonium (fcc) and in ϵ-plutonium (bcc) whilst plutonium is highly soluble in the rare earths, but from gadolinium onwards the solubility of the rare earths in the plutonium allotropes is limited although plutonium is still soluble to about 20 at. % in the heavy rare earth elements.

Recent studies by Havinga, van Vucht and Buschow[32] have shown that in the thorium systems a sequence of intermediate structures occurs at moderate temperatures which is comparable to the sequence seen in light rare earth–heavy rare earth systems, i.e. structures intermediate between fcc and simple hexagonal developed by altering the stacking sequence of the close-packed planes. Thus in the Th–Gd system, the Dutch workers have reported that the structure is fcc for 0–55 at. % Gd, dhcp (La-structure) for 70–75 at. % Gd, rhombohedral (Sm-type) for 82–84 at. % Gd and simple hexagonal for 95–100 at. % Gd. Spot checks on other thorium systems have shown similar structures at a variety of compositions as detailed in Table 35.

TABLE 35. CRYSTAL STRUCTURES OF THORIUM–RARE EARTH ALLOYS[a]

Composition	Crystal structure	Lattice parameters (Å)	
		a	*c*
'$ThGd_5$'	Rhombohedral Sm type	3·610	26·11
'$ThTb_5$'	,,	3·592	25·86
'Th_2Dy_7'	,,	3·554	25·80
'$ThHo_3$'	,,	ND*	
'$ThEr_3$'	,,	ND	
'$ThSm_4$'	Double hexagonal La type	3·644	11·653
'$ThGd_3$'	,,	3·610	11·640
'Th_3Tb_7'	,,	3·585	11·538
'Th_3Dy_7'	,,	3·581	11·507
'Th_3Ho_7'	,,	3·567	11·472
'Th_3Er_7'	,,	3·556	11·438

* ND = Not determined.

[a] E. E. Havinga, J. H. van Vucht and K. H. J. Buschow, *Philips Research Reports* **24** (Oct. 1969) 407.

11. INTRA-ACTINIDES

The alloying behaviour of systems involving two actinide elements shows considerable variability. For immediate neighbours such as Th–Pa, U–Np, Np–Pu and Pu–Am, extensive solubility occurs in the terminal solid solutions and relatively few intermediate phases exist. As the atomic number separation of the two actinide elements is increased, the terminal solid solubility in the complex lower temperature modifications of the early actinides tends to decrease but without any marked increase in the tendency to form intermediate phases. The decreasing solubility reflects the importance of bond angles in the low symmetry structures of uranium, neptunium and plutonium. The intermediate phases tend to extend over very wide composition ranges, only the '$ThPu_2$' phase being of the classical daltonide type of compound.

TABLE 36. LATTICE PARAMETERS AND TRANSITION TEMPERATURES OF INTRA-ACTINIDE INTERMEDIATE PHASES

Composition	Symmetry	Lattice parameters (Å)			X-ray density (g/cm^3)	Melting point (°C)
		a	*b*	*c*		
'$ThPu_2$'[a]	Orthorhombic	9·820 or 7·90	8·164 8·43	6·681 9·79		615(P)
δ-U–Np[b] (31–76 at. % Np)	Cubic ζ-U–Pu type	10·63 (Np-rich) 10·55 (U-rich)				Peritectoid 668 (31 at. % Np)
η-U–Pu[a] (30–97 at. % Pu)	Tetragonal	10·57 (75 at. % Pu)		10·76	17·2	Peritectoid 705 (30 at. % Pu) Eutectoid 278 ($\sim$97 at. % Pu)
ζ-U–Pu[a] (26–75 at. % Pu)	Cubic*	10·692 (Pu-rich) 10·651 (U-rich)			18·95	Peritectoid 590 (28 at. % Pu)
η-Np–Pu[a]	Orthorhombic	10·86 (81 at. % Pu)	10·67	10·43		Peritectoid 508 ($\sim$50 at. % Pu) Eutectoid 288 ($\sim$96 at. % Pu)

* The phase is probably tetragonal since it expands anisotropically, but the axial ratio is essentially unity at room temperature.

[a] O. J. Wick, *Plutonium Handbook*, pp. 212, 221 and 224. Gordon & Breach, New York (1967).

[b] P. G. Mardon and J. H. Pearce, *J. Less Common Metals*, **1** (1959) 467.

Marcon and Portnoff[95] have established a measured density of 15·39 g/cm^3 for '$ThPu_2$' and lattice parameters of 6·22, 11·62 and 7·09Å in disagreement with both of the earlier sets of parameters. On the basis of their results, they propose that the true composition of the compound is Th_3Pu_7.

No information has been published on the physico-chemical properties of the intra-actinide intermediate phases, most investigations of such alloy systems having been more concerned with the marked changes in properties which occur within the terminal solid solutions.

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[95] J. P. Marcon and A. Y. Portnoff, *J. Nucl. Mater.* **28** (1968) 341.

HYDRIDES

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1. INTRODUCTION

Hydrides are known for the elements actinium to curium inclusive. In contrast to the similarities observed in the lanthanide–hydrogen systems, the actinide–hydrogen systems do not resemble each other to any great extent and it is not until neptunium is reached that there is a noticeable similarity between the lanthanide and actinide systems. The presently known compounds are listed in Table 1; it must be emphasized at this point that apart from those formed by thorium, uranium and plutonium, the actinide hydrides have not been extensively studied. This is, of course, due largely to the lack of sufficient amounts of the elements beyond curium.

Libowitz[1] has reviewed the preparation and physical properties of the actinide hydrides and discussed in some detail various ternary systems. His authoritative article[1] and the earlier summary of the work on uranium hydride[2] are recommended for more detailed accounts than that presented here.

2. HYDROGENATION REACTIONS

Actinide metals react readily with hydrogen, the temperature required for initiation of the exothermic reactions depending on factors such as the state of the metal (e.g. finely powdered metals react at lower temperatures), the extent of surface oxidation of the metal and the purity and pressure of the hydrogen. With moderate hydrogen pressures massive uranium metal reacts readily at approximately 250°C to form β-UH_3, thorium reacts between 250° and 300°C to form the dihydride, whilst plutonium forms the dihydride between 100° and 200°C. With further addition of hydrogen the ultimate products for the last two reactions are Th_4H_{15} and plutonium trihydride, respectively. References to the original literature pertaining to these systems will be found in the above-mentioned reviews[1,2].

Table 1. Presently Known Actinide Hydrides[a,b]

Ac	Th	Pa	U	Np	Pu	Am	Cm
AcH_2	ThH_2	—	—	NpH_2	PuH_2	AmH_2	CmH_2
—	—	PaH_3	UH_3	NpH_3	PuH_3	AmH_3	—
—	Th_4H_{15}	—	—	—	—	—	—

[a] Analogous deuterides and tritides are known in certain instances.

[b] Only the stoichiometric phases are shown, but as discussed in the text, the dihydride phases (M = Np, Pu, Am and Cm) are known to take up hydrogen to compositions of *ca.* $MH_{2.7}$ without change in structure but with an associated increase (Np) or decrease (Pu and Am) in the lattice parameter.

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[1] G. G. Libowitz, Chapter 11 in *Metal Hydrides* (W. Mueller, J. P. Blackledge and G. G. Libowitz, Eds.) Academic Press, N.Y. (1968).

[2] J. J. Katz and E. Rabinowitch, Chapter 8 in *The Chemistry of Uranium*, Nat. Nucl. Energy Series Div. VIII, Vol. 5, McGraw-Hill, N.Y. (1951).

Low-temperature reactions involving powdered uranium metal with low partial pressures of hydrogen lead to the formation of mixtures of α- and β-UH_3[3,4]. The α-form has also been obtained by cathodic discharge of uranium in a perchloric acid or sodium hydroxide solution below 20°C[3]. Analogous deuterides are obtained by similar reactions involving deuterium, the rate of reaction being somewhat slower than the corresponding metal–hydrogen reactions.

The neptunium–hydrogen[5] and americium–hydrogen[6] systems are formally similar to the plutonium one, the formation of a dihydride and a trihydride being observed. However, as discussed below there are differences between the Np–H_2 system and those of plutonium and americium. In all three cases absorption of hydrogen into the octahedral interstices of the fluorite structure of the dihydride results in the formation of cubic phases ranging from the stoichiometric composition $MH_{2\cdot 0}$ to approximately $MH_{2\cdot 7}$. However, whereas the lattice parameter, a_0, increases with hydrogen concentration in the neptunium–hydrogen phases[5] a decrease is observed with both plutonium[7,8] and americium[6]. At overall compositions in excess of $MH_{2\cdot 7}$ the formation of the hexagonal trihydrides is observed. In contrast to the behaviour observed with these dihydrides, uranium trihydride possesses a very narrow range of homogeneity.

In the lanthanide series the fcc dihydrides of the earlier elements (La–Sm inclusive) also take up further hydrogen with a related decrease in a_0, ultimately forming trihydrides with no change in structure. With heavier lanthanide elements, however, a transformation to a hexagonal structure occurs before the composition MH_3 is reached.

Of the remaining actinide hydrides the actinium compound, AcH_2[9], was observed to form during the reduction of microgram amounts of the trichloride, and protactinium trihydride[10] was prepared by direct union of the elements between 250° and 300°C. Neither compound has been studied to any great extent and the respective metal–hydrogen systems have not been investigated in detail. More recently[11] a cubic curium hydride ($CmH_2 \rightarrow CmH_{2+x}$) was observed to form when curium metal was heated with excess hydrogen at 200–2250°C; no evidence was observed for the formation of hexagonal AmH_3.

The results of kinetic studies on the uranium–hydrogen and thorium–hydrogen reactions are discussed by Libowitz[1] who also presents details of the Th–H_2, U–H_2 and Pu–H_2 phase diagrams. The U–H_2 phase diagram was recently the subject of a further investigation[12]. Values for the terminal hydrogen solubilities in thorium, uranium and plutonium metal are listed in the review article[1]. It is interesting to note that the solubility of hydrogen in solid uranium metal does not change appreciably with temperature for a given metal phase (α, β or γ), but at the temperature of each phase transition, and at the melting point, there is a sharp increase in solubility[2]. These observations are illustrated in Fig. 1. The solubilities in each phase follow Sievert's Law, i.e. they are proportional to the square root of the partial pressure of hydrogen. Recently derived relationships are given in Table 2[13]. The saturation

[3] R. Caillat, H. Coriou and P. Perio, *Compt. Rend.* **237** (1953) 812.

[4] R. N. R. Mulford, F. H. Ellinger and W. H. Zachariasen, *J. Amer. Chem. Soc.* **76** (1954) 297.

[5] R. N. R. Mulford and T. A. Wiewandt, *J. Phys. Chem.* **69** (1965) 1641.

[6] W. M. Olsen and R. N. R. Mulford, *J. Phys. Chem.* **70** (1966) 2934.

[7] F. H. Ellinger, p. 281 in *The Metal Plutonium* (A. S. Coffinberry and W. N. Miner, Eds.), Univ. Chicago Press, Chicago (1961).

[8] B. J. McDonald and J. B. Fardon, *J. Chem. Soc.* (1956) 781.

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

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

[11] B. M. Bansal and D. Damien, *Inorg. Nucl. Chem. Letters*, **6** (1970) 603.

[12] J. Chevallier, P. Desre and J. Spitz, *J. Nucl. Mat.* **23** (1967) 289.

[13] M. W. Mallett and M. J. Trzeciak, *Amer. Soc. Metals, Trans. Quart.* **50** (1958) 981.

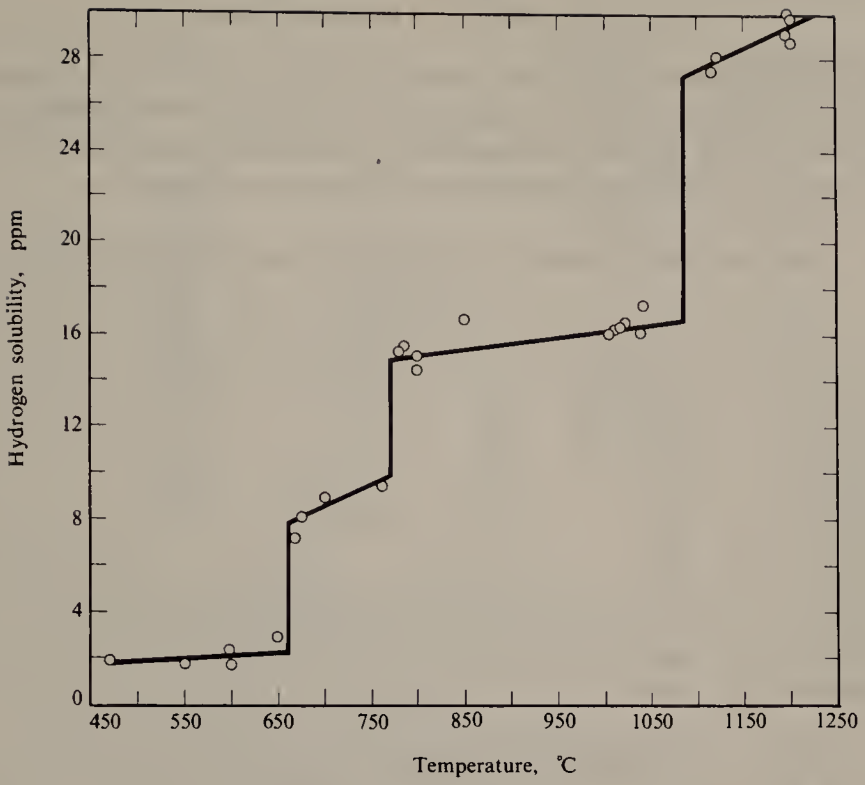

FIG. 1. The solubility of hydrogen in uranium metal in equilibrium with hydrogen at atmospheric pressure. (Reproduced by permission from *The Chemistry of Uranium*, J. J. Katz and E. Rabinowitch, Nat. Nucl. Energy Series Div. VIII, Vol. 5, p. 184. McGraw-Hill, N.Y. (1951).)

solubility of hydrogen in thorium follows the linear relation[14],

$$\log C = 2{\cdot}966 - 1732/T$$

where C is the atom % of hydrogen in the metal.

TABLE 2. SOLUBILITY RELATIONSHIPS FOR HYDROGEN IN URANIUM METAL[a]

	$\log r = \frac{1}{2}\log P_{\text{mm}} - A - B/T$*		Temperature range (°C)
	A	B	
α-U	4·315	388	100–662
β-U	3·219	892	662–769
γ-U	3·679	227	769–1129
{U}	3·201	587	1129–1400

* r = H:U ratio.

[a] M. W. Mallett and M. J. Trzeciak, *Amer. Soc. Metals, Trans. Quart.* **50** (1958) 986.

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[14] D. T. Peterson and D. G. Westlake, *Trans. Metal. Soc. AIME* **215** (1959) 444.

3. PHYSICAL PROPERTIES

Available thermodynamic values are listed in Table 3; for detailed discussions of the calculations on which these values are based and for references to the original literature the reader is referred to the appropriate assessments. Equations describing the temperature dependence of various hydrogenation reactions are shown in Table 4.

TABLE 3. SELECTED THERMODYNAMIC DATA FOR THE ACTINIDE HYDRIDES, DEUTERIDES AND TRITIDES

Compound	$-\Delta H_{f_{298}}$	S°	$\Delta S_{f_{298}}$	$C_{p_{298}}$	Ref.
$\langle ThH_2\rangle$	34·3	14·2			a
$\langle Th_4H_{15}\rangle$	46·5	15·0			a
$\langle \beta\text{-}UH_3\rangle$	30·4	15·2	43·6	11·8	b
$\langle \beta\text{-}UD_3\rangle$	31·0	17·2	46·7	15·8	b
$\langle \beta\text{-}UT_3\rangle$	31·1	26·0	45·1		b
$\langle PuH_3\rangle$	33·0	15·5			c
$\langle NpH_2\rangle$	28·0				d
$\langle PuH_2\rangle$	33·3	14·3			c
$\langle PuH_2\rangle$	37·3	11·8	32·6		e
$\langle PuD_2\rangle$	32·2	16·3	31·2		c, e
$\langle AmH_2\rangle$	40·3				f

[a] M. H. Rand, to be published in *Atomic Energy Review*.

[b] M. H. Rand and O. Kubaschewski, *The Thermochemical Properties of Uranium Compounds*, Oliver & Boyd, London (1963).

[c] F. L. Oetting, *Chem. Rev.* 67 (1967) 261.

[d] R. N. R. Mulford and T. A. Wiewandt, *J. Phys. Chem.* 69 (1965) 1641.

[e] M. H. Rand, *Atomic Energy Review*, Special Issue No. I, 4 (1966) 7.

[f] W. M. Olsen and R. N. R. Mulford, *J. Phys. Chem.* 70 (1966) 2934.

TABLE 4. FREE ENERGIES OF SOME HYDROGENATION REACTIONS

Reaction	$\Delta G = A + BT$ (cal.)		Temperature range (°K)	Ref.
	A	B		
$Th + (H_2) \rightarrow \langle ThH_2\rangle$*	−34,000	29·2		a
$\langle U\rangle_\alpha + \frac{3}{2}(H_2) \rightarrow \langle UH_3\rangle_\beta$	−30,700	43·6	298–900	b
$\langle U\rangle_\alpha + \frac{3}{2}(D_2) \rightarrow \langle UD_3\rangle_\beta$	−31,500	46·6	298–900	b
$\langle U\rangle_\alpha + \frac{3}{2}(T_2) \rightarrow \langle UT_3\rangle_\beta$	−30,675	45·1	500–700	b
$Pu + (H_2) \rightarrow \langle PuH_2\rangle$	−37,300	32·6	298–1100	c
$Pu + (D_2) \rightarrow \langle PuD_2\rangle$	−35,500	31·2		c

* Equation represents ΔG for the region ThH_x to ThH_y ($x = 0·05$ to $0·25$; $y =$ *ca* 1·7).

[a] M. H. Rand, to be published in *Atomic Energy Review*.

[b] M. H. Rand and O. Kubaschewski, *The Thermochemical Properties of Uranium Compounds*, Oliver & Boyd, London (1963).

[c] M. H. Rand, *Atomic Energy Review*, Special Issue No. I, 4 (1966) 7.

TABLE 5. DISSOCIATION PRESSURES FOR THE ACTINIDE HYDRIDES AND DEUTERIDES

Compound	($\log P_{mm} = -A/T + B$) A	($\log P_{mm} = -A/T + B$) B	Temperature range (°K)	Temperature* for 1 atm H_2	Ref.
β-UH_3†	4500	9·28	533–703	703	a
β-UD_3†	4500	9·43	520–690	687	a
UT_3	4471	9·461	591–663	681	b
NpH_3	3736	9·80			c
ThH_2‡	7700	9·54		1156	d
ThH_2‡	7500	9·35	650–875	1159	e
ThH_2‡	7650	9·50		1156	f
NpH_2	6126	9·138	623–898		c
PuH_2	8165	10·01	673–1073	1143	g
PuD_2	7761	9·71	873–1073	1137	g
Th_4H_{15}	4220	9·50		638	d

* Values from ref. 1.

† Values shown here for β-UH_3 and β-UD_3 were chosen to permit a direct comparison of data from one investigation. For details of other investigations of these compounds, the results of which are, in general, in good agreement with those listed, the review by Libowitz[1] is recommended.

‡ The good agreement between the results of the three independent investigations of ThH_2 is obvious.

[a] F. H. Spedding, A. S. Newton, J. C. Warf, O. Johnson, R. W. Nottorf, I. B. Johns and A. H. Daane, *Nucleonics*, 4 (1949) 4.

[b] H. E. Flotow and B. M. Abraham, U.S. Report AECD-3074 (1951).

[c] R. N. R. Mulford and T. A. Wiewandt, *J. Phys. Chem.* **69** (1965) 1641.

[d] R. W. Nottorf, U.S. Report AECD-2984 (1945).

[e] M. W. Mallett and I. E. Campbell, *J. Amer. Chem. Soc.* **73** (1951) 4850.

[f] D. T. Peterson and J. Rexer, *J. Less-Common Metals*, 4 (1962) 92; equation calculated by Libowitz (see ref. 1, p. 510).

[g] R. N. R. Mulford and G. E. Sturdy, *J. Amer. Chem. Soc.* **77** (1955) 3449.

The actinide hydrides are thermally unstable and their dissociation pressures have been extensively investigated[1], especially those of the various thorium, uranium, neptunium and plutonium compounds. Equations describing the temperature dependence of the dissociation pressures are given in Table 5 together with values of the temperatures at which the dissociation pressure is equal to 1 atm of hydrogen. It will be noted that these temperatures decrease in the orders, β-UH_3 > β-UD_3 > β UT_3 and PuH_2 > PuD_2, i.e. the dissociation pressures of the deuterides and tritides are greater than those of the hydrides. In the case of the uranium compounds this is the reverse of the order one might expect from the trend in the heats of formation (Table 3) and the relative values of $-\Delta S_f$ ($UD_3 > UT_3 > UH_3$).

The results of pressure–temperature–composition studies for the uranium–hydrogen[15], neptunium–hydrogen[5], plutonium–hydrogen[16] and americium–hydrogen[6] systems are shown in Figs. 2–5. Details of the thorium–hydrogen system have also been published[17–19]. In the uranium–hydrogen system the pressure on hydrogenation was found to be consistently higher than that on dehydrogenation and a pronounced, reproducible dip was observed on dehydrogenation at 90–98 mole % UH_3. The true cause of this dip has not been ascertained[1].

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[15] F. H. Spedding, A. S. Newton, J. C. Warf, O. Johnson, R. W. Nottorf, I. B. Johns and A. H. Daane, *Nucleonics*, 4 (1949) 4.

[16] R. N. R. Mulford and G. E. Sturdy, *J. Amer. Chem. Soc.* **77** (1955) 3449.

[17] R. W. Nottorf, U.S. Report AECD-2984 (1945).

[18] M. W. Mallett and I. E. Campbell, *J. Amer. Chem. Soc.* **73** (1951) 4850.

[19] D. T. Peterson and J. Rexer, *J. Less-Common Metals*, 4 (1962) 92.

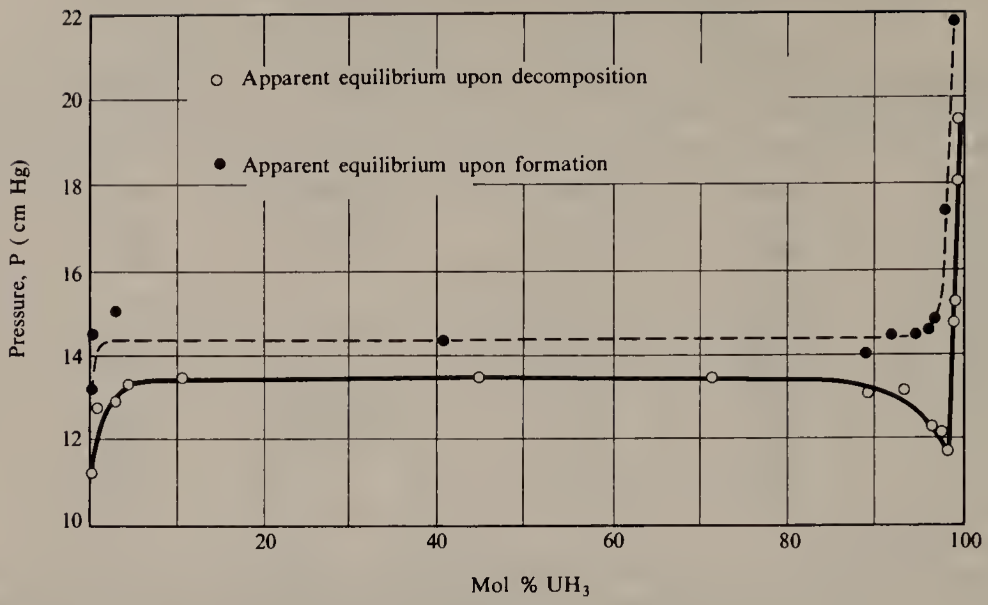

FIG. 2. Pressure-composition isotherm for the uranium–uranium hydride–hydrogen system at 375°C. (Reproduced by permission from F. H. Spedding, *et al.*, *Nucleonics*, 4 (1949) 4.)

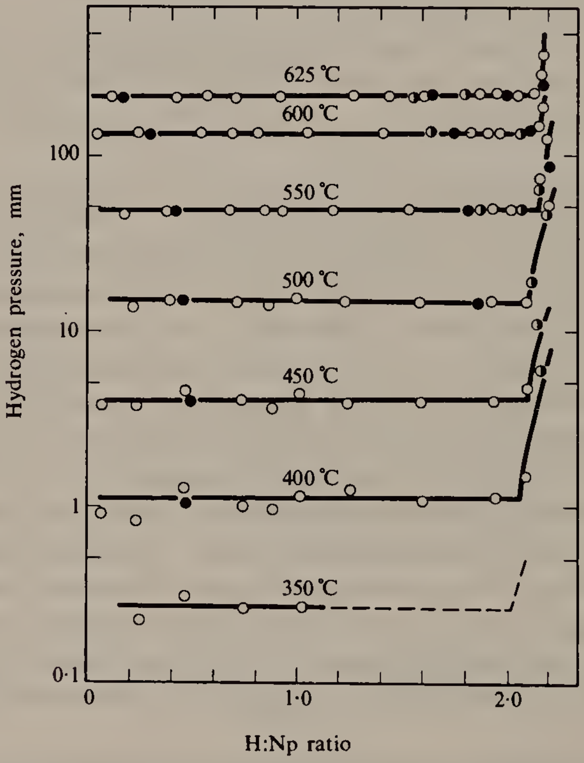

FIG. 3. Pressure isotherms vs. sample composition for the range Np to $NpH_{2\cdot2}$. (Reproduced by permission from R. N. R. Mulford and T. A. Wiewandt, *J. Phys. Chem.* **69** (1965) 1641.)

○ hydrogen addition, sample 1.

● hydrogen removal, sample 1.

◑ sample 2.

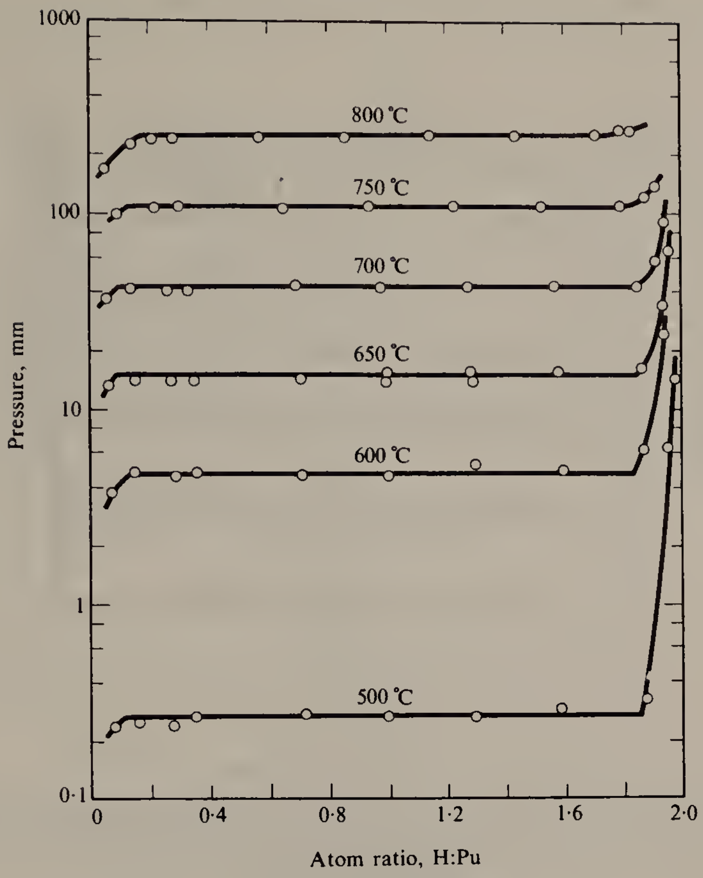

FIG. 4. Pressure isotherms vs. sample composition for the range Pu to $PuH_{2·0}$. (Reproduced by permission from R. N. R. Mulford and F. E. Sturdy, *J. Amer. Chem. Soc.* 77 (1955) 3449.)

In contrast to the behaviour of plutonium dihydride, which becomes poorer in hydrogen as the temperature increases[16] (for example $PuH_{1·88}$ at 500°C and $PuH_{1·86}$ at 600°C, Fig. 4), neptunium dihydride[5] becomes richer in hydrogen as the temperature increases (Fig. 3). The plutonium hydride behaviour is analogous to that observed for the lanthanide hydrides. The lower composition limit for americium dihydride[6] (Fig. 5) is almost temperature-independent between 500° and 800°C.

Crystallographic data for the various hydrides and deuterides are presented in Table 6 together with references to the original literature. Whereas the most frequently observed ThH_2 phase possesses tetragonal symmetry the existence of a second phase, which exhibits the fluorite-type structure observed for AcH_2, NpH_2, PuH_2 and AmH_2, has been reported. Analogous fluorite-type structures are exhibited by the majority of the lanthanide dihydrides. However, whereas the effects of the lanthanide contraction are evident in the lattice parameters (a_0) obtained for the latter series of compounds[20], no such effects (actinide contraction) are apparent from the unit cell dimensions reported for the presently known actinide dihydrides. Metal–hydrogen bond lengths for the dihydrides range from 2·46 Å to 2·314 Å. As mentioned above, absorption of hydrogen in excess of the stoichiometric phase $MH_{2·0}$ results either in an increase (Np) or decrease (Pu and Am) in a_0; this is illustrated by the values shown in Table 6 for $NpH_{2·5}$, $PuH_{2·5}$ and $AmH_{2·67}$. β-UH_3 and PaH_3

[20] A. Pebler and W. E. Wallace, *J. Phys. Chem.* 66 (1962) 148.

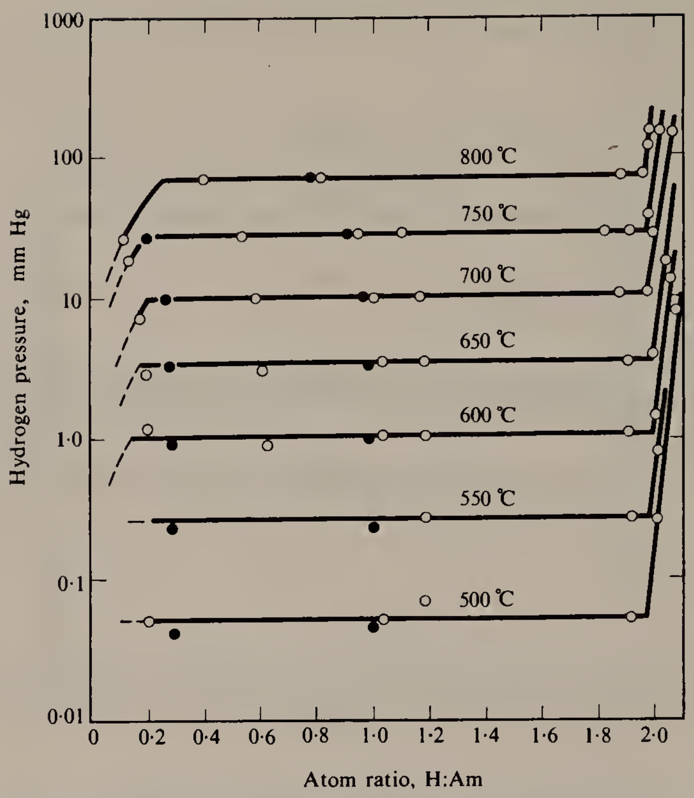

FIG. 5. Pressure isotherms vs. sample composition for the range Am to AmH_2. (Reproduced by permission from W. M. Olsen and R. N. R. Mulford, *J. Phys. Chem.* **70** (1966) 2934.)
○ hydrogen addition.
● hydrogen removal.

crystallize with the β-W type of structure; in the former compound each uranium atom is surrounded by twelve equidistant hydrogen atoms at a distance of 2·32 Å. The trihydrides of neptunium to americium inclusive are isostructural with those formed by the heavier lanthanide elements (Sm, Gd–Tm incl. and Lu). Although Pu–H bond lengths have been reported (Table 6), the recent neutron diffraction study on HoD_3[21] suggests that the structure is more complicated than previously believed and that the true hexagonal cell dimensions are larger than those derived from powder studies [a_0 (true) = a_0 (powder) × $\sqrt{3}$; c_0 (true) = c_0 (powder)]. In Th_4H_{15} each thorium atom is bonded to three hydrogens at 2·46 Å and to nine hydrogens at 2·29 Å.

Comparison of experimentally observed metal–hydrogen distances with those calculated on the basis of ionic bonding, and the values of lattice energies calculated on the same basis, are quoted[1] in favour of the presence of anionic hydrogen in the actinide hydrides.

β-uranium trihydride is ferromagnetic, the reported values for the Curie temperature falling in the range 168° to 181°K. Extrapolation of $1/\chi$ vs. T plots at higher temperatures yield θ values in the range 137° to 182°. The corresponding values for β-UD_3 appear to be slightly lower although once again there is poor agreement between the reported Curie temperatures (167° to 178°K). α-UH_3 is also ferromagnetic and magnetic studies on $PuH_{2\cdot74}$ and $PuD_{2\cdot74}$ have indicated that these phases are either ferro- or ferrimagnetic with a Curie temperature of 107°K. The various magnetic and related studies are discussed by Libowitz[1] and this article is recommended for references to the original literature.

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[21] M. Mansmann and W. E. Wallace, *J. Phys. (Paris)* **25** (1964) 454.

TABLE 6. CRYSTALLOGRAPHIC DATA FOR THE ACTINIDE HYDRIDES AND DEUTERIDES

Compound	Symm.	Space group or structure type	Lattice parameters (Å)		M–H bond length (Å)	ρ_c (g cm^{-3})	Ref.
			a_0	c_0			
PaH_3	C	β-W	6·648	—	2·32		a
α-UH_3	C	O_h^1-$Pm3m$	4·160	—	2·32	11·12	b
α-UD_3	C	O_h^1-$Pm3m$	4·150	—	—	11·33	c
β-UH_3	C	β-W	6·645	—	2·32	10·91	d
β-UD_3	C	β-W	6·633	—	—	11·10	d
NpH_3	H	$D^{16}{}_{4h}$-$P6_3/mmc$	3·77	6·72	—	9·64	e
PuH_3	H	,,	3·78	6·76	2·18→2·41	9·61	f
AmH_3	H	,,	3·77	6·75	—	9·76	j
AcH_2	C	Fluorite	5·670	—	2·46	8·35	g
ThH_2(?α)	T		5·735	4·971	2·39	9·50	h
ThH_2(?β)	C	Fluorite	5·489	—	—	—	h
NpH_2	C	,,	5·343	—	2·314	10·40	e, j
PuH_2	C	,,	5·359	—	2·32	10·40	f
AmH_2	C	,,	5·348	—	2·316	10·6	j
CmH_2	C	,,	5·344	—	2·314	10·7	k
$NpH_{2.5}$	C	,,	5·360	—	—	—	e
$PuH_{2.5}$	C	,,	5·340	—	—	—	f
$AmH_{2.67}$	C	,,	5·338	—	—	—	j
Th_4H_{15}	C	T_d^6–$I\bar{4}3d$	9·11	—	2·29 & 2·46	8·28	i

C, cubic; T, tetragonal; H, hexagonal.

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

[b] R. N. R. Mulford, F. H. Ellinger and W. H. Zachariasen, *J. Amer. Chem. Soc.* **76** (1954) 297.

[c] E. Wicke and K. Otto, *Z. Phys. Chem., Frankfurt*, **31** (1962) 222.

[d] R. E. Rundle, *J. Amer. Chem. Soc.* **69** (1947) 1719.

[e] R. N. R. Mulford and T. A. Wiewandt, *J. Phys. Chem.* **69** (1965) 1641.

[f] F. H. Ellinger, p. 281 in *The Metal Plutonium* (A. S. Cofinberry and W. N. Miner, Eds.), Univ. Chicago Press, Chicago (1961).

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

[h] W. L. Korst, *Acta Cryst.* **15** (1962) 287.

[i] W. H. Zachariasen, *Acta Cryst.* **6** (1953) 393.

[j] W. M. Olsen and R. N. R. Mulford, *J. Phys. Chem.* **70** (1966) 2934.

[k] B. M. Bansal and D. Damien, *Inorg. Nucl. Chem. Letters*, **6** (1970) 603.

4. CHEMICAL PROPERTIES

The chemical properties of thorium, uranium and plutonium hydrides have been studied, particularly those of UH_3, but virtually no information appears to be available for the remaining hydrides in the series. However, such compounds will probably resemble the above three hydrides to a large extent in their behaviour with various halogenating agents, water, air and a variety of gaseous elements.

Thorium, uranium and plutonium hydrides have all been observed to be pyrophoric[2,22] although the stability of plutonium dihydride appears to depend on particle size and the Pu/H ratio[23]. However, it is obviously wise to handle all actinide hydrides in a dry, inert

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[22] J. P. Blackledge, ref. 1, Chapter 5.

[23] F. Brown, H. M. Ockenden and G. A. Welch, *J. Chem. Soc.* (1955) 3932.

atmosphere. One of the main applications of the hydrides is in their conversion to finely divided metal on thermal decomposition. Metals obtained in this manner are finely divided, extremely reactive and, for example, very suitable for alloy formation. In view of the ready thermal decomposition of uranium hydride it is not clear whether all the high-temperature reactions attributed to it do in fact involve the hydride or, at least in part, finely divided metal. A selection of the reactions reported[2] for uranium hydride is shown in Table 7. Amongst the more important are those involving conversion to the tri- or tetrahalides. Thorium dihydride[22] undergoes similar reactions with halogenating agents to yield tetrahalides whilst plutonium trihalides[22] are obtained by analogous hydride–hydrogen halide reactions at moderate temperatures. Similarly plutonium nitride, PuN, is formed when plutonium trihydride is exposed to ammonia gas at 600°C.

The rapid addition of water to uranium and plutonium hydride often results in ignition, whereas thorium dihydride is reported to be stable when immersed in water below 100°C[22]. At higher temperatures (250° to 350°C) Th_4H_{15} reacts smoothly with water to form ThO_2. Oxidizing agents in aqueous solution, for example Ag(I), Hg(II) and Sb(III), convert UH_3 to soluble U(IV) or U(VI) species and similar oxidations occur on dissolution of the trihydride in aqueous hydrochloric, nitric and sulphuric acid[2]. Plutonium hydride dissolves in aqueous hydrochloric and sulphuric acids to yield Pu(III) solutions.

Although uranium trihydride may be safely handled under certain organic solvents (e.g. benzene, toluene, dioxane, alcohol, etc.), contact with halogen-containing solvents such as carbon tetrachloride may result in an explosive reaction[2].

Table 7. A Selection of Reactions between Uranium Trihydride and Various Gaseous Reagents*

Reagent	Conditions (°C)	Products
O_2	Ignites σ R.T.	U_3O_8
N_2†	225–250	Uranium nitrides
Cl_2	200–250	UCl_4
Br_2	200–300	UBr_4
I_2	400	UI_3/UI_4
HF	20–400	UF_4
HCl	250–300	UCl_3
HBr	200	UBr_3
HI	300–400	?UI_3
HCN	400	Carbide/Nitride
H_2S	400–500	US_2/U_2S_3
NH_3	100–200	Uranium nitrides
PH_3	400	U_2P_3
CO_2†	200	UO_2
$COCl_2$	250	UCl_4
CH_3I	275–300	?UI_3
CCl_4	250	UCl_4

* Taken from J. J. Katz and E. Rabinowitch, *The Chemistry of Uranium*, Nat. Nucl. Energy Series Div. VIII, Vol. 5, p. 203. McGraw Hill, N.Y. (1951).

† Although UH_3 may be safely stored under nitrogen or carbon dioxide at room temperature, once the reactions have started they cannot be stopped. However, in the absence of oxygen there is no danger of explosion.

HALIDES, HALATES, PERHALATES, THIOCYANATES, SELENOCYANATES, CYANATES AND CYANIDES

D. BROWN
A.E.R.E., Harwell

1. GENERAL SURVEY OF THE HALIDES

Actinide halides and oxyhalides and related halogeno-complexes have been extensively investigated, particularly the fluorine-containing compounds. Since it is impossible in this treatment to provide a complete literature coverage, the preparation of the compounds will not be dealt with in detail. Certain general points will be given at the start of each section and the interested reader is referred to earlier comprehensive reviews[1–21] for detailed discussions of the extensive literature dealing with the many preparative techniques available.

In order to hold the references at a reasonable number, certain of these reviews will also frequently be cited as the source of various physical and chemical properties. Direct reference will, where possible, only be made to work published during the past few years. This article covers the literature to early 1971.*

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* Whilst this article was in press the first examples of divalent halides containing M^{2+} ions have been characterized. These are $CfBr_2$ (J. R. Peterson and R. D. Baybarz, *Inorg. Nucl. Chem. Letters*, **8** (1972) 101) and AmI_2 (R. D. Baybarz, L. B. Asprey, C. E. Strouse and E. Fukushime, *J. Inorg. Nucl. Chem.* **34** (1972) 3427). These are isostructural with europium analogues.

[1] *The Transuranium Elements* (G. T. Seaborg, J. J. Katz and W. H. Manning, Eds.), Nat. Nucl. Energy Series Div. IV, Vol. 14B, McGraw-Hill, New York (1949).

[2] *The Actinide Elements* (G. T. Seaborg and J. J. Katz, Eds.), Nat. Nucl. Energy Series Div. IV, Vol. 14A, McGraw-Hill, New York (1954).

[3] *The Chemistry of the Actinide Elements*, J. J. Katz and G. T. Seaborg, Methuen, New York (1957).

[4] *The Chemistry of Uranium* (J. J. Katz and E. Rabinowitch, Eds.), Nat. Nucl. Energy Series Div. VIII, Vol. 5, McGraw-Hill, New York (1951).

[5] *Nouveau Traite de Chimie Mineral* (P. Pascall, Ed.), Vols. VII (1962), IX (1963), XV(2) (1961), XV(3) (1962), XV(4) (1967) and XV(5) (1970), Masson et Cie, Paris.

[6] *Halides of the Lanthanides and Actinides*, D. Brown, Wiley, London (1968).

[7] *Plutonium Handbook* (O. J. Wick, Ed.), Vols. I and II, Gordon & Breach, New York (1967).

[8] *Chemistry of Uranium and Transuranium Elements*, V. M. Vdovenko, AEC-tr-6421 (1964).

[9] *The Chemistry of Plutonium*, J. Cleveland, Gordon & Breach, New York (1970).

[10] *Halides of the Actinide Elements*, J. J. Katz and I. Sheft, Chapter 5 in *Advances in Inorganic and Radiochemistry* (H. J. Emeléus and A. G. Sharpe, Eds.), Vol. 2, Academic Press, New York (1960).

[11] *Fluorides of the Actinide Elements*, M. Hodge, Chapter 7 in *Advances in Fluoride Chemistry* Vol. 2 (M. Stacey, J. C. Tatlow and A. G. Sharpe, Eds.), Butterworths, London (1961).

[12] M. J. Steindler, *Plutonium Hexafluoride*, U.S. Report ANL-6753 (1963).

[13] *Compounds of the Actinides*, B. B. Cunningham, Chapter 3 in *Preparative Inorganic Reactions* (W. L. Jolly, Ed.), Vol. 3, Interscience, New York (1966).

[14] Co-ordination chemistry of the actinides, K. W. Bagnall, *Co-ord. Chem. Rev.* **2** (1967) 145.

[15] *The Halogen Chemistry of the Actinides*, K. W. Bagnall, Chapter 7 in *Halogen Chemistry* (V. Gutmann, Ed.), Vol. 3, Academic Press, London (1967).

[16] Die Chimie des Neptuniums, C. Keller, *Fortschritte der Chem. Forschung*, **13** (1969) 1.

[17] *The Actinide Halides and Their Complexes*, D. Brown, Chapter 3 in *Int. Rev. of Science*, Vol. 7 (K. W. Bagnall, Ed.), M.T.P. and Butterworths, London (1972).

[18] D. Brown, Chapter 1 in *Advances in Inorganic and Radiochemistry*, Vol. 12, p. 1.

[19] D. Brown, Chapters 3.5 to 3.8 in Gmelin 71, *The Transuranium Elements* (1972).

[20] K. W. Bagnall, Chapter 18 in Gmelin 71, *The Transuranium Elements* (1972).

[21] R. de Witt, U.S. Report GAT-280 (1960).

TABLE 1. THE PRESENTLY KNOWN ACTINIDE HALIDES*

	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es
Fluorides	AcF_3	—	—	UF_3	NpF_3	PuF_3	AmF_3	CmF_3	BkF_3	CfF_3	—
	—	ThF_4	PaF_4	UF_4	NpF_4	PuF_4	AmF_4	CmF_4	BkF_4	CfF_4	—
	—	—	U_4F_{17}	—	Pu_4F_{17}	—	—	—	—	—	—
	—	—	Pa_2F_9	U_2F_9	—	—	—	—	—	—	—
	—	—	PaF_5	UF_5	NpF_5	—	—	—	—	—	—
	—	—	—	UF_6	NpF_6	PuF_6	—	—	—	—	—
Chlorides	$AcCl_3$	—	—	UCl_3	$NpCl_3$	$PuCl_3$	$AmCl_3$	$CmCl_3$	$BkCl_3$	$CfCl_3$	$EsCl_3$
	—	$ThCl_4$	$PaCl_4$	UCl_4	$NpCl_4$	$PuCl_4$†	—	—	—	—	—
	—	—	$PaCl_5$	UCl_5	—	—	—	—	—	—	—
	—	—	—	UCl_6	—	—	—	—	—	—	—
Bromides	$AcBr_3$	—	—	UBr_3	$NpBr_3$	$PuBr_3$	$AmBr_3$	$CmBr_3$	$BkBr_3$	$CfBr_3$	—
	—	$ThBr_4$	$PaBr_4$	UBr_4	$NpBr_4$	—	—	—	—	—	—
	—	—	$PaBr_5$	UBr_5	—	—	—	—	—	—	—
Iodides	—	ThI_2	—	—	—	—	—	—	—	—	—
	AcI_3	ThI_3	PaI_3	UI_3	NpI_3	PuI_3	AmI_3	CmI_3	BkI_3	CfI_3	—
	—	ThI_4	PaI_4	UI_4	—	—	—	—	—	—	—
	—	—	PaI_5	—	—	—	—	—	—	—	—

* See footnote on page 151.

† Exists only in the gaseous state in the presence of chlorine.

TABLE 2. THE PRESENTLY KNOWN ACTINIDE OXYHALIDES*

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es
Fluorides										
AcOF	ThOF	—	—	—	PuOF	—	—	—	CfOF	—
—	$ThOF_2$	—	'UOF_2'	—	—	—	—	—	—	—
—	—	Pa_2OF_8	U_2OF_8	—	—	—	—	—	—	—
—	—	—	—	$NpOF_3$	—	—	—	—	—	—
—	—	PaO_2F	UO_2F	NpO_2F	—	—	—	—	—	—
—	—	Pa_3O_7F	—	—	—	—	—	—	—	—
—	—	—	UO_2F_2	NpO_2F_2	PuO_2F_2	AmO_2F_2	—	—	—	—
Chlorides										
AcOCl	—	—	UOCl	NpOCl	PuOCl	AmOCl	CmOCl	BkOCl	CfOCl	EsOCl
—	$ThOCl_2$	$PaOCl_2$	$UOCl_2$	$NpOCl_2$	—	—	—	—	—	—
—	—	Pa_2OCl_8	—	—	—	—	—	—	—	—
—	—	—	$UOCl_3$	—	—	—	—	—	—	—
—	—	$Pa_2O_3Cl_4$	—	—	—	—	—	—	—	—
—	—	PaO_2Cl	UO_2Cl	—	—	—	—	—	—	—
—	—	—	UO_2Cl_2	—	—	—	—	—	—	—
Bromides										
AcOBr	—	—	—	—	PuOBr	—	CmOBr	BkOBr	CfOBr	—
—	$ThOBr_2$	$PaOBr_2$	$UOBr_2$	$NpOBr_2$	—	—	—	—	—	—
—	—	$PaOBr_3$	$UOBr_3$	—	—	—	—	—	—	—
—	—	PaO_2Br	UO_2Br	—	—	—	—	—	—	—
—	—	—	UO_2Br_2	—	—	—	—	—	—	—
Iodides										
[AcOI]	—	—	—	NpOI	PuOI	—	—	BkOI	CfOI	—
—	$ThOI_2$	$PaOI_2$	—	—	—	—	—	—	—	—
—	—	$PaOI_3$	—	—	—	—	—	—	—	—
—	—	PaO_2I	—	—	—	—	—	—	—	—
—	—	—	$[UO_2I_2]$	—	—	—	—	—	—	—

* AmOI has very recently been characterized (R. D. Baybarz, L. B. Asprey, C. E. Strouse and E. Fukushima, *J. Inorg. Nucl. Chem.* **34** (1972) 3427).

TABLE 3. IONIC RADII FOR THE ACTINIDE ELEMENTS

Element	Ionic radius (Å)	
	M^{3+a}	M^{4+b}
Ac	1·076*	—
Th	—	0·984‡
Pa	—	0·944‡
U	1·005*	0·929‡
Np	0·986*	0·913‡
Pu	0·974*	0·896‡
Am	0·962*	0·888‡
Cm	0·946*	0·886‡
Bk	0·935*	0·870‡
Bk	0·928†	
Cf	0·915†	

[a] J. R. Peterson and B. B. Cunningham, *J. Inorg. Nucl. Chem.* 30 (1968) 1775.

[b] J. R. Peterson and B. B. Cunningham, *Inorg. Nucl. Chem. Letters*, 3 (1967) 327.

* Calculated from the LaF_3-type trifluoride phase for coordination number = 6.

† Calculated from the YF_3-type trifluoride phase for coordination number = 6.

‡ Calculated from the isostructural series of dioxides for coordination number = 6.

The presently known halides and oxyhalides are listed in Tables 1 and 2, respectively. It is obvious from the range of compounds listed that the decrease in higher oxidation states of the actinides with increasing atomic number (p. 1) is reflected by their halides. The last few elements in the series, fermium, mendelevium, nobelium and lawrencium, have not yet been available in sufficient quantities to permit the chemistry of their halides to be studied. However, it is likely, with the possible exception of divalent nobelium compounds, that the halides formed by these elements will be predominantly trivalent. Certainly the formation of tetravalent compounds beyond californium will be limited to those obtained under strongly oxidizing conditions, e.g. tetrafluorides and tetravalent fluoro-complexes. It is also apparent from Tables 1 and 2 that there is scope for further research aimed, for example, at the characterization of trivalent protactinium halides, pentavalent uranium oxyfluorides and a wide range of trivalent oxyhalides; in addition, neptunium pentachloride and plutonium pentafluoride remain uncharacterized, although thermodynamic calculations suggest that they should be capable of existence. The recent characterization of neptunium pentafluoride (p. 161) should encourage a search for the latter. It is unlikely, however, in view of the results available on plutonium tetrachloride (p. 184), that new tetrahalides, apart possibly from tetrafluorides, will be prepared for elements beyond plutonium. In view of the recent characterization of neptunium(VII), plutonium(VII) and americium(VII) there also exists the possibility that heptavalent oxyfluorides may be obtained for one or more of these elements.

TABLE 4. SELECTED THERMODYNAMIC CONSTANTS FOR THE ACTINIDE HALIDES[a,b,c]

Compound	$-\Delta H_f$ (kcal mole^{-1})	S_{298} (e.u.)	M.p. (°K)	L_f (kcal mole^{-1})	σ_f (cal mole^{-1} °K^{-1})	B.p.^{d} (°K)	L_e^d (kcal mole^{-1})	σ_e^d (cal mole^{-1} °K^{-1})
$\langle AcF_3 \rangle$	(420)							
$\langle UF_3 \rangle$	351^f	(28)	dec.					
$\langle NpF_3 \rangle$	(360)		1698					
$\langle PuF_3 \rangle$	371	30·7	1669	14·3	10·0	2230	65·0	26·1
(PuF_3)	271	81·2						
$\langle AmF_3 \rangle$	(394)	(27·0)	1668					
$\langle CmF_3 \rangle$			1679					
$\langle AcCl_3 \rangle$	(260)		—					
$\langle UCl_3 \rangle$	213·5	38·0	1110	(11·1)	(10·0)	(1930)		23·9
$\langle NpCl_3 \rangle$	(216)		1073					
$\langle PuCl_3 \rangle$	229·8	39·2	1040	10·6^e	10·2			
$\{PuCl_3\}$						2000	49·0	24·5
$(PuCl_3)$	156·1	87·9						
$\langle AmCl_3 \rangle$	249·2		773					
$\langle CmCl_3 \rangle$	(226·4)							
$\langle CfCl_3 \rangle$			848					
$\langle AcBr_3 \rangle$	(220)							
$\langle UBr_3 \rangle$	172·3	(45·0)	1000	10·5	10·5	1810		27·9
$\langle NpBr_3 \rangle$	(174)							
$\langle PuBr_3 \rangle$	187·7	45·7	954	13·2	13·0			
$\{PuBr_3\}$						1736	49·0	28·2
$(PuBr_3)$	112·8	103·1						
$\langle CmBr_3 \rangle$			673					
$\langle AcI_3 \rangle$	(169)							
$\langle UI_3 \rangle$	114·2	(57·0)	1039					
$\langle NpI_3 \rangle$	(120)		1033–45					
$\langle PuI_3 \rangle$	(130)	(56)	(1050)	(12·0)				
$\langle AmI_3 \rangle$	(146)							
$\langle ThF_4 \rangle$	504·6	33·95	1383	10·51	7·6	1976		30·96
(ThF_4)	422·2	83·8						
$\langle PaF_4 \rangle$	(460)	(35·8)						
$\langle UF_4 \rangle$	450	36·3	1309	10·2	7·8	1730		30·7
$\langle NpF_4 \rangle$	(428)							
$\langle PuF_4 \rangle$	425	38·7	1300	15·6	12·0			
(PuF_4)	(352)	(91·5)						
$\langle AmF_4 \rangle$	(400)							
$\langle ThCl_4 \rangle$	284·9	(45·5)	1043	19·85	19·03	1195		30·1
$(ThCl_4)$	221·8	(105·4)						
$\langle PaCl_4 \rangle$	(268)							
$\langle UCl_4 \rangle$	243·6	47·4	863	10·7	12·5	1062		31·8
$\langle NpCl_4 \rangle$	235·7	(47·5)	790					
$\langle PuCl_4 \rangle$	(227)							
$(PuCl_4)$	(189·7)	(98·6)						
$\langle ThBr_4 \rangle$	231·1	(54·5)	952	16·0	16·81	1132		29·6
$(ThBr_4)$	174·7	(111·2)						
$\langle PaBr_4 \rangle$	(212)		—					
$\langle UBr_4 \rangle$	191·1	56·0	792	13·2	16·5	1050		27·1
$\langle NpBr_4 \rangle$	184·5		737–41					
$\langle ThI_4 \rangle$	160·3	(63·5)	843	14·68	17·50	1100		
(ThI_4)	109·1	(117·5)						
$\langle PaI_4 \rangle$	(144)							
$\langle UI_4 \rangle$	121·6	67·0	779	16·9	21·6	1030		30·3
$\langle NpI_4 \rangle$	(113)							
$\langle PuI_4 \rangle$	(100)							
$\langle AmI_4 \rangle$	(87)							
$\langle PaF_5 \rangle$	(540)							

Table 4—(*cont.*)

Compound	$-\Delta H_f$ (kcal mole^{-1})	S_{298} (eu)	M.p. (°K)	L_f (kcal mole^{-1})	σ_f (cal mole^{-1} °K^{-1})	B.p.[d] (°K)	L_e[d] (kcal mole^{-1})	σ_e[d] (cal mole^{-1} °K^{-1})
$\langle \mathrm{UF_5} \rangle$	491·5	45·0	621					
$\langle \mathrm{U_2F_9} \rangle$	472·5	(39·4)						
$\langle \mathrm{U_4F_{17}} \rangle$	461·5	(37·7)						
$\langle \mathrm{NpF_5} \rangle$	(454)							
$\langle \mathrm{PaCl_5} \rangle$			579			(693)	14·65	21·1
$\langle \mathrm{UCl_5} \rangle$	261·5	(58·0)						
$\langle \mathrm{NpCl_5} \rangle$	(246)							
$\langle \mathrm{UF_6} \rangle$	523	54·4	337·2	4·57		330		34·9
$(\mathrm{UF_6})$	511	90·4						
$\langle \mathrm{NpF_6} \rangle$	—	54·76	327·91	4·19	12·79	328·18		
$(\mathrm{NpF_6})$	(463; 459)	89·99						
$\langle \mathrm{PuF_6} \rangle$	430·8	53·0	325	4·2	13·0	335·3	7·2	21·5
$(\mathrm{PuF_6})$	418	88·4						
$\langle \mathrm{UCl_6} \rangle$	270·7	68·3						

[a] Values have been selected from recent review articles (refs. 6, 27–29, 31) and the reader is referred to these for details of the original literature.

[b] Standard symbols are used for this and other tables of thermodynamic data, viz. $\langle\ \rangle$, solid state; $\{\ \}$, liquid state; ( ), vapour state; ΔH_f, heat of formation at 298·15°K; S_{298}, standard entropy; $L_{e,f}$, latent heat of evaporation or fusion; $\sigma_{e,f}$, molar entropy of evaporation or fusion at the m.p. or b.p.; ΔG, free energy of reaction; ΔH, heat of reaction; ΔS, entropy of reaction; C_p, molar heat capacity. Gaseous fluorine, gaseous chlorine, liquid bromine and solid iodine are taken as the standard states at 298·15°K for all values quoted unless otherwise stated.

[c] Values in parentheses are estimated.

[d] Although often listed under $\langle$cpd$\rangle$, these values refer to $\{$cpd$\}$.

[e] Gruen and Dekock (*J. Inorg. Nucl. Chem.* **29** (1967) 2569) prefer the value 14·7 kcal mole^{-1}.

[f] Khanaev and Keipin (*Soviet Radiochem.* **12** (1970) 158) recently determined this value as -357 ± 4 kcal mole^{-1}.

The only "divalent" halide known* for the actinide elements is $\mathrm{ThI_2}$ and, as discussed later (p. 203), even this must be formulated as $\mathrm{Th^{4+}(I)_2(e^-)_2}$. In addition, under conditions where all the lanthanide elements exhibit divalency in $\mathrm{CaF_2}$ and similar matrices, e.g. reduction of $\mathrm{M^{3+}}$ by γ-radiation, solid state electrolysis or exposure to alkaline-earth metal vapours, only americium[22,23] and einsteinium[24] have been observed as divalent ions. Oxidation to the tetravalent state occurs with $\mathrm{Cm^{3+}}$, $\mathrm{Pu^{3+}}$ and $\mathrm{Np^{3+}}$[25,26].

As a consequence of the addition of successive electrons to the inner 5*f* electron shell, the ionic radii of the actinide elements decrease with increasing atomic number. This actinide contraction is illustrated by the ionic radii listed in Table 3. As a result of the size similarities many series of halides and halogeno-complexes of the elements actinium to einsteinium are often isostructural and, indeed, numerous compounds have been identified in only microgram amounts by X-ray diffraction studies. In certain instances, however, there is a change in structure-type along a series of analogous compounds. Such changes, for example at berkelium in the trifluorides (p. 161), at californium in the trichlorides (p. 182), at

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* See footnote on page 151.

[22] N. Edelstein, W. Easley and R. McLaughlin, *J. Chem. Phys.* **44** (1966) 3130.

[23] N. Edelstein and W. Easley, *J. Chem. Phys.* **48** (1968) 2110.

[24] N. Edelstein, J. G. Conway, D. Fujita, W. Kolbe and R. McLaughlin, *J. Chem. Phys.* **52** (1970) 6425; N. Edelstein, *J. Chem. Phys.* **54** (1971) 2488.

[25] R. McLaughlin, R. White, N. Edelstein and J. G. Conway, *J. Chem. Phys.* **48** (1968) 967.

[26] N. Edelstein, W. Easley and R. McLaughlin, Adv. in Chem. Series No. 71, *Lanthanide/Actinide Chemistry*, p. 203 (1967).

Table 5. Heats of Formation and Standard Entropies for Actinide Oxyhalides[a]

Compound	$-\Delta H_f$ (kcal $\mathrm{mole^{-1}}$)	S° (eu)
$\langle \mathrm{AcOF} \rangle$	(265)	—
$\langle \mathrm{PuOF} \rangle$	(269·8)	(21·9)
$\langle \mathrm{PuOCl} \rangle$	222·7	(25·2)
$\langle \mathrm{AmOCl} \rangle$	241·5[b]	—
$\langle \mathrm{PuOBr} \rangle$	206·4	(27·0)
$\langle \mathrm{PuOI} \rangle$	(183)	—
$\langle \mathrm{ThOF_2} \rangle$	401	(24·2)
$\langle \mathrm{UOF_2} \rangle$	352	—
$\langle \mathrm{ThOCl_2} \rangle$	296·1	(27·7)
$\langle \mathrm{PaOCl_2} \rangle$		
$\langle \mathrm{UOCl_2} \rangle$	252·2[c]	33·1
$\langle \mathrm{NpOCl_2} \rangle$	245·8	—
$\langle \mathrm{ThOBr_2} \rangle$	270·0	(33·0)
$\langle \mathrm{PaOBr_2} \rangle$		
$\langle \mathrm{UOBr_2} \rangle$	233·2[c]	(37·7)
$\langle \mathrm{ThOI_2} \rangle$	237·6	(40·0)
$\langle \mathrm{UOCl_3} \rangle$	284·2	(42·0)
$\langle \mathrm{UOBr_3} \rangle$	236·0	(49·0)
$\langle \mathrm{UO_2F_2} \rangle$	399·0	32·4
$\langle \mathrm{UO_2Cl_2} \rangle$	302·9	36·0
$\langle \mathrm{UO_2Br_2} \rangle$	276·6	(40·5)

[a] Values have been selected from review articles (refs. 6, 22, 29, 31) and the reader is referred to these for details of the original literature.

[b] The original literature value was in error according to Fuger[31].

[c] Older values recalculated using the new value for $\Delta H_f\langle \mathrm{UCl_4} \rangle$[31].

neptunium in the tribromides (p. 199) and at americium in the tri-iodides (p. 203), are consistent with the actinide contraction which results in an increased ratio of anion:cation radii. The useful concept of ionic radius ratios for predicting structure types or the existence of a given type of fluoro-complex and the various changes in structure within series of compounds are discussed where appropriate in the later sections.

Selected thermodynamic data for the actinide halides and oxyhalides, and for various halogenation reactions are given in Tables 4 to 8 inclusive and vapour pressure data are listed in Tables 9 and 10. Space does not permit detailed discussion of these data and the reader is referred to authoritative review articles[27–31] for full coverage of the pertinent literature. No experimental thermochemical data are available for actinium or for the elements beyond americium. Estimated heats of formation are available for numerous tri- and tetravalent mixed halides[32].

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[27] M. H. Rand, *Atomic Energy Review* to be published.

[28] M. H. Rand and O. Kubaschewski, *The Thermochemical Properties of Uranium Compounds*, Oliver & Boyd, London (1963).

[29] M. H. Rand, *Atomic Energy Rev.*, Special Issue No. 1, **4** (1966) 7.

[30] F. L. Oetting, *Chem. Rev.* **67** (1967) 261.

[31] J. Fuger, Chapter 5 in *Int. Rev. Sci.* Vol. 7 (K. W. Bagnall, Ed.), M.T.P. and Butterworths, London (1972).

[32] P. G. Maslov and Yu. P. Maslov, *Zh. Obshch. Khim.* **35** (1965) 2112.

TABLE 6. HEAT CAPACITIES FOR CERTAIN ACTINIDE HALIDES[a]
$C_p = a + bT + cT^{-2}$ (cal mole^{-1} °K^{-1})

Compound	C_p at 298°K	a	$b \times 10^3$	$c \times 10^{-5}$	Temperature range (°K)
$\langle PuF_3\rangle$		20·7	8·20		298–1669
$\langle ThF_4\rangle$		26·75	5·854	−1·805	298–1383
$\langle UF_4\rangle$	27·7	25·7	7·00	−0·06	298–1309
$\langle UF_5\rangle$	31·6				
$\langle UF_6\rangle$	40·0	12·6	92·0		273–337
(UF_6)	31·0	22·3	28·5		273–400
(PuF_6)	31·0	37·23	0·274	−5·65	298–1500
$\langle UCl_3\rangle$	24·4	20·8	7·75	1·05	298–900
$\langle ThCl_4\rangle$		28·75	5·561	−1·470	298–1043
$\langle UCl_4\rangle$	28·9	27·2	8·75	−0·79	298–800
(UCl_4)		25·8	14·40	—	890–920
$\langle UCl_6\rangle$	42·0				
$\langle UBr_4\rangle$	30·0	31·4	4·92	−3·15	350–750
$\langle UI_4\rangle$	31·0	34·8	2·38	−4·72	380–720
$\{UI_4\}$		39·6			820–870
$\langle PuOF\rangle$		17·29	5·71		298–1500
$\langle UO_2F_2\rangle$	24·7				
$\langle PuOCl\rangle$		18·29	5·71		298–1500
$\langle UOCl_2\rangle$	22·7				
$\langle UO_2Cl_2\rangle$	25·8				
$\langle PuOBr\rangle$		19·28	5·71		298–1500
$\langle UOBr_2\rangle$	23·4				
$\langle PuOI\rangle$		20·29	5·71		298–1500

[a] Values selected from review articles, refs. 27–30.

TABLE 7. FREE ENERGIES OF SELECTED HALOGENATION REACTIONS
Free Energies of Reaction
$\Delta G = A + BT + CT \log T$ (cal)[a,b]

Reaction	A	B	C	Temperature range (°K)
$U + \frac{3}{2}F_2 \rightarrow UF_3$	−343,000	52·7		298–1405
$Pu + \frac{3}{2}F_2 \rightarrow PuF_3$	−371,000	56·0		298– 913
$\{Pu\} + \frac{3}{2}F_2 \rightarrow \{PuF_3\}$	−370,000	54·6		913–1700
$\{Pu\} + \frac{3}{2}F_2 \rightarrow \{PuF_3\}$	−350,200	43·1		1700–2230
$Th + 2F_2 \rightarrow ThF_4$	−502,590	71·04		298–1383
$U + 2F_2 \rightarrow UF_4$	−448,500	67·4		298–1309
$U + 2F_2 \rightarrow \{UF_4\}$	−433,100	55·6		1309–1405
$\{U\} + 2F_2 \rightarrow \{UF_4\}$	−433,100	55·6		1405–1730
$Pu + 2F_2 \rightarrow PuF_4$	−424,000	70·0		298–1500
$UF_4 + \frac{1}{2}F_2 \rightarrow UF_5$	− 41,200	14·8		298– 565
$UF_4 + F_2 \rightarrow UF_6$	− 73,000	30·4		298– 337
$UF_4 + F_2 \rightarrow (UF_6)$	− 62,300	− 2·8		298–1309
$\{UF_4\} + F_2 \rightarrow (UF_6)$	− 74,900	7·1		1309–1730
$PuF_4 + F_2 \rightarrow (PuF_6)$	6,800	—		298–1500
$PuF_4 + F_2 \rightarrow (PuF_6)$	5,200	2·6		620–1500
$U + \frac{3}{2}Cl_2 \rightarrow UCl_3$	−213,000	51·0		298–1110
$U + \frac{3}{2}Cl_2 \rightarrow \{UCl_3\}$	−200,700	40·0		1110–1405
$Pu + \frac{3}{2}Cl_2 \rightarrow PuCl_3$	−229,400	52·8		298–1040
$\{Pu\} + \frac{3}{2}Cl_2 \rightarrow \{PuCl_3\}$	−215,400	39·4		1040–2000
$Th + 2Cl_2 \rightarrow ThCl_4$	−282,310	67·59		298–1043
$Th + 2Cl_2 \rightarrow \{ThCl_4\}$	−256,970	42·90		1105–1190
$U + 2Cl_2 \rightarrow UCl_4$	−253,100	112·8	−14·3	298– 861
$U + 2Cl_2 \rightarrow \{UCl_4\}$	−236,700	52·0		861–1060
$PuCl_3 + \frac{1}{2}Cl_2 \rightarrow (PuCl_4)$	39,300	−30·0		298–1040
$\{PuCl_3\} + \frac{1}{2}Cl_2 \rightarrow (PuCl_4)$	26,000	−17·0		1040–1500
$UCl_4 + \frac{1}{2}Cl_2 \rightarrow UCl_5$	− 10,100	15·3		298– 600
$UCl_4 + Cl_2 \rightarrow UCl_6$	− 19,200	31·3		298– 450
$UCl_4 + Cl_2 \rightarrow (UCl_6)$	2,600	− 1·5		450– 900
$U + \frac{3}{2}Br_2 \rightarrow UBr_3$	−182,050	53·1		298–1000
$U + \frac{3}{2}Br_2 \rightarrow \{UBr_3\}$	−190,500	60·9		1000–1405
$Pu + \frac{3}{2}Br_2 \rightarrow PuBr_3$	−197,900	53·4		298– 954
$Pu + \frac{3}{2}Br_2 \rightarrow \{PuBr_3\}$	−182,500	37·2		954–1736
$Th + 2Br_2 \rightarrow ThBr_4$	−243,780	70·42		298– 997
$Th + 2Br_2 \rightarrow \{ThBr_4\}$	−222,670	47·65		997–1132
$U + 2Br_2 \rightarrow UBr_4$	−211,000	70·9		298– 792
$U + 2Br_2 \rightarrow \{UBr_4\}$	−194,000	49·2		792–1050
$Th + 2I_2 \rightarrow ThI_4$	−188,600	69·68		298– 864
$Th + 2I_2 \rightarrow \{ThI_4\}$	−169,380	46·55		864–1113
$U + 2I_2 \rightarrow UI_4$	−153,500	62		298– 779
$U + 2I_2 \rightarrow \{UI_4\}$	−134,000	37		779–1030
$UI_3 + \frac{1}{2}I_2 \rightarrow UI_4$	− 20,000	28·3	− 2·5	298– 779

[a] Values are from review articles, refs. 27–29.

[b] Unless indicated, the actinide elements and compounds are taken to be in the solid state with gaseous fluorine, gaseous chlorine, liquid bromine and solid iodine.

TABLE 8. FREE ENERGIES, HEATS AND ENTROPIES OF VAPORIZATION AND SUBLIMATION OF CERTAIN ACTINIDE HALIDES[a]

Compound	$\Delta G = RT \ln p_{\mathrm{atm}} = A + BT + CT \log T$ (cal)			Temperature range (°K)	$\Delta H_{298°}$ (kcal/mole)	$\Delta S_{298°}$ (eu/mole)
	A	B	C			
$\langle \mathrm{PuF_3} \rangle$	101,400	− 90·6	13·8	298–1700	99·6	50·5
$\{\mathrm{PuF_3}\}$	91,200	−114·4	23·0	1700–2500		
$\langle \mathrm{AmF_3} \rangle$	112,650	−155·5	32·2			
$\langle \mathrm{ThF_4} \rangle$	85,950	− 91·55	13·8		82·4	49·9
$\{\mathrm{ThF_4}\}$	80,970	−116·88	23·03			
$\langle \mathrm{UF_4} \rangle$	75,100	− 90·3	13·8	298–1309	73·2	50·2
$\{\mathrm{UF_4}\}$	70,100	−115·2	23·0	1309–1720		
$\langle \mathrm{PuF_4} \rangle$	73,400	− 93·0	13·8	298–1300	71·6	52·8
$\{\mathrm{PuF_4}\}$	50,000	− 32·0	—	1300–1550		
$\langle \mathrm{UF_6} \rangle$	15,150	−109·6	25·3	273– 337		
$\{\mathrm{UF_6}\}$	6,870	− 21·13	—	33– 400		
$\langle \mathrm{PuF_6} \rangle$	15,000	−109·0	25·3	260– 325	11·7	35·4
$\{\mathrm{PuF_6}\}$	7,200	− 21·5	—	325– 350		
$\langle \mathrm{UCl_3} \rangle$	72,000	− 81	13·8	298–1110	70·2	47·3
$\{\mathrm{UCl_3}\}$	65,000	−109	23·0	1110–1930		
$\langle \mathrm{PuCl_3} \rangle$	75,500	− 92·2	13·8	298–1040	73·7	48·7
$\{\mathrm{PuCl_3}\}$	69,100	−110·5	23·0	1040–2000		
$\langle \mathrm{ThCl_4} \rangle$	63,730	− 98·33	13·82	298–1043	63·14	59·9
$\{\mathrm{ThCl_4}\}$	49,090	−119·04	25·33	1043–1183		
$\langle \mathrm{UCl_4} \rangle$	51,900	− 93·0	13·8	298– 863	50·1	52·9
$\{\mathrm{UCl_4}\}$	45,500	−119·3	25·3	863–1062		
$\langle \mathrm{UCl_6} \rangle$	18,300	− 33·5	—	298– 400	18·8	35·1
$\langle \mathrm{UBr_3} \rangle$	75,100	− 91·8	13·8	298–1000	73·4	51·6
$\{\mathrm{UBr_3}\}$	68,600	−112·8	23·0	1000–1810		
$\langle \mathrm{PuBr_3} \rangle$	77,600	−117·6	20·7	298– 954	74·9	57·4
$\{\mathrm{PuBr_3}\}$	66,500	−112·8	23·0	954–1736		
$\langle \mathrm{ThBr_4} \rangle$	57,190	− 95·46	13·82	298– 952	56·4	56·72
$\{\mathrm{ThBr_4}\}$	45,950	−117·94	25·33	952–1124		
$\langle \mathrm{UBr_4} \rangle$	49,400	− 92·7	13·8	298– 792	47·6	52·6
$\{\mathrm{UBr_4}\}$	40,100	−114·6	25·3	792–1050		
$\langle \mathrm{ThI_4} \rangle$	52,960	− 94·21	13·82	298– 839	51·18	54·02
$\{\mathrm{ThI_4}\}$	43,320	−123·12	27·64	839–1105		
$\langle \mathrm{UI_4} \rangle$	56,400	−108·6	16·1	298– 779	54·3	61·7
$\{\mathrm{UI_4}\}$	42,600	−117·5	25·3	779–1030		
$\langle \mathrm{NpCl_4} \rangle$	53,156	−164·1	36·85	552–696	43·7	

[a] Values are from review articles, refs. 24–27.

TABLE 9. VAPOUR PRESSURE DATA FOR TRI-, TETRA- AND PENTAVALENT HALIDES[a]

$\log P_{mm} = -A/T + B$

Compound	Temperature range (°K)	A	B
$\langle PuF_3 \rangle$	1200–1440	21,120	9·410
$\{PuF_3\}$	1440–1770	19,400	8·392
$\langle PuF_3 \rangle$	1243–1475	20,734	9·288
$\langle AmF_3 \rangle$	1126–1469	24,628	34·007–7·048 log T
UCl_3	873–1273	12,000	10·000
$\langle PuCl_3 \rangle$	850–1007	15,910	12·726
$\{PuCl_3\}$	1007–1250	12,587	9·428
UBr_3	873–1273	15,000	12·500
$\langle PuBr_3 \rangle$	800–929	15,281	13·386
$\{PuBr_3\}$	929–1100	12,356	10·237
$\langle PuI_3 \rangle$		15,173	29·18–5·035 log T
$\{PuI_3\}$		13,008	30·16–6·042 log T
$\langle ThF_4 \rangle$		16,860	11·986
$\{ThF_4\}$		15,270	10·821
$\langle UF_4 \rangle$	555–1007	16,509	28·539–4·876 log T
$\{UF_4\}$	1018–1302	16,840	37·086–7·549 log T
$\langle NpF_4 \rangle$	876–1091	15,680	12·820
$\langle PuF_4 \rangle$		14,370	36·07–7·554 log T
$\{PuF_4\}$		18,124	37·97–7·554 log T
$\langle PuF_4 \rangle$	779–1125	14,577	12·1203
$\langle AmF_4 \rangle$	729–908	11,911	9·336
$\langle ThCl_4 \rangle$	974–1036	12,910	14·30
$\{ThCl_4\}$	1051–1183	7,987	9·57
$\langle UCl_4 \rangle$	623–778	10,427	13·30
$\{UCl_4\}$	863–1063	7,205	9·65
$\langle NpCl_4 \rangle$	552–696	9,547	12·904
$\langle ThBr_4 \rangle$	902–952	9,630	11·73
$\{ThBr_4\}$	952–1124	7,549	9·56
$\langle UBr_4 \rangle$	573–723	10,900	14·56
$\{UBr_4\}$	723–898	7,060	9·71
$\{ThI_4\}$	856–1105	7,577	9·09
$\langle UI_4 \rangle$	573–683	11,520	15·53
$\langle \alpha\text{-}UF_5 \rangle$		8,001	13·99
$\{\alpha\text{-}UF_5\}$		5,388	9·82
$\langle PaCl_5 \rangle$	509–578	4,843	10·35
$\{PaCl_5\}$	581–593	3,204	7·50

[a] Apart from those for $\langle UF_4 \rangle$[b] and $\langle NpF_4 \rangle$[c] the values are selected from review articles, refs. 6, 19, 31.

[b] E. G. Chudinov and D. Ya. Choporov, *Russ. J. Phys. Chem.* **44** (1970) 1106.

[c] E. D. Chudinov and D. Ya. Choporov, *Soviet Radiochem.* **12** (1970) 490.

TABLE 10. VAPOUR PRESSURE DATA FOR THE ACTINIDE HEXAFLUORIDES[a,b]

Compound	Temperature range (°C)	$\log P_{mm} =$
$\langle UF_6 \rangle$	0–64	$6{\cdot}38363 + 0{\cdot}0075377t - 942{\cdot}76/(t + 183{\cdot}416)$
$\{UF_6\}$	64–116	$6{\cdot}99464 - 1126{\cdot}288/(t + 221{\cdot}963)$
$\{UF_6\}$	116–230	$7{\cdot}69069 - 1683{\cdot}165/(t + 302{\cdot}148)$
$\langle NpF_6 \rangle$	0–55·10	$18{\cdot}48130 - 2892{\cdot}0/t - 2{\cdot}6990 \log t$
$\{NpF_6\}$	55·10–76·82	$0{\cdot}01023 - 1191{\cdot}1/t + 2{\cdot}5825 \log t$
$\langle PuF_6 \rangle$	0–51·59	$0{\cdot}39024 - 2095{\cdot}0/t + 3{\cdot}4990 \log t$
$\{PuF_6\}$	51·59–77·17	$12{\cdot}14545 - 1807{\cdot}5/t - 1{\cdot}5340 \log t$

[a] G. D. Oliver, H. T. Milton and J. W. Crysard, *J. Amer. Chem. Soc.* **75** (1953) 2827.

[b] E. E. Weaver, J. G. Malm and B. Weinstock, *J. Inorg. Nucl. Chem.* **11** (1959) 104.

2. COMPOUNDS WITH FLUORINE

Binary Fluorides

The presently known binary fluorides are listed in Table 1. This group of compounds reflects the valence state stability trends within the actinide series of elements and it is unlikely, with the possible exception of americium, that the elements beyond plutonium will form other than di-, tri- and tetrafluorides. Thus, high-temperature reactions involving fluorine and compounds of the elements thorium to californium inclusive result in the formation of ThF_4, PaF_5, UF_6, NpF_6, PuF_6, AmF_4, CmF_4, BkF_4 and CfF_4, respectively. Conversely, whilst simple oxide– or hydrated trifluoride–hydrogen fluoride reactions yield the trifluorides of the elements americium to californium inclusive, increasingly powerful reducing conditions are required for the formation of PuF_3, NpF_3 and UF_3. For example, whereas dioxide–hydrogen fluoride–hydrogen reactions result in the formation of the first two compounds, UF_3 is only obtained by high-temperature reduction of uranium tetrafluoride with reagents such as magnesium (500°C), aluminium (900°C) or uranium (1050°C). A similar trend is observed in the conditions required for tetrafluoride formation from, for example, the pentoxide (Pa) or dioxides (U to Pu inclusive). The reactions involve for protactinium, hydrogen fluoride–hydrogen mixtures, for uranium, hydrogen fluoride and for both neptunium and plutonium, hydrogen fluoride–oxygen mixtures.

It is apparent that whereas powerful reducing conditions will be essential for the preparation of thorium and protactinium trifluoride, if indeed they are capable of existence as condensed phases, the trifluorides of the elements einsteinium inclusive will be relatively easy to prepare. The only element likely to form a stable difluoride is nobelium which is known to exist in the divalent state in aqueous solution. In view of the recent preparation of neptunium pentafluoride[33] by reduction of NpF_6 with iodine in iodine pentafluoride, it would be interesting to investigate new methods for the preparation of the unknown plutonium pentafluoride.

In addition to reactions involving fluorine or hydrogen fluoride, many other methods are available for the preparation of actinide fluorides and the interested reader is referred to earlier review articles for details of the preparative methods for the individual compounds[6, 9, 11, 12, 14–19, 21].

Physical and Chemical Properties of the Trifluorides

The trifluorides of the elements up to and including curium crystallize at room temperature with the 9-coordinate LaF_3-type of structure; berkelium trifluoride is dimorphic, possessing this structure at high temperature and the 8-coordinate YF_3-type of structure at low temperature. It is predicted that californium trifluoride will transform to the former structure-type at *ca.* 700°C. The dimorphism observed for berkelium trifluoride[34] is consistent with the analogous structural change observed in the lanthanide trifluorides. Thus, this occurs between promethium and samarium which for coordination number 6 have ionic radii of 0·945 Å and 0·921 Å, respectively, compared with the values of 0·935 Å (LaF_3-type) and 0·928 Å (YF_3-type) for berkelium (Table 3). A view of the 9-coordinate lanthanum trifluoride structure is shown in Fig. 1[35]. The nine fluorines are in an irregular tricapped

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[33] S. Fried and J. Holloway, personal communication (1970).

[34] J. R. Peterson and B. B. Cunningham, *J. Inorg. and Nuclear Chem.* **30** (1968) 1775.

[35] A. Zalkin, D. H. Templeton and T. E. Hopkins, *Inorg. Chem.* **5** (1966) 1466.

Table 11. Crystallographic Data for the Actinide Fluorides

Compound	Colour	Symmetry*/space group	a_0 (Å)	b_0 (Å)	c_0 (Å)	$\beta°$	Ref.
AcF_3	White	H; D^4_{3d}–$P\bar{3}cl$	7·41	—	7·55	—	a
UF_3	Black	,, ,,	7·181	—	7·348	—	a
NpF_3	Purple	,, ,,	7·129	—	7·288	—	a
PuF_3	Violet-blue	,, ,,	7·093	—	7·254	—	a
AmF_3	Pink	,, ,,	7·044	—	7·225	—	b
CmF_3	White	,, ,,	6·999	—	7·179	—	b
BkF_3	Yellow-green	,, ,,	6·97	—	7·140	—	c
BkF_3	Yellow-green	O; D^{16}_{2h}–$Pnma$	6·70	7·09	4·410	—	c
CfF_3	—	,,	6·653	7·041	4·395	—	c
ThF_4	White	M; C^6_{2h}–$C2/c$	12·90	10·93	8·58	126·4	d
PaF_4	Brown	,, ,,	12·83	10·82	8·45	126·4	d
UF_4	Green	,, ,,	12·73	10·753	8·404	126·33	d
NpF_4	Green	,, ,,	12·64	10·70	8·36	126·4	d
PuF_4	Brown	,, ,,	12·59	10·69	8·29	126·0	d
AmF_4	Tan	,, ,,	12·56	10·58	8·25	125·9	d
CmF_4	Brownish-tan	,, ,,	12·51	10·61	8·20	125·8	d
BkF_4	—	,, ,,	12·47	10·58	8·17	125·9	d
CfF_4	Green	,, ,,	12·425	10·468	8·126	126·02	e
PaF_5	White	T; D^{12}_{2d}–$I\bar{4}2d$	11·53	—	5·19		f
α-UF_5	Bluish-white	T; C^5_{4h}–$I4/m$	6·525	—	4·472		g
β-UF_5	Bluish-white	T; D^{12}_{2d}–$I\bar{4}2d$	11·473	—	5·209		g
Pa_2F_9	Black	BCC; —	8·494	—	—		f
U_2F_9	Black	,, —	8·4545	—	—		h
UF_6	White	O; D^{16}_{2h}–$Pnma$	9·900	8·962	5·207		i
NpF_6	Orange	,, ,,	9·910	8·97	5·21		j
PuF_6	Brown	,, ,,	9·95	9·02	5·26		k

* H, hexagonal; O, orthorhombic; M, monoclinic; T, tetragonal; BCC, body-centred cubic.

[a] W. H. Zachariasen, *Acta Cryst.* **2** (1949) 388.

[b] L. B. Asprey, T. K. Keenan and F. H. Kruse, *Inorg. Chem.* **4** (1965) 985.

[c] J. R. Peterson and B. B. Cunningham, *J. Inorg. Nucl. Chem.* **30** (1968) 1775.

[d] T. K. Keenan and L. B. Asprey, *Inorg. Chem.* **8** (1969) 235.

[e] L. B. Asprey, personal communication (1972).

[f] L. Stein, *Inorg. Chem.* **3** (1964) 995.

[g] W. H. Zachariasen, *Acta Cryst.* **2** (1949) 296.

[h] W. H. Zachariasen, *Acta Cryst.* **2** (1949) 390.

[i] J. L. Hoard and J. D. Stroup, Paper 45, U.S.A.E.C. Report TID-5290, Book 1 (1958).

[j] J. G. Malm and B. Weinstock, *Proc. 2nd Int. Conf. Peaceful Uses Atomic Energy*, Vol. 28, p. 125. Geneva (1958).

[k] A. E. Florin, I. A. Tannenbaum and J. F. Lemons, *J. Inorg. Nuclear Chem.* **2** (1956) 368.

trigonal prismatic array around the metal atom. Unit cell dimensions for the actinide trifluorides are listed in Table 11.

Few magnetic data are available for the trifluorides. The effective magnet moment for uranium trifluoride[36] (3·67 B.M.; $\theta = -110°$) is close to that predicted (3·62 B.M.) for a $5f^3$ configuration and this configuration is supported by one interpretation of the results of a study of the paramagnetic resonance[37] of powdered uranium trifluoride. The magnetic susceptibility vs. T plot for plutonium trifluoride[38] is similar to those of samarium(III) compounds suggesting a $5f^5$ electronic configuration. The effective magnet moment for

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[36] M. Berger and M. J. Sienko, *Inorg. Chem.* **6** (1967) 324.

[37] M. C. M. O'Brien, *Proc. Phys. Soc.* 68A (1955) 351.

[38] J. K. Dawson, C. J. Mandelberg and D. Davies, *J. Chem. Soc.* (1951) 2047.

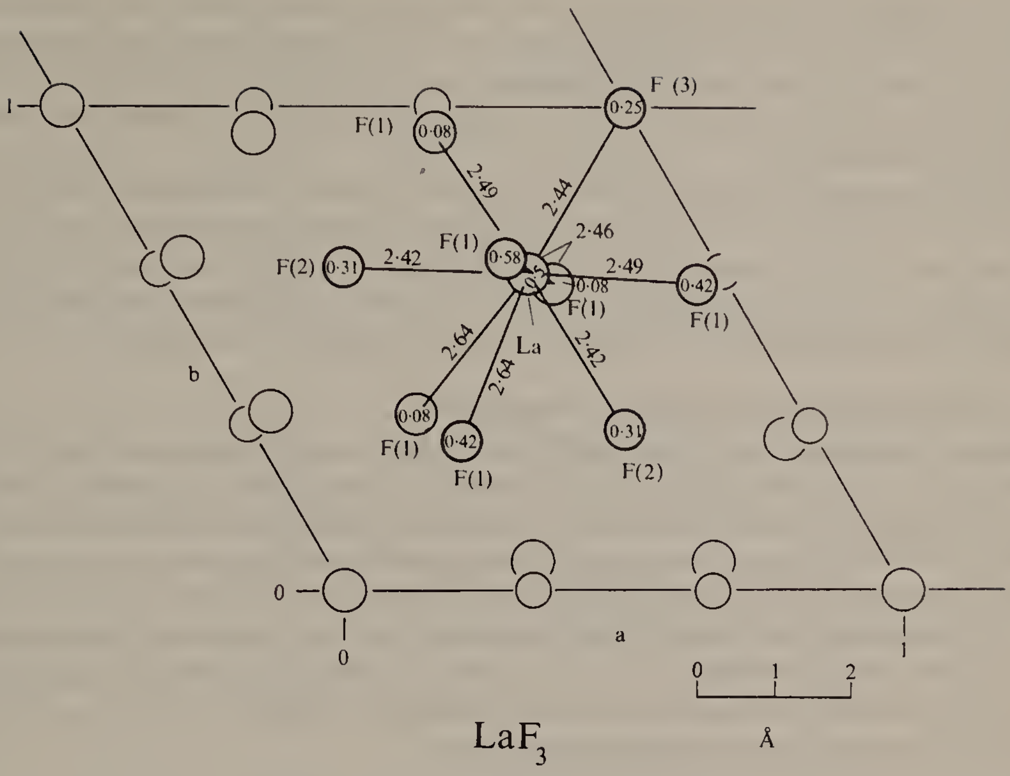

FIG. 1. The nine-fold coordination of lanthanum trifluoride as viewed down the c_0 axis. (Reproduced by permission from A. Zalkin *et al.*, *Inorg. Chem.* 5 (1966) 1466.)

curium trifluoride[39] is 7·71 B.M. ($\theta = -4°$ to $-7°$) whilst susceptibilities recorded for americium trifluoride[40] at 295°, 199° and 77°K are, respectively, 1040, 1290 and 1740 $\times 10^{-6}$ cgs units.

Solid state spectra have been recorded in the visible and near infrared regions for plutonium, americium and curium trifluoride (see refs. 6 and 19); band assignments are not available. Various thermochemical properties of the trifluorides are given in Tables 4, and 6–8 inclusive and the available vapour pressure data (plutonium and americium only) are listed in Table 9.

Few chemical properties have been recorded for the actinide trifluorides[6, 9,11,17,18,19]. Reduction by elements such as barium and calcium, which constitute an important route to the metals, is discussed elsewhere in this volume (p. 5). Plutonium, americium and curium trifluoride are stable in hydrogen at elevated temperatures. Fluorine oxidation at high temperature leads either to hexafluoride (U to Pu inclusive) or tetrafluoride (Am to Cf inclusive) formation and oxidation of uranium trifluoride by the remaining halogen elements results in the formation of mixed tetravalent compounds of the type UF_3X (X = Cl, Br or I).

Plutonium trifluoride undergoes the unusual, reversible reaction,

$$PuF_3 + O_2 \underset{\text{vac.}}{\overset{\text{1 atm } O_2,\ 600°}{\rightleftharpoons}} PuF_4 + PuO_2$$

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[39] A. Sayed-Marel, U.S. Report UCRL-11984 (1965).
[40] W. W. T. Crane, J. C. Wallmann and B. B. Cunningham, U.S. Report UCRL-846 (1950).

with dry oxygen[41,42]; in the presence of water vapour above 300°C, the product is the dioxide. Similarly uranium trifluoride is oxidized to U_3O_8 when heated in air; it dissolves in oxidizing acids to yield soluble uranium(VI) species. Plutonium trifluoride is virtually insoluble in water but dissolves slightly in aqueous acid media to form blue solutions containing plutonium(III).

The only complexes known with neutral donor ligands are trifluoride "hydrates" of plutonium, americium and curium which precipitate from aqueous fluoride media. For the first, compositions in the range $PuF_3 \cdot 0{\cdot}4H_2O$ to $PuF_3 \cdot 0{\cdot}75H_2O$ have been reported; the water appears not to be coordinated and the "hydrates" are readily converted to their respective anhydrous trifluorides. Complex fluoride formation is discussed later (p. 169).

Physical and Chemical Properties of the Tetrafluorides

The tetrafluorides are high-melting solids all of which possess the 8-coordinate UF_4-type of structure[43] (as do ZrF_4 and HfF_4) in which the metal atom is surrounded by eight fluorines arranged as a slightly distorted antiprism (Fig. 2); U–F bond distances range from 2·249 Å to 2·318 Å. Keenan and Asprey[44] have recently reported accurate unit cell parameters for the tetrafluorides (Table 11) and shows that an atomic volume vs. atomic number plot is a smooth curve, as observed also for several series of tetravalent fluoro-complexes (Fig. 3). Little overall decrease in size is predicted for the transberkelium actinide tetrafluorides provided they are isostructural with the earlier members of the series. The tetrafluorides are monomeric in the vapour phase.

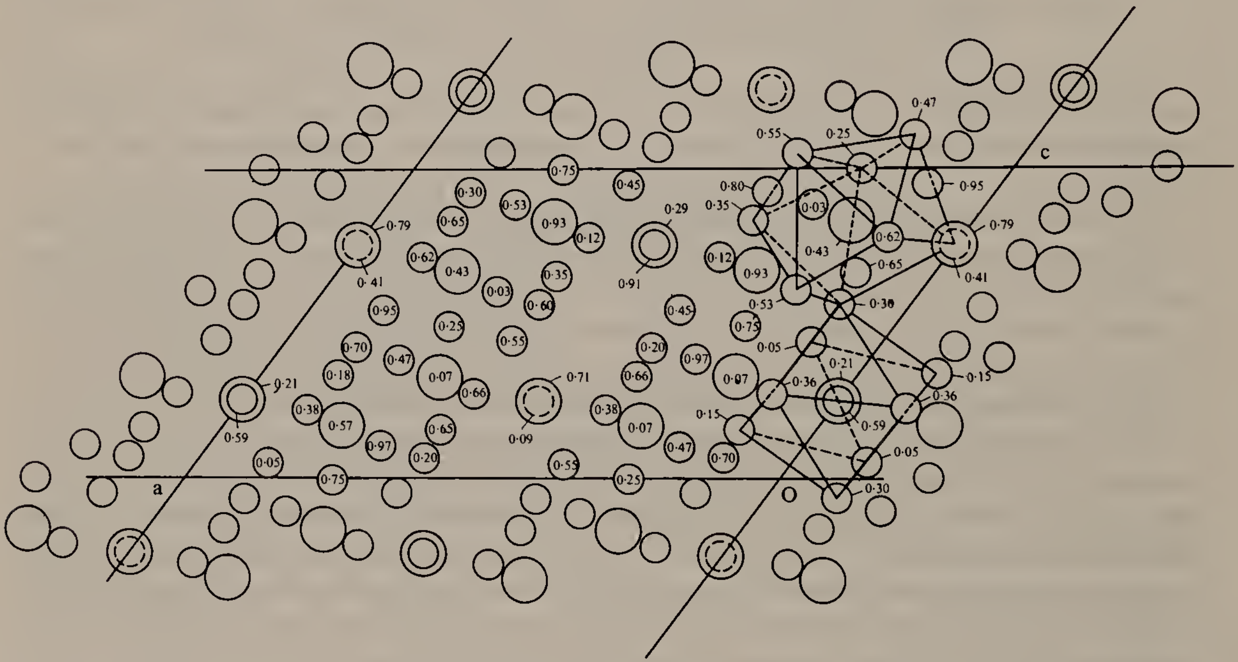

FIG. 2. The structure of UF_4 viewed down the b_0 axis. Numbers represent the positional parameter y as a fraction of the unit cell. (Reproduced by permission from A. C. Larson *et al.*, *Acta Cryst.* **17** (1969) 555.)

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[41] S. Fried and N. R. Davidson, ref. 1, p. 784.

[42] J. K. Dawson, R. M. Elliott, R. Hurst and A. E. Truswell, *J. Chem. Soc.* (1954) 558.

[43] A. C. Larson, R. B. Roof Jnr. and D. T. Cromer, *Acta Cryst.* **17** (1964) 555.

[44] T. K. Keenan and L. B. Asprey, *Inorg. Chem.* **8** (1969) 235.

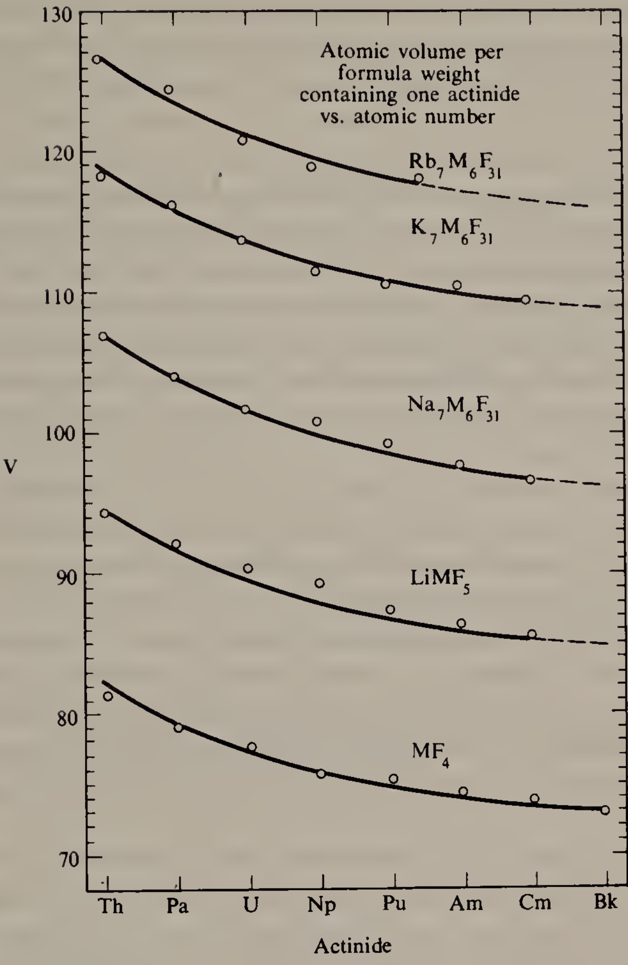

FIG. 3. Volume per formula weight (1 mole of actinide) ratio vs. atomic number for tetravalent actinide fluorides. (Reproduced by permission from T. K. Keenan and L. B. Asprey, *Inorg. Chem.* **8** (1969) 235.)

Magnetic susceptibility data on MF_4–ThF_4 mixtures have been interpreted on the basis of $6d^2$ and $5f^4$ electronic configurations for uranium[45] and plutonium[45,46] tetrafluoride respectively. The former assignment is supported by the results of paramagnetic resonance studies[47] with the powdered tetrafluoride. Visible absorption spectra have been recorded for solid protactinium[48], uranium[49], neptunium[50], americium[51] and curium[51] tetrafluoride. A complete 41-level f^3 intermediate spin–orbit coupling diagram has been constructed on the basis of the neptunium tetrafluoride results. Values of the spin–orbit coupling constant (τ) and the coulomb interaction parameter (F_2) are 2178 and 323·4 cm^{-1}, respectively[50].

Various thermodynamic data are given in Tables 4 and 6–8 inclusive; results of vapour pressure studies are shown in Table 9.

[45] J. K. Dawson, *J. Chem. Soc.* (1951) 429, 2889; (1952) 1185, 1882.
[46] W. B. Lewis and N. Elliott, *J. Chem. Phys.* **27** (1957) 904.
[47] S. N. Gosh, W. Goody and D. Hill, *Phys. Rev.* **96** (1954) 36.
[48] L. B. Asprey, F. H. Kruse, R. A. Penneman, *Inorg. Chem.* **6** (1967) 544.
[49] D. M. Gruen and M. Fred, *J. Amer. Chem. Soc.* **76** (1954) 3850.
[50] L. P. Vargo, M. J. Reisfeld and L. B. Asprey, *J. Chem. Phys.* **53** (1970) 250.
[51] L. B. Asprey and T. K. Keenan, *J. Inorg. Nucl. Chem.* **7** (1958) 27.

Raman and infrared vibrations have been recorded at 614 (R), 420 (R; i.r.), 340 (R) and 180 (R; i.r.) cm^{-1} for uranium tetrafluoride[52]; a metal–fluorine vibration has been recorded at 520 cm^{-1} for gaseous thorium tetrafluoride[53] and at *ca.* 400 cm^{-1} for protactinium tetrafluoride[54].

The chemical properties of uranium tetrafluoride have been fairly extensively investigated, but those of the remaining tetrafluorides have scarcely been studied[6,15,19]. Reduction to the metals is discussed earlier (p. 5); in addition, hydrogen is known to reduce plutonium tetrafluoride to the trifluoride (cf. the conditions required for reduction of uranium tetrafluoride (p. 161) and will probably similarly reduce the later tetrafluorides. Fluorine oxidizes the appropriate compounds to PaF_5, UF_6, NpF_6 and PuF_6, respectively, and bromine tri- and pentafluorides will also oxidize uranium tetrafluoride and neptunium tetrafluoride but not plutonium tetrafluoride. The remaining tetrafluorides are stable towards fluorine at elevated temperature.

Thorium tetrafluoride and the dioxide interact to yield $ThOF_2$[55] (cf. the PuF_4/PuO_2 reaction above), but no similar reaction occurs with UF_4. Intermediate fluorides such as U_2F_9, U_4F_{17} and U_5F_{22}, as well as α-UF_5 and β-UF_5, are formed when UF_4 and UF_6 are heated together at moderate temperatures[6].

The tetrafluorides of thorium to plutonium inclusive are only slightly soluble in water; crystalline hydrates of the type $MF_4 \cdot 2{\cdot}5H_2O$ (M = Th, U and Pu) precipitate from aqueous media and various lower hydrates have been reported for these elements[6,19]. However, since tetravalent americium is unstable in 15 M ammonium fluoride, it is unlikely that tetrafluoride hydrates of the elements beyond plutonium will form in aqueous media.

Physical and Chemical Properties of Intermediate and Pentavalent Fluorides

PaF_5 and β-UF_5 are isostructural as are Pa_2F_9 and U_2F_9 (Table 11). Single-crystal structural data are not available, but on the basis of X-ray powder data, Zachariasen[56] suggests that the uranium atoms in α-UF_5 and β-UF_5 are, respectively, 6- and 7-coordinate whilst those in U_2F_9 are 9-coordinate. The magnetic susceptibility of β-UF_5 shows Curie–Weiss dependence[57] between 125° and 420°K with $\mu_{eff} = 2{\cdot}24$ B.M. ($\theta = -75{\cdot}4°$). Thermodynamic data for the uranium compounds are listed in Tables 4, 6 and 7. They are all thermally unstable, disproportionating at high temperatures to form the tetra- and hexafluoride; vapour pressure results for α-UF_5, obtained in the presence of uranium hexafluoride to limit disproportionation, are given in Table 9. Protactinium pentafluoride is, surprisingly, relatively involatile, subliming only above 500°C *in vacuo*.

Apart from complex fluoride formation (p. 173) few chemical properties are known for the pentafluorides. Both PaF_5 and UF_5 are moisture-sensitive, the latter disproportionating to U(IV) and U(VI) in most aqueous media. The only known complexes with donor ligands appear to be $PaF_5 \cdot H_2O$ and $PaF_5 \cdot 2H_2O$[18].

Physical and Chemical Properties of the Hexafluorides

The available crystallographic data are given in Table 11. Although the molecules in the crystals do not appear to be perfect octahedra, spectral and electron diffraction studies have

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[52] W. Krasser and H. W. Nuernberg, *Spectrochim. Acta*, **26** (1970) 1059.

[53] A. Büchler, J. B. Berkowitz-Muttack and D. H. Dugre, *J. Chem. Phys.* **34** (1961) 2202.

[54] L. Stein, *Proc. Int. Conf. Phys. Chim. Protactinium*, p. 101. C.N.R.S., Paris (1966).

[55] R. W. M. D'Eye, *J. Chem. Soc.* (1958) 196.

[56] W. H. Zachariasen, *Acta Cryst.* **2** (1949) 296, 390.

[57] H. Nguyen-Nghi, H. Marquet-Ellis and A. J. Dianoux, *Compt. Rend.* **259** (1964) 4683.

shown that in the liquid and vapour states the hexafluorides possess regular octahedral symmetry (see refs. 6, 15, 17, 21 and 58). Infrared and Raman bands are listed in Table 12 together with metal–fluorine bond distances derived from electron diffraction studies. Many of the earlier spectral studies have been reviewed by De Witt[21] and by Weinstock and Goodman[58]. Force constant calculations will be found in these and other articles[59–63]. Visible and near infrared spectral data, 2000–21,000 Å, are available for gaseous NpF_6[64] and PuF_6[65]; peaks at 12,970 and 2210 Å (NpF_6) and at 10,075 and 3157 Å (PuF_6) obey Beer's Law and are useful for quantitative analysis of gaseous hexafluoride mixtures.

Uranium and plutonium hexafluoride exhibit weak, almost temperature-independent, paramagnetism; it is suggested that for the latter[66] the first excited state must be at least 1000 cm^{-1} (0·12 eV) above the non-degenerate ground state, f^2, with the two non-bonding electrons occupying the f_β level with spins paired. The g value derived for NpF_6 from magnetic studies[67] on NpF_6/UF_6 mixtures, −0·605, is in agreement with that obtained by N.M.R. studies[68], −0·604.

The actinide hexafluorides are all low-melting solids; the most reliable vapour pressure data are shown in Table 10. Although the volatilities of the liquids increase in the order $PuF_6 < NpF_6 < UF_6$, neptunium hexafluoride is anomalous in possessing the highest vapour pressure in the solid state; this observation is not clearly understood. Various thermodynamic values are listed in Tables 4 and 6–8 inclusive.

TABLE 12. FUNDAMENTAL VIBRATIONAL FREQUENCIES[a] AND METAL–FLUORINE BOND DISTANCES[b] IN THE VAPOUR STATE

Compound	ν_1 (R)	ν_2 (R)	ν_3 (i.r.)	ν_4 (i.r.)	ν_5 (R)	ν_6 (inactive)	M–F (Å)
UF_6	667·1	532·5	624	186·2	202	(142)	1·996
NpF_6	654	535	624	198·6	208	(164)	1·981
PuF_6	(628)	(523)	616	206·0	(211)	(173)	1·971

[a] E. L. Grasner and B. Frlec, *J. Chem. Phys.* 49 (1968) 5135.
[b] M. Kimura, V. Schomaker, D. W. Smith and B. Weinstock, *J. Chem. Phys.* 48 (1968) 4007.

Uranium hexafluoride is technologically important for the separation of the fissile isotope U-235 from natural uranium by gas phase diffusion or centrifugation and, consequently, its physical properties have been extensively investigated. Selected constants are listed in Table 13; these properties and those available for plutonium hexafluoride will not be discussed and the reader is referred to various other compilations[1–19,21], particularly those of De Witt[21] and Steindler[12].

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[58] B. Weinstock and G. L. Goodman, *Adv. Chem. Phys.* 11 (1965) 169.
[59] G. Nagarayan, *Bull. Soc. Chim. Belg.* 71 (1962) 77; 72 (1963) 276.
[60] M. Kimura and K. Kimura, *J. Mol. Spect.* 11 (1963) 368.
[61] S. N. Thakur and D. K. Rosi, *J. Mol. Spect.* 19 (1966) 341.
[62] C. W. F. J. Pistorius, *J. Chem. Phys.* 29 (1958) 1328.
[63] S. J. Cyrin and J. Brunroll, *Acta Chem. Scand.* 22 (1968) 2739.
[64] M. J. Steindler and W. J. Gerding, *Spectrochim. Acta*, 22 (1966) 1197.
[65] M. J. Steindler and W. H. Günther, *Spectrochim. Acta*, 20 (1964) 1319.
[66] D. M. Gruen, J. G. Malm and B. Weinstock, *J. Chem. Phys.* 24 (1956) 905.
[67] C. A. Hutchinson, Tung Tsang and B. Weinstock, *J. Chem. Phys.* 37 (1962) 555.
[68] C. A. Hutchinson and B. Weinstock, *J. Chem. Phys.* 32 (1960) 56, and references therein.

TABLE 13. PHYSICAL CONSTANTS FOR URANIUM HEXAFLUORIDE[a]

Property	Value	Temperature (°C)
Critical temperature (°C)	230·2±0·2	—
Critical pressure (atm)	45·5±0·5	—
Density, solid (g cm^{-3})	5·060±0·005	25
Density, liquid (g cm^{-3})	3·595	70
Viscosity, liquid (centipoise)	0·91	70
Viscosity, gas (micropoise)	199·9	80
Surface tension (dyne cm^{-1})	16·8±0·3	70
Refractive index, liquid (4360 Å)	1·383	70
Molecular refraction (cc, 4360 Å)	22·59±0·08	85
Dielectric constant, liquid	2·18	65
Dielectric constant, gas	1·00292±0·000003	67·4
Thermal conductivity, gas (cal sec^{-1} cm^2 °C cm^{-1})	$1{\cdot}0\times10^{-5}$	5

[a] Taken from ref. 6.

The hexafluorides can be safely handled in Pyrex or quartz, provided water is absent. All three are decomposed to lower fluorides by α-activity, the rate being greatest for plutonium hexafluoride (up to 2% per day); consequently it is advisable to store PuF_6 in the vapour state. Plutonium hexafluoride is also reduced by γ-radiation and, in contrast to uranium hexafluoride, both the neptunium and plutonium compounds are susceptible to photodecomposition. Plutonium hexafluoride is also thermally unstable, but the extent of decomposition at 60–70°C is sufficiently small to permit transport by vacuum distillation or transpiration in helium or fluorine without significant loss.

The hexafluorides decrease in stability from uranium to plutonium[6,15,19]. Thus, uranium hexafluoride is stable towards nitrogen, chlorine, bromine, carbon dioxide and bromine trifluoride, whereas plutonium hexafluoride is reduced by these and a wide range of other reagents[19], in particular sulphur tetrafluoride (30°C) and uranium tetrafluoride (25°C). Both hexafluorides undergo reduction to their respective tetrafluorides in the presence of hydrogen, carbon tetrachloride and carbon disulphide; the UF_6/H_2 reaction has a high energy of activation and is slow even at 600°C. The reduction of UF_6 by hydrogen bromide at 80° provides a useful route to α-UF_5[69]. The chemical reactivity of neptunium hexafluoride, which is presumably intermediate, has scarcely been studied.

All three hexafluorides react violently with water at room temperature; under controlled conditions these reactions yield the hexavalent oxyfluorides, MO_2F_2. Hydrates and complexes with other oxygen donor ligands are unknown.

Phase relations in binary systems such as UF_6–BrF_3, UF_6–BrF_5, UF_6–ClF_3 and UF_6–HF are discussed in detail by De Witt[12]. More recently the UF_6–PuF_6[70], UF_6–MoF_6[71,72], UF_6–WF_6[72,73] and UF_6–NbF_5[74] systems have been studied. The congruently melting compound $UF_6\cdot XeF_2$ is reported to form in the UF_6–XeF_2 phase system[75].

[69] A. S. Wolf, W. E. Hobbs and K. E. Rapp, *Inorg. Chem.* 4 (1965) 755.

[70] L. E. Trevorrow, M. J. Steindler, D. V. Steidl and J. T. Savage, *Inorg. Chem.* 6 (1967) 1060.

[71] L. E. Trevorrow, M. J. Steindler and D. V. Steidl, Adv. Chem. Series 71, *Lanthanide/Actinide Chemistry*, p. 308. Amer. Chem. Soc., Washington (1967).

[72] W. D. Hedge, U.S. Report K-1697 (1968).

[73] V. N. Prusakov and V. K. Ezhov, *Atomneya Energ.* **25** (1968) 35 and 64.

[74] V. N. Prusakov and V. K. Ezhov, *Atomneya Energ.* **28** (1970) 496.

[75] V. K. Ezhov, V. N. Prusakov and B. B. Chaivanova, *Atomneya Energ.* **28** (1970) 497.

Reduction of NpF_6 and PuF_6 on contact with alkali metal fluorides, which leads to the formation of penta- or tetravalent fluoro-complexes, is discussed below. Uranium hexafluoride is not reduced under these conditions and forms stable hexavalent fluoro-complexes.

Fluoro-complexes

Complex fluorides are formed by the actinide elements in the valence states 3–6 inclusive. A wide range of complex types is known for the tetravalent elements with fewer for the tri- and pentavalent elements; only uranium forms stable hexavalent fluoro-complexes. General preparative methods are discussed very briefly in the following sections; more detailed discussions are available elsewhere[6,15,19], and for a systematic treatment of the structural properties of the fluoro-complexes the recent article by Penneman *et al.*[76] is recommended. Crystallographic data are also dealt with in other recent articles[6,15,17,19]. No thermodynamic data are available.

Trivalent Fluoro-complexes

In contrast to the many lanthanide complexes known, very few trivalent actinide complexes have been characterized. However, on the basis of ionic radius ratios (M^+/M^{3+}) Thoma[77] predicts that 1 : 1 complexes ($M^IM^{III}F_4$) will be formed by all the actinide elements for M^I = Na, and for Ac to Es inclusive for M^I = K. The existence of 3 : 1 complexes ($M_3{}^IM^{III}F_6$) is also predicted for the elements U to Lr inclusive for M^I = Rb and Cs. In view of the more recent characterization of K_3UF_6[78], it now appears likely that 3 : 1 complexes will also be formed for U to Lr inclusive when M^I = K.

No complex formation occurs in the LiF–UF_3, LiF–PuF_3 and LiF–AmF_3 systems; on size considerations complex formation (1 : 1) is likely to be first observed with Cf^{3+}. A single equilibrium compound exists in the NaF–UF_3 and NaF–PuF_3 systems, $NaM^{III}F_4$, and $NaAmF_4$ has been observed to form on the hydrogen reduction of $Na_7Am_6F_{31}$. $NaAmF_4$, $KPuF_4$, $KAmF_4$, KPu_2F_7 and KAm_2F_7 have all been prepared by heating the appropriate oxide with sodium carbonate or sodium fluoride in a hydrogen–hydrogen fluoride mixture at 350–650°C. The only other complexes known are those of the type $M_3{}^IUF_6$ (M^I = K, Rb and Cs). The reader is referred to earlier articles[6,17,19,76] for details of the original references pertaining to the preparation and crystallographic properties of these compounds.

Tetravalent Fluoro-complexes

A large range of stoichiometries is found for actinide(IV) fluoro-complexes with univalent cations[6,76]. The complexes known for M^I = Li, Na, K, Rb, Cs and NH_4 are indicated in Table 14 together with the predictions of Thoma[77], modified to take account of more recent studies, concerning the existence of tetravalent complexes.

Several general methods of preparation are available. These include:

(a) Reaction between the appropriate fluorides at elevated temperatures.
(b) Reaction between the appropriate tetrafluoride or dioxide and the alkali metal fluoride or carbonate in hydrogen fluoride or hydrogen fluoride–oxygen mixtures.

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[76] R. A. Penneman, R. R. Ryan and A. Rosenweig, *Structure and Bonding*, in press (1973).
[77] R. E. Thoma, *Inorg. Chem.* **1** (1962) 220.
[78] R. E. Thoma, H. A. Friedman and R. A. Penneman, *J. Amer. Chem. Soc.* **88** (1966) 2046.

TABLE 14. COMPLEX FORMATION IN THE MF_4–MF SYSTEMS

	Lithium Fluoride							Sodium Fluoride								
		Stoichiometry							Stoichiometry							
MF_4	M^+/M^{4+} ratio	4:1	3:1	1:1	1:2	1:4	1:6	M^+/M^{4+} ratio	4:1	3:1	7:2	2:1	7:6	1:1*	1:2
ThF_4	0·69		a	a	a	a	a	0·99	a	a	a	a	a	a†	a
PaF_4	0·71		b	a		b		1·02		a		b	a		b
UF_4	0·73	a	a	a		a		1·05		a	a	a	a	a	a
NpF_4	0·74		b	a		b		1·06		b		a	a		
PuF_4	0·76	a	b	a		b		1·09		b		a	a		
AmF_4	0·76		b	a		b		1·10		b		b	a		
CmF_4	0·77		b	a		b		1·11		b		b	a		
BkF_4	0·77		b	b		b		1·11		b		b	a		
CfF_4			b	b		b				b		b	a		

	Potassium Fluoride									Rubidium Fluoride									
		Stoichiometry									Stoichiometry								
MF_4	M^+/M^{4+} ratio	5:1	3:1	7:2	2:1	7:6	1:2	1:3	1:6	M^+/M^{4+} ratio	5:1	3:1	7:2	2:1	7:6	1:1	2:3	1:3	1:6
ThF_4	1·34	a	a†	a	a	a	a	a	a	1·49	a	a	a	a	a			a	a
PaF_4	1·38		a		b	a	b	b	b	1·54		b		b	a			b	b
UF_4	1·43		a		a	a	a	a	a	1·59		a		a	a	a	a	a	a
NpF_4	1·44		b		b	a	a			1·61		b		a	a	b			
PuF_4	1·48		b		a	a	a			1·64		b		a	a	b			
AmF_4	1·49		b		b	a				1·66		b		a	c	b			
CmF_4	1·51		b		b	a				1·68		b		a	c	b			
BkF_4	1·51		b		b	a				1·68		b		b		b			
CfF_4			b		b	b						b		b		b			

	Caesium Fluoride								Ammonium Fluoride						
	M^+/M^{4+} ratio	Stoichiometry							M^+/M^{4+} ratio	Stoichiometry					
MF_4		3:1	2:1	1:1	2:3	1:2	1:3	1:6		4:1	3:1	2:1	7:6	1:1	1:3
ThF_4	1·69	*a*	*a*	*a*	*a*	*a*	*a*	*a*	1·43	*a*	*a*			*a*	
PaF_4	1·74	*b*	*b*	*b*	*b*	*b*			1·48	*a*				*b*	
UF_4	1·80	*a*	*a*	*a*	*a*	*a*		*a*	1·53	*a*		*a*	*a*	*a*	*a*
NpF_4	1·82	*b*	*b*	*b*					1·54	*a*		*b*	*a*	*b*	
PuF_4	1·86	*b*	*a*	*a*					1·57	*a*		*a*	*a*	*a*	*a*
AmF_4	1·88	*b*	*b*	*b*					1·59	*a*					
CmF_4	1·90	*b*	*b*	*b*					1·61						
BkF_4	1·90	*b*	*b*	*b*					1·61						
CfF_4		*b*	*b*	*b*											

a, Complex known.
b, Complex formation predicted[77].
c, Complex formation predicted by Thoma[77], but attempts to prepare them have been unsuccessful.
* Some complexes reported as 1:1 are more probably, on the basis of X-ray data, the 7:6 species.
† Metastable phase.

(c) Evaporation of acidic solutions containing the stoichiometric amounts of the appropriate elements followed by treatment at 300°C with hydrogen–hydrogen fluoride mixtures (Np), hydrogen fluoride alone (Pu) or fluorine (Am and Cm).
(d) Precipitation from aqueous solution followed by heating in air, *vacuo* or fluorine.
(e) Hydrogen reduction of pentavalent fluoro-complexes (Pa) or reduction of the hexafluoride (Pu) on contact with the appropriate alkali metal fluoride.
(f) The thermal decomposition of tetravalent complexes of higher stoichiometry, e.g. $(NH_4)_4M^{IV}F_8$ (U and Pu).

For details of individual preparations and of various phase diagrams, earlier review articles are recommended[6,15,17,19].

Analogous complexes formed by the elements Th to Cf inclusive are frequently isostructural and, indeed, the majority of the complexes known for elements beyond americium have been identified by X-ray powder diffraction analysis. Some interesting structures have been reported for certain of the tetravalent complexes and in view of the large tetravalent ionic radii (Table 3) it is not surprising to find that all exhibit high coordination numbers. Complexes of the type $LiM^{IV}F_5$ (M^{IV} = Th to Cm inclusive) all possess tetragonal symmetry[79] with the $LiUF_5$-type of structure[80] in which the U^{4+} atom has nine fluorine nearest neighbours arranged as a tri-capped trigonal prism. Adjacent prisms share edges and corners to form a network; U–F bond distances range from 2·26 to 2·59 Å.

The 7:6 complexes are all isostructural with $Na_7Zr_6F_{31}$, possessing rhombohedral symmetry, space group C^2_{3i}–$R\bar{3}$[6,76]. The basic structural unit is an approximately square antiprism formed by eight fluorines around the metal atom; six such antiprisms share corners to form an octahedral array which encloses a cavity containing one additional fluorine atom[81].

Full structural data are also available for $(NH_4)_4UF_8$[82] with which all the 4:1 ammonium complexes apart from $(NH_4)_4ThF_8$ are isostructural[76]. In $(NH_4)_4UF_8$ there is a discrete 8-coordinate, dodecahedral array of fluorines around the uranium atom with U–F bond distances between 2·25 and 2·33 Å[82]. In contrast to this, the slightly larger Th atom in $(NH_4)_4ThF_8$ is 9-coordinate[83], the fluorines being arranged in a distorted tri-capped trigonal prismatic array (cf. K_2PaF_7, p. 175) with prisms sharing edges to form chains. Th–F bond distances for shared and unshared fluorine atoms are 2·59 and 2·25 Å, respectively; one fluorine is not bonded and lies 4·98 Å from the nearest thorium atom.

Other series of isostructural complexes include that of the type $KM_2^{IV}F_9$ (M^{IV} = Th–Pu inclusive)[76]. KU_2F_9 possesses orthorhombic symmetry, space group D^{16}_{2h}-*Pnma*; each uranium atom is surrounded by a trigonal prismatic array of fluorine atoms with a pyramid on each of the three faces. The U–9F bond distances range from 2·29 to 2·39 Å[84]. A similar stereochemistry is found for β_1-K_2UF_6 for which U–F shared and unshared bond lengths are, respectively, 2·38 and 2·22 Å[85]. β_1-K_2ThF_6, β_1-K_2NpF_6 and Rb_2ThF_6 are isostructural[19,76]. The remaining 2 : 1 rubidium complexes (U–Cm inclusive) all possess the 8-coordinate Rb_2UF_6-type of structure in which eight fluorines are arranged as a dodecahedron around each metal atom[76].

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[79] T. K. Keenan, *Inorg. Nucl. Chem. Letters*, **2** (1966) 153.
[80] G. D. Brunton, *Acta Cryst.* **21** (1964) 814.
[81] J. H. Burns, R. D. Ellison and H. A. Levy, *Acta Cryst.* **24B** (1968) 230.
[82] A. Rosenweig and D. T. Cromer, *Acta Cryst.* **26B** (1970) 38.
[83] R. R. Ryan, R. A. Penneman and A. Rosenweig, *Acta Cryst.* **25B** (1969) 1958.
[84] G. Brunton, *Acta Cryst.* **25B** (1969) 1919.
[85] G. Brunton, *Acta Cryst.* **25B** (1969) 2163.

Compilations of unit cell data are available[6,19,76] for the tetravalent fluoro-complexes and these will not be repeated here. The reader is also referred to these articles[6,19,76] for detailed discussions of the structural aspects of other tetravalent actinide fluoro-complexes including those of the type $M^{II}M^{IV}F_6$ (M^{II} = Ca, Sr, Ba, Pb, Cd and Eu; M^{IV} = variously Th, U, Np and Pu) which possess the LaF_3-type of structure.

The value of molar refractivity in the determination of transition metal fluoro-complex composition is discussed in detail by Penneman[86]. Essentially he demonstrates that the molar refractivities of a series of complex fluorides containing a common alkali fluoride are a linear function of composition. For example, the refractivities of a series such as $UF_4 \cdot NaF$, $UF_4 \cdot 2NaF$ and $UF_4 \cdot 3NaF$ can be expressed as:

$$R_{UF_4 \cdot nNaF} = R_{UF_4} + nR_{NaF} \ (n = 1, 2 \text{ or } 3)$$

Similar relationships hold for the tetravalent complexes containing the Li, K, Rb, NH_4 and Cs cations, each linear plot having a different slope but the same origin at R_{UF_4}. It should also be noted that the coordination number of the actinide (or lanthanide) ion and the presence or absence of shared fluorine atoms have little or no effect on the linearity of the refractivity. This additivity also applies to tri- and pentavalent fluoro-complexes.

Pentavalent Fluoro-complexes

Three types of pentavalent fluoro-complexes are known, $M^IM^VF_6$, $M^I_2M^VF_7$ and $M^I_3M^VF_8$, for the elements Pa to Np inclusive and examples of the first two types are known for plutonium. References to the original preparations are given elsewhere[6,19]. Whereas all three types can be crystallized from aqueous hydrofluoric acid solution for Pa(V), only *hexa*fluorouranates(V) can be prepared in this manner. Other uranium(V) complexes are obtained by a variety of solid state reactions, which may also be employed for the hexafluoro-complexes, whereas the neptunium(V) and plutonium(V) complexes are only obtained by fluorine oxidation of tetravalent compounds mixed with the appropriate univalent fluoride or by reduction of the hexafluoride by contacting it with an alkali metal fluoride. In certain instances, e.g. $NOUF_6$, NO_2UF_6, $N_2H_6(UF_6)_2$, $(N_2H_6)UF_7$, NH_4UF_6, reduction of uranium hexafluoride by the appropriate reagents may be employed. However, uranium hexafluoride, unlike NpF_6 and PuF_6, is not reduced on contact with alkali metal fluorides at room temperature. The presently known complexes are shown in Table 15.

TABLE 15. SOME PENTAVALENT ACTINIDE FLUORO-COMPLEXES*

Complex type	M^V	M^I
$M^IM^VF_6$	Pa	Na, K, Rb, Cs, NH_4
	U	Li, Na, K, Rb, Cs, NH_4, Ag, Tl, NO, NO_2, N_2H_6
$M^I_2M^VF_7$	Pa	K, Rb, Cs, NH_4
	U	K, Rb, Cs, NH_4
$M^I_3M^VF_8$	Pa	Li, Na, K, Rb, Cs
	U	Na, K, Rb, Cs, NH_4, Ag, Tl

* The only neptunium and plutonium complexes known are $CsNpF_6$, $CsPuF_6$, Rb_2NpF_7, Rb_2PuF_7 and Na_3NpF_8[6,17].

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[86] R. A. Penneman, *Inorg. Chem.* 8 (1969) 1379.

The first examples of hydrated uranium(V) fluoro-complexes, $M^{II}U_2F_{12}\cdot 4H_2O$ (M^{II} = Co, Ni and Cu), were reported recently[87]; they precipitate on the addition of the appropriate difluoride to β-UF_5 in 48–50% hydrofluoric acid.

The available crystallographic data are listed in Table 16 together with an indication, if the information is available, of the structure types of the compounds. Several of the 1:1 complexes are isostructural with $RbPaF_6$ in which the protactinium atom is 8-coordinate[88], the fluorines being arranged as a dodecahedron with Pa–F distances of 2·35 Å (four shared fluorines) and 2·08 Å (four unshared fluorines). With the larger caesium atom and slightly smaller U(V), Np(V) and Pu(V) ions, however, there is a structural change and compounds of the type $CsM^{V}F_6$ (M^{V} = U, Np and Pu) exhibit the 6-coordinate $KOsF_6$-type of structure[76]. The derived ionic radius for U^{5+} in $CsUF_6$ is 0·73 Å.

TABLE 16. CRYSTALLOGRAPHIC DATA FOR THE PENTAVALENT FLUORO-COMPLEXES[a]

Compound	Colour	Symmetry	Structure type	a_0 (Å)	b_0 (Å)	c_0 (Å)	$\beta°$
$LiUF_6$	Pale blue	R ($R\bar{3}$)*	$LiSbF_6$	5·262	—	14·295	
$NaPaF_6$	White	T	—	5·35	—	3·98	
α-$NaUF_6$	Pale blue	R	$LisSbF_6$	5·596	—	15·526	
β-$NaUF_6$	Pale blue	C ($Fm3m$)	$NaTaF_6$	8·608	—	—	
$KPaF_6$	White	O	$RbPaF_6$	7·98	11·54	5·64	
KUF_6	Yellow-green	O	$RbPaF_6$	7·96	11·46	5·61	
NH_4PaF_6	White	O	$RbPaF_6$	8·03	11·90	5·84	
NH_4UF_6	Yellow-green	O	$RbPaF_6$	8·03	11·89	5·83	
$RbPaF_6$	White	O ($Cmca$)	$RbPaF_6$	8·048	12·025	5·861	
$RbUF_6$	Yellow-green	O	$RbPaF_6$	8·06	11·89	5·82	
$CsPaF_6$	White	O	$RbPaF_6$	8·06	12·56	6·14	
$CsUF_6$	Pale blue	R ($R\bar{3}$)	$CsUF_6$	8·021	—	8·430	
$CsNpF_6$	Pink-violet	R	$CsUF_6$	8·017	—	8·386	
$CsPuF_6$	Green	R	$CsUF_6$	8·006	—	8·370	
$NOUF_6$	Green	C ($Ia3$)	$NOUF_6$	10·464	—	—	
$AgUF_6$	—	T	—	5·42	—	7·95	
K_2PaF_7	White	M ($C2/c$)	K_2PaF_7	13·960	6·742	8·145	125·17
Cs_2PaF_7	White	M	K_2PaF_7	14·937	7·270	8·266	125·32
Rb_2NpF_7	Lilac	M ($P2_1/c$)	K_2NbF_7	6·26	13·42	8·90	90
Rb_2PuF_7	Green	M	K_2NbF_7	6·27	13·41	8·88	90
Li_3PaF_8	White	T ($P4_22_12$)	—	10·386	—	10·890	
Na_3PaF_8	White	T ($I4/mmm$)	Na_3PaF_8	5·493	—	10·970.	
Na_3UF_8	Pale blue	T	Na_3PaF_8	5·470	—	10·940	
Na_3NpF_8	Lilac	T	Na_3PaF_8	5·443	—	10·837	
K_3PaF_8	White	C ($Fm3m$)	—	9·235	—	—	
K_3UF_8	Pale blue	C ,,	—	9·20	—		
Rb_3PaF_8	White	C ,,	—	9·60	—	—	
Cs_3PaF_8	White	C ,,	—	9·937	—	—	
Ag_3UF_8	—	C	—	4·36	—	—	
Tl_3UF_8	—	C	—	4·75	—	—	

[a] Parameters are taken from refs. 6 and 76 in which details of the original literature are provided.

* R, rhombohedral (hexagonal parameters given); T, tetragonal; C, cubic; O, orthorhombic; M, monoclinic.

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[87] F. Montoloy and P. Plurien, *Compt. Rend.* **267C** (1968) 1036.

[88] J. H. Burns, H. A. Levy and O. L. Keller Jr., *Acta Cryst.* **24B** (1968) 1675.

All the 2:1 protactinium(V) fluoro-complexes possess the 9-coordinate K_2PaF_7-type of structure[89] (Table 16), whereas the heptafluorouranates(V) and Rb_2NpF_7 and Rb_2PuF_7 crystallize[76] with the 7-coordinate K_2TaF_7-type of structure; this again is presumably a consequence of the actinide contraction.

The octafluoro-complexes, $Na_3M^VF_8$ (M^V = Pa to Np inclusive), possess the 8-coordinate Na_3PaF_8-type of structure. In Na_3PaF_8 each protactinium atom is surrounded by eight equidistant fluorine atoms (Pa–F, 2·21 Å) at the vertices of an almost perfect cube[90]. The F–F distances (2·47 and 2·60 Å) indicate tetragonal distortion with D_{4h} symmetry. Interestingly, for the apparently isostructural uranium complex, Na_3UF_8, NMR studies indicate non-equivalence of the eight fluorine atoms suggesting that the UF_8^{3-} has symmetry lower than D_{4h}[91]. This deduction is supported by magnetic susceptibility studies[92].

Magnetic susceptibility data have also been recorded for $N_2H_6UF_7$ and several hexafluorouranates(V)[6]. Paramagnetic resonance studies have yielded g values of $-0{\cdot}768$, $-0{\cdot}764$ and $-0{\cdot}709$ for $LiUF_6$, $NaUF_6$ and $CsUF_6$, respectively[93]. Rather surprisingly, signals were not observed for the K, NH_4, Rb, Ag and Tl complexes.

Combined coulomb, spin–orbit and octahedral crystal-field spectroscopic parameters deduced from spectral studies on $CsNpF_6$[94, 95] are, respectively, $E^1 = 3144$, $E^2 = 16{\cdot}75$, $E^3 = 257{\cdot}9$, $\tau = 2230$, $B_0^4 = 1071$ and $B_0^6 = 551$ cm^{-1}. Infrared M–F bands have been recorded for certain 1:1 complexes (503–550 cm^{-1}), 2:1 complexes (430–438 and 356 cm^{-1}) and 3:1 complexes (395–422 cm^{-1})[6]. Raman vibrations occur at 590 cm^{-1} and 545 cm^{-1} for solid $RbPaF_6$ and Rb_2PaF_7, respectively[96], and at 628 cm^{-1} for certain hexafluorouranates(V) in anhydrous hydrogen fluorine[97].

Hexavalent Fluoro-complexes

Only uranium forms hexavalent fluoro-complexes. A variety of heptafluoro-complexes of the type M^IUF_7 (M^I = Na, K, Cs, NH_4, N_2H_5, NO and NO_2) are obtained either by direct union of the component fluorides or by reacting them together in solvents such as perfluoroheptane, tetrachloroethane, chlorine trifluoride or anhydrous hydrogen fluoride[6,17,98]. Na_2UF_8 is obtained by condensing uranium hexafluoride onto sodium fluoride, or by thermal decomposition of $NaUF_7$[98]; at higher temperatures uranium hexafluoride is lost with the formation of Na_3UF_9. Octafluoro-uranates(VI) are also known for M^I = K, Rb and Cs; the stability of these complexes increases with the atomic weight of the alkali metal[99]. No lithium compound is known. Complexes of the type $M^I_3U_{12}F_{15}$ (M^I = Na and K) are also known[76].

The structure proposed for Na_2UF_8[98], which possesses tetragonal symmetry, space group D^{17}_{4h}–$I4/mmm$, is similar to that described above for Na_3PaF_8 except that the sodium is removed from the tetragonal axis. Dainoux and Rigny[100] find from NMR studies,

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[89] D. Brown, S. F. A. Kettle and A. J. Smith, *J. Chem. Soc.* (A) (1967) 1429.
[90] D. Brown, J. F. Easey and C. E. F. Rickard, *J. Chem. Soc.* (A) (1969) 1161.
[91] E. Fukushima and H. G. Hecht, *J. Chem. Phys.* **54** (1971) 4341.
[92] P. Rigny, A. J. Dianoux and P. Plurien, according to ref. 76.
[93] P. Rigny and P. Plurien, *J. Phys. Chem. Solids*, **28** (1967) 2589.
[94] L. P. Varga, L. B. Asprey, T. K. Keenan and R. A. Penneman, *J. Chem. Phys.* **52** (1970) 1664.
[95] L. P. Varga, J. D. Brown, M. J. Reisfeld and R. D. Swan, *J. Chem. Phys.* **52** (1970) 4233.
[96] L. O. Keller, Jr. and A. Chetham-Strode, ref. 54, p. 119.
[97] B. Frlec and H. H. Hyman, *Inorg. Chem.* **6** (1967) 2233.
[98] J. G. Malm, H. Selig and S. Siegel, *Inorg. Chem.* **5** (1966) 130.
[99] I. Peka and J. Vachuska, *Coll. Czech. Chem. Comm.* **32** (1967) 426.
[100] A. J. Dainoux and P. Rigny, *J. de Physique* **29** (1968) 791.

however, that the UF_8^{3-} group has lower symmetry than D_{4h}. Complete structural data are not available for the remaining hexavalent complexes although some unit cell sizes are known[6,76].

NH_4UF_7 decomposes to UF_5 at 170° in a vacuum; other heptafluorouranates(V), M^I = K, Rb and Cs, decompose to yield tetravalent complexes of the type M^IUF_5 when heated. $CsUF_7$ initially yields $CsUF_6$ which loses fluorine above 585°C.

Oxyfluorides

The presently known oxyfluorides are shown in Table 2. With the possible exception of protactinium it is likely that the remaining elements through to lawrencium will form trivalent compounds, but in view of the PuF_4/PuO_2 reaction described earlier (p. 163) and the fact that the existence of UOF_2 is questionable, the only new oxydifluoride likely to be prepared is $PaOF_2$. There is obviously scope for further investigation of the U(V) oxyfluoride system and, under the correct conditions, other Pa(V) compounds may exist. However, the elements beyond americium are unlikely to form other than trivalent oxyfluorides.

No general method of preparation of the oxyfluorides is known. Both PuOF and CfOF have, in fact, only been obtained accidentally as a result of the hydrolysis of the corresponding trifluoride. $ThOF_2$ is obtained by interaction of thorium tetrafluoride and thoria at high temperature and it is claimed that UOF_2, which does not form when UF_4 and UO_2 are heated together, can be precipitated from aqueous solution. Thermal decomposition of protactinium pentafluoride hydrates leads to the successive formation of Pa_2OF_8, PaO_2F and Pa_3O_7F (alternative methods are available for the preparation of the first) whilst $NpOF_3$ and NpO_2F are obtained, respectively, by heating Np_2O_5 in gaseous hydrogen fluoride and by controlled hydrogen reduction of NpO_2F_2.

The hexavalent compounds MO_2F_2 (M = U to Pu) form on hydrolysis of the appropriate hexafluoride, but AmO_2F_2 is only obtained by treatment of $NaAmO_2CO_3$ with hydrogen fluoride containing fluorine at −196°C. UO_2F_2 and NpO_2F_2 are obtained by a variety of other methods including high-temperature trioxide–hydrogen fluoride and trioxide–fluorine reactions.

The above preparative methods are discussed in detail and original references are provided in other reviews[6,15,17,19].

Physical and Chemical Properties of the Trivalent Oxyfluorides

The trivalent compounds are high-melting, non-volatile solids of which AcOF, ThOF and CfOF possess the cubic fluorite-type of structure (Table 17). In CfOF[101] the oxygens and fluorines are randomly distributed over the anion sites 2·408 Å from the metal atom. PuOF, on the other hand[102], crystallizes with a tetragonal modification of the fluorite structure in which the bond distances are Pu–4O, 2·57 Å and Pu–4F, 2·39 Å. The tetragonal phase is apparently stabilized by the presence of excess fluoride over the composition MOF; at this stoichiometric composition it is unstable relative to the rhombohedral structure known for certain lanthanide(III) oxyfluorides.

The few available thermodynamic values are given in Tables 5 and 6. The chemical properties of these oxyfluorides have not been studied.

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[101] J. R. Peterson and J. H. Burns, *J. Inorg. Nuclear Chem.* **30** (1968) 2955.

[102] W. H. Zachariasen, *Acta Cryst.* **4** (1951) 231.

TABLE 17. CRYSTALLOGRAPHIC DATA FOR ACTINIDE OXYFLUORIDES

Compound	Colour	Symmetry*/ Space group	a_0 (Å)	b_0 (Å)	c_0 (Å)	β°	Ref.
AcOF	White	C; O^{5}_{h}–$Fm3m$	5·931	—	—		a
ThOF		,, ,,	5·68	—	—		b
PuOF		T; D^{7}_{h}–$P4/nmm$	4·05	—	5·72		a
CfOF	Green	C; O^{5}_{h}–$Fm3m$	5·561	—	—		c
$ThOF_2$	White	O;	14·07	4·041	7·25		d
UO_2F		M; —	8·22	6·81	32·08	90·5	e
Pa_2OF_8	White	BCC; —	8·406				f
PaO_2F	White	O; —	6·894	12·043	4·143		g
Pa_3O_7F	White	O; C^{11}_{2v}–$Cmm2$	6·947	12·030	4·203		g
$NpOF_3$	Green	R†; D^{5}_{3d}–$R\bar{3}m$	4·185	—	15·799		h
"NpO_2F"	Green	T; —	8·341	—	7·193		h
UO_2F_2	Yellow	R†; D^{5}_{3d}–$R\bar{3}m$	4·192	—	15·66		i
NpO_2F_2	Pink	R†; ,,	4·185	—	15·79		h
PuO_2F_2	White	R†; ,,	4·154	—	15·81		j
AmO_2F_2	Light brown	R†; ,,	4·136	—	15·85		k

* C, cubic; T, tetragonal; O, orthorhombic; M, monoclinic; BCC, body centred cubic; R, rhombohedral.

† Hexagonal lattice parameters given.

[a] W. H. Zachariasen, *Acta Cryst.* 4 (1951) 231.

[b] J. Lucas and J. P. Rannon, *Compt. Rend.* **266C** (1968) 1056.

[c] J. R. Peterson and J. H. Burns, *J. Inorg. Nucl. Chem.* **30** (1968) 2955.

[d] R. W. M. D'Eye, *J. Chem. Soc.* (1958) 196.

[e] S. Kemmler-Sack, *Z. anorg. u. allgem. Chem.* **364** (1969) 88.

[f] L. Stein, *Inorg. Chem.* 3 (1964) 995.

[g] D. Brown and J. F. Easey, *J. Chem. Soc.* (A) (1970) 3378.

[h] K. W. Bagnall, D. Brown and J. F. Easey, *J. Chem. Soc.* (A) (1968) 2223.

[i] M. Atoji and M. J. McDermott, *Acta Cryst.* **26B** (1970) 1540.

[j] I. F. Alenchickova, L. L. Zaitseva, L. V. Lipis, N. S. Nikolaev, V. V. Fomin and N. T. Chebotarev, *Zhur. Neorg. Khim.* 3 (1958) 951.

[k] T. K. Keenan, *Inorg. Nucl. Chem. Letters*, **4** (1968) 381.

Physical and Chemical Properties of the Tetravalent Oxydifluorides

$ThOF_2$ possesses orthorhombic symmetry (Table 17); structural data are not available. Somewhat surprisingly UOF_2 is stated to be stable at 700°C[103], an observation which does not agree with the lack of compound formation in the UF_4–UO_2[104] and UF_4–ThO_2 systems[105] between 400° and 1100°C. Thermodynamic data are listed in Table 5.

Physical and Chemical Properties of the Pentavalent Oxyfluorides

Full structural data are not available for any pentavalent oxyfluoride and no thermodynamic or vapour pressure studies have been reported. Unit cell dimensions are listed in Table 17 and infrared data are shown in Table 18.

Apart from Pa_2OF_8 and U_2OF_8, the compounds are air-stable at room temperature. The former decomposes when heated in air at 250–290°C to form PaO_2F, a white solid which decomposes to yield Pa_3O_7F at 500° to 600°C[106]. The last is converted to Pa_2O_5 above

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[103] V. M. Vdovenko, G. A. Romanov, and L. V. Solntseva, *Radiokhimiya*, **9** (1967) 727.

[104] D. Brown, J. F. Easey and J. Edwards, unpublished observations.

[105] G. Fonteneau and J. Lucas, *Compt. Rend.* **269C** (1969) 760.

[106] D. Brown and J. F. Easey, *J. Chem. Soc.* (A) (1970) 3378.

TABLE 18. INFRARED DATA FOR THE ACTINIDE OXYHALIDES (cm^{-1})

Compound	ν_{M-O}	ν_{M-F}	Ref.
Pa_2OF_8	790, 740, 690	450	a
PaO_2F*	500, 435, 377		b
Pa_3O_7F*	625, 429, 328, 277		b
$NpOF_3$	985	852, 350, 300	c
NpO_2F	800	277	c
UO_2F_2	990		d
NpO_2F_2	980	446, 277, 250	c
PuO_2F_2	975		e

* Assignments not made. These results indicate polymeric oxygen-bridged structures.

[a] L. Stein, *Inorg. Chem.* 3 (1964) 995.

[b] D. Brown and J. F. Easey, *J. Chem. Soc.* (A) (1970) 3378.

[c] K. W. Bagnall, D. Brown and J. F. Easey, *J. Chem. Soc.* (A) (1970) 2223.

[d] H. R. Hoekstra, *Inorg. Chem.* 2 (1963) 492.

[e] I. F. Alenchikova, L. L. Zaitseva, L. V. Lipis, N. S. Nikolaev, V. V. Fomin and N. T. Chebotarev, *Zhur. Neorg. Khim.* 3 (1958) 951.

650°C in air. PaO_2F reacts readily with hydrogen–hydrogen fluoride mixtures at 450°C to yield PaF_4. In contrast to the behaviour of Pa_2OF_8, the uranium analogue disproportionates at 300°C in a vacuum to form a mixture of uranyl fluoride, uranium hexafluoride and uranium tetrafluoride[6].

Physical and Chemical Properties of the Hexavalent Oxyfluorides

The four hexavalent compounds are isostructural, possessing the 8-coordinate UO_2F_2-type of structure in which each uranium atom is bonded to six fluorine atoms; the uranium–oxygen distance is 1·74 Å and the uranium–fluorine distance is 2·429 Å[107]. On the basis of recent spectral studies (ref. d, Table 18) in which ν_3 for UO_2F_2 is observed at 990 cm^{-1}, a U–O bond length of 1·71 Å is deduced. Thermodynamic data (UO_2F_2 only) are given in Tables 5 and 6 and infrared data are listed in Table 18.

Apart from those of UO_2F_2, little is known of the chemical properties of this series of compounds. Fluorine converts UO_2F_2 to the hexafluoride above 270°C and will presumably react similarly with neptunyl(VI) and plutonyl(VI) fluoride. UO_2F_2 is reduced to the dioxide in an excess of hydrogen at 450°C and to a mixture of uranium tetrafluoride and uranium dioxide by sulphur at 500–600°C. Controlled reduction of NpO_2F_2 by hydrogen at 300–325°C leads to the formation of NpO_2F.

The hexavalent oxyfluorides are soluble in water and the UO_2F_2–H_2O, UO_2F_2–HF–H_2O and PuO_2F_2–HF–H_2O phase diagrams have been studied in detail[6,19]. Hydrated compounds are known for uranyl(VI) and plutonyl(VI) fluoride, e.g. $UO_2F_2\cdot 2H_2O$, $UO_2F_2\cdot 3H_2O$, $UO_2F_2\cdot 2HF\cdot 4H_2O$, $PuO_2F_2\cdot H_2O$ and $PuO_2F_2\cdot 2HF\cdot 4H_2O$. The only other complexes known to form with donor ligands are a series of uranyl fluoride adducts with ammonia, $UO_2F_2\cdot xNH_3 (x = 2, 3 \text{ or } 4)$.

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[107] W. H. Zachariasen, *Acta Cryst.* 1 (1948) 277.

Oxyfluoro-complexes

Neither trivalent nor tetravalent actinide oxyfluoro-complexes are known.

The pentavalent uranium complex $(NEt_4)_2UOF_5 \cdot 2H_2O$, which is converted to the anhydrous compound *in vacuo*, was recently prepared[108] by the addition of "undried NEt_4F to $(NEt_4)UCl_6$ in acetone–ethanol mixtures"; it is likely that analogous protactinium(V) compounds will exist. Pentavalent complexes of the type $M^IM^VO_2F_2$ are obtained from aqueous solution[6,15,19] (M^I = K, Rb and NH_4; M^V = variously Np, Pu and Am) and a series of uranium(V) complexes of the type $M^IM^{II}U_2O_6F$ (M^I = Na, K, Rb and Tl; M^{II} = Ba, Sr and Pb) have been prepared by heating together appropriate oxide–fluoride mixtures at 500–900°C in a vacuum.[109]

A wide range of uranyl(VI) fluoro-complexes have been identified in the M^IF–UO_2F_2–H_2O systems (M^I = alkali metal)[6,15,17]. By varying the ratio of CsF to UO_2F_2, for example, the complexes $CsUO_2F_3 \cdot H_2O$, $CsUO_2F_3$, $Cs_2UO_2F_4 \cdot H_2O$ and $Cs_3UO_2F_5$ can all be prepared from dilute aqueous hydrofluoric acid and many analogous complexes have been prepared with other alkali metal cations. In addition, numerous complexes of the types $M^IUO_2F_3 \cdot xH_2O$, $M^I(UO_2)_2F_5 \cdot xH_2O$ and $M^I(UO_2)_3F_7 \cdot xH_2O$ (where M^I = an organic base and x varies from 0 to 6) have been recorded[6,15,17]. $(NH_4)_3UO_2F_5$ is the solid phase in equilibrium with ammonium fluoride and uranyl fluoride in water and the preparation of the hydrazinium complex $(N_2H_5)_3UO_2F_5 \cdot 1 \cdot 5H_2O$ has been described. Hydrated complexes of the type $M^{II}UO_2F_4 \cdot 4H_2O$ (M^{II} = Zn, Cd, Cu, Mn, Co and Ni) crystallize from aqueous solution. Additional classes of complexes now known include MUO_3F (M = Na and K), $M^I(UO_2)_2F_5$ (M^I = K and Rb) and $M^I(UO_2)_3F_7 \cdot 4H_2O$ (M^I = K and Rb).

The M^IF–NpO_2F_2–H_2O systems have not been studied, but ozone oxidation of either neptunium(IV) or (V) in a saturated potassium fluoride solution results in precipitation of the green, water-soluble solid $K_3NpO_2F_5$[110].

Two series of complexes of the types $M^IPuO_2F_3 \cdot H_2O$ (M^I = Na, K, Rb, Cs and NH_4) and $M^I_2PuO_2F_4$ (M^I = Na, K, Rb and NH_4) are obtained from 1·3% hydrogen fluoride by varying the ratio of alkali metal to plutonyl fluoride[111]. The analogous 1:1 quinolinium complex is also known[6].

Properties of the Pentavalent Oxyfluoro-complexes

Compounds of the type $M^IM^VO_2F_2$ are all isostructural, possessing rhombohedral symmetry, space group D^5_{3d}–$R\bar{3}m$. Unit cell dimensions are listed in Table 19. Thermodynamic, magnetic and infrared data are not available. $(NEt_4)_2UOF_5$[108] exhibits U–O vibrations at 853 and 870 cm^{-1}; its structure is unknown. The complexes of the type $M^IM^{II}U_2O_6F$ all possess cubic symmetry (O^7_h–$Fd3m$) with a_0 values between 11·1 and 11·4 Å[109]. Magnetic and spectral results[109] suggest that U–O octahedra exist in $KSrU_2O_6F$, $RbSrU_2O_6F$, $KBaU_2O_6F$ and $RbBaU_2O_6F$; this arrangement is disordered in the remaining complexes.

The plutonium(V) complexes have been observed to undergo oxidation to plutonium

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[108] J. L. Ryan, *J. Inorg. Nuclear Chem.* **33** (1971) 153.

[109] S. Kemmler-Sack, *Z. anorg. u. allgem. Chem.* **363** (1968) 282 and 295.

[110] C. E. Thalmeyer and D. Cohen, Chapter 10 in ref. 71.

[111] I. L. Alenchikova, L. L. Zaitseva, L. V. Lipis, N. S. Nikolaev, V. V. Fomin, and N. J. Chebotarev, *Russ. J. Inorg. Chem.* **6** (1961) 771.

TABLE 19. CRYSTALLOGRAPHIC DATA FOR CERTAIN PENTAVALENT AND HEXAVALENT OXYFLUORO-COMPLEXES

Compound	Colour	Symmetry* Space group	a_0 (Å)	b_0 (Å)	c_0 (Å)	Ref.
$KNpO_2F_2$	—	R†; D^5_{3d}–$R\bar{3}m$	6·80	—	36·32	a
$KAmO_2F_2$	Tan	,, ,,	6·76	—	36·25	b
$RbNpO_2F_2$	Grey-green	,, ,,	6·85	—	36·18	c
$RbPuO_2F_2$	Lavender	,, ,,	6·796	—	36·17	c
$RbAmO_2F_2$	Tan	,, ,,	6·789	—	36·15	c
$NH_4PuO_2F_2$	Lavender	,, ,,	6·817	—	36·16	c
$K_3UO_2F_5$	Yellow	T; C^6_{4h}–$I4_1/a$	9·160	—	18·167	d
$K_3NpO_2F_5$	Green	,, ,,	9·12	—	18·12	a
$(NH_4)_3UO_2F_5$	Yellow	M; C^3_s–Cm	29·22	9·48 β = 136·11°	13·51	e
$Cs_3UO_2F_5$	Yellow	C; —	9·869	—	—	f
$KPuO_2F_3.H_2O$	—	C; —	8·126	—	—	g
$RbPuO_2F_3.H_2O$	—	C; —	8·458	—	—	g
$CsPuO_2F_3.H_2O$	—	C; —	8·916	—	—	g

* R, rhombohedral; T, tetragonal; M, monoclinic; C, cubic.

† Hexagonal parameters listed.

[a] C. E. Thalmeyer and D. Cohen, Chapter 10 in *Actinide/Lanthanide Chemistry* (P. R. Fields and T. Moeller, Eds.), Adv. in Chem. Series 71, Amer. Chem. Soc., Washington (1967).

[b] L. B. Asprey, F. H. Ellinger and W. H. Zachariasen, *J. Amer. Chem. Soc.* 76 (1954) 5235.

[c] T. K. Keenan, *Inorg. Chem.* 4 (1965) 1500.

[d] W. H. Zachariasen, *Acta Cryst.* 7 (1954) 783.

[e] H. Brusset, H. Gillier-Pandraud and Nguyen-Quy-Dao, *Acta Cryst.* 25B (1969) 67.

[f] A. N. Rebenko, F. A. Brusentsev and A. A. Opalovskii, *Izv. Sib. Otd. Nauk. SSSR, Ser. Khim. Nauk.* (1) (1968) 136.

[g] I. F. Alenchikova, L. L. Zaitseva, L. V. Lipis, N. S. Nikolaev, V. V. Fomin and N. T. Chebotarev, *Russ. J. Inorg. Chem.* 6 (1961) 777.

(VI) in water whilst $RbAmO_2F_2$ is reduced to Rb_2AmF_6 on contact with acidic rubidium fluoride.

Little else appears to be known concerning the properties of the pentavalent complexes.

Properties of the Hexavalent Oxyfluoro-complexes

Unit cell dimensions for complexes of the type $M^I_3M^{VI}O_2F_5$ are listed in Table 19. The structure of $K_3UO_2F_5$ comprises pentagonal bipyramidal $UO_2F_5{}^{2-}$ units in which the U–O and U–F distances are, respectively, 1·76 and 2·24 Å[112]. The pentagonal bipyramidal arrangement is distorted in $(NH_4)_3UO_2F_5$[113] for which the U–O and U–F bond lengths are 1·9 and 2·2 Å, respectively.

Papers dealing with the effects of cation size on the position of the asymmetric uranium–oxygen stretching vibration (ν_3) in complexes of the type $M^I_3UO_2F_5$ and the calculation of force constants have been summarized in an earlier review[17]. ν_3 occurs between 847 and 887 cm^{-1} in the infrared spectra of such complexes with the O–U–O bending mode at 266–289 cm^{-1}. Uranium–fluorine stretching vibrations have been assigned in the range 350–430 cm^{-1} with O–U–F and F–U–F vibrations between 211 and 221 cm^{-1} and 188 and 200 cm^{-1}, respectively. For complexes of the type $M^IUO_2F_3$ terminal U–F vibrations

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[112] W. H. Zachariasen, *Acta Cryst.* 7 (1954) 783.

[113] H. Brusset, H. Gillier-Pandraud and Nguyen-Quy-Dao, *Acta Cryst.* 25B (1969) 67.

occur between 350 and 430 cm^{-1} with bridging vibrations around 300 cm^{-1} and the O–U–O bending mode at approximately 250 cm^{-1}. Neptunium–oxygen and neptunium–fluorine vibrations for $K_3NpO_2F_5$ are reported[110] to occur at 850 and 740 cm^{-1} and 480 and 365 cm^{-1}, respectively.

3. COMPOUNDS WITH CHLORINE

Binary chlorides

The known actinide chlorides are listed in Table 1. The valence state stability trends are again evident for this series of compounds. Thus, chlorine oxidation of the appropriate metal or lower chloride leads to the formation of uranium hexachloride, neptunium tetrachloride and plutonium trichloride, respectively. Thorium metal reacts with chlorine to yield the tetrachloride and although it has not been investigated, the analogous reaction involving protactinium (or protactinium tetrachloride) will undoubtedly yield the pentachloride. In addition, whereas the trichlorides of the elements Pu to Es inclusive are readily obtained, for example by sesquioxide–hydrogen chloride reactions, reducing conditions are necessary for the preparation of both uranium and neptunium trichloride, for example tetrahalide–zinc reactions at high temperature. Thorium, uranium and neptunium tetrachloride are obtained from a variety of reactions involving the appropriate oxide and reagents such as carbon tetrachloride, carbonyl chloride and hexachloropropene. The last is particularly useful for the conversion of UO_3, U_3O_8 or Np(V) hydroxide to the appropriate tetrachloride. Protactinium tetrachloride, on the other hand, is only obtained under reducing conditions, e.g. the reaction between protactinium pentachloride and aluminium. The extensive literature dealing with the preparation of the individual chlorides, particularly those of thorium and uranium, is reviewed elsewhere[6,15,17,19].

In view of the above stability trends and the fact that plutonium tetrachloride is known to exist only in the gaseous phase in the presence of chlorine[114] it is unlikely that new actinide tetrachlorides will be prepared; however, the elements fermium to lawrencium will form trichlorides and, possibly, a dichloride will exist for nobelium. Actinide dichlorides are, as yet, unknown, although the distribution of americium between liquid plutonium metal and the fused salt mixture $PuCl_3$–NaCl–KCl (698° to 775°C) indicates[115] that Am^{2+} may be formed by the reaction:

$$\mathrm{Am(l)} + \frac{2}{3}\mathrm{PuCl_3} \rightleftharpoons \frac{2}{3}\mathrm{Pu(l)} + \mathrm{AmCl_2}$$

It would be interesting to have more information on the formation of divalent americium under these conditions (cf. Am^{2+} in CaF_2, p. 155). There have been claims for the preparation of $ThCl_2$, but a recent study[116] of the $ThCl_4$–Th and $ThCl_4$–Al systems indicated that no reduction occurred; uranium and plutonium metal have solubilities in their respective trichlorides of 4·0 mole % (at the eutectic, 800°) and 7·0 mole % (at the eutectic, 740°), respectively. It would be interesting to have information on the reactions between protactinium tetrachloride and metals such as zinc and barium (or, better still, protactinium metal itself) since these may result in the formation of protactinium trichloride.

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[114] D. M. Gruen and C. W. DeKock, *J. Inorg. Nucl. Chem.* **29** (1967) 2569.

[115] L. J. Mullins, A. J. Beaumont, and J. A. Leary, U.S. Report LA-3562 (1966).

[116] J. E. Fuller, U.S. Report IS-T-301 (1968).

Physical and Chemical Properties of the Trichlorides

As a consequence of the actinide contraction, a structural change occurs at californium (Table 20). The earlier members of the series possess the 9-coordinate UCl_3-type of structure only, whereas californium trichloride is dimorphic, the second form crystallizing with the 8-coordinate $PuBr_3$-type of structure (p. 197). $EsCl_3$ exhibits the UCl_3-type of structure at 425°C and it is predicted that at room temperature it will possess the 8-coordinate structure. The only single-crystal data available are those for $AmCl_3$[117] in which each americium atom is surrounded by a trigonal prismatic array of six chlorines (Am–Cl, 2·874 Å) with three chlorines (Am–Cl, 2·975 Å) situated just outside the prism faces.

TABLE 20. CRYSTALLOGRAPHIC DATA FOR ACTINIDE CHLORIDES

Compound	Colour	Symmetry/ Space group	a_0 (Å)	b_0 (Å)	c_0 (Å)	$\beta°$	Ref.
$AcCl_3$*	White	H; C^2_{6h}–$C6_3/m$	7·62	—	4·55	—	a
UCl_3	Green	,, ,,	7·440	—	4·321	—	b
$NpCl_3$	Green	,, ,,	7·413	—	4·282		b
$PuCl_3$*	Green	,, ,,	7·395	—	4·246		a
$AmCl_3$†	Pink	,, ,,	7·382	—	4·214		c
$CmCl_3$	White	,, ,,	7·380	—	4·186		d
$BkCl_3$	Green	,, ,,	7·382	—	4·127		c
$CfCl_3$	Green	,, ,,	7·393	—	4·090		f
$CfCl_3$	Green	O; D^{17}_{2h}–$Ccmm$	3·869	11·750	8·561		g
$EsCl_3$‡	—	H; C^2_{6h}–$C6_3/m$	7·47	—	4·10		h
$EsCl_3$§	—	,, ,,	7·40	—	4·07		h
$ThCl_4$†	White	T; D^{19}_{4h}–$I4/amd$	8·473	—	7·468		i
$PaCl_4$	Greenish-yellow	,, ,,	8·377	—	7·482		j
UCl_4	Green	,, ,,	8·296	—	7·487		k
$NpCl_4$	Red-brown	,, ,,	8·250	—	7·460		l
$PaCl_5$†	Yellow	M; C^6_{2h}–$C2/c$	8·00	11·42	8·43	106·38	m
UCl_5†	Brown	M; C^5_{2h}–$P2_1/n$	7·99	10·69	8·48	91·5	n
UCl_6†	Dark-green	H; D^3_d–$C\bar{3}m$	10·97	—	6·04		o

* Values converted from Kx units.
† Structural data given in references quoted.
‡ Parameters measured at *ca.* 425°C.
§ Parameters calculated for 25°C.

[a] W. H. Zachariasen, *J. Chem. Phys.* **16** (1948) 254.
[b] D. Brown and J. Edwards, *J. Chem. Soc. Dalton* (1972) 1757.
[c] J. H. Burns and J. R. Peterson, *Acta Cryst.* **26B** (1970) 1885.
[d] J. C. Wallmann, J. Fuger, J. R. Peterson and J. L. Green, *J. Inorg. Nucl. Chem.* **29** (1967) 1745.
[e] J. R. Peterson and B. B. Cunningham, *J. Inorg. Nucl. Chem.* **30** (1968) 823.
[f] J. L. Green and B. B. Cunningham, *Inorg. Nucl. Chem. Letters*, **3** (1967) 343.
[g] J. H. Burns, personal communication (1970).
[h] D. K. Fujita, B. B. Cunningham and T. C. Parsons, *Inorg. Nucl. Chem. Letters*, **5** (1969) 307.
[i] K. Mucker, G. S. Smith, Q. Johnson and R. E. Elson, *Acta Cryst.* **25B** (1969) 2362.
[j] D. Brown and P. J. Jones, *J. Chem. Soc.* (A) (1967) 719.
[k] R. L. Mooney, *Acta Cryst.* **2** (1949) 189.
[l] W. H. Zachariasen, ref. 1, p. 1482.
[m] R. P. Dodge, G. S. Smith, Q. Johnson and R. E. Elson, *Acta Cryst.* **22** (1967) 85.
[n] G. S. Smith, Q. Johnson and R. E. Elson, *Acta Cryst.* **22** (1967) 300.
[o] W. H. Zachariasen, *Acta Cryst.* **1** (1948) 285.

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[117] J. H. Burns and J. R. Peterson, *Acta Cryst.* **26B** (1970) 1885.

Magnetic susceptibility results appear to be available only for uranium trichloride[118] and plutonium trichloride[38]; the data are consistent with $5f^3$ and $5f^5$ electronic configurations, respectively. Paramagnetic resonance studies support the former configuration[119]. Publications dealing with absorption, emission and fluorescence spectra of the actinide trichlorides are summarized elsewhere[6,19]. The more recent analyses of the free-ion energy levels now include configuration–interaction parameters as well as spin–orbit and electrostatic parameters; values are given in Table 21. An excellent article by Carnall[120] deals with current studies and improved theoretical treatments in this interesting field. The only values currently available for Cf^{3+} in lanthanum trichloride are 4000 and 300 cm^{-1} for τ and F_2, respectively.

TABLE 21. ELECTROSTATIC, SPIN–ORBIT AND CONFIGURATION–INTERACTION PARAMETERS (cm^{-1}) FOR TRIVALENT TRANSURANIUM IONS

Parameter	$Np^{3+}/LaBr_3$	$Pu^{3+}/LaCl_3$	$PuCl_3$	$AmCl_3$	$Cm^{3+}/LaCl_3$
E^0	15,920	14,930·5	—	—	4939·29
E^1	3394·3	3726·7	3634·5	3582·8	4621·47
E^2	14·19	14·99	15·356	17·276	17·70
E^3	317·5	350·18	342·15	334·30	399·42
τ	1969·2	2260·2	2272·2	2593·3	2841·66
α	35·0	36·5	31·064	21·634	57·08
β	−802·4	−1171	−675·00	−158·48	−4761·60
γ	—	—	29·743	1240·4	—
Reference	a	b	c	d	e

[a] W. F. Krupke and J. B. Gruber, *J. Chem. Phys.* **46** (1967) 542.
[b] J. G. Conway and K. Rajnak, *J. Chem. Phys.* **44** (1966) 348.
[c] W. T. Carnall, P. R. Fields and R. G. Pappalardo, *J. Chem. Phys.* in press, 1971.
[d] R. G. Pappalardo, W. T. Carnall and P. R. Fields, *J. Chem. Phys.* **51** (1969) 1182.
[e] J. B. Gruber, W. R. Cochran, J. G. Conway and A. T. Nicol, *J. Chem. Phys.* **45** (1966) 1423.

Thermodynamic values for the trichlorides are given in Tables 4 and 6–8 inclusive; available vapour pressure data are listed in Table 9 (UCl_3 and $PuCl_3$ only).

The chemical properties of the trichlorides have not been extensively studied; in fact only microgram amounts of certain of the later compounds in the series have been prepared. Although uranium and plutonium trichloride are reduced to their respective metals by elements such as calcium and lithium, such reactions have little application in metal production. Uranium trichloride is oxidized to higher chlorides by chlorine (cf. the $PuCl_3$–Cl_2 reaction, p. 184) to the tetrafluoride by gaseous hydrogen fluoride at high temperature and to tetravalent mixed halides by bromine and iodine.

The trichlorides are moisture-sensitive and hydrates of the type $M^{III}Cl_3 \cdot 6H_2O$ are known (M^{III} = Pu, Am, and Bk); lower hydrates, $PuCl_3 \cdot H_2O$ and $PuCl_3 \cdot 3H_2O$, have been identified for plutonium. It is predicted, on size considerations, that both uranium and neptunium trichloride will form heptahydrates[121]. The trichloride hexahydrates are isostructural with their lanthanide analogues; full structural data are available for $AmCl_3 \cdot$

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[118] P. Handler and C. A. Hutchinson, *J. Chem. Phys.* **25** (1956) 1210.
[119] C. A. Hutchinson, P. M. Llewellyn, E. Wong and P. Dorain, *Phys. Rev.* **102** (1956) 292.
[120] T. W. Carnell, Paper presented at the Int. Conf. Co-ord. Chem. Krakow-Zakopane, Poland (1970).
[121] J. H. Burns and J. R. Peterson, *Inorg. Chem.* **10** (1971) 147.

$6H_2O$[121]. The only other complexes known with donor ligands appear to be the ammoniates $UCl_3 \cdot NH_3$, $UCl_3 \cdot 3NH_3$ and $UCl_3 \cdot 7NH_3$[6,15], and the recently reported methyl cyanide complex $UCl_3 \cdot CH_3CN$[122].

Chloro-complex formation is discussed later (p. 189).

Physical and Chemical Properties of the Tetrachlorides

The solid tetrachlorides are all isostructural (Table 20). A recent study of thorium tetrachloride[123] has shown that each metal atom is 8-coordinate, the chlorines being arranged as a dodecahedron with two sets of four at distances of 2·718 and 2·903 Å, respectively. The corresponding Np–Cl distances, based on powder results, are 2·61 and 2·86 Å, respectively. Electron diffraction studies on gaseous thorium and uranium tetrachloride suggest C_{2v} symmetry with bond distances in the monomeric species of Th–Cl, 2·58 Å and U–Cl, 2·53 Å[124]. Association in the liquid phase is indicated by the values of Trouton's constant for thorium tetrachloride (31) and uranium tetrachloride (31–36).

Spectra have been recorded for both crystalline and gaseous uranium tetrachloride, the most recent investigation covering the region 400–50,000 cm^{-1} for tetrachloride molecules isolated in a nitrogen matrix at liquid helium temperature. The results are interpreted[125] on the basis of tetrahedral symmetry for the isolated molecules and the numerous bands observed in the 4000–24,000 cm^{-1} range are assigned to pure electronic transitions from the ${}^3H_4(\Gamma_5)$ ground state to excited states of the $5f^2$ configuration.

Plutonium tetrachloride exists in the vapour state in the presence of chlorine[114]; the spectrum at 928°C is shown in Fig. 4 and the temperature dependence of the equilibrium

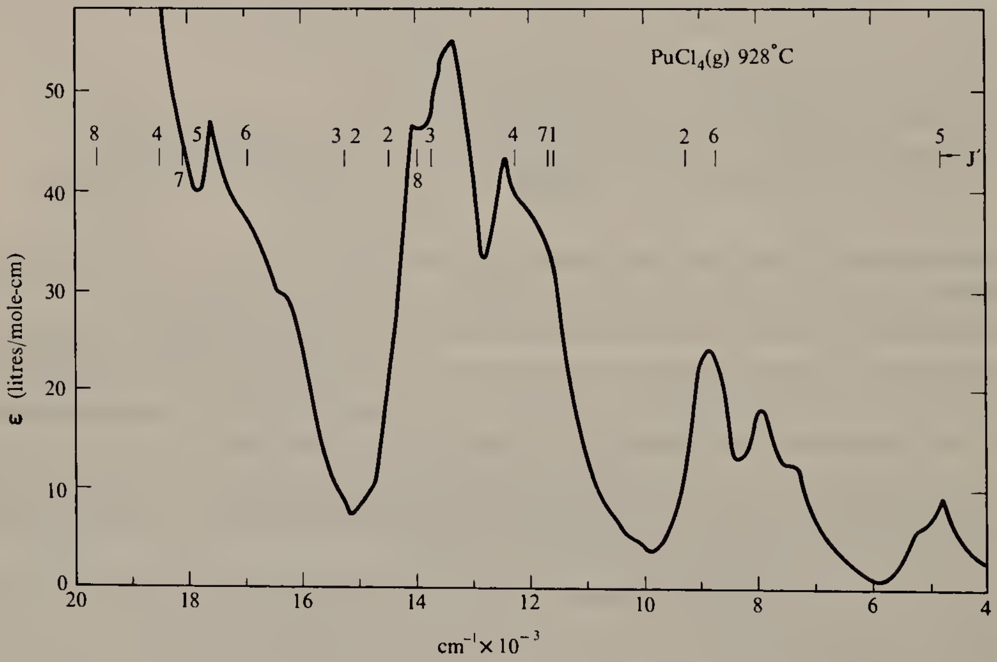

FIG. 4. The absorption spectrum of gaseous $PuCl_4$. (Reproduced by permission from D. M. Gruen and C. W. Dekock, *J. Inorg. Nucl. Chem.* **29** (1967) 2569.)

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[122] J. MacCordick and C. Brun, *Compt. Rend.* **270C** (1970) 620.
[123] K. Mucker, G. S. Smith, Q. Johnson and R. E. Elson, *Acta Cryst.* **25B** (1969) 2362.
[124] U. S. Ezhov, P. A. Akishin and N. G. Rambidi, *Zhur. Struct. Khim.* **10** (1969) 763.
[125] J. R. Clifton, D. M. Gruen and A. Ron, *J. Chem. Phys.* **51** (1969) 224, and references therein.

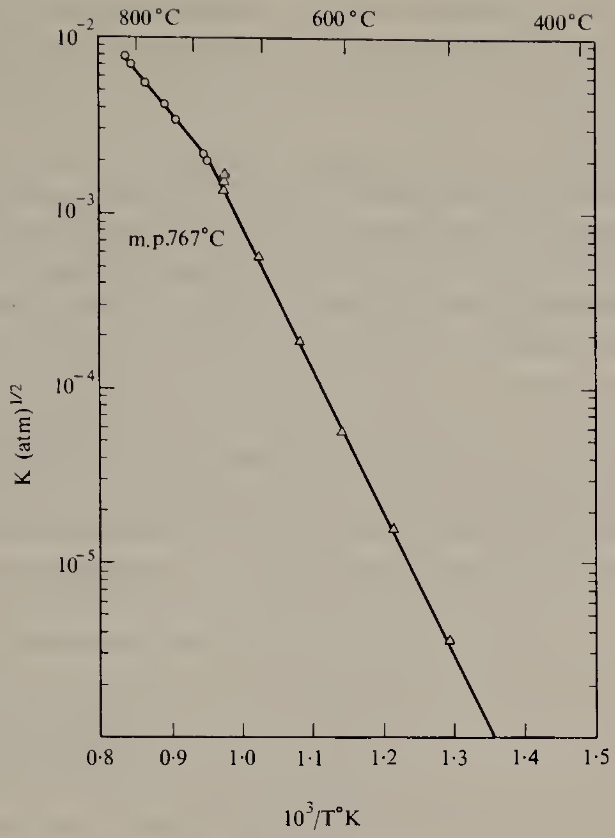

FIG. 5. The equilibrium constant K vs. $10^3/T$°K for the reaction $PuCl_3(s, l) + \frac{1}{2}Cl_2(g) \rightarrow PuCl_4(g)$. (Reproduced by permission from D. M. Gruen and C. W. Dekock, *J. Inorg. Nucl. Chem.* **29** (1967) 2569.)

△ s, g equilibria.
○ l, g equilibria.

constant (K) for the reaction:

$$PuCl_3(s, l) + \tfrac{1}{2}Cl_2(g) \rightarrow PuCl_4(g)$$

is illustrated in Fig. 5. The molar free energy of the reaction is represented by $\Delta G = 23{,}000 - 14{\cdot}1\ T$ (cal), 1052–1183°K. Thermodynamic data for the remaining tetrachlorides are listed in Tables 4 and 6–8 inclusive and vapour pressure data are summarized in Table 9.

The magnetic moment of uranium tetrachloride[126], 3·29 B.M. ($\theta = -62°$), is lower than that predicted by Russell-Saunders (3·58 B.M.) or *j–j* coupling (3·83 B.M.). No magnetic studies have been reported for $PaCl_4$ or $NpCl_4$.

Apart from those of thorium and uranium tetrachloride, the chemical properties of these compounds have barely been studied, although recent interest has centred on the preparation of tetrachloride complexes with donor ligands for all the elements Th to Pu inclusive (p. 186).

The tetrachlorides are water-soluble, moisture-sensitive solids, but hydrates are known only for thorium tetrachloride, both $PaCl_4$ and UCl_4 being oxidized on prolonged exposure to the atmosphere. Fluorine converts thorium and uranium tetrachloride to their respective tetra- and hexafluorides, and chlorine, which will undoubtedly oxidize protactinium tetrachloride, converts uranium tetrachloride to the penta- or hexachloride at moderate temperatures. Hydrogen fluoride converts both uranium and thorium tetrachloride to the

[126] J. K. Dawson, *J. Chem. Soc.* (1951) 429.

corresponding tetrafluoride whereas reactions between the former and hydrogen bromide or hydrogen iodide result in the formation of trivalent or tetravalent halides depending on the conditions. Ignition in moist air results in the formation of oxides, viz. ThO_2, Pa_2O_5, U_3O_8 and NpO_2.

Reduction of $ThCl_4$ and UCl_4 by elements such as sodium, potassium and calcium results in the formation of their respective elements, but such reactions are inferior to those involving the tetrafluorides. Under milder reducing conditions, e.g. hydrogen or zinc at moderate temperatures, UCl_4 and $NpCl_4$ are converted to trichlorides. The reduction of protactinium tetrachloride has not been studied. Conversion to tetravalent oxydihalides and the preparation of hexachloro-complexes are discussed later (pp. 192 and 189, respectively).

The tetrahalides tend to be insoluble in non-polar solvents such as carbon tetrachloride, benzene and isopentane, but they dissolve in, and form complexes with, solvents such as nitromethane, methyl cyanide and the lower alcohols. Numerous complexes with oxygen or nitrogen donor ligands are now known, particularly for thorium and uranium tetrachloride. In the few instances where an investigation has included all the tetrachlorides, interesting differences in behaviour have been observed[6,14,15,17]. Although solid plutonium tetra-

TABLE 22. A SELECTION OF THE COMPLEXES FORMED BETWEEN ACTINIDE TETRACHLORIDES AND DONOR LIGANDS[a,b]

Ligand	Stoichiometry for				
	$ThCl_4$	$PaCl_4$	UCl_4	$NpCl_4$	$PuCl_4$
Acetamide		*a*	1:6	1:6	1:6
N,N-Dimethylacetamide	1:4	*b*	*b*	*b*	*b*
	1:3	1:3	*b*	*b*	*b*
	b	1:2·5	1:2·5	1:2·5	1:2·5
Dimethylformamide	1:4	*a*	*b*	*a*	*a*
	b	*a*	1:2·5	*a*	*a*
Dimethylsulphoxide[d]	*a*	*c*	1:7	1:7	1:7
	1:5	1:5	1:5	1:5	*b*
	1:3	1:3	1:3	1:3	1:3
Diethylsulphoxide	1:4	*a*	*b*	*b*	*b*
	1:3	*a*	1:3	1:3	1:3
Diphenylsulphoxide	1:4	*a*	1:4	1:4	*b*
	b	*a*	1:3	1:3	1:3
Triphenylphosphine oxide	1:2	1:2	1:2	1:2	1:2
Hexamethylphosphoramide	1:2	1:2	1:2	1:2	1:2
Trimethylphosphine oxide	1:2	*a*	1:2	1:2	*a*
	1:6	*a*	1:6	1:6	1:6
Octamethylpyrophosphoramide	1:2	*a*	1:1·5	1:1·5	1:1·5
$(R_2PO)_2CH_2$; R = Me and Et	1:1	*a*	1:1	*a*	*a*
Methyl cyanide	1:4	1:4	1:4	1:4	*a*
Ammonia	1:6	*a*	1:4	*a*	*a*

[a] This is a very brief selection of the known complexes (see refs. 6, 14, 15, 17 and 20) illustrating effects due to the actinide contraction and due to increased steric hindrance within a series of related ligands.

[b] Infrared studies indicate coordination via the oxygen atom in the various amide, sulphoxide and phosphine oxide complexes.

a, Not studied.

b, Not formed.

c, Oxidation observed under conditions required for formation.

d, The 1:7 complexes and 1:3 complexes, respectively, decrease and increase in stability from thorium through to plutonium.

chloride does not exist, several complexes of the type $PuCl_4 \cdot xL$ ($x = 2$ to 7, L = oxygen donor ligand) can be obtained by reactions involving Cs_2PuCl_6 and the appropriate ligand in non-aqueous solvents, or plutonium(IV) in aqueous hydrochloric and the appropriate ligand (sulphoxides only). It is impossible to discuss the many known complexes in this article; a selection is shown in Table 22 and the interested reader is referred to reviews which cover the literature to 1970[6,14,15,17,20]. It would be interesting to have structural information on the many potentially high coordination number complexes. The only information available to date[127] indicates that in $ThCl_4 \cdot 5DMSO$ (DMSO, dimethylsulphoxide) each thorium atom is 8-coordinate, the compound being ionic, $[ThCl_3 \cdot 5DMSO]^+[Cl]^-$. The arrangement of the three chlorine atoms and five oxygen atoms around the thorium is approximately dodecahedral.

The Physical and Chemical Properties of the Pentachlorides

Protactinium and uranium pentachloride are not isostructural (Table 20). The metal atom in the former is 7-coordinate, being surrounded by an irregular pentagonal bipyramidal array of chlorine atoms linked in infinite chains by sharing pentagon edges[128]. The various bond angles and lengths in an isolated $PaCl_7$ unit are shown in Fig. 6. Uranium pentachloride, on the other hand, possesses a structure based on a cubic close packing of chlorine atoms in which uranium atoms occupy one-fifth of the octahedral holes[129]. Two such octahedra share an edge to form a dimeric U_2Cl_{10} unit with U–Cl bridging and non-bridging distances of 2·67 to 2·70 Å and 2·43 to 2·44 Å, respectively. Uranium pentachloride, which is dimeric in carbon tetrachloride, is unique amongst the known pentachlorides in also vaporizing as a dimer[130]. The magnetic behaviour of uranium pentachloride has been reported by different groups[6] to be consistent with a $6d^1$ or a $5f^1$ electronic configuration for the U^{5+} ion. Thermodynamic data for uranium pentachloride are given in Tables 4 and 7. It is thermally unstable with respect to uranium tetra- and hexachloride and consequently no melting point is available. Spectral studies have been reported for uranium pentachloride in various solvents[131] and in the vapour state[130].

Both compounds are extremely moisture-sensitive. They react with oxygen to yield oxyhalides (p. 192) and are reduced to their respective tetrahalides by hydrogen at elevated temperatures. Fluorine and chlorine oxidize uranium pentachloride to the hexafluoride and hexachloride respectively. Hydrates are unknown, but stable complexes of the types $M^VCl_5 \cdot L$ and $M^VCl_5 \cdot 2L$ are formed with trialkyl or triarylphosphine oxides[6,14,15,17]. Similar 1 : 1 complexes are known for uranium pentachloride[132] with a variety of N, P, As, S, Se and Te donor ligands and also with trichloroacrylyl chloride ($Cl_2 \cdot C \cdot CCl \cdot COCl$). In view of the instability of UCl_5 in aqueous solution all complexes must be prepared in non-aqueous solvents. Attempts to stabilize neptunium pentachloride as the 1 : 1 or 1 : 2 triphenylphosphine oxide complex have been unsuccessful[133] (cf. $PuCl_4 \cdot 2TPPO$ and $PuBr_4 \cdot 2TPPO$, pp. 186 and 199, respectively).

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[127] K. W. Bagnall, personal communication (1971).

[128] R. P. Dodge, G. S. Smith, Q. Johnson and R. E. Elson, *Acta Cryst.* **22** (1967) 85.

[129] G. S. Smith, Q. Johnson and R. E. Elson, *Acta Cryst.* **22** (1967) 300.

[130] D. M. Gruen and R. L. McBeth, *Inorg. Chem.* **8** (1969) 2625.

[131] J. Selbin and J. D. Ortego, *Chem. Rev.* **69** (1969) 657.

[132] J. Selbin, N. Ahmad and M. J. Pribble, *J. Inorg. Nucl. Chem.* **32** (1970) 3249.

[133] D. Brown, D. G. Holah and C. E. F. Rickard, *Chem. Comm.* (1968) 651.

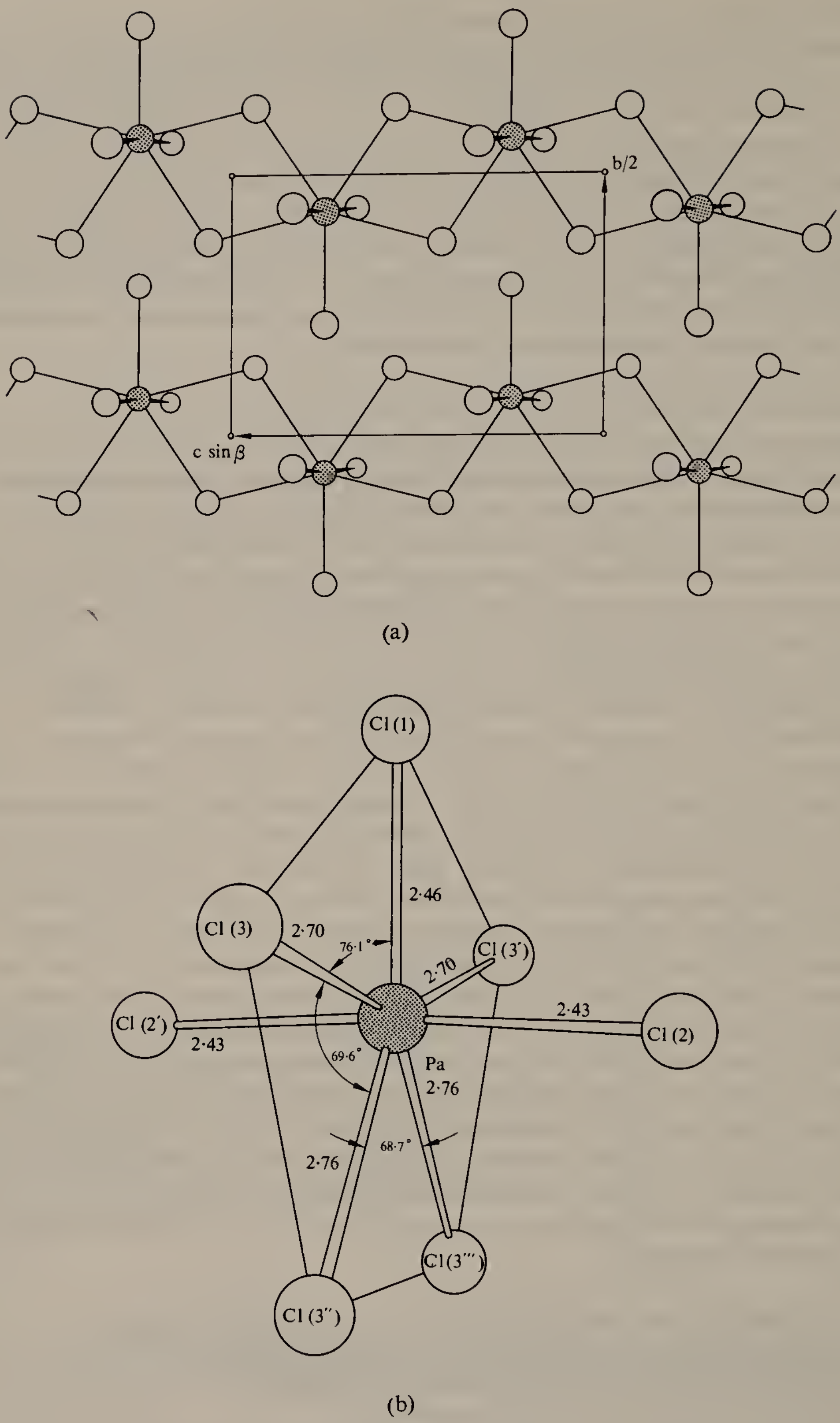

FIG. 6. The structure of $PaCl_5$.

(a) Portion of the infinite chains; coordination around each Pa atom is pentagonal bipyramidal.

(b) Bond distances (Å) and angles within an isolated $PaCl_7$ unit.

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Physical and Chemical Properties of Uranium Hexachloride

A typical molecular structure is exhibited by uranium hexachloride (Table 20) with individual UCl_6 molecules in a three-dimensional array; six chlorines form an almost perfect octahedron around the uranium atom with U–Cl distances of 2·42 Å[134]. The single bond covalent radius of U^{6+} is calculated to be 1·43 Å.

Uranium hexachloride is a blackish-green, air-sensitive solid which sublimes at 75–100° *in vacuo*. Anhydrous hydrogen fluoride converts it to the pentafluoride and it reacts with uranium hexafluoride to yield the tetrafluoride. It reacts violently with water to form uranyl(VI) chloride. The only recorded complex appears to be an incompletely characterized yellow solid formed on the addition of dipyridyl to the hexachloride in carbon tetrachloride[6]. Little else is known about the chemical behaviour of uranium hexachloride.

Chloro-complexes

Relatively few trivalent chloro-complexes are known and no hexavalent complexes have yet been obtained. General preparative methods are briefly discussed in the following sections; more detailed accounts are available elsewhere[6,15,17,19].

Trivalent Chloro-complexes

Anhydrous hexachloro-complexes of the types $M^I{}_3M^{III}Cl_6$ (M^I = Cs, NEt_4 and Ph_3PH; M^{III} = variously Pu and Am) and $Cs_2NaM^{III}Cl_6$ (M^{III} = Am and Bk) are obtained from both aqueous and non-aqueous solvents. Hydrated uranium(III) compounds of the type $M^IUCl_4{\cdot}5H_2O$ (M^I = K, Rb and NH_4) have recently been isolated from oxygen-free, concentrated hydrochloric acid and this observation[135] should stimulate interest in the preparation of analogous neptunium(III) and plutonium(III) complexes; $CsAmCl_4{\cdot}xH_2O$ (x = *ca.* 4) is also known.

Complexes identified during M^ICl–$PuCl_3$ and $M^{II}Cl_2$–$PuCl_3$ phase studies[19] include those of the types $M^I{}_3PuCl_6$ (M^I = K, Rb and Cs), $M^I{}_2PuCl_5$ (M^I = K and Rb), $M^IPu_2Cl_7$ (M^I = Rb and Cs) and $M^{II}{}_3PuCl_6$ (M^{II} = Sr and Ba). Complex formation is not observed in the systems, LiCl–UCl_3, LiCl–$PuCl_3$, NaCl–UCl_3, NaCl–$PuCl_3$, $CaCl_2$–$PuCl_3$, $BaCl_2$–UCl_3, and $MgCl_2$–$PuCl_3$.

$Cs_2NaAmCl_6$ and $Cs_2NaBkCl_6$ possess face-centred cubic symmetry (Table 23); in the latter each berkelium atom is surrounded by an octahedral array of six chlorines each at a distance of 2·58 Å[136]. The magnetic moments of the tetrachlorouranate(III) hydrates range from 3·32 to 3·36 B.M.[135] (θ between 80° and 68°). Metal–chlorine stretching vibrations are listed in Table 23.

Tetravalent Chloro-complexes

Chloro-complexes of the tetravalent actinide elements have been widely investigated[6,15,17,19]. Compounds of the type $M^I{}_2M^{IV}Cl_6$ (M^I = variously Cs, NMe_4, Ph_3PH, NEt_4, Ph_4As, etc.; M^{IV} = Th to Pu inclusive and Bk) crystallize from aqueous hydrochloric acid or from solvents such as ethanol, nitromethane and methyl cyanide. Alternatively, hexachlorothorates(IV) (M^I = Li to Cs inclusive) and hexachlorouranates(IV) (M^I = Li to K

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[134] W. H. Zachariasen, *Acta Cryst.* **1** (1948) 285.
[135] R. Barnard, J. I. Bullock and L. F. Larkworthy, *Chem. Comm.* (1968) 960.
[136] L. R. Morss and J. Fuger, *Inorg. Chem.* **8** (1969) 1433.

TABLE 23. CRYSTALLOGRAPHIC AND INFRARED DATA FOR CERTAIN ACTINIDE CHLORO- AND OXYCHLORO-COMPLEXES

Compound	Colour	Symmetry/ Space group	a_0 (Å)	b_0 (Å)	c_0 (Å)	β°	ν_{M-Cl}*	Ref.
$Cs_2NaAmCl_6$	Yellow	C; $O^5{}_h$–$Fm3m$	10·86				242	a
$Cs_2NaBkCl_6$§	White	C; ,,	10·805				—	b
Cs_2PaCl_6†	Yellow	Trig; K_2GeF_6	7·546		6·056		266	c
Cs_2PuCl_6†§	Pale yellow	Trig; ,,	7·430		6·030		—	d
Cs_2BkCl_6§	Orange	H; $C^4{}_{6v}$–$P6_3mc$	7·450		12·098		—	b
$(NMe_4)_2ThCl_6$†	White	C; $O^5{}_h$–$Fm3m$	13·12				258	e
$(NEt_4)_2UCl_6$†	Green	O; $D^{23}{}_{2h}$–$Fmmm$	14·23	14·73	13·33		253	e
$Cs_2UO_2Cl_4$§	Yellow	M; $C^3{}_{2h}$–$C2/m$	11·92	7·71	5·83	99·46	¶	f
$Cs_2AmO_2Cl_4$	Yellow	C; —	15·10				¶	a
$(NMe_4)_2UO_2Cl_4$	Yellow	T; $C^5{}_{4h}$–$I4/m$	9·12		11·77		—	g
$(NMe_4)_2PuO_2Cl_4$	Yellow	T; ,,	9·20		11·90		—	g
$(NHEt_3)_2UO_2Cl_4$	Yellow	T; ,,	13·50		24·32		—	h
$(NEt_4)_2UO_2Cl_4$	Yellow	M; —	16·30	10·00	12·90	142	—	g
$(NEt_4)_2PuO_2Cl_4$	Yellow	T; $C^5{}_{4h}$–$I4/m$	10·0		12·90		—	g
$Cs_{0\cdot9}UO_3Cl_{0\cdot9}$§	Yellow	M; $C^3{}_{2h}$–$P2_1/m$	8·74	4·11	7·71	105·34	—	i, j
$K_4U_5O_{16}Cl_2$	Yellow	M; $C^5{}_{2h}$–$P2_1/c$	9·96	6·99	19·60	134·97	—	i
$Cs(UO_2)_2Cl_5$	Yellow	O; —	11·17	12·80	8·38		—	k

C, cubic; Trig., Trigonal; H, hexagonal; O, orthorhombic; M, monoclinic; T, tetragonal.

* ν_3 for tetravalent hexachloro-complexes of Th to Pu inclusive lies in the range 255–267 cm^{-1} [6].

† The series M^{IV} = Th to Pu are isostructural[6].

§ Full structural data are given in reference cited.

¶ See Table 25 and p. 196.

[a] K. W. Bagnall, J. B. Laidler and M. A. A. Stewart, *J. Chem. Soc.* (A) (1968) 133.

[b] L. R. Morss and J. Fuger, *Inorg. Chem.* **8** (1969) 1433.

[c] D. Brown and P. J. Jones, *J. Chem. Soc.* (A) (1967) 243.

[d] W. H. Zachariasen, *Acta Cryst.* **1** (1948) 268.

[e] D. Brown, *J. Chem. Soc.* (A) (1966), 766.

[f] D. A. Hall, A. D. Rae and T. N. Waters, *Acta Cryst.* **20** (1966) 160.

[g] E. Staritzky and J. Singer, *Acta Cryst.* **5** (1952) 536.

[h] H. Brusset, Gnuyen-Quy-Dao and F. Hoffner, *Bull. Soc. Chim. Fr.* (1970) 1759.

[i] J. G. Allpress, J. S. Anderson and A. N. Hambly, *J. Inorg. Nucl. Chem.* **30** (1968) 1195.

[j] J. G. Allpress and A. D. Wadsley, *Acta Cryst.* **17** (1964) 41.

[k] A. S. Bavz, I. I. Kapshukov, M. P. Vorobei and O. V. Skiba, *J. Struct. Chem.* **11** (1970) 872.

inclusive) have been prepared by heating together the component chlorides, and certain hexachloroplutonates(IV) (M^I = Na to Cs inclusive) form when the appropriate chloride and plutonium trichloride are heated together in chlorine at temperatures *ca.* 50°C above the melting point of the alkali-metal chloride.

Uranium(IV) complexes of the type $M^{II}UCl_6$ (M^{II} = Ca, Sr and Ba) are also known and there is an unsubstantiated report[137] of the existence of certain octachlorothorates(IV). A vapour phase complex, $UCl_4 \cdot Al_2Cl_6$, is also known; it is appreciably more volatile than uranium tetrachloride itself[130,138].

Selected crystallographic and infrared data are listed in Table 23, together with an indication of series of isostructural compounds. Raman and infrared studies on hexa-

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[137] E. Chauvenet, *Compt. Rend.* **148** (1909) 1519; *Ann. Chim. Phys.* **23** (1911) 425.

[138] D. M. Gruen and R. L. McBeth, *Inorg. Nucl. Chem. Letters*, **4** (1968) 299.

chlorouranates(IV) in methyl cyanide have resulted[139] in the following assignments: 262 (ν_3, M–Cl, i.r.), 121 (ν_5, δ Cl–M–Cl, R), 237 (ν_2, M–Cl, R) and 299 (ν_1, M–Cl, R). The magnetic susceptibilities of the hexachlorouranates(IV) are temperature-independent below *ca.* 350°K indicating a $5f^2$ electronic configuration with a non-magnetic ground state of A_1 ($^3H_4$) with no permanent population of the excited states[6, 15]. Temperature dependence is, however, observed at higher temperatures[140], presumably as a consequence of the thermal population of higher levels of the $^3H_4$ term. Both Cs_2NpCl_6 and Cs_2PuCl_6 exhibit Curie–Weiss dependence below room temperature[6]; for the former $\mu_{eff}=3{\cdot}10$ B.M. with $\theta=-71°$. On the basis of paramagnetic resonance and spectral studies on Cs_2PaCl_6 in a Cs_2ZrCl_6 matrix, it is reported that the Pa^{4+} ion has a $5f^1$ electronic configuration in this complex[141,142]. Results of solid state spectral studies on hexachlorouranates(IV) are discussed in terms of vibronic and pure electronic transitions by Satten *et al*,[144].

Measured heats of formation[143] for Cs_2ThCl_6, Cs_2UCl_6, Cs_2NpCl_6 and Cs_2PuCl_6 are, respectively, $-508{\cdot}7$, $-476{\cdot}7$, $-468{\cdot}5$ and $-466{\cdot}9$ kcal mole^{-1} and for the uranium(IV) complexes[31] K_2UCl_6, $KUCl_5$, Na_2UCl_6 and $KNaUCl_6$ the values are $-461{\cdot}8$, $-353{\cdot}3$, $-441{\cdot}6$ and $-452{\cdot}0$ kcal mole^{-1}, respectively.

Pentavalent Chloro-complexes

Only uranium and protactinium are known to form pentavalent chloro-complexes. Attempts to obtain hexachloroneptunates(V) have been unsuccessful. Hexachloro-complexes $M^IM^VCl_6$ (M^I=NMe_4, NEt_4, Ph_4As, Rb, Cs etc.; M^V=Pa or U) are conveniently obtained[6,15,17,131] from reactions in non-aqueous solvents such as thionyl chloride, thionyl chloride–iodine monochloride mixtures or methyl cyanide. High-temperature chlorination (using thionyl chloride) of UO_3 or U_3O_8 and the appropriate metal chloride, and chlorine oxidation of tetravalent chloro-complexes in nitromethane also yield hexachlorouranates(V). The octachloro-complexes $(NO)_3PaCl_8$, $(NMe_4)_3PaCl_8$ and $(NMe_4)_3UCl_8$ are also known[6], and the formation of $UCl_5{\cdot}AlCl_3$ in the vapour phase has been observed. The free energy change for the reaction[130]

$$UCl_4(s) + AlCl_3(g) + \tfrac{1}{2}Cl_2(g) \rightarrow UCl_5.AlCl_3(g)$$

is given by the equation

$$\Delta G = 8914 - 10{\cdot}74T \text{ cal mole}^{-1} \ (440\text{–}630°\text{K})$$

The vapour phase spectrum of the complex is very similar to that of the U_2Cl_{10} dimer and those of the solid hexachlorouranates(V), indicating the existence of species of the type $AlCl_4(UCl_6)$. Visible and near infrared spectra recorded for the uranium(V) complexes are discussed in detail in recent articles[108,131,145] together with band assignments for $5f^1$ systems. Infrared M–Cl vibrations are observed around 305–310 cm^{-1} (ν_3) and 122 cm^{-1} (ν_4) for hexachlorouranates(V)[6,108] and at 290 cm^{-1} for $(NMe_4)_3PaCl_8$[6]. Magnetic susceptibility data are available for certain of the uranium(V) complexes[6,15,131] and recent ESR measurements have yielded g values of $1{\cdot}1$ (probably −ve)[131].

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[140] W. Trzebiatowski and J. Mulak, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **18** (1970) 121.
[141] J. D. Axe, H. J. Stapleton and R. Kyi, *J. Chem. Phys.* **32** (1960) 1216.
[142] J. D. Axe, H. J. Stapleton and C. D. Jefferies, *Phys. Rev.* **121** (1960) 1630.
[143] J. Fuger and D. Brown, *J. Chem. Soc.* (A) (1971) 841.
[144] R. A. Satten, C. L. Schreiber and E. Y. Wong, *J. Chem. Phys.* **42** (1965) 165, and references therein.
[145] J. Selbin, J. D. Ortego and N. Gritzer, *Inorg. Chem.* **7** (1968) 976.

Oxychlorides

The presently known oxychlorides are listed in Table 2. It is unlikely that elements beyond neptunium will form tetravalent oxydichlorides, but the elements beyond einsteinium will all probably form trivalent oxychlorides and neptunium will possibly form other pentavalent compounds. In view of the difficulties associated with reduction of thorium(IV) and protactinium(IV), trivalent oxychlorides are unlikely to be characterized for these elements.

Trivalent compounds have either been obtained accidentally on sublimation of the trichloride or by heating the appropriate oxide or trichloride in controlled hydrogen chloride–water vapour mixtures between 500° and 550°C. The tetravalent compounds are all conveniently prepared by MCl_4–MO_2 or MCl_4–Sb_2O_3 reactions *in vacuo*; the latter type of reaction has also been employed for the preparation of protactinium(V) oxychlorides which are alternatively obtained by reactions between the pentachloride and oxygen at moderate temperatures and by the thermal decomposition of Pa_2OCl_8 in a vacuum.

$UOCl_3$ is best prepared by the reaction between UO_3 and $MoCl_5$ at 200–220°C *in vacuo* and UO_2Cl is the product of the reaction between UO_2Cl_2 and UO_2 at 590°C. Oxidation of uranium tetrachloride in oxygen leads to the formation of UO_2Cl_2.

These and various other reactions leading to the formation of actinide oxyhalides are discussed in detail in recent reviews[6,15,17,19,131].

Physical and Chemical Properties of the Trivalent Oxychlorides

All the trivalent oxychlorides possess the PbClF-type of structure (Table 24). Temperature coefficients for the unit cell parameters of CfOCl are $\alpha_{a_0}=1\cdot14\times10^{-5}\ ^\circ C^{-1}$ and $\alpha_{c_0}=1\cdot85\times10^{-5}\ ^\circ C^{-1}$.[146] The vapour phase hydrolysis of $PuCl_3$[147] and $AmCl_3$[148] has been investigated; thermodynamic values are given in Tables 5 and 6. The magnetic moment of CmOCl is 7·58 B.M.[39]; no other magnetic studies have been reported.

Little is known concerning the chemical behaviour of the non-volatile oxychlorides. They are non-hygroscopic, and PuOCl is stated to be insoluble in water and soluble in aqueous acid solutions[149].

Physical and Chemical Properties of the Tetravalent Oxyhalides

The isostructural oxydichlorides possess the unusual structure recently reported for $PaOCl_2$[150] (Table 24 and Fig. 7). This consists of infinite polymeric chains along the short c_0 axis cross linked in the a_0b_0 plane. Protactinium atoms are 7-, 8- and 9-coordinate, with oxygen atoms 3- and 4-coordinate. Infrared observations are consistent with such a polymeric structure, all the bands occurring below 600 cm^{-1}.[151]

Few chemical properties have been recorded for the oxydihalides. They are thermally unstable and when heated above *ca.* 550°C *in vacuo* disproportionate to yield a sublimate of the tetrachloride and a residue of the dioxide. Available thermodynamic data are listed in Tables 5 and 6. Neither magnetic nor solid state spectral studies have been reported. Complexes with donor ligands are unknown.

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[146] D. K. Fujita, U.S. Report UCRL-19507 (1969).

[147] I. Sheft and N. Davidson, ref. 1, p. 841.

[148] C. W. Koch and B. B. Cunningham, *J. Amer. Chem. Soc.* **76** (1954) 1470.

[149] B. M. Abraham, B. B. Brody, N. R. Davidson, F. Hagemann, I. Karle, J. J. Katz and M. J. Wolf, ref. 1, p. 740.

[150] R. P. Dodge, G. S. Smith, Q. Johnson and R. E. Elson, *Acta Cryst.* **24B** (1968) 304.

[151] K. W. Bagnall, D. Brown and J. F. Easey, *J. Chem. Soc.* (A) (1968) 288.

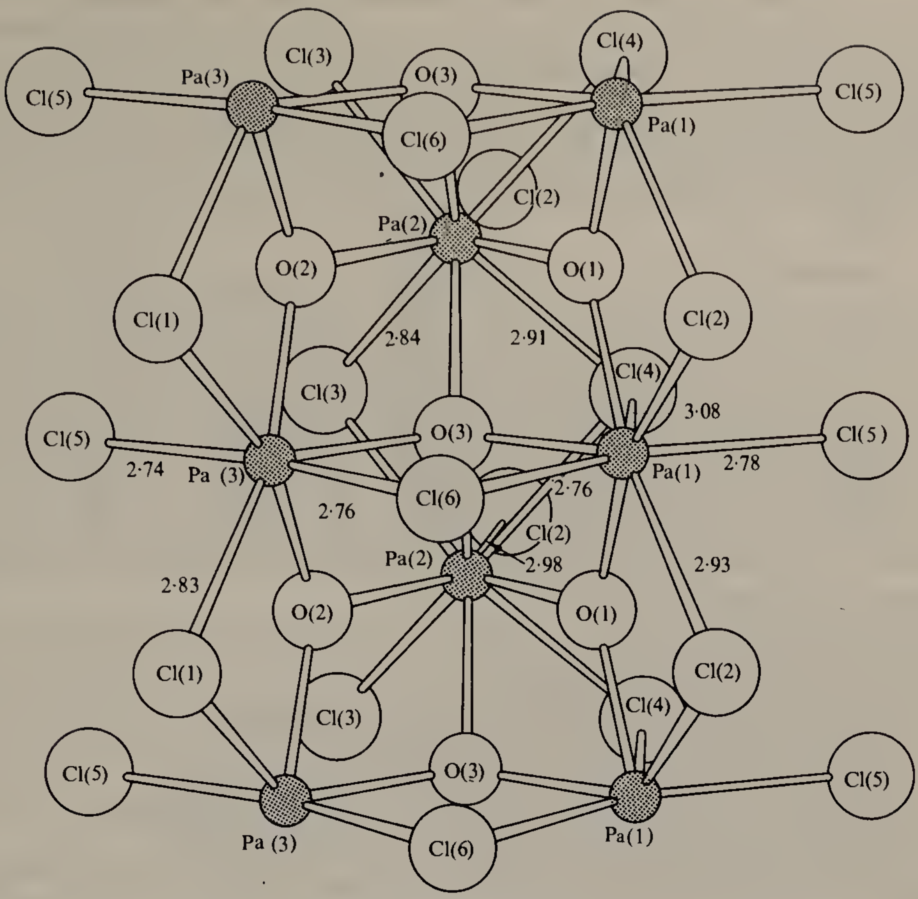

FIG. 7. The structure of $PaOCl_2$. (Reproduced by permission from R. P. Dodge *et al.*, *Acta Cryst.* **24B** (1968) 304.)

Physical and Chemical Properties of the Pentavalent Oxychlorides

No structural information is available, but infrared studies[152] suggest that the Pa(V) oxychlorides are probably polymeric, all bands occurring below 600 cm^{-1}. Thermodynamic values ($UOCl_3$ only) are given in Table 5. The only magnetic data available are for UO_2Cl for which $\mu_{eff} = 1 \cdot 86$ B.M. ($\theta = -95°$).

The protactinium(V) compounds are all thermally unstable, each disproportionating *in vacuo* to yield the pentachloride and the next lower oxychloride. For example[152],

$$3Pa_2OCl_8 \xrightarrow{250°C} 4PaCl_5 + Pa_2O_3Cl_4$$

and

$$2Pa_2O_3Cl_4 \xrightarrow{520°C} PaCl_5 + 3PaO_2Cl$$

Uranium(V) oxytrichloride, on the other hand, is reported to decompose above 700°C to give a mixture of tetrachloride, pentachloride, dioxide and a phase of composition $U_2O_3Cl_3$[153].

The pentavalent oxychlorides are all moisture-sensitive; little is known concerning their chemistry. The only complex known with an oxygen donor ligand is $PaOCl_3 \cdot 2TPPO$[154].

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[152] D. Brown and P. J. Jones, *J. Chem. Soc.* (A) (1966) 874.

[153] I. V. Budayev and N. Vol'sky, *Proc. 2nd Int. Conf. Peaceful Uses Atomic Energy*, Vol. 28, p. 316. Geneva (1958).

[154] D. Brown and C. E. F. Rickard, *J. Chem. Soc.* (A) (1971) 81.

TABLE 24. CRYSTALLOGRAPHIC DATA FOR ACTINIDE OXYCHLORIDES

Compound	Colour	Symmetry/ Space group	a_0 (Å)	b_0 (Å)	c_0 (Å)	Ref.
AcOCl*	White	T; D^{7}_{4h}–*P4/nmm*	4·248	—	7·084	a
UOCl	Red	,, ,,	4·000	—	6·85	b
NpOCl		,, ,,	4·028	—	6·836	c
PuOCl*	Blue-green	,, ,,	4·014	—	6·793	a
AmOCl		,, ,,	4·000	—	6·78	d
BkOCl	Green	,, ,,	3·966	—	6·71	e
CfOCl		,, ,,	3·956	—	6·662	f
EsOCl†		,, ,,	3·97	—	6·75	g
$ThOCl_2$	White	O; C^{8}_{2v}–*Pbam*	15·494	18·095	4·018	h
$PaOCl_2$	Mustard	,, ,,	15·332	17·903	4·012	h
$UOCl_2$	Green	,, ,,	15·255	17·828	3·992	h
$NpOCl_2$	Orange	,, ,,	15·209	17·670	3·948	h
UO_2Cl_2	Yellow	O; D^{16}_{2h}–*Pnma*	5·725	8·409	8·720	i

* Parameters converted from Kx units.
† Parameters at *ca.* 430°C.

T, tetragonal; O, orthorhombic.
[a] W. H. Zachariasen, *Acta Cryst.* **2** (1949) 388.
[b] S. A. Shchukarov and A. I. Efimov, *Zhur. Neorg. Khim.* **2** (1957) 2304.
[c] D. Brown and J. Edwards, *J. Chem. Soc. Dalton* (1972) 1957.
[d] D. H. Templeton and C. H. Dauben, *J. Amer. Chem. Soc.* **75** (1953) 4560.
[e] J. R. Peterson and B. B. Cunningham, *Inorg. Nucl. Chem. Letters*, **3** (1967) 579.
[f] J. C. Copeland and B. B. Cunningham, *J. Inorg. Nucl. Chem.* **31** (1969) 733.
[g] D. K. Fujita, B. B. Cunningham and J. C. Parsons, *Inorg. Nucl. Chem. Letters*, **5** (1969) 307.
[h] K. W. Bagnall, D. Brown and J. F. Easey, *J. Chem. Soc.* (A) (1968) 288.
[i] P. S. Debets, *Acta Cryst.* **24B** (1968) 400.

Physical and Chemical Properties of Uranyl Chloride

Thermodynamic data are given in Tables 5 and 6, and unit cell parameters are included in Table 24.

Uranyl chloride is a yellow solid (m.p. 751°K) which is converted to U_3O_8 on ignition in air. It is moisture-sensitive and the monohydrate $UO_2Cl_2 \cdot H_2O$ and a higher hydrate $UO_2Cl_2 \cdot xH_2O$ ($x > 3$) are known. Numerous complexes with oxygen donor ligands, e.g. amides, triarylphosphine oxides and diarylsulphoxides, are known in which coordination of the ligand takes place via the oxygen atom[6,14,15,17]. A range of complexes with a variety of nitrogen donor ligands is also known. The uranium–oxygen stretching vibration occurs in the range 920 to 960 cm^{-1} in many of these complexes; bands in the region 250 to 265 cm^{-1} have been assigned to the O–U–O bending mode with U–Cl vibrations between 238 and 243 cm^{-1} in complexes of the type $UO_2Cl_2 \cdot 2L$ ($L = Ph_3PO$ and Ph_3AsO)[155]. In uranyl chloride itself the asymmetric (i.r.) and symmetric (R) stretching vibrations for the UO_2^{2+} group occur at 960 and 871 cm^{-1}, respectively. The force constant is calculated to be 7·40 Mdyn $Å^{-1}$ and the U=O bond distance as 1·72 Å[156].

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[155] F. A. Hart and J. E. Newberry, *J. Inorg. Nucl. Chem.* **30** (1968) 318.
[156] J. I. Bullock, *J. Chem. Soc.* (A) (1969) 781.

Oxychloro-complexes

A few pentavalent actinide oxychloro-complexes of the types $M^{I}_2M^{V}OCl_5$ (M^{I}= univalent cation; M^{V}=Pa, U and Np) and $M^{I}_3M^{V}O_2Cl_4$ (M^{V}=Np and Am) are known together with a wide variety of actinyl (VI) complexes, $M^{I}_2M^{VI}O_2Cl_4$ (M^{I}=univalent cation; M^{VI}=U, Np, Pu and Am), but no trivalent or tetravalent complexes have yet been characterized.

Pentavalent Oxychloro-complexes

Cs_2NpOCl_5 and $(Ph_4As)_2NpOCl_5$ have been isolated from aqueous hydrochloric acid[157], but the Pa(V) and U(V) complexes $(NEt_4)_2PaOCl_5$[154], $(NEt_4)_2UOCl_5$[108] and $(Ph_4As)_2UOCl_5$[108] are only obtained from the hexachlorometallates(V) or similar complexes in the presence of controlled amounts of water by crystallization from solvents such as methyl cyanide and nitromethane. The bisethoxychloro-complex $NEt_4Pa(OEt)_2Cl_4$ has also been characterized[154]. The dioxytetrachloro-complexes $Cs_3NpO_2Cl_4$[157] and $Cs_3AmO_2Cl_4$[158] are obtained by precipitation from dilute hydrochloric acid–ethanol mixtures.

There are interesting differences in the positions of the M–O stretching vibrations for the various $M^{I}_2MOCl_5$ complexes (Table 25). Although one might expect a relatively long Pa=O bond in view of the position of the metal–oxygen vibration (830 cm^{-1}) in $(NEt_4)_2$-$PaOCl_5$ (monoclinic, space group C^6_{4h}-Cc with a_0=14·131, b_0=14·218, c_0=13·235 Å and

TABLE 25. INFRARED AND RAMAN ASSIGNMENTS FOR SOME PENTAVALENT AND HEXAVALENT OXYHALOGENO-COMPLEXES*

Compound	Colour	$\nu_{M=O}$ (cm^{-1})	δ_{O-U-O} (cm^{-1})	ν_{M-Cl} (cm^{-1})*	Ref.
$(NEt_4)_2PaOCl_5$	Yellow	830		289, 251	a
$(NEt_4)_2UOCl_5$	Blue	913, 813		296, 253, 197, 120	b
Cs_2NpOCl_5	Pale-yellow	921		275 (252)	c
$(Ph_4As)_2NpOCl_5$	Pale-yellow	907		271 (237)	c
$Cs_3NpO_2Cl_4$	Green	810, 794		264 (245, 217)	c
$Cs_3AmO_2Cl_4$	Green	800		290	d
$Cs_2UO_2Cl_4$	Yellow	922, 831 (R)	265	264(R), 240, 131(R)	e, f
$Cs_2NpO_2Cl_4$†	Yellow	919	271	244	c
$Cs_2AmO_2Cl_4$†	Dark red	902	313	244	d
$Cs_2AmO_2Cl_4$†	Dark red	902	303	230	d
$(NEt_4)_2PaOBr_5$	Yellow	840		—	a
$(NEt_4)_2UOBr_5.2{\cdot}5NEt_4Br$	Green	919, 817		190, 80	b
$(NMe_4)_2UO_2Br_4$	Yellow	—, 832(R)	256	198(R), 170, 89(R)	f
$Cs_2UO_2Br_4$	Yellow	920, 836(R)			e

* Unless indicated, bands shown refer to i.r. data; bands in parentheses are observed but not assigned.

† Assignments have been modified in the light of more recent studies on uranyl(VI) complexes (see p. 196).

[a] D. Brown and C. E. F. Rickard, *J. Chem. Soc.* (A) (1971) 81.

[b] J. L. Ryan, *J. Inorg. Nucl. Chem.* 33 (1971) 153.

[c] K. W. Bagnall and J. B. Laidler, *J. Chem. Soc.* (A) (1966), 516.

[d] K. W. Bagnall, J. B. Laidler and M. A. A. Stewart, *J. Chem. Soc.* (A) (1968) 133.

[e] J. I. Bullock, *J. Chem. Soc.* (A) (1969) 781.

[f] J. E. Newberry, *Spectrochim. Acta*, A25, (1969) 1699.

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[157] K. W. Bagnall and J. B. Laidler, *J. Chem. Soc.* (A) (1966) 516.

[158] K. W. Bagnall, J. B. Laidler and M. A. A. Stewart, *J. Chem. Soc.* (A) (1968) 133.

$\beta=91\cdot04°$) a recent structure determination[159] has shown this to be only 1·74 Å. The *trans* Pa–Cl bond length is 2·42 Å with the remaining four Pa–Cl distances in the distorted octahedron ranging from 2·59 to 2·72 Å. The electronic and infrared spectra of the uranium(V) oxypentachloro-complexes are discussed in a recent publication[108].

The positions of the metal–oxygen stretching vibrations for the dioxytetrachloro-complexes (Table 24) indicate the presence of discrete MO_2^+ ions.

Hexavalent Oxychloro-complexes

Anhydrous actinyl(VI) tetrachloro-complexes, $M^I_2M^{VI}O_2Cl_4$ (M^I=a wide range of large univalent cations, especially for U; M^{VI}=U, Np and Pu), are obtained in a variety of ways. The single known americium(VI) complex, $Cs_2AmO_2Cl_4$, is prepared by treating the pentavalent compound $Cs_3AmO_2Cl_4$ with concentrated hydrochloric acid[158]. Dihydrates of the uranyl(VI) complexes with small cations (K, Rb and NH_4) crystallize preferentially from aqueous solution and salts of the types $M^I_2UO_3Cl_2$ (M^I=K and NH_4) and $M^I_xUO_3Cl_x$ (M^I=K, Rb and Cs) are obtained by high-temperature reactions involving uranium oxides. The crystallographic data available for certain of these complexes are discussed together with the preparative methods in recent reviews[6,15,17,19]. Unit cell dimensions are listed in Table 23.

Recent interest has been concentrated on infrared and Raman studies dealing with the effects of cation size on the asymmetric U–O stretching vibration (ν_3) in the dioxytetrachlorouranates(VI), and the calculation of U–O bond lengths and force-constants (see ref. 17 for a summary). In complexes of the type $M^I_2UO_2Cl_4$ the symmetric Raman active uranium–oxygen stretching vibration (ν_1) is observed between 831 and 840 cm^{-1}, the bending mode (i.r. active) occurs between 256 and 265 cm^{-1} with U–Cl vibrations at *ca.* 240 cm^{-1} (i.r.), *ca.* 260 cm^{-1} (R) and *ca.* 130 cm^{-1} (R). The results for $Cs_2UO_2Cl_4$ are shown in Table 25. In view of these recent spectral studies it is likely that bands at 303 and 315 cm^{-1} previously assigned[158] to Am–Cl stretching vibrations in the two crystal modifications of $Cs_2AmO_2Cl_4$ are in fact associated with the O–Am–O bending mode; similarly the assignment[157] of a Np–Cl vibration at 271 cm^{-1} is probably in error, this really being the O–Np–O bending mode whilst an unassigned band at 245 cm^{-1} is associated with the Np–Cl stretching vibration. These modifications to the original assignments are included in Table 25. Similar modifications are quite probably required for the $Cs_3AmO_2Cl_4$ assignments.

Five pure electronic levels (6880, 13,277, 14,425, 17,478 and 1,9351 cm^{-1}, respectively) have been identified as a result of visible and i.r. studies on the NpO_2^{2+} ion in $Cs_2UO_2Cl_4$. The first is assigned to a transition within the $5f^1$ configuration; the remainder probably arise from an excited configuration[160]. Solution and solid state spectra are also available for certain neptunyl(VI) and plutonyl(VI) chloro-complexes[161].

4. COMPOUNDS WITH BROMINE

Binary bromides

As a consequence of the lower oxidizing power of bromine and its inability to stabilize higher valence state compounds, fewer actinide bromides are known than chlorides and fluorides (Table 1). In view of the valence state stability trends within this series of elements,

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[159] D. Brown, P. T. Moseley and C. J. Reynolds, *J. Chem. Soc. Dalton* (1972) 857.

[160] O. M. Staffsudd, A. F. Leung and E. Y. Wong, *Phys. Rev.* **180** (1969) 339.

[161] J. L. Ryan, *Inorg. Chem.* **2** (1963) 348.

the only new compounds likely to be obtained in the future are the tribromides of protactinium and of the elements einsteinium to lawrencium inclusive and, possibly, that of thorium, together with dibromides of some of the elements.*

Direct combination of bromine and the appropriate element leads to the formation of $ThBr_4$, $PaBr_5$, UBr_4 (or under controlled conditions either UBr_3 or UBr_5), $NpBr_4$ and $PuBr_3$, respectively. Protactinium tetrabromide, uranium tribromide and neptunium tribromide are formed by reduction of their respective higher bromides by reagents such as hydrogen or aluminium. A variety of oxide–brominating agent reactions are available for the preparation of the tribromides of the elements plutonium to californium inclusive and the trichloride–ammonium bromide reaction has been employed in certain instances. Detailed accounts of the various preparative methods are available[6,15,17,19]

The Physical and Chemical Properties of the Tribromides

As a consequence of the actinide contraction, structural changes occur in the tribromides, the earlier members (Ac to α-$NpBr_3$) possessing the 9-coordinate UCl_3-type of structure (p. 182) and later members (β-$NpBr_3$ to $BkBr_3$) possessing the 8-coordinate $PuBr_3$-type of structure. The latter is a layer-type structure with each Pu atom bonded to two bromines at 3·06 Å and six at 3·08 Å. The structure of $CfBr_3$ is unknown, but it is quite different from that of $PuBr_3$. The appropriate references are given together with unit cell dimensions in Table 26.

Available thermodynamic values are given in Tables 4 and 6–8 inclusive and vapour pressure data are listed in Table 9. Magnetic susceptibility results for uranium tribromide[45] are very similar to those of the trichloride indicating a $5f^3$ electronic configuration; $\mu_{eff}=$ 3·29 B.M. (with $\theta=-25°$). No other magnetic properties have been recorded. Solid state spectral data are available for $AmBr_3$[162], for the Np^{3+} ion in a $LaBr_3$-matrix[163] and the spectrum of gaseous $PuBr_3$ has been measured[114] in the range 4000 to 42,000 cm^{-1}. Pertinent results obtained from the $Np^{3+}/LaBr_3$ study are given in Table 21.

Hexahydrates have been characterized[6,17,19] for certain (U, Np, Pu, Am and Cf) of the moisture-sensitive tribromides and evidence points to the existence of monohydrates. The hexahydrates are isostructural with their trichloride analogues. Plutonium, americium and curium tribromide are all stable in hydrogen at elevated temperatures and the first is not oxidized by bromine vapour. No evidence for the existence of a lower bromide was found during an investigation of the UBr_3-U phase system.

Apart from the hydrates mentioned above, the only other known complex with donor ligands is $UBr_3 \cdot 8NH_3$. Hexabromo-complexes are discussed later.

The Physical and Chemical Properties of the Tetrabromides

β-$ThBr_4$ and $PaBr_4$ are isostructural with the actinide tetrachlorides (p. 184), the two M–4Br distances in the latter being 2·77 and 3·07 Å, respectively. The structures of the remaining tetrabromides are unknown (Table 26). Gaseous thorium and uranium tetrabromide exist as distorted tetrahedra (C_{2v} symmetry) with M–Br bond distances of 2·72 and 2·66 Å, respectively[124].

Vapour pressure data are listed in Table 9 and various thermodynamic values are given in Tables 4 and 6–8 inclusive. The magnetic moment of UBr_4 is 3·12 B.M. ($\theta=-35°$).

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* See footnote, page 151.

[162] R. G. Pappalardo, W. T. Carnell and P. R. Fields, *J. Chem. Phys.* **51** (1969) 1182.

[163] W. F. Krupke and J. B. Gruber, *J. Chem. Phys.* **46** (1967) 542.

TABLE 26. CRYSTALLOGRAPHIC DATA FOR THE ACTINIDE BROMIDES AND OXYBROMIDES

Compound	Colour	Symmetry/ Space group	a_0 (Å)	b_0 (Å)	c_0 (Å)	$\beta°$	Ref.
$AcBr_3$*		H; C^2_{6h}–$C6_3/m$	8·076	—	4·689		a, b
UBr_3	Red	,, ,,	7·938	—	4·438		c
α-$NpBr_3$	Green	,, ,,	7·916	—	4·390		c
β-$NpBr_3$	Green	O; D^{17}_{2h}–$Ccmm$	12·618	4·108	9·153		c
$PuBr_3$	Green	,, ,,	12·617	4·097	9·147		c
$AmBr_3$	White	,, ,,	12·661	4·064	9·144		d
$CmBr_3$	White	,, ,,	12·660	4·048	9·124		d
$BkBr_3$	Yellow-green	,, ,,	12·60	4·10	9·10		e
β-$ThBr_4$	White	T; D^{19}_{4h}–$I4/amd$	8·945	—	7·930		f
$PaBr_4$	Brown	,, ,,	8·824	—	7·957		g
UBr_4	Brown	M; —	10·92	8·69	7·05	93·15	h
$NpBr_4$	Dark red	M; —	10·89	8·74	7·05	94·19	i
α-$ThBr_4$	White	O; —	13·610	12·050	7·821		j
β-$PaBr_5$	Dark red	M; C^5_{2h}–$P2_1/n$	8·48	11·205	8·95	91·1	k
AcOBr*		T; D^7_{4h}–$P4/nmm$	4·278	—	7·415		a, b
PuOBr*	Green	T; D^7_{4h}–$P4/nmm$	4·022	—	7·571		l
BkOBr	White	,, ,,	3·95	—	8·10		e
CfOBr	Green	,, ,,	3·90	—	8·11		m
CfOBr	White	,, ,,	3·90	—	8·12		n
$PaOBr_3$	Green	M; C^3_2–$C2$	16·911	3·871	9·334	113·67	o
$UOBr_3$	Brown	M; C^3_2–$C2$	16·24	3·7	9·0	110·5	p

* Original values converted from Kx units.
H, hexagonal; O, orthorhombic; T, tetragonal; M, monoclinic.

[a] S. Fried, F. Hagemann and W. H. Zachariasen, *J. Amer. Chem. Soc.* **72** (1950) 771.
[b] W. H. Zachariasen, *Acta Cryst.* **1** (1948) 265.
[c] D. Brown and J. Edwards, *J. Chem. Soc. Dalton* (1 72) 1757.
[d] L. B. Asprey, T. K. Keenan and F. H. Kruse, *Inorg. Chem.* **4** (1965) 985.
[e] D. Cohen, S. Fried, S. Siegel and B. Tani, *Inorg. Nucl. Chem. Letters*, **4** (1968) 257.
[f] R. W. M. D'Eye, *J. Chem. Soc.* (1950) 2764.
[g] D. Brown and P. J. Jones, *J. Chem. Soc.* (A) (1967) 719.
[h] R. M. Douglass and E. Staritzky, *Anal. Chem.* **29** (1957) 459.
[i] D. Brown, J. Hill and C. E. F. Rickard, *J. Chem. Soc.* (A) (1970) 476.
[j] D. E. Scaife, *Inorg. Chem.* **5** (1965) 162.
[k] D. Brown, T. Petcher and A. J. Smith, *Acta Cryst.* **25B** (1969) 178.
[l] W. H. Zachariasen, *Acta Cryst.* **2** (1949) 388.
[m] D. K. Fujita, U.S. Report UCRL-19507 (1969).
[n] S. Fried, D. Cohen, S. Siegel and B. Tani, *Inorg. Nucl. Chem. Letters*, **4** (1968) 495.
[o] D. Brown, T. J. Petcher and A. J. Smith, *Nature*, **217** (1968) 738.
[p] J. C. Levet, Personal communication (1972).

Low-temperature spectra have been recorded for uranium tetrabromide, the observed bands being assigned to transitions from the $^3H_4(T_5)$ ground state to excited states of the $5f^2$ configuration[125]. Magnetic and spectral data are not available for the other tetrabromides.

The moisture-sensitive tetrabromides do not form stable hydrates, but a variety of complexes with donor ligands such as amides, triarylphosphine oxides, dialkylsulphoxides and methyl cyanide have been characterized. For detailed discussions of such complexes recent review articles are recommended[14,15,17,20]. A brief summary of certain of these compounds is shown in Table 27.

The conversion of the tetrabromides to oxydibromides and the preparation of hexabromometallates(IV) are discussed later (pp. 201 and 200, respectively).

Table 27. Examples of Tetravalent and Hexavalent Bromide Complexes with Donor Ligands*

Ligand	Stoichiometry for					
	$ThBr_4$	$PaBr_4$	UBr_4	$NpBr_4$	$PuBr_4$	UO_2Br_2
N,N-Dimethylacetamide	1:5	1:5	1:5	*a*	*a*	
	1:2·5	1:2·5	1:2·5	*a*	*a*	
						1:2
Hexamethylphosphoramide	1:3	*b*	*b*	*b*	*b*	
	1:2	1:2	1:2	1:2	1:2	1:2
Triphenylphosphine oxide	1:3	*b*	*b*	*b*	*b*	
	1:2	1:2	1:2	1:2	1:2	1:2
Dimethylsulphoxide	1:6	*a*	1:6	*a*	*a*	*a*
Methyl cyanide	1:4	1:4	1:4	1:4	1:4	
						1:1

* For full details of these and related complexes, see refs. 6, 14, 15, 17 and 20.

[a] System not studied.

[b] Complex formation not observed at this stoichiometry.

The Physical and Chemical Properties of the Pentabromides

Two crystal modifications of protactinium pentabromide (α and β) are known; uranium pentabromide is isostructural with the β-form[164]. β-$PaBr_5$ (Table 26) is dimeric[165], each protactinium being 6-coordinate with Pa–Br distances of 2·83 and 2·84 Å (bridging) and 2·52 to 2·67 Å (non-bridging); the structure is similar to that of UCl_5 (p. 187). The calculated single-bond, covalent radius for Pa^{5+} in β-$PaBr_5$ is 1·44 Å. Thermodynamic, magnetic and vapour pressure data are not available.

Both compounds are moisture-sensitive and stable hydrates are unknown. A few complexes with oxygen and nitrogen donor ligands have, however, been prepared under anhydrous conditions. These include[6,14,17] $MBr_5 \cdot L$ (M = U and Pa; L = triphenylphosphine oxide and hexamethylphosphoramide), $PaBr_5 \cdot 2L$ (L = triphenylphosphine oxide) and $PaBr_5 \cdot 3L$ (L = methyl cyanide and dimethylacetamide).

Conversion of the pentabromides to oxybromides and hexabromo-complexes are both discussed later (pp. 201 and 200, respectively).

Bromo-complexes

Tri-, tetra-, and pentavalent bromo-complexes are known for a variety of actinide elements, but none form stable hexavalent complexes. General preparative methods are briefly outlined in the following sections, but the reader is referred to available reviews for details of the original literature[6,15,17,19].

Trivalent Bromo-complexes

Ryan[166] recently obtained trivalent hexabromo-complexes of Pu(III) and Am(III) from ethanol saturated with hydrogen bromide but failed to obtain the analogous U(III) complexes owing to rapid oxidation even in the absence of air. Solution spectra have been

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[164] F. Lux, D. Dempf and K. W. Bagnall, *Chem. Ber.* **103** (1970) 2807.

[165] D. Brown, T. J. Petcher and A. J. Smith, *Acta Cryst.* **25B** (1969) 178.

[166] J. L. Ryan, ref. 71, p. 331.

recorded for the plutonium complex $(Ph_3PH)_3PuBr_6$, but, apart from the comment that this oxidizes to the $PuBr_6^{2-}$ species on exposure to air, no other properties have been recorded.

Tetravalent Bromo-complexes

Hexabromo-complexes, $M_2^IM^{IV}Br_6$, are known for the elements thorium to plutonium inclusive[6,15,19]. Complexes such as $(NEt_4)_2M^{IV}Br_6$ (M = U, Np and Pu) crystallize from ethanolic hydrogen bromide solution on the addition of acetone. However, anhydrous thorium, protactinium, uranium and neptunium hexabromo-complexes are more conveniently prepared by reactions between the appropriate tetrabromide and a univalent bromide, MBr (M = variously NMe_4, NEt_4, Ph_3PBu, Ph_3PBz, Ph_3PH and Et_3PH), in non-aqueous solvents such as methyl cyanide. Alkali-metal hexabromouranates(IV) have also been obtained by heating either sodium or potassium bromide in uranium tetrabromide vapour, but there appears to have been no thorough investigation of any MBr– or MBr_2–$M^{IV}Br_4$ phase system.

The tetramethylammonium complexes $(NMe_4)_2ThBr_6$, $(NMe_4)_2PaBr_6$ and $(NMe_4)_2UBr_6$, like their hexachloro-analogues, possess face-centred cubic symmetry; unit cell dimensions, are 13·49, 13·40 and 13·37 Å, respectively[6]. Metal bromine stretching vibrations (ν_3) are observed around 180 cm^{-1} for certain of the thorium(IV), protactinium(IV) and uranium(IV) complexes.

The uranium(IV) hexabromo-complexes exhibit almost temperature-independent paramagnetism below 300°K.[167] This observation is in agreement with the non-magnetic ground state $A_1(^3H_4)$; assuming no thermal population of excited states, the observed susceptibility is likely to be due to an unusually large high-frequency term arising from an interaction between the ground state and the first excited state $T_1(^3H_4)$.

Pentavalent Bromo-complexes

Hexabromoprotactinates(V), M^IPaBr_6 (M^I = NMe_4 and NEt_4), crystallize when the component halides are mixed in anhydrous methyl cyanide[168]. Alternatively both protactinium(V) and uranium(V) bromo-complexes are obtained by metathesis of the appropriate hexachloro-complex with liquid boron tribromide[169]. Bromine oxidation of uranium tetrabromide (or a U(IV) hexabromo-complex) in methyl cyanide or nitromethane in the presence of suitable univalent bromides, e.g. NEt_4Br and Ph_4AsBr, provides a second convenient route to hexabromouranates(V)[108].

The orange-red protactinium(V) and brown-black uranium(V) complexes are extremely moisture-sensitive, but they can be safely handled in anhydrous, oxygen-free solvents and spectral data are available for hexabromouranates(V) both in the solid state[108,169] and in solvents such as methylene dichloride[169]. These are very similar to those of the hexachlorouranates(V); the results are discussed in detail by Ryan[108]. Infrared stretching vibrations have been recorded at 214 cm^{-1} (ν_3), 87 cm^{-1} (ν_4), 68 and 62 cm^{-1} (ν_6) for NEt_4UBr_6[108] and at *ca.* 216 cm^{-1} (ν_3) for NEt_4PaBr_6 and NMe_4PaBr_6[168].

No structural, magnetic or thermodynamic data are available.

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[167] J. P. Day and L. M. Venanzi, *J. Chem. Soc.* (A) (1966) 197.

[168] D. Brown and P. J. Jones, *J. Chem. Soc.* (A) (1967) 247.

[169] D. Brown, J. Hill and C. E. F. Rickard, *J. Chem. Soc.* (A) (1970) 476.

Oxybromides

The presently known actinide oxybromides are listed in Table 2. It is likely that NpOBr, AmOBr and the corresponding compounds of the elements einsteinium to lawrencium inclusive will be capable of existence, but new tetravalent, pentavalent or hexavalent compounds are unlikely to be obtained.

The trivalent compounds are conveniently prepared by heating the appropriate tribromide in moist hydrogen bromide vapour at 450° to 550°C. Tetravalent oxydibromides, $MOBr_2$, are readily obtained by tetrabromide–dioxide or tetrabromide–antimony sesquioxide reactions at moderate temperatures in a vacuum. The pentabromide–antimony sesquioxide reaction is useful for the preparation of $PaOBr_3$ and PaO_2Br which are alternatively obtained by reactions between protactinium pentabromide and oxygen. The former type of reaction, MBr_5–Sb_2O_3, may also prove useful for the formation of pentavalent uranium oxybromides. $UOBr_3$ and UO_2Br have been produced by the controlled reduction of uranium trioxide using carbon tetrabromide vapour (110°) and hydrogen bromide (250°), respectively. Oxidation of uranium tetrabromide (150–160°) or uranium(V) oxytribromide (148°) are amongst several methods reported to yield uranyl(VI) bromide, UO_2Br_2.

The interested reader is referred to recent reviews[6,15,17] for further discussion of the above preparative methods and for references to the original literature.

The Physical and Chemical Properties of the Trivalent Oxybromides

In common with the trivalent lanthanide oxytribromides[6] and the actinide oxychlorides (p. 192) and actinide oxyiodides (p. 207) the trivalent oxybromides possess the PbFCl-type of structure (Table 26); the Pu–4O and Pu–4Br distances in this layer-type structure are, respectively, 2·34 and 3·21 Å. Thermodynamic data (PuOBr only) are given in Tables 5 and 6; neither magnetic nor spectral data are available.

The chemical properties of this series of compounds have not been studied; this is hardly surprising, however, when one recalls that, apart from PuOBr, only microgram amounts of the oxybromides have been prepared.

The Physical and Chemical Properties of the Tetravalent Oxybromides

Although structural information is not available, it appears likely, in view of the fact that i.r. bands only occur below 600 cm^{-1} for the isostructural oxydibromides of thorium(IV) to neptunium(IV) inclusive[151], that these compounds possess polymeric structures involving extensive oxygen-bridging similar to that reported for $PaOCl_2$ (p. 192).

Thermodynamic values are presented in Tables 5 and 6. Magnetic and spectral studies have not been reported. The compounds are non-volatile solids which disproportionate when heated at *ca.* 550° to 600°C in a vacuum to yield their respective tetrabromides and dioxides. They dissolve readily in dilute acid solutions and yield their respective stable oxides on ignition in air at *ca.* 850°C.

The Physical and Chemical Properties of the Pentavalent Oxybromides

Protactinium(V) oxytribromide (Table 26) crystallizes with a structure which comprises chains of 7-coordinate protactinium atoms linked by bridging oxygen atoms (3- or 4-coordinate) and bridging bromine atoms. The Pa–O distances range from 2·06 to 2·25 Å with Pa–Br bridging distances of 2·76 and 3·02 Å and Pa–Br terminal distances of 2·56 to

2·69 Å[170]. Pa–O stretching vibrations are observed[171] only below 600 cm^{-1} for both $PaOBr_3$ and PaO_2Br. Levet has recently shown[171a] that, contrary to earlier results[172,173], $UOBr_3$ and UO_2Br are isostructural with their protactinium analogues and that the former, like $PaOBr_3$, exhibits bands only below 600 cm^{-1} in its infrared spectrum.

Thermodynamic values are shown in Table 5. The magnetic moment recorded for UO_2Br is 1·76 B.M. ($\theta = -200°$).[173]

$PaOBr_3$, like the higher pentavalent protactinium oxychlorides and $PaOI_3$, is thermally unstable in a vacuum, disproportionating to yield the volatile pentabromide and non-volatile dioxymonobromide[174]

$$2PaOBr_3 \xrightarrow{500°C} PaBr_5 + PaO_2Br$$

An adduct with hydrogen bromide, $UO_2Br \cdot HBr$, is known and the complex $PaOBr_3 \cdot 2Ph_3PO$ has been characterized; it crystallizes on the controlled hydrolysis of $Pa(OEt)_2Br_3 \cdot Ph_3PO$ in methyl cyanide[154]. No other complexes are known.

The Physical and Chemical Properties of Uranyl Bromide

The structure of uranyl bromide is unknown; the strong U–O stretching vibration occurs (i.r.) at 905 cm^{-1} with other bands at 948, 930 and 825 cm^{-1}.[175] Some thermodynamic data are given in Table 5.

Anhydrous uranyl bromide is a dark red solid which evolves bromine slowly at room temperature; it is deliquescent and the yellow trihydrate $UO_2Br_2 \cdot 3H_2O$ may be obtained under controlled conditions. UO_2Br_2 is soluble in many polar organic solvents such as acetone, ether and various alcohols. It forms stable complexes with oxygen and nitrogen donor ligands,[6,14,15,17] a brief selection of which is shown in Table 27.

Oxybromo-complexes

Uranyl(VI) oxybromo-complexes are known and very recently the first examples of pentavalent actinide oxybromo-complexes, $M^I_2M^VOBr_5$ (M^I = a univalent cation, M^V = Pa[154] and U[108]), have been characterized. Neither tri- nor tetravalent complexes are known.

Pentavalent Oxybromo-complexes

$(NEt_4)_2PaOBr_5$, $(Ph_4As)_2UOBr_5$ and $(NEt_4)_2UOBr_5 \cdot 2{\cdot}5NEt_4Br$ have been prepared[108,154] by controlled hydrolysis of $NEt_4Pa(OEt)_2Br_4$, Ph_4AsUBr_6 and NEt_4UBr_6, respectively. All are air-sensitive compounds, those of uranium(V) undergoing disproportionation to U(IV) and U(VI). Structural data are not available. Infrared assignments are shown in Table 25 and the electronic and i.r. spectra of the uranium(V) complexes are discussed by Ryan[108]. Once again (cf. the chloro-analogues, Table 25) two i.r. active vibrations are observed for the U=O group whereas a single band is observed in the spectrum of $(NEt_4)_2PaOCl_5$.

[170] D. Brown, T. J. Petcher and A. J. Smith, *Nature*, **217** (1968) 738.
[171] D. Brown, J. F. Easey and P. J. Jones, *J. Chem. Soc.* (A) (1967) 1698.
[171a] J. C. Levet, Personal communication (1972).
[172] J. C. Levet, *Compt. Rend.* **260** (1965) 4775.
[173] J. C. Levet, *Compt. Rend.* **268C** (1969) 703.
[174] D. Brown and P. J. Jones, *J. Chem. Soc.* (A) (1966) 262.
[175] J. Prigent, *Compt. Rend.* **247** (1958) 1737.

Treatment with boron tribromide converts $(NEt_4)_2PaOBr_5$ to the hexabromoprotactinate(V), NEt_4PaBr_6, at room temperature.

Hexavalent Oxybromo-complexes

Only uranium(VI) forms oxybromo-complexes[6,15]. Compounds of the type $M^I{}_2UO_2Br_4$ (M^I = a univalent cation) are obtained by reacting the component halides in anhydrous methyl cyanide. Although the anhydrous caesium salt $Cs_2UO_2Br_4$ crystallizes from aqueous hydrobromic acid, dihydrates are obtained under these conditions for the smaller cations ($M^I = NH_4$ and K). Additional complexes of the type $M^I{}_2UO_3Br_2$ (M^I = K and NH_4) are also known and KUO_3Br has been characterized.

$Cs_2UO_2Br_4$ possesses monoclinic symmetry[176] with $a_0 = 9{\cdot}90$, $b_0 = 9{\cdot}808$ and $c_0 = 6{\cdot}39$ Å, $\beta = 103{\cdot}5°$. The U–Br and U–O distances in the distorted octahedron are 2·82 and 1·69 Å, respectively. Recent i.r. and Raman studies have been summarized elsewhere[17]; assignments for $Cs_2UO_2Br_4$ and $(NMe_4)_2UO_2Br_4$ are listed in Table 25.

5. COMPOUNDS WITH IODINE

Binary iodides

Relatively few actinide iodides are known (Table 1), and in view of the valence state stability trends within the actinide series of elements, it is unlikely, with the possible exception of NpI_4, that other than tri-iodides (Es to Lw) and di-iodides* will be prepared in the future. Although ThI_2 is formally divalent, recent structural studies[177] on the β-form have confirmed the indications obtained from specific resistance and magnetic (diamagnetic) ($\chi_m = -80 \pm 20 \times 10^{-6}$ emu) measurements that this compound should be formulated $Th^{4+}(e^-)_2I_2$ (cf. the di-iodides of lanthanum, cerium and praseodymium[6]). Thus, the structure consists of four two-dimensionally infinite layers alternating between trigonal–prismatic and trigonal–antiprismatic layers. Trigonal–prismatic and antiprismatic polyhedra of iodine atoms surround the thorium atoms in the prismatic and antiprismatic layers, respectively. The Th–I bond lengths in these layers are, respectively 3·20 and 3·22 Å (Fig. 8) compared with distances between 3·13 and 3·29 Å observed for 8-coordinate thorium tetraiodide (p. 203) indicating the presence of Th^{4+} ions in β-ThI_2. The extra electrons are presumed to be delocalized within the layers.

Metal–iodine reactions result in the formation of ThI_4, PaI_5, UI_4 (or under controlled conditions UI_3), NpI_3 and PuI_3, respectively, whilst the formation of PaI_4, ThI_3 and ThI_2 requires increasingly strong reducing conditions. Prolonged vacuum thermal decomposition of protactinium pentaiodide appears to result in the formation of PaI_3. These and various other preparative methods are discussed in earlier review articles[6,15,17,19] to which the reader is referred for references to the original literature.

The Physical and Chemical Properties of the Tri-iodides

The tri-iodides of the elements protactinium to americium (α-form) possess the 8-coordinate $PuBr_3$-type of structure whereas those of curium to californium, and β-AmI_3, crystallize with the 6-coordinate BiI_3-type of structure (Table 28). Unit cell dimensions are not available for ThI_3, but it is known not to be isostructural with the other earlier

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* See footnote page 151.

[176] Yu. N. Mikhailov, V. G. Kuznetsov and E. S. Kovaleva, *J. Struct. Chem.* 6 (1965) 752.

[177] L. J. Guggenberger and R. A. Jacobsen, *Inorg. Chem.* 7 (1968) 2257.

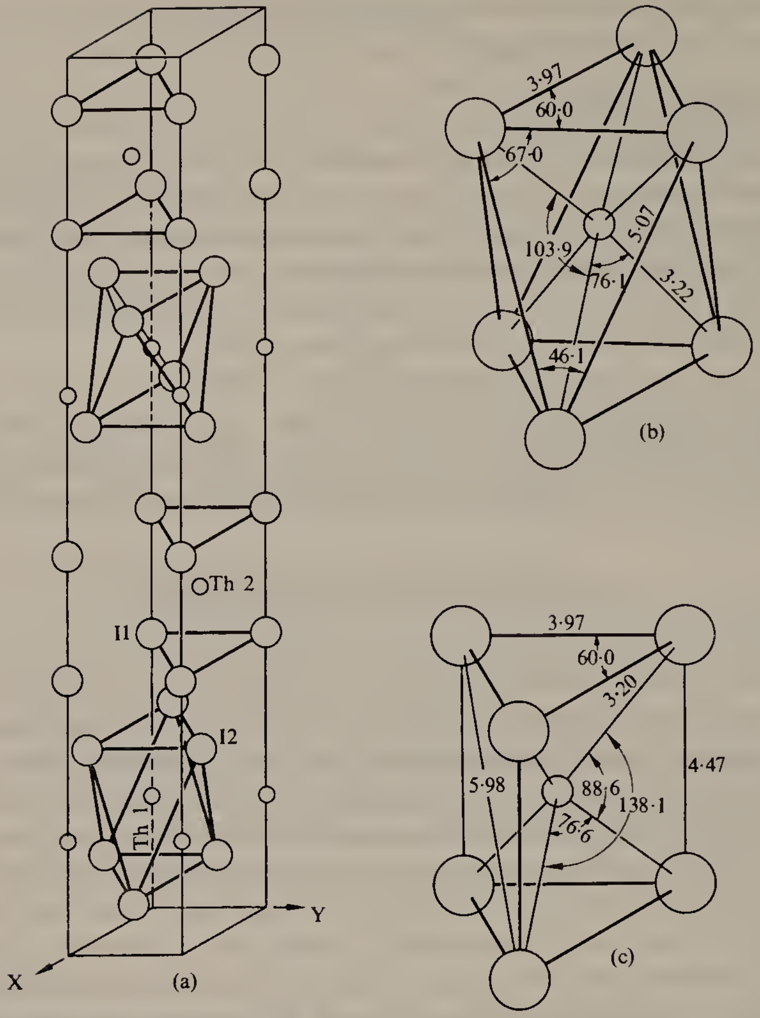

FIG. 8. The structure of ThI_2.
(a) Contents of one unit cell.
(b) Coordination polyhedron in the trigonal-antiprismatic layers.
(c) Coordination polyhedron in the trigonal-prismatic layers.
(Reproduced by permission from L. J. Guggenberger and R. A. Jacobson, *Inorg. Chem.* 7 (1968) 2257.)

members of this series. Apart from thorium and protactinium tri-iodide the compounds are volatile at high temperature in a vacuum; available vapour pressure data are listed in Table 9 and thermodynamic values are listed in Table 4. Magnetic[45] and spectral data[162] are available only for uranium and americium tri-iodide, respectively.

Few chemical properties have been recorded for the actinide tri-iodides, many of which have only been prepared in sub-milligram amounts. Iodine will oxidize uranium tri-iodide to the tetraiodide; americium and curium tri-iodide are both stable in hydrogen at 900°C (cf. the reduction of samarium tri-iodide to the di-iodide[6]). Thorium tri-iodide reacts vigorously with water with the evolution of hydrogen. Hydrates and complexes with other donor ligands are unknown.

The Physical and Chemical Properties of the Tetraiodides

Thorium tetraiodide (Table 28) possesses a structure in which each thorium atom is

TABLE 28. CRYSTALLOGRAPHIC DATA FOR ACTINIDE IODIDES* AND OXYIODIDES

Compound	Colour	Symmetry/ Space group	a_0 (Å)	b_0 (Å)	c_0 (Å)	β°	Ref.
β-ThI_2	Gold	H; $D^4{}_{6h}$–$P6_3/mmc$	3·97	—	31·75		a
PaI_3	Black	O; $D^{17}{}_{2h}$–$Ccmm$	4·33	14·00	10·02		b
UI_3	Black	,, ,,	4·328	13·996	9·984		c
NpI_3	Purple	,, ,,	4·326	13·980	9·982		c
PuI_3	Green	,, ,,	4·326	13·962	9·974		c
α-AmI_3†		,, ,,	4·31	14·03	9·92		d
β-AmI_3	Yellow	H; $C^2{}_{3i}$–$R\bar{3}$	7·42	—	20·55		e
CmI_3	White	,, ,,	7·44	—	20·40		e
BkI_3	Yellow	,, ,,	7·50	—	20·40		f
CfI_3	Lemon-yellow	,, ,,	7·55	—	20·80		g
NpOI	Burgundy	T; $D^{17}{}_{2h}$–$P4/nmm$	4·051	—	9·193		c
PuOI*	Green	,, ,,	4·052	—	9·18		d
BkOI	White	,, ,,	4·00	—	9·14		f
CfOI	Tan	,, ,,	3·97	—	9·14		g
CfOI	Tan	,, ,,	3·97	—	9·13		h
ThI_4	White	M; $C^5{}_{2h}$–$P^2{}_1/n$	13·216	8·068	7·766	98·68	i

* See footnote, p. 151.

† Converted from Kx units.

H, hexagonal; O, orthorhombic; T, tetragonal; M, monoclinic.

[a] L. J. Guggenheimer and R. A. Jacobsen, *Inorg. Chem.* 7 (1968) 2257.

[b] V. Scherrer, F. Weigel and M. Van Ghemen, *Inorg. Nucl. Chem. Letters*, 3 (1967) 589.

[c] D. Brown and J. Edwards, *J. Chem. Soc. Dalton* (1972) 1757.

[d] W. H. Zachariasen, *Acta Cryst.* 1 (1948) 265.

[e] L. B. Asprey, T. K. Keenan and F. H. Kruse, *Inorg. Chem.* 4 (1965) 985.

[f] D. Cohen, S. Fried, S. Siegel and B. Tani, *Inorg. Nucl. Chem. Letters*, 4 (1968) 257.

[g] S. Fried, D. Cohen, S. Siegel and B. Tani, *Inorg. Nucl. Chem. Letters*, 4 (1968) 495.

[h] D. K. Fujita, U.S. Report UCRL-19507 (1969).

[i] A. Zalkin, J. D. Forrester and D. H. Templeton, *Inorg. Chem.* 3 (1964) 639.

surrounded by eight iodine atoms (Th–I in the range 3·13 to 3·29 Å) arranged as a distorted square antiprism.[178] Although structural information is not available for PaI_4 or UI_4, X-ray powder studies have recently shown[179] that the latter is not isostructural with ThI_4. Thermodynamic data are included in Tables 4 and 6–8 inclusive and vapour pressure data are listed in Table 9.

Thorium tetraiodide is reduced by thorium metal at high temperatures with the formation of ThI_3, α-ThI_2 or β-ThI_2; the thorium–iodine phase system, constructed on the basis of such reductions,[180] is shown in Fig. 9. Hydrogen or zinc reduction of uranium tetraiodide yield the tri-iodide and when heated in oxygen UI_4 is converted to U_3O_8. Hydrates are unknown for the moisture-sensitive tetraiodides, but a few complexes with other donor ligands have been characterized[6,14,15,17], e.g. $ThI_4 \cdot 4CH_3CN$, $PaI_4 \cdot 4CH_3CN$, $UI_4 \cdot 6DMA$ (DMA = dimethylacetamide), $UI_4 \cdot 4DMA$ and the urea complexes $MI_4 \cdot 8L$ (M = Th and U). Very recently the first examples of actinide tetrahalide–isocyanide complexes, $UI_4 \cdot 4CNC_6H_{11}$ and $ThI_4 \cdot 4CNC_6H_{11}$, were characterized; ν_{C-N} shifts from 2135 cm^{-1} to 2190 cm^{-1} on complex formation.[181] Hexadio-complexes are discussed later (p. 206).

[178] A. Zalkin, J. D. Forrester and D. H. Templeton, *Inorg. Chem.* 3 (1964) 639.

[179] D. Brown, J. Edwards and P. T. Moseley, unpublished observations (1971).

[180] D. E. Scaife and A. W. Wylie, *J. Chem. Soc.* (1964) 5450.

[181] F. Lux and U.-E. Bufe, *Angew. Chem. Int. Ed. (Eng.)* 10 (1971) 274.

The Physical and Chemical Properties of Protactinium Pentaiodide

No thermodynamic, vapour pressure or structural information is available for protactinium pentaiodide.

It is a black, air-sensitive compound which is converted to pentavalent oxyiodides on being heated with antimony sesquioxide and to the mixed halide PaI_2Br_3 when melted with protactinium pentabromide[171]. Reduction with aluminium yields the dark green tetraiodide.

Iodo-complexes

The only known iodo-complexes are a single pentavalent compound $(Ph_3AsMe)PaI_6$ and a series of hexaiodometallates(IV), $M^{I}_2M^{IV}I_6$ (M^{I} = variously NBu_4, Ph_4As and Ph_3AsMe;

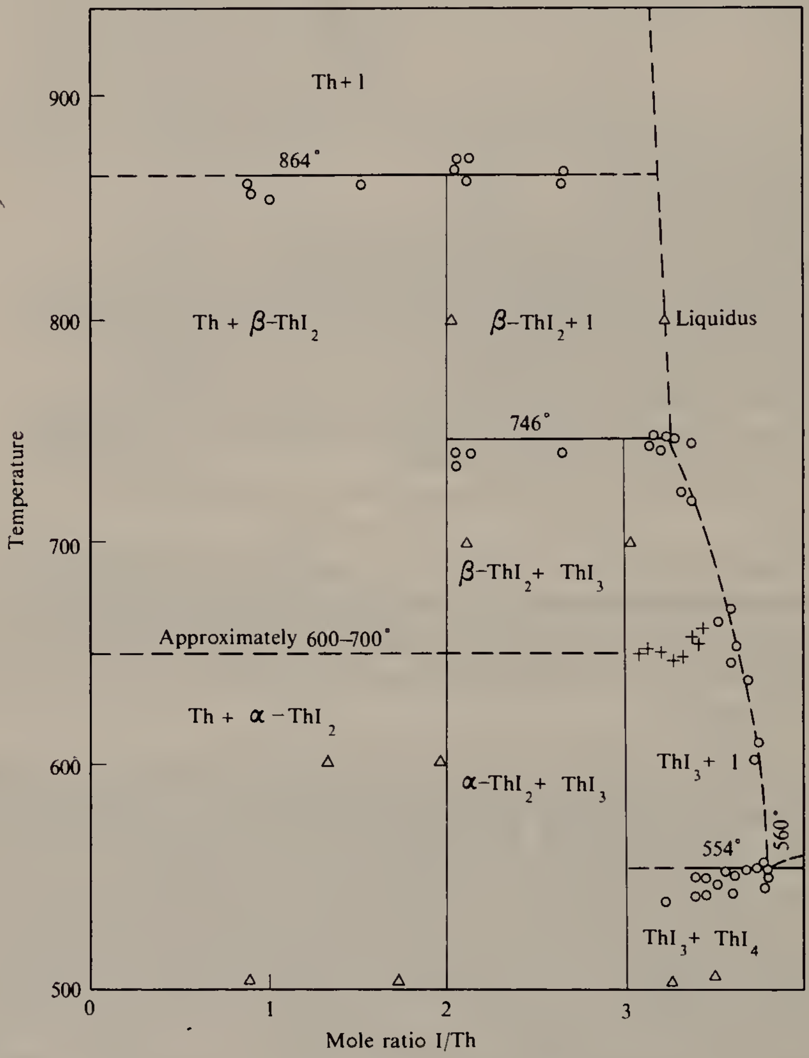

Fig. 9. The thorium–iodine system.

△ Results for D.T.A.; horizontals represent the average for many results, not all of which are shown.

○ Equilibrated samples quenched from these points.

(Reproduced by permission from D. E. Scaife and A. W. Wylie, *J. Chem. Soc.* (1964) 5450.)

M^{IV} = Th, Pa and U). All are conveniently prepared by reactions involving the appropriate penta- or tetraiodide and the univalent iodide in anhydrous methyl cyanide. Attempts to prepare hexaiodouranates(V) have been unsuccessful[108].

Oxyiodides

The few known oxyiodides are shown in Table 2. Although many other trivalent oxyiodides could certainly be characterized, it is unlikely, with the possible exception of UOI_2, that new higher valence state compounds will be prepared.

Although anhydrous uranyl iodide, UO_2I_2, has never been fully characterized, the complexes $UO_2I_2 \cdot 4DMF$ (DMF = dimethylformamide), $UO_2I_2 \cdot 2Ph_3PO$ and $UO_2I_2 \cdot 5CO(NH_2)_2$ are known[6,17] together with a monohydrate of the last.

Trivalent oxyiodides have either been obtained accidentally as residues from the sublimation of the tri-iodides or by heating the tri-iodide in moist gaseous hydrogen iodide. However, in view of the recent preparation of NpOI[179] by heating together stoichiometric amounts of neptunium tri-iodide and antimony sesquioxide *in vacuo*, it is likely that the MI_3–Sb_2O_3 reaction will prove to be a general method of preparation for this type of compound. Similar reactions involving ThI_4 and PaI_5 have resulted in the formation of $ThOI_2$, $PaOI_3$ and PaO_2I; the first is also obtained by the more conventional MI_4–MO_2 reaction. Apart from the NpI_3–Sb_2O_3 reaction, these preparative methods are discussed in more detail elsewhere[6,15,17,19].

The Physical and Chemical Properties of the Trivalent Oxyiodides

The known trivalent compounds possess the PbFCl-type of structure (Table 28); the Pu–O and Pu–I distances are, respectively, 2·32 and 3·44 Å. Estimated thermodynamic values for PuOI are given in Tables 5 and 6.

The chemical properties of these compounds have not been investigated.

The Physical and Chemical Properties of the Tetravalent Oxyiodides

The X-ray powder data available for the isostructural thorium(IV)[182] and protactinium(IV)[183] compounds, $ThOI_2$ and $PaOI_2$, respectively, have not been interpreted; on the basis of i.r. studies[151] (all bands below 550 cm^{-1}) it is likely that they will possess polymeric oxygen-bridged structures (cf. $PaOCl_2$, p. 192). Thermodynamic data for $ThOI_2$ are given in Table 5.

The chemical properties of these compounds have not been studied in detail. A red form of $ThOI_2$[184] obtained by heating together ThO_2 and ThI_4 in the presence of thorium metal or thorium di-iodide is believed to be coloured as the result of slight reduction. It is readily converted to white $ThOI_2$ by heating with a trace of iodine.

The Physical and Chemical Properties of the Pentavalent Oxyiodides

Structural data are not available for either $PaOI_3$ or PaO_2I; i.r. bands are observed[171] only below 600 cm^{-1} indicating the absence of discrete PaO^{3+} or PaO_2^+ groups. $PaOI_3$, like Pa_2OCl_8 and $PaOBr_3$, is thermally unstable decomposing above 450°C,

$$2PaOI_3 \rightarrow PaI_5 + PaO_2I$$

Both compounds are air-sensitive. Complexes with donor ligands are unknown.

[182] D. E. Scaife, A. G. Turnbull and A. W. Wylie, *J. Chem. Soc.* (1965) 1432.
[183] D. Brown and P. J. Jones, *J. Chem. Soc.* (A) (1967) 719.
[184] J. D. Corbett, R. A. Guidotti and D. Adolphson, *Inorg. Chem.* **8** (1969) 163.

Oxyiodo-complexes

The only known actinide oxyiodo-complex appears to be the hexavalent uranium compound $(Ph_3BuP)_2UO_2I_4$ obtained from a reaction in methyl cyanide[185]. The uranium–oxygen stretching vibration (ν_3) occurs at 925 cm^{-1} in the infrared spectrum of this compound.

6. MIXED HALIDES

In addition to the numerous halides already discussed, a number of less important mixed halides are known for uranium(III), UX_2Y (X and Y = Cl, Br or I), uranium(IV), UX_3Y, UX_2Y_2, and UX_2YZ (X, Y and Z = F, Cl, Br or I) and protactinium(V), $PaBr_3I_2$. Since little new work of consequence has been published since these compounds were last reviewed, the reader is referred to the earlier review articles[6,186]. It is obvious that by modifying the preparative conditions the above list could be considerably extended, and that similar compounds could be prepared for the remaining actinide elements in their various valence states. A few mixed halide complexes with donor ligands are also known[6], e.g. $UI_2Cl_2 \cdot 5DMA$ (DMA = N,N-dimethylacetamide), $UCI_3 \cdot 5DMA$ and $UCl_3I \cdot 8CO(NH_2)_2$.

Mixed halogeno- and oxyhalogeno-complexes have been prepared[6] for uranium(IV), $M^I_2UX_2Y_2$ (X and Y = Cl and Br, respectively) and uranyl(VI), $M^I_2UO_2Cl_2Br_2$ (M^I = Na, K and Cs), $Cs_2UO_2X_3Y$ (X and Y = Cl or Br) and $(Ph_3BuP)_2UO_2X_2Y_2$ (X and Y = Cl, Br or I).

7. HALATES AND PERHALATES

By comparison with the chemistry of the halides, that of the actinide halates has been relatively neglected. Thus, apart from anhydrous uranyl(VI) perchlorate, only a few perchlorate complexes with oxygen donor ligands are known for thorium(IV), uranium(IV) and uranyl(VI); only brief details are available on the chemistry of presently known tetravalent iodates of thorium, neptunium and plutonium and for the uranyl(VI) hydrate, and the only element so far reported to form a tri-iodate is plutonium. Information on the actinide bromates appears to be limited to the very early work of Rammelsburg[187] and of Cleve[188].

Perchlorates

Anhydrous tetraperchlorates are unknown. Thorium tetraperchlorate hydrates of variable water content, $Th(ClO_4)_4 \cdot xH_2O$ ($x = 2, 3, 4, 6$ or 8 depending on the preparative conditions), crystallize from aqueous solution[189–191], but analogous uranium compounds are unknown. $Th(ClO_4)_4 \cdot 4H_2O$ possesses orthorhombic symmetry[192], space group $D_h{}^4$–$P2_12_12_1$

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[185] P. J. Day and L. M. Venanzi, *J. Chem. Soc.* (A) (1966) 1363.

[186] Ref. 4, p. 539.

[187] C. Rammelsberg, *Ann. Phys. Chem. Pogg.* **55** (1842) 69.

[188] P. Clève, *Bull. Soc. Chim.* **21** (1874) 115.

[189] B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.* (1961) 3091.

[190] V. I. Rigin, *Tr. Sibirsk. Tekhnol. Inst.* No. 36 (1963) 79; according to *C.A.* **61**, 11379e.

[191] A. R. Warrier, P. Ramamurthy, C. C. Patel and P. S. Narayanan, *Ind. J. Chem.* **2** (1964) 131.

[192] P. Ramamurthy and C. C. Patel, *J. Inorg. Nucl. Chem.* **25** (1963) 310.

with $a_0 = 4.44$, $b_0 = 16.51$ and $c_0 = 11.35$ Å; controlled thermal decomposition is reported to result in the intermediate formation of $ThO(ClO_4)_2$, the ultimate product being thoria[193].

Stable thorium and uranium tetraperchlorate complexes with oxygen donor ligands have been characterized. A selection is shown in Table 29 together with information on the ligand shifts observed on coordination via the oxygen atom. These may be prepared by direct reaction between thorium tetraperchlorate hydrates and the appropriate ligand in either aqueous or non-aqueous media or by metathesis of the corresponding tetrachloride complex (Th and U) with silver perchlorate in acetone. The water of hydration is readily removed from the N,N-dimethylacetamide complexes *in vacuo* at room temperature; exposure of the anhydrous complex to the atmosphere results in the formation of the stable trihydrates. Infrared studies have shown the perchlorate groups to be ionic in the various hydrates and complexes with donor ligands. References to the appropriate publications are included in Table 29.

TABLE 29. A SELECTION OF ACTINIDE PERCHLORATE COMPLEXES WITH DONOR LIGANDS

Compound	Colour	$\nu_{L=O}$	$\Delta\nu_{L=O}$	Ref.
$Th(ClO_4)_4 \cdot 6DMA$	White	1614	33	a
$U(ClO_4)_4 \cdot 6DMA$	Green	1618	29	b
$Th(ClO_4)_4 \cdot 6DMA \cdot 3H_2O$	White	1613	34	a
$U(ClO_4)_4 \cdot 6DMA \cdot 3H_2O$	Green	1616	31	b
$Th(ClO_4)_4 \cdot 6DMSO$	White	946	105	c
$Th(ClO_4)_4 \cdot 4OMPA$	White	1140	98	d
$Th(ClO_4)_4 \cdot 7AN$	White	1585; 1575	86; 97	e
$Th(ClO_4)_4 \cdot 8PNO$	White	1218	25	f

DMA, N,N-dimethylacetamide; DMSO, dimethylsulphoxide; AN, antipyrine; PNO, pyridine-N-oxide.

[a] K. W. Bagnall, D. Brown, P. J. Jones and P. S. Robinson, *J. Chem. Soc.* (1964) 2531.
[b] K. W. Bagnall and D. Brown, *J. Chem. Soc.* (1962) 1655.
[c] V. Krishnan and C. C. Patel, *J. Inorg. Nucl. Chem.* **26** (1964) 2201.
[d] M. D. Joesten, *Inorg. Chem.* **6** (1967) 1598.
[e] V. V. Savant, P. Ramamurthy and C. C. Patel, *J. Less-Common Metals*, **22** (1970) 479.
[f] P. Ramamurthy and C. C. Patel, *Can. J. Chem.* **42** (1964) 856.

Uranyl perchlorate heptahydrate, $UO_2(ClO_4)_2 \cdot 7H_2O$, appears to be the stable phase which crystallizes from aqueous solution[194] although it is reported that the pentahydrate[195] has also been obtained. Vacuum dehydration of the former (m.p. 60°C) over sulphuric acid leads to the successive formation of the pentahydrate (m.p. 116°C) and the trihydrate (m.p. 148°C). The latter is converted to anhydrous uranyl perchlorate via the intermediate formation of the monohydrate at 100–140°C *in vacuo*[194]. Analogous neptunyl(VI) compounds appear to be unknown and the only solid plutonyl(VI) compound known appears to be $PuO_2(ClO_4)_2 \cdot 6H_2O$.[196] Infrared studies indicate the presence of ionic perchlorates in the hepta- and pentahydrates, of monodentate perchlorates in the trihydrate, and of

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[193] P. Ramamurthy and C. C. Patel, *Ind. J. Chem.* **3** (1965) 134.

[194] V. M. Vdovenko, L. G. Mashirov, V. K. Blokhina, I. G. Suglobova and D. N. Suglobov, *Sov. Rad.* **5** (1963) 67.

[195] G. Gordon and H. Taube, *J. Inorg. Nucl. Chem.* **16** (1961) 272.

[196] A. Ekstrom, M. S. Farrell and J. J. Lawrence, *J. Inorg. Nucl. Chem.* **30** (1968) 660.

TABLE 30. INFRARED ASSIGNMENTS FOR URANYL PERCHLORATE AND ITS HYDRATES (CM^{-1}) [a]

Compound	Proposed symmetry and assignments									UO_{2as}^{2+}	UO_{2sym}^{2+}
	T_d										
	ν_3	ν_1	ν_4							ν_3	ν_1
$UO_2(ClO_4)_2\cdot 7H_2O$	1110	932	624							958	888
$UO_2(ClO_4)_2\cdot 5H_2O$	1030–1060	930	624							958	890
	C_{3v}										
	ν_4	ν_1	ν_2	ν_5	ν_3	ν_6					
$UO_2(ClO_4)_2\cdot 3H_2O$	1192; 1162	1035; 1017	874	645	619	960				967	892
	C_s										
	ν_8	ν_6	ν_1	ν_2	ν_7	ν_9	ν_3	ν_5	ν_4		
$UO_2(ClO_4)_2\cdot H_2O$	1250; 1231	1136; 1114	1075	996	646	633	613	470	450	974	896
$UO_2(ClO_4)_2$	1270; 1234	1148; 1116	1048	974	640	627	600	481	455	996	900

[a] V. M. Vdovenko, L. G. Mashirov and D. M. Suglobov, *Sov. Radiochem.* **6** (1964) 289.

bidentate perchlorates in both the monohydrate and the anhydrous compound[197]. The observed bands are listed in Table 30.

Uranyl perchlorate complexes with oxygen donor ligands have been characterized; a selection of these yellow compounds is shown in Table 31 together with infrared data where available and references to the original literature. Ionic perchlorate groups appear to be present in the 1:5 complexes (cf. $UO_2(ClO_4)_2\cdot 5H_2O$, Table 30) and in $UO_2(ClO_4)_2\cdot$ 3OMPA, but the presence of extra bands in the spectra of complexes containing fewer monodentate ligands indicates the presence of either mono- or bidentate perchlorates[198]. The effect of the electron–donor properties of the ligands on the position of the asymmetric uranium–oxygen stretching vibration is discussed in detail by Vdovenko and co-workers[198,199]. No X-ray structural data appear to be available for any of the uranyl perchlorate compounds and no thermodynamic data have been reported.

Although solid hexavalent perchlorato-complexes are unknown, there is evidence that in the presence of the tetradecylammonium or tridecylammonium, cations in the species $UO_2(ClO_4)_3^-$ and $UO_2(ClO_4)_4^{2-}$ exist in benzene solution[200]; $UO_2(ClO_4)_2$ itself is

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[197] V. M. Vdovenko, L. G. Mashirov and D. N. Suglobov, *Sov. Radiochem.* **6** (1964) 289.

[198] V. M. Vdovenko, L. G. Mashirov and D. N. Suglobov, *Sov. Radiochem.* **9** (1967) 37; *Dokl. Akad. Nauk. SSR* **163** (1965) 100.

[199] V. M. Vdovenko, L. G. Mashirov and D. N. Suglobov, *Doklady Chem.* **167** (1966) 436.

[200] V. M. Vdovenko, A. I. Skoblo and D. N. Suglobov, *Sov. Radiochem.* **6** (1964) 658.

TABLE 31. INFRARED DATA FOR SOME URANYL PERCHLORATE COMPLEXES AND REFERENCES FOR PREPARATIVE METHODS

Compound*	$\nu_{UO_2^{2+}{}_{as}}$ (cm^{-1})	$\nu_{ClO_4^-}$ (cm^{-1})	Ref.
$UO_2(ClO_4)_2$:L = 1:5 with			
Py	886	1098	a
PyNO	907	1081	a, j
ANP	907	1096	a, b
DMSO			g
DMSeO	899	1100	f
DMF	920	1100	a, i
DPSO		1095	e
TSO			g
HMPA			d
URD			k
$UO_2(ClO_4)_2$:L = 1:3 with			
OMPA		1090	c
CAM	952	873, 1015, 1174	a
CH_3CN	962	864, 1020, 1173	a
$UO_2(ClO_4)_2$:L = 1:2 with			
TBP	952	854, 1015, 1173, 885, 972, 1136, 1230	a
TBPO			h
CH_3NO_2	972	903, 972, 1140, 1229	a
DBE	960	851, 1020, 1183, 890, 972, 1147, 1229	a

* Py, pyridine; PyNO, pyridine-N-oxide; ANP, antipyrene; DMSO, dimethylsulphoxide; DMSeO, dimethylselenoxide; DMF, dimethylformamide; DPSO, diphenylsulphoxide; TSO, thioxane oxide; HMPA, hexamethylphosphoramide; URD, urea, 1:3-dimethylurea or 1:3-diethylurea; OMPA, octamethylpyrophosphoramide; CAM, camphor; TBP, tributylphosphate; TBPO, tributylphosphine oxide; DBE, dibutylether.

[a] V. M. Vdovenko, L. G. Mashirov and D. H. Suglobov, *Soviet Radiochem.* 9 (1967) 37.

[b] V. V. Savant, P. Ramamurthy and C. C. Patel, *J. Less-Common Metals*, **22** (1970) 479.

[c] M. D. Joesten, *Inorg. Chem.* 6 (1967) 1598.

[d] A. K. Majumdar, R. G. Battacharyya and D. C. Bera, *Chem. & Ind.* (1971) 730.

[e] A. K. Majumdar and R. G. Battacharyya, *Chem. & Ind.* (1970) 95.

[f] V. R. Paetzold and G. Bochmann, *Z. anorg. Chem.* **368** (1969) 202.

[g] J. O. Edwards and J. A. Stritar, *Science* **142** (1963) 1651.

[h] S. M. Sinitsyna and N. M. Sinitsyn, *Doklady Chem.* **168** (1966) 467.

[i] W. R. Walker, *J. Inorg. Nuclear Chem.* **26** (1964) 1753.

[j] P. Ramamurthy and C. C. Patel, *Can. J. Chem.* **42** (1964) 856.

[k] A. Deptula, *Nukleonika*, **10** (1965) 765.

insoluble in benzene. Infrared data indicate the presence of bidentate and monodentate perchlorate groups in $UO_2(ClO_4)_3^-$ and $UO_2(ClO_4)_4^{2-}$, respectively, the change being attributed to steric effects.

Iodates

Plutonium tri-iodate is obtained as a light-brown precipitate on the addition of aqueous potassium iodate to Pu(III) solutions in aqueous sulphuric acid[201]. The chemistry of this compound, the only known trivalent actinide iodate, has not been studied.

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[201] H. Anderson, ref. 1, p. 825.

Thorium[202,203], neptunium[204] and plutonium[205–207] tetraiodate hydrates precipitate from aqueous nitric acid on the addition of an excess of potassium iodate or iodic acid. The water of hydration may be removed by heating the product at *ca.* 100°C[205,207]; anhydrous thorium tetraiodate may be precipitated directly at 80°C[203]. Carrier experiments[208,209] involving cerium tetraiodate and tracer berkelium indicate the existence of a tetravalent berkelium iodate. Earlier reports[210] of the formation of compounds such as $4Th(IO_3)_4 \cdot KIO_3 \cdot 18H_2O$ have been shown to be incorrect[202]. The chemistry of the tetraiodates has barely been studied[19], the emphasis in the case of thorium being on the separation obtained from the lanthanide elements on precipitation from aqueous acidic media. The symmetric stretching and bending vibrations are observed for $Th(IO_3)_4$ at 770 and 410 cm^{-1}, respectively[211].

Uranyl iodate hydrates, $UO_2(IO_3)_2 \cdot 2H_2O$ or $UO_2(IO_3)_2 \cdot H_2O$, precipitate from aqueous nitric acid on the addition of iodic acid[212–215]. An earlier report[214] concerning the precipitation of the complex $KUO_2(IO_3)_3 \cdot 3H_2O$ from saturated potassium iodate solution has not been confirmed during a more recent investigation of the $UO_2(IO_3)_2$–KIO_3–H_2O system[215]. Neptunyl(VI) iodates are unknown and the only evidence for the existence of a plutonyl(VI) compound is the report that a white precipitate of possible composition $PuO_2(IO_3)_2 \cdot 6HIO_3 \cdot xH_2O$ is obtained from aqueous solution[201].

Periodates

The only information concerning the existence of actinide periodates appears to be the unconfirmed, reported existence of $ThHIO_6 \cdot 5H_2O$[216], $(KIO_4)_2 \cdot (UO_2)_2 \cdot O_2 \cdot 5H_2O$[217], and a phase of composition $UO_2(IO_4)_2 \cdot 2UO_3$[218]. Further investigations are obviously necessary before these compounds are accepted.

8. THIOCYANATES, SELENOCYANATES, CYANATES AND CYANIDES

Prior to the recent characterization of tetravalent protactinium, neptunium and plutonium octathiocyanato-complexes[219] and a series of neptunium and plutonium tetrathiocyanate complexes with trialkyl and triaryl phosphine oxide ligands[220], actinide thiocyanates

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[202] T. Moeller and N. D. Fritz, *Anal. Chem.* **20** (1948) 1055.

[203] Sh. A. Musaev, *Azerb. Khim. Zh.* No. 6 (1962) 87; according to *C.A.* **59**, 1258a.

[204] E. S. Kritchevsky and J. C. Hindman, unpublished observations according to B. B. Cunningham and J. C. Hindman, ref. 2, p. 475.

[205] B. B. Cunningham and L. B. Werner, *J. Amer. Chem. Soc.* **71** (1949) 1521.

[206] J. K. Dawson and R. M. Elliott, Brit. Report AERE-C/R 1207 (1953).

[207] I. S. Sklyarenko and T. M. Chubukova, *J. Anal. Chem. USSR* **18** (1963) 425.

[208] B. Weaver, *Anal. Chem.* **40** (1968) 1894.

[209] J. J. Fardy and B. Weaver, *Anal. Chem.* **41** (1969) 1299.

[210] Yu. A. Chernikov and T. A. Uspenskaya, *Zavodeskaya Lab.* 9 (1940) 276.

[211] W. E. Dasent and T. C. Waddington, *J. Chem. Soc.* (1960) 2429.

[212] P. Artmann, *Z. anorg. Chem.* 79 (1912) 327.

[213] T. W. Richards and B. S. Merigold, *Z. anorg. Chem.* **31** (1902) 235.

[214] P. Artmann, *Z. anorg. Chem.* **80** (1913) 280.

[215] A. E. Klygin, I. D. Smirnova and N. A. Nikol'skaya, *Russ. J. Inorg. Chem.* **4** (1959) 754.

[216] P. C. R. Choudhury, *J. Ind. Chem. Soc.* **18** (1941) 335.

[217] F. Burriel and C. Goyanes, *Anales real. soc. espan. fis. y quim* (*Madrid*) **50B** (1954) 281.

[218] B. Singh, A. Singh and R. Singh, *Res. Bull. East Panjab. Univ.* No. 23 (1952) 121.

[219] Z. M. S. Al-Kazzaz, K. W. Bagnall and D. Brown, *J. Chem. Soc. Dalton* (1972) 2273.

[220] Z. M. S. Al-Kazzaz, K. W. Bagnall and D. Brown, *J. Inorg. Nucl. Chem.* in press (1973).

were known only for thorium(IV), uranium(IV) and uranium(VI). It will be obvious from the following brief account that there is scope for further interesting studies in this field, particularly with the tri- and pentavalent actinide elements.

Simple, anhydrous tetrathiocyanates are unknown although the hydrate $Th(NCS)_4 \cdot 4H_2O$ and a range of tetravalent complexes with a variety of oxygen-donor ligands (M^{IV} = Th, U, Np and Pu) have been characterized. In addition, numerous octathiocyanato-complexes, $M^I_4M^{IV}(NCS)_8$, and several hydrated complexes are known for the elements thorium to plutonium inclusive. The only actinyl(VI) ion for which thiocyanates are known is UO_2^{2+}; neutral complexes with oxygen donor ligands and a range of anionic complexes have been characterized.

Actinide cyanides are unknown. However, uranium(IV) chlorocyanides have been stabilized as their ammoniates and the single anionic compound $(NEt_4)_2UCl_4(CN)_2$ is known[221]. There is also some evidence for the existence of the mixed complex $K_2UO_2(CN)_2(NO_3)_2$.

Bagnall[222] has recently reviewed the chemistry of the actinide thiocyanates and cyanides and this article is recommended for full details of the preparation and properties of these compounds. The presently known compounds will be only briefly discussed in the following sections. Thermodynamic data are not available. Although few structural studies have been reported, infrared evidence indicates that bonding occurs via the nitrogen atom of the SCN^- ion and, therefore, where formulae are given they are written to indicate this.

Tetravalent Thiocyanate Complexes with Donor Ligands

Complexes of the type $M^{IV}(NCS)_4 \cdot 4L$ and $M(NCS)_4 \cdot 2L^I$ (L = monodentate oxygen donor ligand; L^I = bidentate oxygen donor ligand) are readily obtained for M^{IV} = Th, U, Np and Pu by reactions involving potassium thiocyanate and the appropriate tetrachloride complex in non-aqueous solvents such as methyl cyanide or nitromethane[220,223,224]. Although analogous protactinium(IV) complexes are unknown, there is no reason to suppose that they cannot be prepared provided oxygen-free solvents are employed.

Available infrared data for these complexes are shown in Table 32; in the majority of cases the C=N stretching vibration occurs as a doublet or triplet. No structural information is available and, in view of the structure recently reported for $(NEt_4)_4U(NCS)_8$ (p. 215), it would be interesting to have such information on these potentially 8-coordinate compounds.

Uranyl Thiocyanate Complexes with Donor Ligands

A selection of the known uranyl thiocyanate complexes is given in Table 33 together with available infrared data. Compared with the above tetravalent complexes, somewhat smaller ligand shifts ($\Delta\nu_{P=O}$ or $\Delta\nu_{C=O}$) are observed on complex formation and in two instances the position of the $\nu_{C=N}$ stretching vibration indicates the presence of bridging thiocyanate groups ($UO_2(NCS_2)_2 \cdot 2TBP$ and $UO_2(NCS)_2 \cdot H_2O$). Structural data are not available for any of these compounds. References to the original literature are cited in Table 33; others will be found in the article by Bagnall[222].

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[221] K. W. Bagnall and J. O. Baptista, *J. Inorg. Nuclear Chem.* **32** (1970) 2283.
[222] K. W. Bagnall, *Int. Rev. Sci.* 7 (1971) 139.
[223] K. W. Bagnall, D. Brown and R. Colton, *J. Chem. Soc.* (1964) 2527.
[224] K. W. Bagnall, D. Brown, P. J. Jones, and P. S. Robinson, *J. Chem. Soc.* (1964) 2531.

TABLE 32. TETRAVALENT THIOCYANATE COMPLEXES WITH DONOR LIGANDS

Compound*	Colour	ν_{C-N}	$\nu_{L=O}$†	$\Delta\nu_{L=O}$†	Ref.
$Th(NCS)_4\cdot 4DMA$	White	2033	1605	41	a
$U(NCS)_4\cdot 4DMA$	Green	2047	1606	42	b
$Th(NCS)_4\cdot 4TMPO$	White	2038, 2056, 2078	1098	62	c
$U(NCS)_4\cdot 4TMPO$	Green	2025, 2060, 2080	1090	70	c
$Np(NCS)_4\cdot 4TMPO$	Yellow-brown	2035, 2060, 2085	1094	66	c
$Pu(NCS)_4\cdot 4TMPO$	Brown	2020, 2045, 2065	1100	60	c
$Th(NCS)_4\cdot 4HMPA$	White	2060, 2070	1098	103	c
$U(NCS)_4\cdot 4HMPA$	Green	2060, 2070	1090	111	c
$Np(NCS)_4\cdot 4HMPA$	Yellow-brown	2073	1098	103	c
$Th(NCS)_4\cdot 4TPPO$	White	2060, 2080	1068	123	c
$U(NCS)_4\cdot TPPO$	Green	2020, 2050, 2070	1065	126	c
$Np(NCS)_4\cdot 4TPPO$	Yellow	2029, 2064	1078	113	c
$Th(NCS)_4\cdot 2OMPA$	White	2005, 2035, 2060	1150	83	c
$U(NCS)_4\cdot 2OMPA$	Green	2025, 2050	1152	81	c
$Np(NCS)_4\cdot 2OMPA$	Pale-yellow	2053	1163	70	c

* DMA, dimethylacetamide; TMPO, trimethylphosphine oxide; HMPA, hexamethylphosphoramide; TPPO; triphenylphosphine oxide; OMPA, octamethylpyrophosphoramide.

† L = C or P.

[a] K. W. Bagnall, D. Brown, P. J. Jones and P. S. Robinson, *J. Chem. Soc.* (1964) 2531.

[b] K. W. Bagnall, D. Brown and R. Colton, *J. Chem. Soc.* (1964) 2527.

[c] Z. M. S. Al-Kazzaz, K. W. Bagnall and D. Brown, *J. Inorg. Nucl. Chem.* (1973) in press.

TABLE 33. URANYL THIOCYANATE COMPLEXES WITH DONOR LIGANDS

Compound*	Colour	ν_{C-N}	$\nu_{U=O}$	$\nu_{L=O}$‡	$\Delta\nu_{L=O}$‡	Ref.
$UO_2(NCS)_2\cdot 3U$	Orange	2068, 2091	910	1632, 1648		a
$UO_2(NCS)_2\cdot 2U\cdot H_2O$	Yellow	2070, 2094	927	1635, 1650		a
$UO_2(NCS)_2\cdot 3AP$	Yellow	2058	916	1604	63	a
$UO_2(NCS)_2\cdot 3THF$	Yellow	2031, 2060	935			a
$UO_2(NCS)_2\cdot 3QNO$	Yellow	2072, 2100				b
$UO_2(NCS)_2\cdot 2DMA\cdot H_2O$	Yellow	2072, 2095	939	1660	20	a
$UO_2(NCS)_2\cdot 2TBP$	Yellow	2036, 2110†	944		87	c
$UO_2(NCS)_2\cdot 3DMSO$	Yellow	2042, 2062	914		66	a
$UO_2(NCS)_2\cdot 2TPPO$	Yellow	2052		1138, 1085	57, 110	d
$UO_2(NCS)_2\cdot 3TASO$	Yellow	2019		833	45	d
$UO_2(NCS)_2\cdot 3H_2O$	Yellow	2057	937			c
$UO_2(NCS)_2\cdot H_2O$	Yellow	2103†, 1910	944			c
$UO_2(NCS)_2\cdot 2HMPA$	Yellow	2125†, 2080, 2045	920			e
$UO_2(NCS)_2\cdot 3HMPA$	Yellow	2080	920			e

* U, urea; AP, antipyrene; THF, tetrahydrofuran; QNO, quinoline-N-oxide; DMA, dimethylacetamide; TBP, tributylphosphate; DMSO, dimethylsulphoxide; TPPO, triphenylphosphine oxide; TASO, triphenylarsine oxide.

† Indicative of bridging thiocyanate groups.

‡ L = C, P or As.

[a] R. N. Shchelokov, I. M. Shul'gina and I. I. Chernyaev, *Dokl. Akad. Nauk. SSSR* **168** (1966) 1338; *Doklady Chem.* 166–8 (1966) 640.

[b] A. K. Majumdar and R. G. Battacharyya, *Science and Culture, Calcutta*, **35** (1969) 271.

[c] V. M. Vdovenko, A. I. Skoblo and D. N. Suglobov, *Russ. J. Inorg. Chem.* **13** (1968) 1577.

[d] F. S. Hart and J. E. Newberry, *J. Inorg. Nucl. Chem.* **28** (1966) 1334.

[e] A. K. Majumdar, R. G. Battacharyya and D. C. Bera, *Chem. & Ind.* (1971), 730.

Tetravalent Anionic Thiocyanato-complexes

Anhydrous octathiocyanato-complexes of the type $M^I_4M^{IV}(NCS)_8$ (M^{IV} = variously Th, Pa, U, Np and Pu) are isolated by suitable metatheses in either non-aqueous[219,223,225] (M^I = K, Cs and NEt_4) or aqueous[226,227] (M^I = Rb, NH_4 and α–α dipyridyl) solvents. The latter type of reaction also results in the formation of hydrates[226,228], such as $M^I_4M^{IV}(NCS)_8 \cdot 2H_2O$ and $M^I_4M^{IV}(NCS)_8 \cdot H_2O$ (M^I = Rb, Cs and NH_4; M^{IV} = Th and U), which slowly lose water in a desiccator over concentrated sulphuric acid and when heated between 60° and 100°C. Reactions involving stoichiometric amounts of reagents lead to the formation of penta- or heptathiocyanato-complexes, e.g. $RbTH(NCS)_5 \cdot 3H_2O$ and $(NH_4)_3Th(NCS)_7 \cdot 5H_2O$, respectively[228].

The available crystallographic data are presented in Table 34. Structural studies on $(NEt_4)_4U(NCS)_8$ recently showed[229] each uranium atom to be surrounded by eight nitrogen atoms at the vertices of a cube with a U–N bond length of 2·38 Å. This is only the second example of cubic 8-coordination (cf. Na_3PaF_8, p. 175) to be reported. The bonding in cubic 8-coordinate compounds is stated to require *f* orbital participation, probably hybrid orbitals between fd^3sp^3 or f^4d^3s. Observed i.r. stretching bands[219,223,225,227] fall into the following ranges for the various octathiocyanato-complexes which have been studied, $\nu_{C=N}$, 2012 to 1098 cm^{-1}, ν_{C-S}, 794 to 834 cm^{-1}, and δ_{NCS}, 474 to 482 cm^{-1}. As many as four bands are observed for $\nu_{C=N}$ in the solid hydrated complexes, but the tetraethylammonium complexes, $(NEt_4)_4M(NCS)_8$, exhibit relatively simple spectra with a single strong peak at *ca.* 2060 cm^{-1}. On the basis of i.r. data it is suggested[227] that certain of the octathiocyanato-dihydrates $M^I_4M^{IV}(NCS)_8 \cdot 2H_2O$ (M^I = Rb and Cs; M^{IV} = Th and U) exist in acetone solution with archimedean antiprismatic configurations (D_{4d} sym.) whereas in the solid state they exhibit dodecahedral stereochemistry (D_{2d} sym.). The single strong band in the i.r. spectra of the tetraethylammonium octathiocyanatometallates(IV)[219,226] is consistent with the cubic stereochemistry deduced from the single-crystal X-ray studies.

TABLE 34. UNIT CELL DIMENSIONS FOR TETRAVALENT AND HEXAVALENT THIOCYANATO-COMPLEXES

Compound	Colour	Symmetry/ Space group	a_0 (Å)	b_0 (Å)	c_0 (Å)	β°	Ref.
$(NEt_4)_4Th(NCS)_8$	White	T; *I4/mmm*				—	a
$(NEt_4)_4Pa(NCS)_8$	Blue	,, ,,	11·649	—	23·053	—	a
$(NEt_4)_4U(NCS)_8$	Green	,, ,,	11·64	—	23·01	—	a, b
$(NEt_4)_4Np(NCS)_8$	Brown	,, ,,	11·627	—	22·894	—	a
$(NEt_4)_4Pu(NCS)_8$		,, ,,	11·592	—	22·876	—	a
$Cs_4Th(NCS)_8 \cdot 2H_2O$	White	M; C^5_{2h}–$P2_1n$	13·520	13·969	16·226	90	c, d
$Cs_4U(NCS)_8 \cdot 2H_2O$	Green	O; D^{12}_{14h}–*Pnab*	13·15	13·20	15·75	—	d
$Cs_3UO_2(NCS)_5$	Yellow	O; D^{16}_{2h}–*Pnma*	13·629	13·249	11·556	—	d

[a] Z. M. S. Al-Kazzaz, K. W. Bagnall and D. Brown, *J. Chem. Soc. Dalton* (A) (1972) 2273.
[b] R. Countryman and W. S. McDonald, *J. Inorg. Nuclear Chem.* 33 (1971) 2213.
[c] A. K. Molodkin and C. A. Skotnikova, *Russ. J. Inorg. Chem.* 7 (1962) 1548.
[d] E. G. Arutyunyan and M. A. Porai-Koshits, *J. Struct. Chem. USSR* 4 (1963) 96.

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[225] P. Gans and J. W. Marriage, *J. Chem. Soc. Dalton* (A) (1972) 2273.
[226] V. P. Markov and E. N. Traggeim, *Russ. J. Inorg. Chem.* 6 (1961) 1175.
[227] I. E. Grey and P. W. Smith, *Austral. J. Chem.* 22 (1969) 311.
[228] A. K. Molodkin and G. A. Skotnikova, *Russ. J. Inorg. Chem.* 7 (1962) 800; 9 (1964) 32.
[229] R. Countryman and W. S. McDonald, *J. Inorg. Nucl. Chem.* 33 (1971) 2213.

TABLE 35. EXAMPLES OF URANYL(VI) THIOCYANATO-COMPLEXES[a]

Complex type	M^I
$M^I[UO_2(NCS)_3]$	$N(C_{10}H_{21})_4$
$M^I[UO_2(NCS)_3 \cdot 2H_2O]$	K, Rb, NH_4
$M^I_3[UO_2(NCS)_5]$	Cs, dipyH, $N(C_{10}H_{21})_4$, $NH(C_2H_5)_3$
$M^I_3[UO_2(NCS)_5] \cdot H_2O$	pyridine, piperidine, quinoline, triethylamine
$M^I_3[UO_2(NCS)_5] \cdot 2H_2O$	K, NH4
$M^I_2[(UO_2)_3(NCS)_8]$	$N(C_{10}H_{21})_4$

[a] For full preparative details for these and related complexes, the review by Bagnall[222] is recommended.

Solid state and solution spectra have been recorded in the visible and near infrared regions for the anhydrous tetraethylammonium and caesium complexes[219].

Uranyl Thiocyanato-complexes

A variety of anhydrous and hydrated 1:1 and 3:1 uranyl(VI) complex thiocyanates are known (Table 35) and a single 2:1 complex, $(NH_4)_2[UO_2(NCS)_4 \cdot 2H_2O]$,[230] has been reported. In addition, an unusual mixed complex $Cs_3(NH_4)_3[UO_2(NCS)_5]_2$ apparently exists[231]; it would be interesting to have infrared or structural information on this complex to see whether bridging thiocyanate groups are present in the apparently dimeric anion. The preparation of all these compounds is discussed in detail by Bagnall[222].

The various infrared vibrations for the pentathiocyanato-monohydrates are observed[232] in the ranges 920–925 cm^{-1} ($\nu_{U-O_{as}}$), 2045 to 2100 (ν_{C-N}), 805 to 815 (ν_{C-S}) and 482 to 490 (δ_{NCS}). The only structural data available at present indicate that in $Cs_3UO_2(NCS)_5$ (Table 34) the stereochemistry around the uranium atom is pentagonal bipyramidal with U–O and U–N distances of 1·65 and 2·45 Å, respectively[233].

In addition to the above-mentioned hydrated complexes, 1:1 complexes of the type $M^I[UO_2(NCS)_3 \cdot 2L]$ are known where L is a donor ligand such as urea, tributylphosphate and tributylphosphine oxide. These compounds and various mixed thiocyanato-chloro, thiocyanato-acetato and thiocyanato-oxalato complexes of uranyl(VI) are discussed by Bagnall[222].

Selenocyanates and Selenocyanato-complexes

The only actinide selenocyanate compounds which appear to have been characterized are the tetravalent thorium complexes $Th(NCSe)_4 \cdot 4DMF$, $Na_2Th(NCSe)_6 \cdot 3DMF$, $K_2Th(NCSe)_6 \cdot 4{\cdot}5DMF$ and $K_4Th(NCSe)_8 \cdot 2DMF$ which crystallize when stoichiometric amounts of thorium tetranitrate and the appropriate alkali metal selenocyanate are allowed to react in dimethylformamide[234] (DMF, dimethylformamide). As in the thiocyanato-complexes discussed above, bonding is via the nitrogen atom. The C–N, C–Se and C–O vibrations occur in the ranges 2065–2075, 675–678 and 1658–1660 cm^{-1}, respect-

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[230] V. P. Markov and E. N. Traggeim, *Russ. J. Inorg. Chem.* 5 (1960) 724.
[231] V. P. Markov, E. N. Traggeim and I. M. Shul'gina, *Russ. J. Inorg. Chem.* 9 (1964) 305.
[232] K. Andrä and H. Böhland, *Z. Chem.* 5 (1965) 145.
[233] E. G. Arutyunyan and M. A. Porai-Koshits, *J. Struct. Chem.* 4 (1963) 96.
[234] A. M. Golub and V. A. Kalibabchuk, *Russ. J. Inorg. Chem.* 12 (1967) 1249.

ively. The yellow solids are unstable and decompose in air at room temperature with the liberation of selenium.

Cyanides and Cyanates

Actinide cyanide chemistry has barely been investigated and apart from an early, unconfirmed report of the existence of $K_2UO_2(CN)_4$[235] the only compounds characterized to date are $UCl_3 \cdot (CN) \cdot 4NH_3$, impure samples of $(NEt_4)_2[UCl_4(CN)_2]$[221] and the mixed uranyl(VI) complex $K_2UO_2(CN)_2(NO_3)_2$[236] for which no supporting analytical data are provided. The green ammine complex precipitates when sodium or potassium cyanide is added to uranium tetrachloride in anhydrous liquid ammonia; $\nu_{C—N}$ is observed as a single band at 2120 cm^{-1}. Products from analogous reactions involving other uranium tetrahalides and the thorium tetrahalides have not yet been fully characterized[221]. In contrast to these reactions in liquid ammonia, alkali metal cyanides and uranium tetrachloride appear not to react in anhydrous liquid hydrocyanic acid; the only product is a UCL_4–HCN adduct of unknown composition[221].

The only information available on actinide cyanates is contained in early publications by Pascal[237] who reports the formation of $UO_2(CNO)_2$, $K[UO_2(CNO)_3]$, $K_2[UO_2(CNO)_4]$ and $K[(UO_2)_2(CNO)_5]$ by metathesis in alcoholic media. Obviously further studies are desirable before the existence of these compounds can be accepted.

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[235] J. Aloy, *Ann. Chim. Phys.* **24** (1901) 417.

[236] S. P. McGlynn, J. K. Smith and W. C. Neely, *J. Chem. Phys.* **35** (1961) 105.

[237] P. Pascal, *Compt. Rend.* **157** (1913) 933; *Bull. Soc. Chim. Fr.* **15** (1914) 11.

BINARY AND TERNARY OXIDES, HYDROXIDES AND HYDROUS OXIDES, PEROXIDES, PHOSPHATES AND ARSENATES

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1. BINARY OXIDES

The binary oxides, MO_x, of the actinide elements form an interesting but complex class of compounds. In addition to the stoichiometric oxides, a wide range of intermediate oxide phases exists, sometimes with remarkable phase widths. The most important actinide oxides are the dioxides, MO_2, which crystallize with the fluorite (CaF_2) structure, and which are known for the elements thorium to californium, inclusive. With the exception of PaO_2, which has not been investigated in detail, these dioxides lose oxygen at high temperatures and form sub-stoichiometric oxides, MO_{2-x}, with oxygen vacancies in the anionic part of the unit cell. Protactinium and uranium dioxide also take up additional oxygen to give superstoichiometric oxides, MO_{2+x}, even on standing in air at room temperature. Most actinide oxides occur in several crystal modifications, e.g. at least five Pa_2O_5, seven UO_3, and five Cm_2O_3 modifications are known.

The lattice constants of the three best known lanthanide and actinide sesquioxide modifications (hexagonal, monoclinic and cubic) and of the actinide dioxides are plotted in Figs. 1 and 2 respectively as a function of the atomic number. The lattice constants of the lanthanide sesquioxides and those of the actinide dioxides show a constant decrease with increasing atomic number, i.e. with decreasing ionic radius, whereas distinct irregularities not associated with any crystal-chemical factors occur in the case of the actinide sesquioxides. This effect may be attributed to radiation damage to the crystal lattice by the inherent high α-activity or to non-stoichiometric oxides. In this connection it should be remembered that the investigations of curium and transcurium oxides have involved only micro- or ultramicro-quantities of sometimes relatively short-lived isotopes. Further investigations with long-lived isotopes (e.g. ^{248}Cm instead of ^{244}Cm or ^{254}Es instead of ^{253}Es) in quantities sufficient for the analytical determination of the exact composition are obviously desirable.

No modern critical review on binary actinide oxides exists. A survey of published data is to be found in Pascal's *Nouveau Traité de Chimie Minérale*[1a], whereas selected physical and chemical properties are given in the *High Temperature Oxide* series[1b,1c]. Up-to-date contributions dealing with the chemistry of the transuranium oxides have been published in the *Gmelin Handbuch, Transuranelemente*[2a] and in the author's *The Chemistry of the Transuranium Elements*[2b], both published in 1971–2. Details of the oxide chemistry of plutonium will be found in Wick's *Plutonium Handbook*[2c] and in Cleveland's *The Chemistry*

[1a] *Nouveau Traité de Chimie Minérale*, P. Pascal (Ed.), Vols. 9 and 15, Masson et Cie, Paris (1961 ff).

[1b] R. C. Anderson, *Thoria and Yttria*, in *High Temperature Oxides*, A. M. Alper (Ed.), Part II, p. 1. Academic Press, New York (1970).

[1c] L. R. Eyring, *Refractory Oxides of the Lanthanide and Actinide Elements*, in *High Temperature Oxides*, A. M. Alper (Ed.), Part II, p. 41. Academic Press, New York (1970).

[2a] C. Keller, *Oxide der Transurane*, in *Gmelin Handbuch der Anorganischen Chemie*, Band 71, Teil C, *Transurane*, Verlag Chemie, Weinheim (1972).

[2b] C. Keller, *The Chemistry of the Transuranium Elements*, Verlag Chemie, Weinheim (1971).

[2c] *Plutonium Handbook*, O. J. Wick (Ed.), Gordon & Breach, New York (1967).

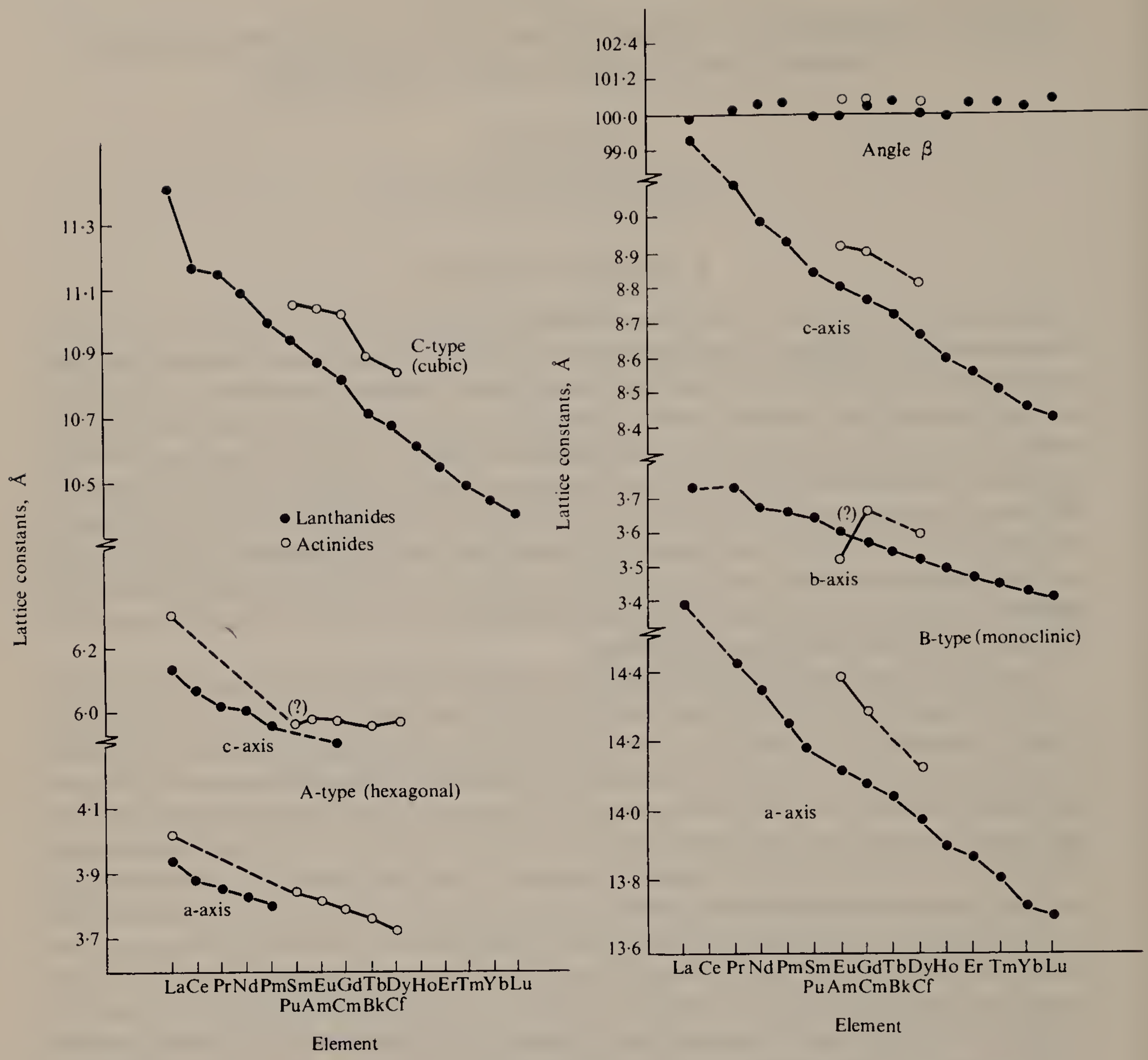

FIG. 1. Lattice constants of the hexagonal, monoclinic and cubic modifications of the lanthanide and actinide sesquioxides as a function of the atomic number.

of Plutonium[2d]. A summary of the chemical, physical and technological properties of UO_2 is given in Bell's *Uranium Dioxide*[2e], published about eleven years ago.

Actinium oxide

The only known actinium oxide, hexagonal Ac_2O_3 ($a = 4{\cdot}07$ Å, $c = 6{\cdot}29$ Å, $\rho = 9{\cdot}19$ g/cm^3), has been obtained by thermal decomposition of the oxalate $Ac_2(C_2O_4)_3 \cdot aq$ at 1100°C[3]. It reacts with H_2S at 1400°C to form cubic Ac_2S_3. No other data are available at present.

[2d] J. M. Cleveland, *The Chemistry of Plutonium*, Gordon & Breach, New York (1970).

[2e] *Uranium Dioxide, Properties and Nuclear Applications*, J. Belle (Ed.), USAEC, Washington D.C. (1961).

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

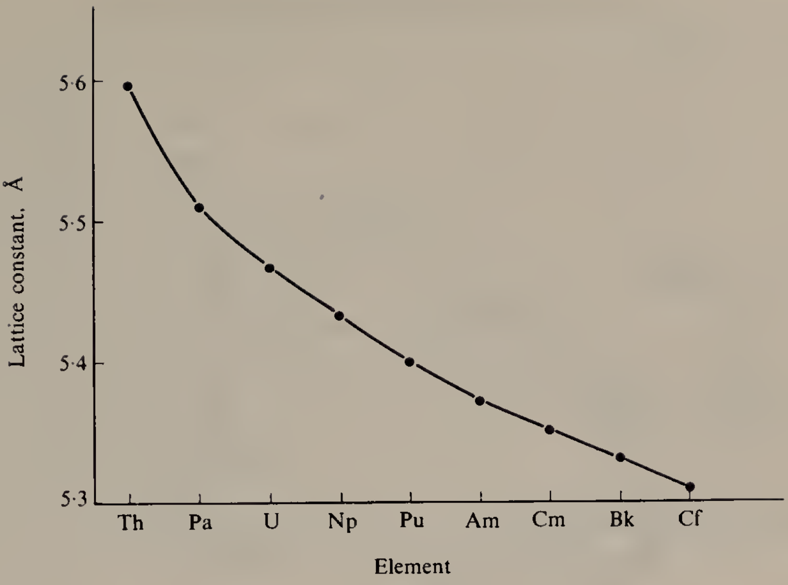

FIG. 2. Lattice constants of the actinide dioxides as a function of the atomic number.

Thorium oxide

Thorium dioxide (thoria), ThO_2, the only compound in the thorium–oxygen system, exists up to its melting point of 3390°C (the highest known for an oxide) as a single cubic phase with the fluorite structure (space group *Fm*3*m*). At high temperatures in a low oxygen pressure, thoria blackens with loss of oxygen. The oxygen deficiency for ThO_{2-x} between 1400°C and 1900°C from 10^{-2} to 10^{-6} atm oxygen pressure may be approximated by the relationship[4]

$$\log x \approx -1{\cdot}870-0{\cdot}340\times10^4/T(^\circ\mathrm{K})-0{\cdot}166\times\log p(\mathrm{atm})$$

Reheating in air at lower temperatures restores the white color. In contact with molten thorium metal at sufficiently high temperatures, thoria shows larger deviations from stoichiometry. The limiting oxygen-to-thorium ratio varies from 1·985 at about 1735°C to a minimum at about 2700°C, increasing to 1·997 at the melting point[5]. The thorium–oxygen phase diagram is shown in Fig. 3.

Thoria is commonly prepared by calcination (800–1200°C) of the oxalate obtained by precipitation from a solution of the purified nitrate. The properties of this oxide can be modified by firing to higher temperatures. Spherical particles of ThO_2 and other actinide oxides may be obtained using the "sol-gel process"[6]. In this process a dispersed hydrosol is prepared by steam decomposition of thorium nitrate or of an aqueous thorium nitrate solution. The resulting oxide is digested with dilute nitric acid to form a sol which is then converted to a gel containing about 3% water by low-temperature evaporation. The ThO_2 microcrystallites are of the order of 100 Å in diameter. The gel loses additional water and nitrate on heating and sinters to a density of 9·9 g/cm^3 (theoretical value 10·001 g/cm^3) between 1000° and 1150°C. In an alternative process the sol is converted to gel by the

[4] S. C. Carniglia, S. D. Brown and T. F. Schroeder, *J. Am. Ceram. Soc.* **54** (1971) 13.

[5] R. Benz, *J. Nucl. Mat.* **29** (1969) 43.

[6] D. E. Ferguson, O. C. Dean and D. A. Douglas, *Proc. 3rd Int. Conf. on the Peaceful Uses of Atomic Energy*, Vol. 10, p. 307. Geneva (1965).

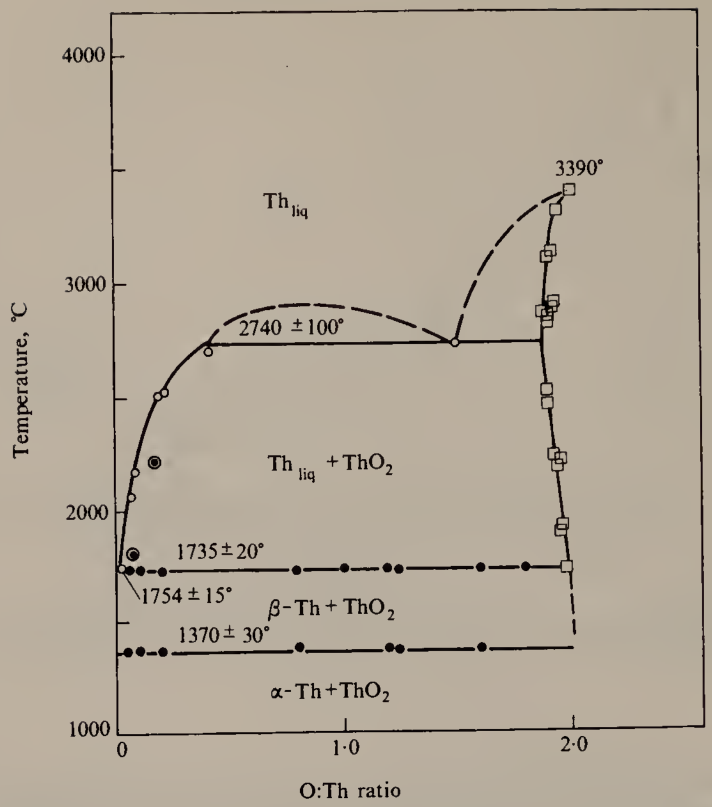

FIG. 3. The thorium–oxygen phase diagram. (Reproduced with permission from ref. 5.)

organic liquid extraction of water from sol droplets[7]. The organic liquid is usually an alcohol with an affinity for water but which is immiscible with the sol. The product is a fine powder composed of small spheres.

Thoria is stable to quite high temperatures. Some decomposition to $ThO_{(g)}$ and oxygen occurs on vaporization above 2000°C. Thorium monoxide is stable only in the gaseous state; on cooling in a vacuum it decomposes to the metal and dioxide. The free energy of formation from 2000°K to 3000°K for $ThO_{(g)}$, $ThO_{2(g)}$, and $ThO_{2(s)}$ may be calculated using the relationships

$$\Delta G(\mathrm{ThO_{(g)}}) = -10{,}300-14{\cdot}4T\,\mathrm{cal/mol}$$

$$\Delta G(\mathrm{ThO_{2(g)}}) = -138{,}600+11{\cdot}4T\,\mathrm{cal/mol}$$

and

$$\Delta G(\mathrm{ThO_{2(s)}}) = -296{,}000+46{\cdot}38T\,\mathrm{cal/mol}\text{ respectively}$$

which indicate that the stability of $ThO_{(g)}$ increases with temperature whilst that of $ThO_{2(g)}$ decreases.

ThO_2 that has not been heated above about 550°C will dissolve readily in 8 to 16 M HNO_3 containing a small amount of fluoride. High-fired thoria requires refluxing with concentrated nitric acid plus larger amounts of fluoride, the dissolution being very slow. Hydrochloric acid, even with added HF, is without effect on high-fired ThO_2. Digestion with fuming sulfuric acid or fusion with $NaHSO_4$($Na_2S_2O_7$, NH_4HSO_4) converts thoria to the water-soluble sulfate. Small samples of ThO_2 can be dissolved in 30% HCl+$HClO_4$ at 310°C in a sealed tube.

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[7] P. A. Haas and S. D. Clinton, *Ind. Eng. Chem., Process Design Develop.* **5** (1966) 236.

TABLE 1. PHYSICOCHEMICAL PROPERTIES OF ThO_2[a–c]

Lattice constant: $a = 5{\cdot}5971$ Å at 25°C
Density: $\rho = 10{\cdot}001$ g/cm^3
Thermal expansion (°C): $a_T = 5{\cdot}59588 + 4{\cdot}570 \times 10^5 \times T + 6{\cdot}27 \times 10^{-9} \times T^2$
Melting point: $M_p = 3390$°C
Boiling point: $B_p = 4400$°C
Heat of formation: $\Delta H_{298^\circ K} = -(293{\cdot}2 \pm 0{\cdot}4)$ kcal/mol
Free energy of formation: $\Delta G_{298^\circ K} = -279{\cdot}4$ kcal/mol
Enthalpy: $H_T - H_{298^\circ K} = -5774{\cdot}21 + 16{\cdot}5643\,T + 1{\cdot}11607 \times 10^{-3}T^2 + 2{\cdot}19547 \times 10^5/T$ cal/mol
Entropy: $S_{298^\circ K} = 15{\cdot}59 \pm 0{\cdot}02$ cal/mol deg
Heat of vaporization: $\Delta H_{298^\circ K} = 170{\cdot}3$ kcal/mol
Heat of fusion: $\Delta H_f = 21{\cdot}4$ kcal/mol
Heat capacity: $C_p = 14{\cdot}6 + 0{\cdot}0051\,T$(°K) cal/mol deg from R.T. to 1000°C
Vapor pressure: $\log p\,(ThO_2(g)(atm)) = 8{\cdot}26 - 3{\cdot}55 \times 10^4/T$(°K) from 2000° to 3000°K
Dielectric constant: $\epsilon = 18{\cdot}9$ (for 300 kc/sec)
Compressibility: $\beta = 0{\cdot}518 \times 10^{-12}$ cm^2/dyn
Young's modulus: $1{\cdot}98 \times 10^3$ kbar
Thermal conductivity: $\lambda = (1-P)(1 + 1{\cdot}49\,P)(0{\cdot}79 + 0{\cdot}185\,T)$ W/cm deg from 250° to 1800°K, P = pore volume fraction
Magnetic susceptibility: $\chi = -(26{\cdot}3 \pm 0{\cdot}3) \times 10^{-6}$ cm^3/mol

[a] C. Keller, *The Chemistry of the Transuranium Elements*, Verlag Chemie, Weinheim (1971).

[b] R. C. Anderson, *Thoria and Yttria* in *High Temperature Oxides*, A. M. Alper (Ed.), Part II, p. 1, Academic Press, New York (1970).

[c] S. Peterson and C. E. Curtis, *Thorium Ceramics Data Manual*, Report ORNL-4503, Vol. I (1970).

Some of the physical properties of thorium dioxide are given in Table 1. At low to moderate temperatures thoria can be considered an insulating material. However, it has some of the characteristics of semiconductors. It is an electronic conductor whose level of conductivity is dependent on temperature and oxygen partial pressure. For "pure" ThO_2 in the high oxygen pressure regions a $p(O_2)^{1/4}$ dependence of electrical conductivity is recorded[8]. At intermediate oxygen partial pressures this relationship breaks down and the ionic contribution becomes very significant. Substitution of Th^{4+} for Y^{3+} or Ca^{2+} leads to structures which exhibit a level of anionic conductivity comparable to that of the electronic conductivity plus or minus a factor of ten. The concentration of anionic vacancies is now large with respect to the number of electronic charge carriers normally present in pure ThO_2, and furthermore, this concentration is fixed by composition and to a first approximation is independent of $p(O_2)$.

Thorium oxide has a refractive index of 2·110 for $\lambda = 564{\cdot}1\,\mu$m, a relatively high value for oxides[9]. A theoretically dense sample of Thoralox ceramic, containing 2 m/o CaO in solid solution shows transmission cut-offs at 0·27 μm and 9·5 μm for a 1·56 mm thick sample[10], very close to the same values found for ThO_2 single crystals. The reflectivity of single crystal ThO_2 rises from 40% at 20 μm to 90% at 3·4 μm and then drops to near zero at 1·7 to 1·8 μm[11].

Protactinium oxides

In addition to the dioxide, PaO_2, and at least five modifications of the pentoxide, Pa_2O_5,

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[8] M. F. Lasker and R. A. Rapp, *Z. Phys. Chem.* (*Neue Folge*) 49 (1966) 198.

[9] W. P. Ellis and R. M. Lindstrom, *Opt. Acta* **11** (1964) 287.

[10] P. J. Jørgensen, in R. C. Anderson, *Thoria and Yttria*, in *High Temperature Oxides*, A. M. Alper (Ed.) Part II, p. 22, Academic Press, New York (1970).

[11] J. D. Axe and G. D. Pettit, *Phys. Rev.* **151** (1966) 676.

four intermediate oxides have been identified in the PaO_2–Pa_2O_5 region by X-ray powder diffraction methods[12–14].

Protactinium pentoxide is obtained by heating the hydrated oxide $Pa_2O_5 \cdot aq$ or any other binary protactinium(IV) or (V) compound in air or oxygen to temperatures above 650°C. The amorphous, hydrated oxide is obtained by precipitation of protactinium(V) from aqueous solution on the addition of aqueous ammonia. At low temperatures, fcc Pa_2O_5 is obtained, whilst at higher temperatures modifications with less symmetric structures are formed (Table 2). Pa_2O_5 seems to be strictly stoichiometric and is, therefore, useful in analytical work.

Hydrogen reduction of Pa_2O_5 at 1550°C yields the black dioxide PaO_2, which crystallizes with the fluorite type of structure like all other actinide dioxides. During a very careful study of the oxidation of the dioxide and the reduction of the pentoxide, four intermediate oxides with relatively small homogeneity regions have been characterized (Table 2). Protactinium monoxide, like all other actinide monoxides, has not yet been obtained pure; it has only been identified by X-ray methods as a surface layer on protactinium metal.

Uranium oxides

The uranium–oxygen system is one of the most complex oxide systems known. Despite many thorough investigations, contradictory results have often been obtained and many

TABLE 2. CRYSTALLOGRAPHIC DATA FOR BINARY PROTACTINIUM OXIDES

Composition	Colour	Symmetry	Lattice parameters				Range of existence (°C)	Ref.
			a (Å)	b (Å)	c (Å)	α (°)		
Pa_2O_5	White	Cubic	5·446	—	—	—	650–700	a
Pa_2O_5	White	Tetragonal†	5·429	—	5·503	—	700–1000	b
Pa_2O_5	White	Hexagonal	3·817	—	13·220	—	1000–1500	b
Pa_2O_5	White	Rhombohedral	5·424	—	—	89·76	1250–1400	b
Pa_2O_5	White	Orthorhombic	6·92	4·02	4·18	—	?	a
$PaO_{2.42}$ – $PaO_{2.44}$	White (?)	Rhombohedral	5·449	—	—	89·65	—	b
$PaO_{2.40}$ – $PaO_{2.42}$	White (?)	Tetragonal	5·480	—	5·416	—	—	b
$PaO_{2.33}$	Black	Tetragonal	5·425	—	5·568	—	—	b
$PaO_{2.18}$ – $PaO_{2.21}$	Black	Cubic	5·473	—	—	—	—	b
PaO_2	Black	Cubic	5·505	—	—	—	—	a, b
PaO	—	Cubic	4·961	—	—	—	—	a

† Stchouzkoy *et al.*[c] quote *a* and *c* values twice those listed.

[a] P. A. Sellers, S. M. Fried, R. E. Elson and W. H. Zachariasen, *Acta Cryst.* **76** (1945) 5935.

[b] L. E. J. Roberts and A. Walter, in *Physico-Chimie du Protactinium*, Colloques Internationaux du Centre National de la Recherche Scientifique, No. 154, p. 51. Paris (1966).

[c] T. Stchouzkoy, H. Pézérat, G. Bouissières and R. Muxart, *Compt. Rend.* **259** (1964) 3016.

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[12] L. E. J. Roberts and A. Walter, in *Physico-Chimie du Protactinium*, Colloques Internationaux du Centre National de la Recherche Scientifique No. 154, p. 51. Paris (1966).

[13] T. Stchouzkoy, H. Pézérat and R. Muxart, in *Physico-Chimie du Protactinium*, Colloques Internationaux due Centre National de la Recherche Scientifique, No. 154, p. 61. Paris (1966).

[14] P. A. Sellers, S. M. Fried, R. E. Elson and W. H. Zachariasen, *J. Am. Chem. Soc.* **76** (1954) 5935.

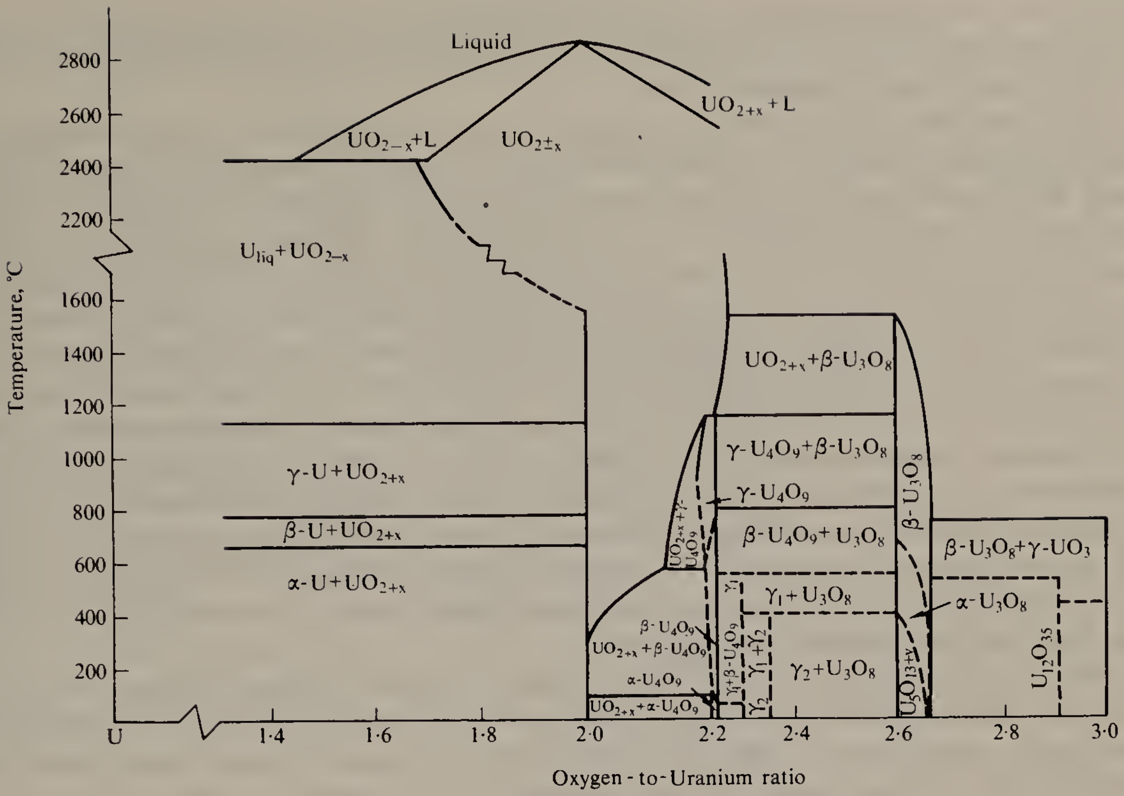

FIG. 4. The uranium–oxygen phase diagram.

questions remain, not only concerning chemical and physical properties, but also the phase diagram. The basic interest in the uranium–oxygen system is due mainly to the application of uranium dioxide as a nuclear fuel in power reactors.

Phase Relationships and Structural Investigations

The binary oxides $UO_{2\pm x}$, U_4O_9, U_3O_7, U_3O_8, and UO_3 have been described in the uranium–oxygen system together with several other intermediate oxides which have not been investigated to the same extent. Most of these oxides are polymorphic and are oxide phases with different ranges of composition rather than stoichiometric compounds. The crystallographic data for the binary uranium oxides are summarized in Table 3. Figure 4 shows the phase relationships in the uranium–oxygen system. It is a composite diagram incorporating the results of several investigations.

The UO_{2+x}–$UO_{2.67}$ *Region.* Reduction of the higher uranium oxides at about 1000°C yields the brown dioxide, UO_2, which loses oxygen only in a high vacuum above 1800°C[15]. On cooling, the resulting UO_{2-x} decomposes to UO_2+metallic uranium. The sub-stoichiometry of UO_{2-x} extends from $UO_{1.994}$ at 1200°C through $UO_{1.7}$ at 2300°C to $UO_{1.65}$ at the monotectic temperature of the U–UO_2 system, 2425°C. At still higher temperatures up to the melting point of UO_2 (2865°C) the variation in the O:U ratio decreases. The sub-stoichiometric phases are best prepared by reactions between UO_2 and metallic uranium rather than by reduction of UO_2 with hydrogen.

When heated in air or in oxygen, UO_2 is transformed into U_3O_8 via several intermediate oxides, including the fluorite phase UO_{2+x} and/or U_4O_9, the exact route depending on the

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[15] R. E. Latta and R. E. Fryxell, *J. Nucl. Mat.* 35 (1970) 195.

temperature and oxygen pressure. Different studies have also demonstrated by DTA and DTG measurements that the oxidation of UO_2 and U_4O_9 to U_3O_8 proceeds via U_3O_7 ($UO_{2.33}$) as a definite compound[16,17].

UO_2 crystallizes in the fluorite structure with isotropic vibration of both U and O. At high temperature, however, a strong anisotropic vibration of the oxygen atoms occurs along the cube diagonals towards the center of the cube. The fluorite phase UO_{2+x} also possesses the cubic fluorite lattice, the excess oxygen being randomly distributed at the edge centers ($00\frac{1}{2}$, $0\frac{1}{2}0$, $\frac{1}{2}00$) or at the center ($\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$) of the fluorite lattice. Following the incorporation of additional oxygen the neighboring oxygen atoms become slightly displaced to minimize the lattice strain. For example, on the incorporation of an additional oxygen atom at the center of the cube the oxygen atoms at ($\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4}$) are displaced along the cube diagonals to (*uuu*) with $u \sim 0{\cdot}20$ (Fig. 5)[18]. Intensity variations of neutron diffraction patterns show that the extra oxygen atoms in UO_{2+x} occupy positions that are distributed at random throughout the structure, so that, although the same space group symmetry *Fm3m* is preserved, this now relates only to the "statistical" cell, obtained by superimposing all the cells in the structure. It has also been demonstrated that the randomly distributed defects are not individual oxygen atoms but complexes which consist of vacant, normal oxygen sites and two different interstitial oxygen sites.

The composition range of the UO_{2+x}-phase is strongly temperature-dependent, the value of x increasing from about zero at 300°C to 0·17 at 900°C. Above 1123°, x rises only slowly with temperature to about 0·28 at 1600°C. At approximately $UO_{2.23}$ the "disordered" UO_{2+x}-phase passes into the "ordered" U_4O_{9-y}-phase. A cubic superstructure has been found for U_4O_{9-y}, with 256 U atoms in 4×4×4 elementary cells of the fluorite

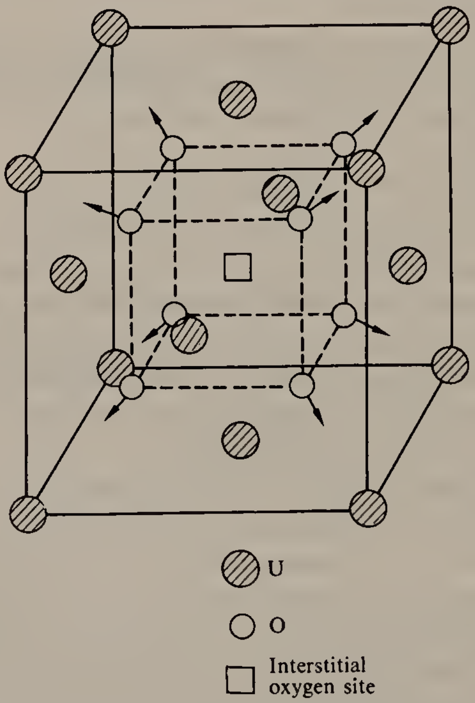

FIG. 5. Displacement of the oxygen atoms in the UO_2 lattice located at $\pm(\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4})$ following the incorporation of an additional oxygen atom at $(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$[18].

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[16] P. Imris, *J. Inorg. Nucl. Chem.* **27** (1965) 2135.

[17] H. Landspersky and J. Vachuska, *J. Inorg. Nucl. Chem.* **28** (1966) 2767.

[18] B. T. M. Willis, *J. Physique (Paris)* **25** (1964) 431.

TABLE 3. CRYSTALLOGRAPHIC DATA FOR BINARY URANIUM OXIDES

Compound	Symmetry	Space group	Lattice constants						Ref.
			a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	
UO (?)	Cubic	*Fm3m*	4·92	—	—	—	—	—	a
UO_2	Cubic	*Fm3m*	5·468	—	—	—	—	—	‡
α-U_4O_{9-y}	Pseudocubic	—	n·5·4338	—	—	90·078	—	—	b
β-U_4O_{9-y}	Cubic	$I\bar{4}3d$	n·5·4338	—	—	—	—	—	b
$U_{16}O_{37}$	Tetragonal†	—	5·417	—	5·497	—	—	—	c
U_8O_{19}	Monoclinic	—	5·378	5·559	5·378	90·29	—	—	d
β-U_2O_5	Tetragonal	—	3·813	—	13·18	—	—	—	c
γ-U_2O_5	Monoclinic	—	5·410	5·481	5·410	—	90·49	—	c
U_8O_{21}	Orthorhombic	—	6·751	3·176	8·286	—	—	—	c
α-U_3O_8	Orthorhombic	*C2mm*	6·716	11·960	4·1469	—	—	—	e
β-U_3O_8	Orthorhombic	*Cmcm*	7·069	11·445	8·303	—	—	—	e
α-UO_3	Orthorhombic	*C2mm*	3·913	6·936	4·167	—	—	—	f
β-UO_3	Monoclinic	$P2_1$	10·34	14·33	3·910	—	99·03	—	g
γ-UO_3	Orthorhombic	*Fddd*	9·813	19·93	9·711	—	—	—	h
δ-UO_3	Cubic	—	4·146	—	—	—	—	—	i
ϵ-UO_3	Triclinic	—	4·002	3·841	4·165	98·10	90·20	120·17	k
ξ-UO_3	Orthorhombic	$P2_12_12_1$	7·511	5·466	5·224	—	—	—	l
α-$UO_2(OH)_2$	Orthorhombic	*Cmca*	4·242	10·302	6·868	—	—	—	m
β-$UO_2(OH)_2$	Orthorhombic	*Pbca*	5·635	6·285	9·919	—	—	—	n

† Cell parameters refer to the pseudo-cell.

‡ Generally accepted value (see, e.g. G. H. Winslow, *High Temp. Sci.* 3 (1971) 361).

[a] R. E. Rundle, N. C. Baenzinger, A. S. Wilson and R. A. McDonald, *J. Am. Chem. Soc.* **70** (1949) 99.

[b] B. Belbeoch and J. C. Boivineau, *Bull. Soc. Mineral. Cristallogr.* **90** (1967) 558.

[c] H. R. Hoekstra, S. Siegel and F. X. Gallagher, *J. Inorg. Nucl. Chem.* **32** (1970) 3237.

[d] H. R. Hoekstra, S. Siegel and P. Charpin, *J. Inorg. Nucl. Chem.* **30** (1968) 519.

[e] B. O. Loopstra, *Acta Cryst.* **B26** (1970) 656.

[f] α-UO_3 is an imperfectly crystalline form of orthorhombic $UO_{2\cdot9}$: B. O. Loopstra and E. H. P. Cordfunke, *Rec. Trav. Chim. Pay-Bas* **85** (1966) 135.

[g] P. C. Debets, *Acta Cryst.* **21** (1966) 589.

[b] S. Siegel and H. R. Hoekstra, *Inorg. Nucl. Chem. Letters* **7** (1971) 455.

[i] E. Wait, *J. Inorg. Nucl. Chem.* **1** (1955) 309.

[k] L. M. Kovba, L. M. Vidavskii and E. G. Lavut, *Zhur. Strukt. Khim.* **4** (1963) 627.

[l] S. Siegel, H. R. Hoekstra and E. Sherry, *Acta Cryst.* **20** (1966) 292.

[m] J. C. Taylor, *Acta Cryst.* **B27** (1971) 1088.

[n] R. B. Roof, Jr., D. T. Cromer and A. C. Larson, *Acta Cryst.* **17** (1964) 701.

lattice[19]. Neutron diffraction studies of a U_4O_9 single crystal indicate an even larger (8 ×) cubic superlattice[20].

Three different modifications of U_4O_9 are known:

(a) α-U_4O_9 is formed at temperatures $\leqslant 65°C$. The structure of this modification is slightly deformed with respect to the cubic β-U_4O_9[21]. The transformation temperature is found to vary with slight changes of composition, and also seems to be dependent on quenching conditions[22,23].

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[19] B. Belbeoch, C. Piekarski and P. Perio, *Acta Cryst.* **14** (1961) 837.

[20] N. Masaki and K. Doi, *Acta Cryst.* **B24** (1968) 1393.

[21] B. Belbeoch and J. C. Boinvineau, *Bull. Soc. fr. Minéral. Cristallogr.* 90 (1967) 558.

[22] K. Naito, T. Ishii, Y. Hamaguchi and K. Oshima, *Solid State Commun.* 5 (1967) 349.

[23] T. Ishi, K. Naito and K. Oshima, *Solid State Commun.* 8 (1970) 677.

(b) β-U_4O_9 forms between 65°C and about 560°C[24]. Relatively large parts of this purely cubic U_4O_9 structure consist of stoichiometric UO_2 in the U_4O_9 cell. According to a neutron diffraction study[18] the distribution of oxygen may indicate an idealized formula $U_{12}O_{21}O_4{}'O_2{}''$. That is, on the average there are, in $3UO_2$ subcells, four oxygen atoms in position O′ and two oxygens in position O″ with the rest on normal lattice positions. The channeling behavior of 1 MeV He^+ ions and deuterons in U_4O_9 indicates the existence of a high concentration of displaced oxygen atoms located more than ~0·20 Å from the interstitial holes or from normal lattice positions. The channeling data show that the uranium sublattice is only slightly disturbed[25].

(c) γ-U_4O_9 forms between 560°C and 1123°C; this modification seems to be a partially disordered cubic U_4O_9[24].

Another presumably metastable oxide $UO_{2\cdot 19}$, obtained by oxidation between 300°C and 750°C of thin, single-crystal films of UO_2, crystallizes with a tetragonal fluorite superstructure of the type $a{=}b{=}4a_{UO_2}$ and $c{=}a_{UO_2}$[26]. The formation of the UO_{2+x} superstructures from the UO_2 fluorite lattice can be explained as follows. The oxygen atoms are first randomly distributed in the UO_2 lattice until a long-range order, and hence a superstructure, appears at a certain oxygen content. At high temperatures the state of order is again disturbed; in the case of U_4O_9 the order $\rightleftharpoons$ disorder transition to UO_{2+x} occurs at 1123°C[27]. At this temperature the three oxides UO_{2+x}, $UO_{2.245}(U_4O_{9-y})$ and $UO_{2.61}$ are in equilibrium.

The UO_{2+x} phase has a higher entropy than the U_4O_9 phase, although it is appreciably lower than the value calculated for a completely random distribution of the excess oxygen. This means that submicro-regions of the ordered U_4O_9-structure must still be present in UO_{2+x}[21].

In the region $UO_{2.25}$–$UO_{2.6}$ we find below 500°C two further ordered, intermediate phases whose structures can be derived from the fluorite structure. The γ_1-phase with $2{\cdot}33 \leqslant O{:}U \leqslant 2{\cdot}38$ decomposes at about 400°C to give the γ_2-phase$+UO_{2.61}$. The γ_2-phase $(2{\cdot}30 \leqslant O{:}U \leqslant 2{\cdot}35)$ passes into $U_4O_9+UO_{2.61}$ at 550°C. The oxidation and thermal decomposition of all uranium oxides in air or oxygen at normal pressure and 800–900°C yield $U_3O_8(UO_{2.67})$. Under controlled conditions stoichiometric U_3O_8 is obtained and this compound is therefore used for the gravimetric determination of uranium. U_3O_8 contains both uranium(V) and (VI), $U^{V}{}_2U^{VI}O_8$.

At least two different U_3O_8 modifications are known. When heated in air to about 800°C, the orthorhombic, dark-green α-U_3O_8 is obtained[28]. Orthorhombic β-U_3O_8, very often designed as $UO_{2.6}$, U_5O_{13} or U_8O_{21}, seems to be a high-temperature phase with a considerable range of stoichiometry. Both modifications have structures which are closely related to the "ideal" UO_3 composition. In α-U_3O_8 each uranium atom has seven oxygen neighbors with a pentagonal bipyramidal coordination. In β-U_3O_8 two uranium atoms are pentagonal bipyramidal and the third is surrounded by a distorted octahedron of oxygen atoms.

Marked changes in the relative stability of uranium oxides occur at high pressures, e.g. three different $UO_{2.5}$ modifications have been detected[29]:

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[25] H. Matzke, J. A. Davies and N. G. E. Johansson, *Canad. J. Phys.* **49** (1971) 2215.
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[27] L. E. J. Roberts and A. J. Walter, *J. Inorg. Nucl. Chem.* **22** (1961) 213.
[28] B. O. Loopstra, *Acta Cryst.* **B26** (1970) 656.
[29] H. R. Hoekstra, S. Siegel and F. X. Gallagher, *J. Inorg. Nucl. Chem.* **32** (1970) 3237.

α-U_2O_5 is prepared at 500°C at 15 kbar via the reaction

$$UO_2+U_3O_8 \rightarrow 2\ \alpha\text{-}U_2O_5$$

β-U_2O_5, with a hexagonal type of structure, is stable at 40–50 kbar and temperatures in excess of 800°C

monoclinic γ-U_2O_5 is stable at >60 kbar and temperatures of at least 800°C.

U_3O_8 is stable at relatively low pressures, but disproportionates to α- or β-U_2O_5 and ξ-UO_3 as the pressure is increased. Monoclinic U_3O_7, with the high density of 11·34 g/cm^3, has been prepared from mixtures of UO_2 and U_3O_8 at 30–40 kbar and 500–1400°C[30].

The $UO_{2.67}$–UO_3 *Region.* Uranium trioxide, UO_3, exists in at least six crystal modifications (α-UO_3 to ϵ-UO_3 and high-pressure ξ-UO_3) and one amorphous form (Table 3). The relative instability of UO_3 necessitates the use of moderate temperatures (400°C to 700°C) in its preparation. This limitation leads to difficulties in preparing pure phases, especially in the case of the amorphous oxide and α-UO_3 (Table 4). It has been shown that residual traces of nitrogen (from nitrate and ammoniums ions) and carbon (from carbonate and organic residues) are extremely difficult to remove without decomposition of the trioxide and sometimes influence the formation of a special polymorph. For example, the decomposition of carefully washed uranyl peroxide $UO_4 \cdot 2H_2O$ gives rise to the formation of amorphous UO_3, whereas the non-washed $UO_4 \cdot 2H_2O$ yields α-UO_3[31]. For this reason it is preferable, whenever possible, to use U_3O_8 as a starting material.

TABLE 4. MODES OF PREPARATION AND COLORS OF URANIUM TRIOXIDE PHASES

Type	Color†	Conditions
Amorphous UO_3†	Orange	Ignition of $UO_4 \cdot 2H_2O$, $UO_3 \cdot 2H_2O$, $UO_2C_2O_4 \cdot 3H_2O$, or $(NH_4)_4UO_2(CO_3)_3$ in air to 400°C
α-UO_3	Tan (orange, red)	Amorphous UO_3 heated in 40 atm O_2 at 470–500°C or thermal decomposition of non-washed $UO_4 \cdot 2H_2O$ at 525–575°C
β-UO_3	Orange, red	U_3O_8 heated in 40 atm O_2 at 500–550°C Ignition of $(NH_4)_2U_7O_{22}$ in air to 500°C
γ-UO_3	Yellow	Ignition of $UO_2(NO_3)_2 \cdot 6H_2O$ in air at 400–600°C Heat α-, β-, δ-, ϵ- and amorphous UO_3 in 40 atm O_2 at 650°C
δ-UO_3	Dark red	Ignition of β-$UO_3 \cdot H_2O$ in air to 375°C (> 24 hr)
ϵ-UO_3	Red	Heat U_3O_8 in NO_2 at 250–375°C

† The color is dependent to some extent on the method of preparation.

On heating to higher temperatures at normal pressure all crystalline UO_3 modifications decompose directly to U_3O_8 with the exception of amorphous UO_3 which gives $UO_{2.9}$ ($U_{12}O_{35}$) as an intermediate[32]. $UO_{2.9}$ seems to be a distinct compound in the uranium–oxygen system. γ-UO_3 is the most stable UO_3-modification; at 650°C and $p(O_2) = 40$ atm all modifications will be converted to γ-UO_3. At normal pressure γ-UO_3 decomposes at 650–680°C.

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[30] H. R. Hoekstra, S. Siegel and P. Charpin, *J. Inorg. Nucl. Chem.* **30** (1968) 519.

[31] E. H. P. Cordfunke, *J. Inorg. Nucl. Chem.* **23** (1961) 285.

[32] H. R. Hoekstra and S. Siegel, *J. Inorg. Nucl. Chem.* **18** (1961) 154.

Detailed structural investigations have been undertaken for α-, β-, γ-, δ-, and ξ-UO_3[33–38]. Whereas no short U–O bond lengths are observed in both modifications of U_3O_8, uranyl groups with O–U–O bond lengths between 1·7 Å and 1·9 Å are present in α-, β-, γ-, and ξ-UO_3. Uranium trioxide, therefore, is unique in that it represents a composition in which pure uranyl bonding can exist without other influences. In β-UO_3, for example, of the ten uranium atoms in the monoclinic unit cell, six are 6-coordinate whilst four have seven oxygen neighbors at distances of 2·7 Å or less. Uranium atoms with different coordinations are also found in γ-UO_3, in which chains of 6-coordinate uranium atoms lie in parallel planes and are interconnected by 7-coordinate uranium atoms. In high-pressure ξ-UO_3 (prepared at 30 kbar and 1100°C), however, each uranium atom is bonded to seven oxygen atoms with a puckered pentagonal array around the uranyl group. It is highly probable that α-UO_3 and ϵ-UO_3 have similar geometric configurations. This would mean that only cubic δ-UO_3, with the ReO_3-type of structure, does not contain more than one kind of uranium atom, if, that is, the proposed structure is correct.

Physical and Chemical Properties

During the last twenty years uranium dioxide has become especially important as a nuclear fuel for research and power reactors. Consequently, its physical and chemical properties, the most important of which are summarized in Table 5, have been thoroughly investigated. UO_2 is a refractory compound with a high melting point and a lattice energy of −2351 kcal/mol (U_4O_9: −2320 kcal/mol)[39]. The heats of formation of the different binary uranium oxides and uranium oxide-hydrates are given in Table 6. The value for UO_2 fits very well into the series of the other actinide dioxides. Surprisingly there is practically no difference between the heats of formation of the different UO_3 modifications.

Most of the physical properties depend to a large extent on the exact oxygen-to-uranium ratio and considerable changes are often observed when going from stoichiometric $UO_{2\cdot00}$ to sub- or superstoichiometric oxides.

A characteristic example is the variation of the free energy of solution of oxygen $\Delta G(O_2)$ in uranium oxides near the dioxide composition (Fig. 6). An enormous change in oxygen potential occurs between $UO_{1\cdot99}$ and $UO_{2\cdot01}$. This large difference is to be expected, because oxygen is going into vacant anion sites when O:U < 2·00 and into interstitial positions in the lattice when O:M > 2·00[40]. Correspondingly, the equilibrium oxygen pressure over UO_{2+x} increases sharply with increasing values of x, going at 1400°C, e.g. from about 10^{-8} atm at $UO_{2.01}$ to about 10^{-5} atm at $UO_{2.10}$[41].

Relatively high oxygen pressures have been found for oxygen-rich uranium oxides. The oxygen partial pressure for diphasic regions may be calculated using the following equations:

$\log p(O_2)$ (atm) $= 8\cdot78 - 17{,}460/T$ (°K) for the UO_{2+x}–$UO_{2.6}$ region from 1123°C to 1450°C[27] and
$\log p(O_2)$ (torr) $= 16\cdot192 - 12{,}338/T$ (°K) for the U_3O_8–γ-UO_3 region from 512°C to 600°C[42]

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[33] B. O. Loopstra and E. H. P. Cordfunke, *Rec. Trav. Chim. Pay-Bas*, **85** (1966) 135.
[34] P. C. Debets, *Acta Cryst.* **21** (1966) 589.
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[36] S. Siegel and H. R. Hoekstra, *Inorg. Nucl. Chem. Letters*, **7** (1971) 455.
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[42] E. H. P. Cordfunke and P. Aling, *Trans. Faraday Soc.* **61** (1965) 1.

Table 5. Physicochemical Properties of Uranium Dioxide

1. For solid UO_2

Lattice constant: $a = 5{\cdot}468$ Å
Density: $\rho = 10{\cdot}97$ g/cm^3
Thermal expansion coefficient: $\alpha = 25{\cdot}0 \times 10^{-6} + 12{\cdot}7 \times 10^{-9}\,T\,(^\circ\mathrm{C})\ \mathrm{deg}^{-1}$ [a]
Melting point: $M_p = 2865^\circ$C [b]
Néel temperature: $T_N = 30{\cdot}8^\circ$K [c]
Heat of formation: $\Delta H_{298^\circ\mathrm{K}} = -(259{\cdot}3 \pm 0{\cdot}2)$ kcal/mol [d]
Entropy: $S_{298^\circ\mathrm{K}}(UO_{2.005}) = 18{\cdot}41$ cal/mol deg [a]
Enthalpy: (a) from 298°K to 1500°K [e]
$H_T - H_{298^\circ\mathrm{K}} = (-\,6725{\cdot}69 + 18{\cdot}4272\,T + 1{\cdot}01027 \times 10^{-3}T^2 + 3{\cdot}40429 \times 10^5/T)$ cal/mol
(b) from 1500°K to 2715°K [f]
$H_T - H_{298^\circ\mathrm{K}} = (-\,6{\cdot}36 + 0{\cdot}0180\,T + 1{\cdot}95 \times 10^{-6}T^2 + 2{\cdot}46 \times 10^2/T)$ kcal/mol
Heat capacity: (a) from 298°K to 1500°K [e]
$C_p = 18{\cdot}4272 + 2{\cdot}0205 \times 10^{-3}T - 3{\cdot}40429 \times 10^5/T$ cal/mol deg
(b) from 1300°K to about 3100°K [g]
$C_p\,(UO_{2+x}) = 18{\cdot}1 + 1{\cdot}2 \times 10^{-3}\,T + 1{\cdot}85 \times 10^{11} \times T^{-2} \times [\exp(-\,46{,}000/RT)]$ cal/mol deg
Heat of combustion of $3UO_x(2{\cdot}000 \leqslant x \leqslant 2{\cdot}041)$ to U_3O_8 [d]:
$-\Delta H_{298^\circ\mathrm{K}} = [74{\cdot}49 - 90{\cdot}96\,(x - 2{\cdot}0216)]$ kcal/mol
Heat of fusion: $\Delta H_f = 18{\cdot}2$ kcal/mol [h]
Heat of sublimation (2080°K to 2705°K):
$\Delta H_S = (143{\cdot}1 \pm 3{\cdot}0)$ kcal/mol [i]
Vapor pressure of uranium-bearing species above stoichiometric urania (extrapolated)[i]:
$\log p(\mathrm{atm}) = (8{\cdot}61 \pm 0{\cdot}27) - (31{,}284 \pm 64)/T$
Dielectric constant: $\epsilon = 24$ [k]
Compressibility: $\beta = 0{\cdot}62 \times 10^{-12}$ cm^2/dyn [l]
Young's modulus: 1913 kbar (94·6% theor. density and 12–20 μm grain size) [m]
Hardness: 6 to 7 on Mohs' scale [l]
Index of refraction: $\left.\begin{array}{l} 2{\cdot}29 \pm 0{\cdot}03 \text{ at } 8000\text{Å} \\ 2{\cdot}58 \pm 0{\cdot}22 \text{ at } 4500\text{Å} \end{array}\right\}$—for thin UO_2 films evaporated onto fused silica [l]
Thermal conductivity: $1/\lambda(\mathrm{W/cm\ deg}) = 11{\cdot}75 + 0{\cdot}02375\,T\,(^\circ\mathrm{C})$, recommended for 95% theoretical density and composition $UO_{2.005 \pm 0.005}$ from R.T. to 1300°C [n]

2. For liquid UO_2

Density: $(8{\cdot}74 \pm 0{\cdot}16)$ g/cm^3 just above the melting point (2800°C (?)) [o]
Coefficient of thermal expansion: $\alpha = 3{\cdot}5 \times 10^{-5}$/deg between 2800°C to 3100°C
Enthalpy: $H_T - H_{298^\circ\mathrm{K}} = -11153{\cdot}8 + 32{\cdot}457\,T$ cal/mol up to 3500°K [p]
Surface tension: 400 to 600 dyn/cm [q]
Compressibility: $3{\cdot}59 \times 10^{-12}$ to $3{\cdot}77 \times 10^{-12}$ from 2860°C to 2920°C [q]

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[g] C. Affortit, *High Temp.-High Pressures* **1** (1969) 27.
[h] R. A. Hein, P. N. Flagella and J. B. Conway, *J. Am. Ceram. Soc.* **51** (1968) 291.
[i] M. Tetenbaum and P. D. Hunt, *J. Nucl. Mat.* **34** (1970) 86.
[k] J. D. Axe and G. D. Pettit, *Phys. Rev.* **151** (1966) 676.
[l] Cited in *Uranium Dioxide, Properties and Nuclear Applications*, J. Belle (Ed.), USAEC, Washington, D.C. (1963).
[m] *Thermal Conductivity of Uranium Dioxide*, Technical Report Series No. 59, IAEA, Vienna (1966).
[n] R. A. Hall, *J. Nucl. Mat.* **37** (1970) 314.
[o] J. A. Christensen, *J. Am. Ceram. Soc.* **46** (1963) 607.
[p] L. Leibowitz, M. G. Chasanov, L. W. Mishler and D. F. Fischer, *J. Nucl. Mat.* **39** (1971) 115.
[q] S. Rosen, J. M. Simmons, E. A. Aitken, B. R. T. Frost, A. D. Tevebaugh and W. F. Sheely, *Proc. 4th United Nations International Conference on the Peaceful Uses of Atomic Energy*, Paper A/CONF. 49/P/069, Geneva (1971).

TABLE 6. ENTHALPIES OF FORMATION AND STANDARD ENTROPIES OF URANIUM OXIDES AND OXIDE-HYDRATES[a]

Compound	$-\Delta H_{298}$ (kcal/mol)	S_{298} (cal/mol deg)
UO_2	259·3 ± 0·2	18·63 ± 0·1
U_4O_9	1078·8 ± 1·4	19·96 ± 0·04($UO_{2\cdot25}$)
β-U_3O_7	818·9 ± 1	
U_3O_8	854·4 ± 0·6	22·51 ± 0·04(α-U_3O_8)
α-UO_3	291·8 ± 1	
β-UO_3	292·6 ± 1	
γ-UO_3	293·5 ± 1	23·6 ± 0·1
δ-UO_3	290	
ϵ-UO_3	291 ± 1	
β-$UO_3 \cdot H_2O$	367·4 ± 1	
$UO_3 \cdot 2H_2O$	437·3 ± 1	
$UO_4 \cdot 2H_2O$	436	

[a] J. Fuger, *Thermodynamic Properties of Simple Actinide Compounds*, in *MTP International Review of Science*, p. 57. Butterworth, London (1971).

The vapor species over stoichiometric UO_2 is $UO_{2(g)}$, whereas principally $UO_{(g)}$, with small amounts of $U_{(g)}$ and $UO_{2(g)}$, is found over liquid U–UO_2 mixtures from 1600° to 2500°K[43,44]. The volatility of uranium oxides increases in an oxygen atmosphere, probably due to the formation of $UO_{3(g)}$.

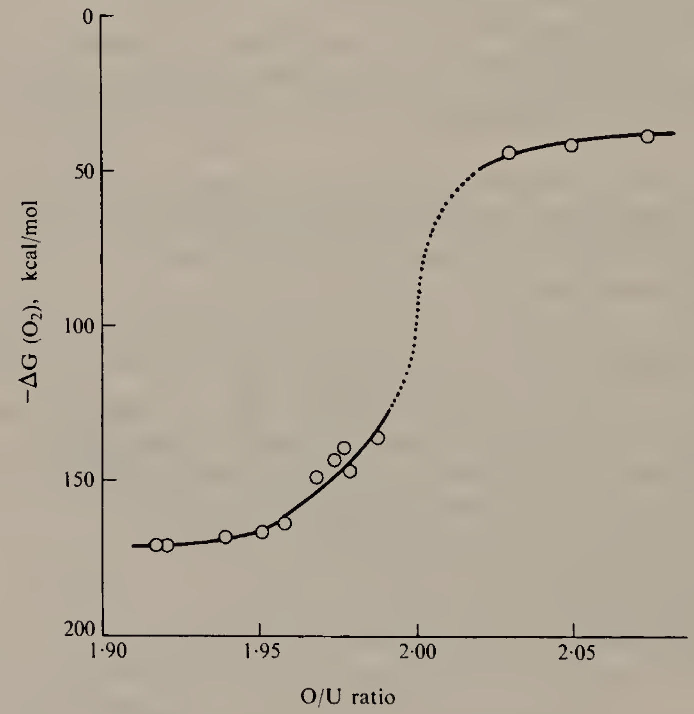

FIG. 6. Variation of $\Delta G(O_2)$ with oxygen-to-uranium ratio at 2200°K. (Reproduced with permission from ref. 40.)

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Neutron diffraction studies have shown that UO_2 is antiferromagnetic below 30·8°K with an effective magnetic moment of about 1·8 μ_B per uranium atom[45]. The magnetic structure consists of alternating ferromagnetic sheets. The neutron diffraction data suggest that the ground state for a U^{4+} ion in UO_2 is a triplet T_2 state. Low-temperature magnetic susceptibility measurements of different uranium oxides showed a maximum at 6·4°K which was larger the higher the oxygen content[46]. This effect is attributed to a defect cluster which is the same in all the oxides.

NMR studies of ^{17}O-enriched UO_2 have shown that direct covalency and overlap contributions to the hyperfine splitting are of secondary importance and that the major contribution to the hyperfine interaction arises from the involvement of excited metal orbitals (such as 7*s* or 6*d*) and/or by exchange polarization of core electrons. In UO_2 the dominant relaxation mechanism is due to electron spin exchange[47].

U_4O_9 is paramagnetic[48], the susceptibility for 1/4 U_4O_9 after correction for diamagnetism between 77°K and 550°K is $420\times10^{-6}+0{\cdot}530/(T+55)$ cm³/mol. Electrical conductivity measurements of uranium oxides have shown that UO_{2-x} and $U_3O_{8(-x)}$ are *n*-type semiconductors whilst UO_{2+x} is a *p*-type semiconductor[49].

All uranium oxides dissolve readily in concentrated nitric or perchloric acids. Freshly prepared, stoichiometric $UO_{2.00}$ is slowly oxidized, even at room temperature. It is presumed that the oxidized surface layer is amorphous UO_3[50].

Single crystals of the uranium oxides may be obtained by, for example, transport reactions, vacuum sublimation, and floating zone techniques. $UO_{2.00}$ single crystals may be oxidized to UO_{2+x} without loss of single-crystal character.

Neptunium oxides

In the neptunium–oxygen system the following binary oxides have been described: NpO(?), Np_3O_8, Np_2O_5 and NpO_2. Attempts to prepare anhydrous NpO_3 by the oxidation of NpO_2 with oxygen at 28 atm or by the action of atomic oxygen on various compounds of pentavalent and hexavalent neptunium have so far been unsuccessful. Crystallographic data for these oxides are summarized in Table 7.

Np_3O_8, which is isostructural with the analogous uranium compound, can be obtained by oxidation of neptunium(IV) or neptunium(V) hydroxide with air or NO_2 at 300–400°C and by thermal decomposition at 275°C in air of a precipitate described as "ammonium, dineptunate(VI) hydrate"[51]. Np_3O_8 is very unstable to heat: above 500°C it loses oxygen and is converted to NpO_2. Dissolution in dilute mineral acids yields a solution containing $NpO_2{}^+$ and $NpO_2{}^{2+}$ in the ratio of 2:1 (Cf: U_3O_8).

Dark-brown to black-brown Np_2O_5 forms on the decomposition of $NpO_3\cdot H_2O$ at 330°C in a vacuum. It is also obtained by bubbling ozone through molten $LiClO_4$ containing neptunium or by the reaction between neptunium metal and molten $LiClO_4$[52]. Dissolution of the $LiClO_4$ melts in water yields a precipitate which corresponds to the composition

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[45] H. U. Rahman and W. A. Runciman, *J. Phys. Chem. Solids* 27 (1966) 1833.

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TABLE 7. CRYSTALLOGRAPHIC DATA FOR NEPTUNIUM OXIDES [a]

Compound	Symmetry	Space group	Color	Lattice constants				Density (g/cm³)
				a (Å)	b (Å)	c (Å)	α (°)	
NpO (?)	Cubic	$Fm3m$	Black (?)	5·01				
NpO_2	Cubic	$Fm3m$	Brown-green	5·434				11·14
Np_2O_5	Monoclinic		Dark brown	4·183	6·584	4·086	0·32	
Np_3O_8	Orthorhombic		Dark brown	6·584	4·086	4·183		

[a] Compilation from C. Keller, *Die Transuranoxide*, in *Gmelin Handbuch der Anorganischen Chemie Transurane*, Band 71, Teil C. Verlag Chemie, Weinheim (1972).

Np_2O_5 after drying at 100°C. A solution of Np_2O_5 in dilute mineral acids shows only the absorption bands of pentavalent neptunium. The precise phase relationships in the system NpO_2–Np_3O_8 are not yet known. It is probable that a single-phase region is present in the interval $NpO_{2.50}$–$NpO_{2.67}$[51].

Yellowish-green neptunium dioxide, NpO_2, the most stable oxide of neptunium, is obtained by the thermal decomposition of numerous neptunium compounds, e.g. of the hydroxide, oxalate, nitrate, 8-hydroxyquinolate, etc., at 600–1000°C. Like all other actinide dioxides, it crystallizes with the fluorite structure. Its lattice constant fits very well into the series of the actinide dioxides (Fig. 2). Single crystals of NpO_2 are prepared from PbF_2–B_2O_3–NpO_2 or Li_2O–MoO_2–NpO_2 molten salt solutions at 1250–1350°C[53] or by electrochemical reduction of neptunyl chloride in molten LiCl–KCl between 700° and 800°C, both on pyrolytic graphite and platinum cathodes[54].

NpO_2 has a very low vapor pressure (approximately 5×10^{-6} atm at 2000°C) which may be calculated by the relation

$$\log p\,(\text{atm}) = (8\cdot39\pm0\cdot13)-(31{,}100\pm300)/T\,(°\text{K})$$

in the range of 2000–2500°K[55]. The ionic species (detected by mass spectrometry) in the gas phase are $NpO_{2(g)}$ and, to a smaller extent, $NpO_{(g)}$. The dissociation energies of $NpO_{2(g)}$ and $NpO_{(g)}$ are 14·3 and 7·4 eV, respectively; the heat of sublimation of NpO_2 is 142·3 kcal/mol. The free energy of formation of NpO_2 from 1850°K to 2475°K may be calculated from the relationships

$$NpO_{2(s)}:\ \Delta G = -254\cdot10+40\cdot5\times10^{-3}T\,(°\text{K})\ (\text{kcal mol}^{-1})$$

and

$$NpO_{2(g)}:\ \Delta G = -113\cdot0+3\cdot5\times10^{-3}T\,(°\text{K})\ (\text{kcal mol}^{-1})$$

The heat of formation of NpO_2, $\Delta H_{298°\text{K}}$, is −256·7 kcal/mol[56] and the standard entropy and heat content are 19.19 cal/mol deg and 15·8 cal/mol deg[57], respectively.

The heat content curve for NpO_2 shows an anomaly at 25·5°K, as does that of UO_2 at 30·8°K, which may be ascribed to an antiferromagnetic component below this temperature[57]. Investigations of the Mössbauer spectra have confirmed an antiferromagnetic

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[53] C. B. Finch and G. W. Clark, *J. Crystal Growth*, **6** (1969) 245.
[54] L. Martinot, A. Machiels, J. Fuger and G. Duyckaerts, *Bull. Soc. Chim. Belges*, **79** (1970) 125.
[55] R. J. Ackermann, R. L. Faircloth, E. G. Rauh and R. J. Thorn, *J. Inorg. Nucl. Chem.* **28** (1966) 111.
[56] E. J. Huber, Jr. and C. E. Holley, Jr., *J. Chem. Eng. Data*, **13** (1968) 545.
[57] E. F. Westrum, Jr., J. B. Hatcher and D. W. Osborne, *J. Chem. Phys.* **21** (1953) 419.

ordering in NpO_2 below 22°K[58], whilst neutron-diffraction studies, even at 4·5°K, produced no indications of a magnetic ordering[59]; this seems to be due to the very small antiferromagnetic moment of Np^{4+} (0·01 μ_B).

The following magnetic data were obtained for NpO_2[58,60] from powder and single-crystal studies:

$$\mu_{\text{eff}} = 2{\cdot}95\ \mu_B, \qquad \Delta = 125°\text{K below } 300°\text{K}$$
$$\mu_{\text{eff}} = 3{\cdot}25\ \mu_B, \qquad \Delta = 181°\text{K between } 300°\text{K and } 800°\text{K}$$

High-fired NpO_2 dissolves in hot concentrated nitric acid containing small amounts of fluoride, and with oxidation to Np(VI) in hot concentrated perchloric acid.

Plutonium oxides

Phase Relationships and Structural Investigations

Like uranium, plutonium forms non-stoichiometric oxides. However, whereas UO_2 readily takes up oxygen at interstitial sites and forms superstoichiometric oxides, PuO_2 loses oxygen above 1400°C and forms sub-stoichiometric oxides, Pu_{2-x}. No superstoichiometric plutonium oxides have so far been found. Nevertheless, PuO_2 absorbs oxygen readily at the surface, so that finely divided PuO_2 can have an O:Pu ratio greater than 2.

The following binary oxides have been described: PuO(?), C-$Pu_2O_{3(+x)}$(=$PuO_{1.51(1.52)}$), C′-$Pu_2O_{3(+x)}$ (=$PuO_{1.62+x}$), A-Pu_2O_3 (=β-Pu_2O_3), $PuO_{1.995}$($PuO_{1.98}$) and PuO_2. The lattice constants of these compounds are summarized in Table 8. The phase diagram for the $PuO_{1.50}$ to PuO_2 region is shown in Fig. 7 which combines data from different research groups. The results indicate that the characteristic difference between the Pu–O system and the very similar Ce–O, Pr–O, and Tb–O systems is the non-occurrence of intermediate phases, with distorted fluorite lattices, in the Pu–O system[61].

Stoichiometric PuO_2, which crystallizes in the fluorite lattice like all actinide dioxides, is formed when plutonium(IV) peroxide, oxalate, hydroxide, or nitrate is heated in a stream

TABLE 8. CRYSTALLOGRAPHIC DATA FOR BINARY PLUTONIUM OXIDES[a]

Compound	Symmetry	Space group	Color	Lattice constants	
				a (Å)	*c* (Å)
PuO_2	Cubic	*Fm*3*m*	Yellow-brown	5·3960	
$PuO_{1.995}$($PuO_{1.98}$)	Cubic	*Fm*3*m*		5·3967	
C-Pu_2O_3($PuO_{1.51(1.52)}$)	Cubic	*Ia*3	Black	11·03–11·07	
C′-Pu_2O_3($PuO_{1.62}$–$PuO_{1.69}$)	Cubic	*Ia*3	Black	10·95–11·10	
A-Pu_2O_3(β-Pu_2O_3)	Hexagonal	$P\bar{3}m1$	Black	3·841	5·958
PuO	Cubic	*Fm*3*m*	Gray-black	4·960	

[a] C. Keller, *The Chemistry of the Transuranium Elements*, Verlag Chemie, Weinheim (1971).

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[58] B. D. Dunlop, G. M. Kalvius, D. J. Lam and M. B. Brodsky, *J. Phys. Chem. Solids*, **29** (1965) 1365.
[59] D. E. Cox and B. C. Frazer, *J. Phys. Chem. Solids*, **28** (1967) 1649.
[60] H. M. Smith and G. W. Clark, Report ORNL-4470, p. 4 (1970).
[61] C. Sari, U. Benedict and H. Blank, Report EUR-3563e (1967).

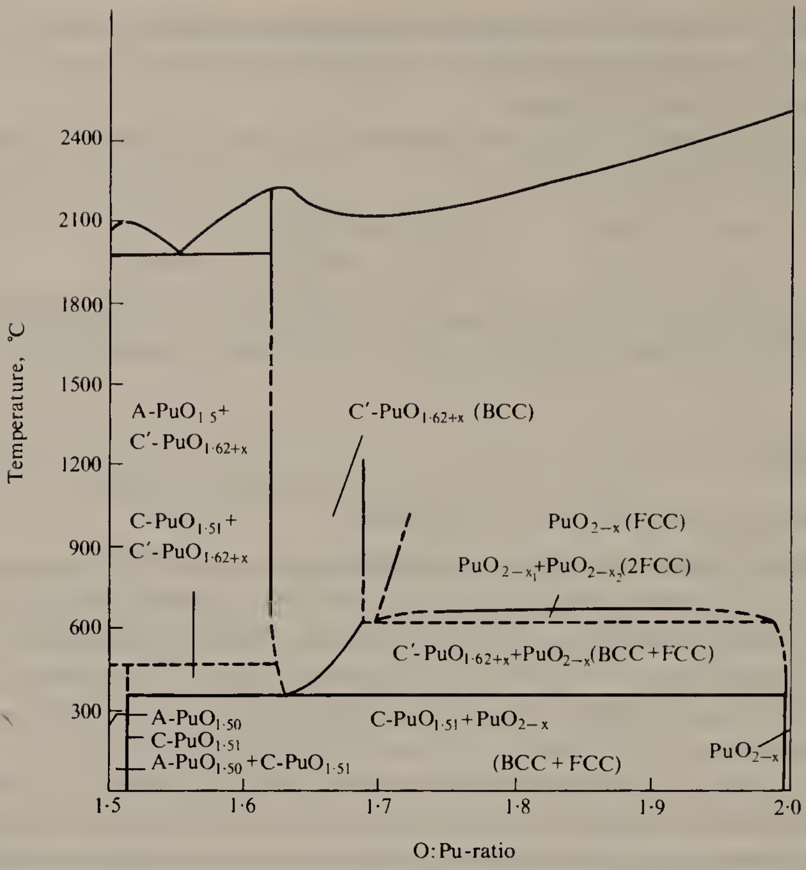

FIG. 7. Phase relationships in the plutonium–oxygen system. (Composite diagram including data from C. Sari, U. Benedict and H. Blank, Report EUR-3563e (1967) and from B. Riley, *Sci. Ceram.* 5 (1970) 83.)

of oxygen at 800°C to 1000°C. Well-formed PuO_2 single crystals can be isolated from silicate melts[62] or by decomposition of $Pu(SO_4)_2$ in LiCl–KCl and $KCl–PbCl_2$ eutectics[63].

Oxygen is liberated when PuO_2 is heated in an inert or reducing atmosphere above 1200°C, resulting in the formation of PuO_{2-x}. Since the Pu^{3+} so formed has a larger ionic radius than Pu^{4+}, the loss of oxygen by PuO_2 is associated with lattice expansion. Heating and quenching of PuO_2 from temperatures up to 1700°C under 10 atm of oxygen, or from 400°C and 70 atm of oxygen, do not significantly affect the lattice parameter or the O:Pu ratio. Furthermore, no oxidation has been achieved by the action of ozone, atomic oxygen or nitrogen dioxide on PuO_2 at temperatures between 500°C and 1000°C. This demonstrates that $PuO_{2.00}$ is the limiting composition of the oxygen-rich part of the Pu–O system.

Hexagonal A-Pu_2O_3 has a strictly stoichiometric composition. It is obtained pure by the reduction of PuO_2 with carbon or metallic plutonium[64]. Between the compositions A-Pu_2O_3 and C'-Pu_2O_3 a eutectic (m.p. 1970°C) of composition $PuO_{1.55}$ is observed[65]. C-Pu_2O_3($PuO_{1.52}$) and C'-Pu_2O_3($PuO_{1.62+x}$) are obtained by reduction of PuO_2 with carbon or hydrogen at high temperatures. C'-Pu_2O_3 is stable only at temperatures above 300°C. Its phase width increases with temperature from $PuO_{1.62}$–$PuO_{1.63}$ at 350°C to a

[62] K. D. Phipps and D. B. Sullenger, *Science*, **145** (1964) 1048.
[63] M. Schlechter, *J. Nucl. Mat.* 37 (1970) 82.
[64] R. E. Skavdahl, USAEC Report HW-77906 (1964).
[65] B. Riley, *Sci. Ceram.* 5 (1970) 83.

constant value of $PuO_{1.62}$–$PuO_{1.69}$ above 600°C[61]. A eutectic point at 2280°C exists between C′-Pu_2O_3 and PuO_2. The vaporization of Pu_2O_3 occurs according to the reaction

$$Pu_2O_{3(s)} \rightarrow PuO_{2(g)} + PuO_{(g)}$$

Solid plutonium monoxide has only been obtained as a surface layer on metallic plutonium. However, PuO can be stabilized by the formation of solid solutions with PuC and/or PuN to give the oxide–carbide Pu(O, C), the oxide–nitride Pu(O, N) and/or the oxide–carbide–nitride Pu(O, C, N). All these compounds crystallize with the rocksalt structure. As demonstrated by mass spectrometry, PuO undoubtedly exists in the gaseous state[66]. For example, the vapor pressure of $PuO_{2(g)}$ and $PuO_{(g)}$ over $PuO_{1.83}$ may be calculated using the relationships

$$\text{for } PuO_{2(g)}\text{: } \log p(\text{atm}) = (6{\cdot}710 \pm 0{\cdot}270) - (27{,}810 \pm 600)/T$$

and

$$\text{for } PuO_{(g)}\text{: } \log p(\text{atm}) = (7{\cdot}750 \pm 0{\cdot}110) - (30{,}330 \pm 240)/T$$

PuO_2 is of considerable importance as a nuclear fuel for breeder and power reactors. High-density plutonium oxide pellets are best produced by sintering the starting material at 1500°C in a stream of moist hydrogen. Sintered specimens with densities of 10·5 to 10·7 g/cm³ are obtained (92–93% of the theoretical density), but partial reduction of PuO_2 to PuO_{2-x} cannot be prevented[67]. The lattice constant of $^{239}PuO_2$ increases when samples are

TABLE 9. PHYSICOCHEMICAL PROPERTIES OF PuO_2[a–e]

Melting point: $M_p = (2390 \pm 20)$°C
Thermal expansion: $\alpha = 11{\cdot}0 \times 10^{-6}\ \text{deg}^{-1}$ from 20°C to 1000°C
Heat of formation: $\Delta H_{298°K} = -(252{\cdot}35 \pm 0{\cdot}17)$ kcal/mol
Entropy: $S_{298°K}(PuO_{2(s)}) = 16{\cdot}34$ cal/mol deg
$S_{298°K}(PuO_{2(g)}) = 70{\cdot}6$ cal/mol deg
Enthalpy: (a) from 192°K to 1400°K
$H_T - H_{298°K} = -\ 8468 + 22{\cdot}18\,T + 1{\cdot}040 \times 10^{-4}\,T^2 + 4{\cdot}935 \times 10^5/T$ cal/mol
(b) from 1400°K to 2175°K
$H_T - H_{298°K} = -\ 6{\cdot}36 + 0{\cdot}018\,T + 1{\cdot}95 \times 10^{-6}\,T^2 + 2{\cdot}46 \times 10^2/T$ kcal/mol
Free energy of formation: $\Delta G(PuO_{2(s)}) = -253{,}480 - 3{\cdot}45 \times T \times \log T + 52{\cdot}48\,T$ cal/mol from 298°K to 1500°K
$\Delta G(PuO_{2(g)}) = -\ 114{,}400 + 7{\cdot}7\,T$ cal/mol from 1700°K to 2000°K
Heat capacity: (a) from 11·9°K to 28·8°K
$C_p = 1{\cdot}350 \times 10^{-2}\,T + 2{\cdot}877 \times 10^{-5}T^3$ cal/mol deg
(b) from 192°K to 1400°K
$C_p = 22{\cdot}18 + 2{\cdot}080 \times 10^{-4}T - 4{\cdot}935 \times 10^5/T^2$ cal/mol deg
Heat of fusion: $\Delta H_f = (16{\cdot}8 \pm 1{\cdot}3)$ kcal/mol
Heat of evaporation: $\Delta H_{298°K} = 153{\cdot}8$ kcal/mol
Vapor pressure: $\log p\,(PuO_2(\text{atm})) = (8{\cdot}072 \pm 0{\cdot}239) - (29{,}240 \pm 530)/T(°K)$
Debye temperature: $T_D = 415$°K
Index of refraction: 2·4
Thermal conductivity: $\lambda = 0{\cdot}06$ W/cm deg at 300°C and
$\lambda = 0{\cdot}025$ W/cm deg at 1200°C, extrapolated to 0% porosity

[a] C. Keller, *The Chemistry of the Transuranium Elements*, Verlag Chemie, Weinheim (1971).

[b] C. Keller, *Oxide der Transurane*, in *Gmelin Handbuch der Anorganischen Chemie*, *Transurane*, Band 71, Teil C. Verlag Chemie, Weinheim (1972).

[c] J. M. Cleveland, *The Chemistry of Plutonium*, Gordon & Breach, New York (1970).

[d] *Plutonium Handbook*, O. J. Wick (Ed.), Gordon & Breach, New York (1969).

[e] LeRoy Eyring, *Refractory Oxides of the Lanthanide and Actinide Elements*, in *High Temperature Oxides*, Part II, p. 41. Academic Press, New York (1970).

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[66] J. E. Battles, J. W. Reiskus and W. A. Shinn, Report ANL-7575, p. 77 (1969).

[67] P. E. Potter, *J. Nucl. Mat.* **15** (1965) 1.

TABLE 10. PHYSICOCHEMICAL PROPERTIES OF THE LOWER PLUTONIUM OXIDES[a–e]

(a) A-Pu_2O_3
Melting point: $M_p = 2085°C$
Thermal expansion: $\left.\begin{array}{l} \alpha_a = 6 \times 10^{-6}\ \text{deg}^{-1} \\ \alpha_c = 30 \times 10^{-6}\ \text{deg}^{-1} \end{array}\right\}$ from 25°C to 300°C
Heat of formation: $\Delta H_{298°K} = -(408 \cdot 7 \pm 3 \cdot 0)$ kcal/mol
Entropy: $S_{298°K} = (34 \cdot 0 \pm 5 \cdot 0)$ cal/mol deg
Free energy of formation: $\Delta G = -406{,}700 + 62 \cdot 71\ T(°K)$ cal/mol from 298°K to 2000°K
Heat capacity: $C_p = 36 \cdot 6 + 3 \cdot 12 \times 10^{-3}\ T - 5 \cdot 6 \times 10^5/T^2$ cal/mol deg

(b) C-Pu_2O_3
Stability range: $\leqslant \sim 350°C$
Thermal expansion: $\alpha = 9 \cdot 0 \times 10^{-6}\ \text{deg}^{-1}$ from 25°C to 300°C
Heat of formation: $\Delta H_{298°K}(PuO_{1.51}) = -(206 \cdot 3 \pm 2 \cdot 5)$ kcal/mol
Entropy: $S_{298°K} = 17 \cdot 2$ cal/mol deg
Heat capacity: $C_p = 18 \cdot 7 + 8 \cdot 0 \times 10^{-4}\ T - 2 \cdot 8 \times 10^5/T^2$ cal/mol deg
Néel temperature: $T_N = 16°K$

(c) C′-Pu_2O_3
Melting point: $M_p = 2360°C$
Thermal expansion: $\alpha = 8 \cdot 5 \times 10^{-6}\ \text{deg}^{-1}$ for $PuO_{1.618}$ from 300°C to 900°C
Heat of formation: $\Delta H_{298°K} = -(213 \cdot 9 \pm 1 \cdot 5)$ kcal/mol (for $PuO_{1.61}$)
Entropy: $S_{298°K} = 19 \cdot 2$ cal/mol deg
Heat capacity: $C_p = 18 \cdot 7 + 8 \cdot 0 \times 10^{-4}\ T - 2 \cdot 8 \times 10^5/T^2$ cal/mol deg

[a] C. Keller, *The Chemistry of the Transuranium Elements*, Verlag Chemie, Weinheim (1971).

[b] C. Keller, *Oxide der Transurane*, in *Gmelin Handbuch der Anorganischen Chemie, Transurane*, Band 71, Teil C. Verlag Chemie, Weinheim (1972).

[c] J. M. Cleveland, *The Chemistry of Plutonium*, Gordon & Breach, New York (1970).

[d] *Plutonium Handbook*, O. J. Wick (Ed.), Gordon & Breach, New York (1969).

[e] LeRoy Eyring, *Refractory Oxides of the Lanthanide and Actinide Elements*, in *High Temperature Oxides*, Part II, p. 41. Academic Press, New York (1970).

stored due to self-irradiation effects. The increase may be calculated[68] using the equation

$$\Delta a/a = 3 \cdot 38 \times 10^{-3}(1 - e^{-1.23 \times 10^4 \lambda t(d)})$$

At saturation equilibrium approximately 0·5–1 point defects are contained per unit cell. The radiation damage can be annealed by heating at 800–900°C.

Physical and Chemical Properties

The physicochemical properties of the various plutonium oxides are listed in Tables 9 and 10.

PuO_2 is a highly refractory compound with a high melting point. As mentioned for the uranium–oxygen phases (p. 230) the physical properties depend to a very large extent on the exact stoichiometry of the oxide. For example, the electric resistance decreases from about 10^{12} to 10^{14} ohm cm for PuO_2 at room temperature to 8×10^4 ohm cm for $PuO_{1.72}$[69]. PuO_2 is a *p*-type conductor whereas PuO_{2-x} is an *n*-type conductor.

The vapor pressure, and hence the volatility, of PuO_2 is very low. However, it is noticeably higher in air than in pure oxygen, indicating that a lower oxide, PuO, evaporates in addition to PuO_2. The oxygen-to-plutonium ratio in congruently evaporating plutonium oxides decreases with rising temperature from 1·92 at 1600°K to 1·84 at 2400°K[70]. The

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[68] K. Mendelssohn, E. King, J. A. Lee, M. H. Rand, C. S. Griffin and R. S. Street, in *Plutonium*-1965, A. E. Kay and M. B. Waldron (Eds.), p. 189. Chapman & Hill, London (1967).

[69] C. E. McNeilly, *J. Nucl. Mat.* **11** (1964) 53.

[70] R. W. Ohse and V. Ciani, *Pure Appl. Chem. Suppl.* (1969) 365.

partial oxygen pressure above PuO_{2-x} is very low. For $PuO_{1.99}$ it increases from 2×10^{-18} atm at 1100°C to 2×10^{-9} atm at 1600°C.

The molar susceptibility of $PuO_{2.00}$, 534×10^{-6} cm^3/mol, is temperature-independent between 4°K and 1000°K[71]. The thermal conductivity of PuO_2 is smaller than that of UO_2; it decreases with diminishing O:Pu ratio.

The green–brown to yellow–brown dioxide is chemically inert. After being heated at high temperature, it dissolves extremely slowly and incompletely in hydrochloric or nitric acids, except in the presence of small quantities of fluoride. Fusion with $KHSO_4$, KHF_2, or Na_2O_2/NaOH is, therefore, often used to dissolve PuO_2. On the other hand, low-fired PuO_2 dissolves in hot concentrated sulfuric acid. The rate of dissolution in hydrochloric acid containing potassium iodide offers a means of assessing the reactivity of PuO_2 obtained by different means and heated to various temperatures[72]. Neutron-irradiated plutonium dioxide dissolves much more readily than the unexposed substance, the rate of dissolution increasing with the burn-up.

Americium oxides

In the americium–oxygen system the following compounds have been described to date: $AmO_{2(-x)}$, $AmO_{1.59}$(C-$AmO_{1.5+x}$), $AmO_{1.62+x}$(C'-Am_2O_3), B-Am_2O_3, A-Am_2O_3 and AmO. The lattice parameters of these binary oxides are summarized in Table 11.

A preliminary phase diagram of the americium–oxygen system up to temperatures of

TABLE 11. CRYSTALLOGRAPHIC DATA FOR BINARY TRANSPLUTONIUM OXIDES[a]

Compound	Symmetry	Space group	Lattice constants a (Å)	b (Å)	c (Å)	β (°)
AmO_2	Cubic	$Fm3m$	5·376			
A-Am_2O_3	Hexagonal	$P\bar{3}m1$	3·805		5·96	
B-Am_2O_3	Monoclinic	$C2/m$	14·38	3·52	8·92	100·4
C-$AmO_{1.5(+x)}$	Cubic	$Ia3$	11·03			
AmO	Cubic	$Fm3m$	5·045			
CmO_2	Cubic	$Fm3m$	5·359†			
A-Cm_2O_3‡	Hexagonal	$P\bar{3}m1$	3·791†		5·968	
B-Cm_2O_3	Monoclinic	$C2/m$	14·282	3·652	8·900	100·31
C-Cm_2O_3	Cubic	$Ia3$	10·99			
BkO_2	Cubic	$Fm3m$	5·334			
A-Bk_2O_3‡	Hexagonal	$P3m1$	3·754		5·958	
C-Bk_2O_3	Cubic	$Ia3$	10·880			
CfO_2	Cubic	$Fm3m$	5·310			
A-Cf_2O_3‡	Hexagonal	$P\bar{3}m1$	3·72		5·96	
B-Cf_2O_3	Monoclinic	$C2/m$	14·124	3·591	8·809	100·31
C-Cf_2O_3	Cubic	$Ia3$	10·838			
C-Es_2O_3‡	Cubic	$Ia3$	10·766			

[a] Compilation from C. Keller, *The Chemistry of the Transuranium Elements*, Verlag Chemie, Weinheim (1971).

† For $^{248}CmO_2$ and A-$^{248}Cm_2O_3$.

‡ R. J. Haire and R. D. Baybarz, *J. Inorg. Nucl. Chem.* **35** (1972) 489.

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[71] G. Raphael and R. Lallement, *Solid State Commun.* **6** (1968) 383.

[72] C. W. Bjorklund and E. Staritzky, USAEC Report LA-1689 (1954).

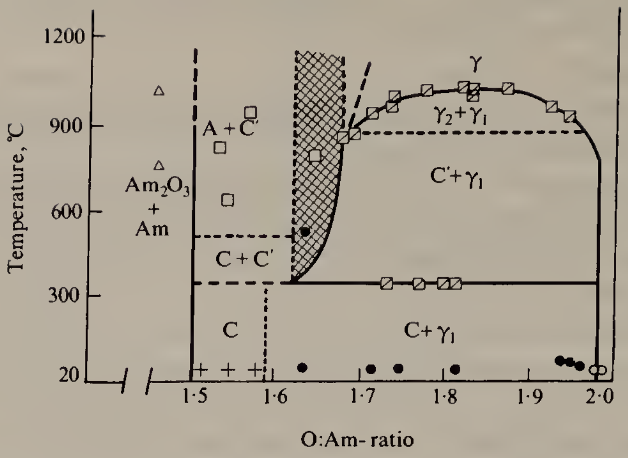

FIG. 8. Phase relationships in the americium–oxygen system. (Reproduced with permission from ref. 73.)

1200°C is given in Fig. 8[73]. At temperatures above 1020°C and for $1\cdot7 \leqslant \text{O:Am} \leqslant 2\cdot0$ an oxygen-deficient fcc single phase AmO_{2-x} exists. At temperatures below about 700°C, the phase width of AmO_{2-x} is relatively small, ranging from $AmO_{2.00}$ to $AmO_{1.98}$. In the low O:Am region a bcc phase with approximate phase width $AmO_{1.50}$ to $AmO_{1.59}$(C-$AmO_{1.5+x}$) exists at room temperature. At temperatures higher than 350°C this phase takes up additional oxygen and extends into the region $1\cdot62 \leqslant \text{O:Am} \leqslant 1\cdot68$ (C'-$AmO_{1.62+x}$). For higher O:Am ratios this phase is in equilibrium with AmO_{2-x} up to 1020°C while for lower O:Am ratios it is in equilibrium with hexagonal A-$AmO_{1.5}$. Thus, the Am–O and Pu–O system are very similar.

Americium dioxide is obtained as a dark-brown powder by heating americium compounds such as $Am_2(C_2O_4)_3\cdot aq$ and $Am(OH)_3$ to 700–800°C in oxygen. It is stable up to about 1000°C. At higher temperatures the formation of the oxygen-deficient phase AmO_{2-x} is observed[74]. Like all actinide dioxides AmO_2 crystallizes in the cubic fluorite structure. Owing to the high radioactivity of ^{241}Am, a lattice expansion of $^{241}AmO_2$ occurs which follows the relationship[75]

$$\Delta a/a = 3\cdot5 \times 10^{-3}\,(1 - e^{-0.042t(d)})$$

The vapor pressures of AmO_2 and AmO between 1600°K and 2200°K are given by the relationships

$$AmO_2\text{: } \log p\ (\text{atm}) = (7\cdot28 \pm 0\cdot19) - (28{,}260 \pm 360)/T\ (°\text{K})$$

and,

$$AmO\text{: } \log p(\text{atm}) = (8\cdot19 \pm 0\cdot41) - (25{,}650 \pm 760)/T\ (°\text{K})$$

Thus, the vapor pressures for americium oxides are higher than these for plutonium oxides[76]. The heat of formation, $\Delta H_{298°K}$, of AmO_2 is $-239\cdot9$ kcal/mol[77].

Reduction of AmO_2 with hydrogen yields either cubic or hexagonal Am_2O_3. Red–brown C-$Am_2O_{3(+x)}$ is formed only below 450°C whilst beige A-Am_2O_3 (with the hexagonal

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[73] C. Sari and E. Zamorani, *J. Nucl. Mat.* **37** (1970) 324.

[74] T. D. Chikalla and L. Eyring, *J. Inorg. Nucl. Chem.* **29** (1967) 2281.

[75] C. Keller, *The Solid State Chemistry of Americium Oxides*, in *Lanthanide/Actinide Chemistry*, Adv. Chem. Series, No. 71, p. 228, American Chemical Society, Washington D.C. (1967).

[76] R. J. Ackerman, R. L. Faircloth and M. H. Rand, *J. Phys. Chem.* **70** (1966) 3698.

[77] L. Eyring, H. R. Rohr and B. B. Cunningham, *J. Am. Chem. Soc.* **74** (1952) 1186.

La_2O_3 type of structure) forms at 850°C. Monoclinic B-Am_2O_3 has been obtained by rapid quenching from high temperatures[78].

Americium monoxide is often observed as a surface layer on americium metal. It has been reported that AmO can be obtained pure from the reaction between americium metal and the stoichiometric quantity of oxygen. For this purpose, the metal is heated for several days at 850°C in an evacuated ampoule with the calculated amount of Ag_2O. AmO is black, brittle and has a metallic appearance[79].

All americium oxides are soluble in mineral acids. AmO_2 dissolves readily in hydrochloric acid with evolution of chlorine and in nitric and sulfuric acids with evolution of oxygen.

Curium oxides

The following compounds have been characterized in the curium–oxygen system: CmO_2, CmO_{2-x} (α-phase), $CmO_{1.82}$ (δ-phase), $CmO_{1.72}$ (τ-phase), $CmO_{1.5+x}$ (σ-phase), A-Cm_2O_3, B-Cm_2O_3, C-Cm_2O_3, X-Cm_2O_3, and H-Cm_2O_3. The δ- and τ-phases have not been detected by X-ray methods, probably due to the lattice damage caused by the high radioactivity of ^{244}Cm.

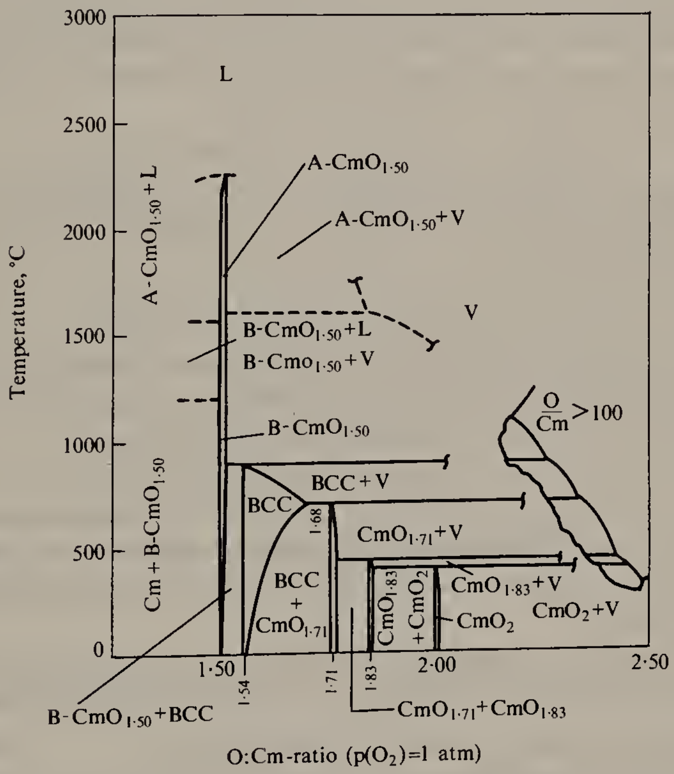

FIG. 9. Phase relationships in the curium–oxygen system. (Reproduced with permission from ref. 80.)

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[78] T. D. Chikalla and L. Eyring, *J. Inorg. Nucl. Chem.* **30** (1968) 133.
[79] Y. Akimoto, *J. Inorg. Nucl. Chem.* **29** (1967) 2650.

A preliminary phase diagram of the curium–oxygen system is given in Fig. 9[80], and the lattice constants of the curium oxides are summarized in Table 11.

Black $CmO_{2\cdot00}$ is obtained by oxidation of lower curium oxides at about 300°C in oxygen. At higher temperatures, even at $p(O_2) = 1$ atm, CmO_2 loses oxygen, passing through the α-phase CmO_{2-x} and changing into $CmO_{1\cdot82}$[81]. This δ-phase has a small phase width, $1\cdot821 \leqslant O:Cm \leqslant 1\cdot849$. At about 500°C the composition is that of the τ-phase $CmO_{1\cdot721}$ which appears to be stable up to 700–1000°C.

The curium–oxygen system is the only actinide oxide system in which all five M_2O_3 modifications characteristic of lanthanide sesquioxides are known. Metastable bcc Cm_2O_3(C-$CmO_{1\cdot5}$) is obtained from CmO_2 at 600–700°C in high vacuum or by reduction with hydrogen. C-Cm_2O_3 is capable of incorporating excess oxygen into the lattice (σ-phase) without change in structure. It decomposes to monoclinic B-Cm_2O_3 at 900°C in air. B-Cm_2O_3 is thermodynamically stable at room temperature. At 1615°C it transforms reversibly to the hexagonal A-Cm_2O_3[82]. Two additional solid state transformations occurring at 2000°C and 2110°C are probably due to the formation of new high-temperature phases designated H and X. Including the melting point of 2275°C[83] we, therefore, have the following reversible transformations for Cm_2O_3,

$$\text{B-}Cm_2O_3 \underset{}{\overset{1615°C}{\rightleftharpoons}} \text{A-}Cm_2O_3 \overset{2000°C}{\rightleftharpoons} \text{H-}Cm_2O_3 \overset{2210°C}{\rightleftharpoons} \text{X-}Cm_2O_3 \overset{2275°C}{\rightleftharpoons} Cm_2O_{3(liq)},$$

Gd_2O_3 has a remarkable effect on the B → A transformation temperature of Cm_2O_3. The transformation temperature rises from 1615°C for pure Cm_2O_3 to about 1700°C and 1770°C for solid solutions containing 11·4 and 25·6 mol% Gd_2O_3, respectively[84].

Curium oxide vaporizes congruently as Cm_2O_3, probably to $CmO_{(g)}$ and $O_{(g)}$[80]. The volatility, calculated as Cm_2O_3, is given by the equation

$$\log p(\text{atm}) = (7\cdot32 \pm 0\cdot26) - (29{,}050 \pm 590)/T\,(°\text{K})$$

The heat and entropy of vaporization are $\Delta H_{2200°K} = 133\cdot0$ kcal/mol and $\Delta S_{2200°K} = 33\cdot5$ cal/mol deg, respectively. The thermal conductivity of theoretically dense $^{224}Cm_2O_3$ can be represented[85] by the relationship

$$1/\lambda\ (\text{W/cm deg}) = 35\cdot42 + 0\cdot0155/\ T\,(°\text{K})$$

Samples of $^{244}CmO_2$ kept at room temperature undergo an expansion of the lattice parameter, limited to a saturation value which is reached in a few days[86]. The increase in the lattice constant of vacuum sealed $^{244}CmO_2$ fits the equation

$$\Delta a/a = (2\cdot33 \pm 0\cdot04) \times 10^{-3}\ (1e^{-1.59t(d)})$$

At liquid nitrogen temperature, a further expansion can be observed, but only with $^{244}CmO_2$ sealed in oxygen. This low-temperature expansion anneals out at room temperature in 2 days, whereas complete annealing of the initial room temperature expansion requires 10 days at 360°C.

Cubic C-Cm_2O_3 transforms spontaneously within a few weeks into hexagonal A-Cm_2O_3 under the influence of its own α-radiation[87,88], whereas the radiation induced trans-

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[88] H. O. Haug, *J. Inorg. Nucl. Chem.* **29** (1967) 2753.

formation of hexagonal A-Cm_2O_3 to monoclinic B-Cm_2O_3 occurs at about 500°C. In contrast to CmO_2 and C-Cm_2O_3 the hexagonal lattice of A-Cm_2O_3 undergoes contraction during its spontaneous formation from the cubic modification.

The radiation-induced transformation of C-Cm_2O_3 into A-Cm_2O_3 can be explained as follows[88a]: In C-Cm_2O_3, 25% of the fluorite-type anion sites are vacant. As a result of intensive α-bombardment these "anion vacancies" (which are ordered in groups of four on $(111)_c$ planes) disorder and aggregate on every fourth $(111)_c$ plane. Crystallographic shear across these (now vacant) planes eliminates all the vacant anion sites by annihilating 25% of the fluorite type (111) anion planes. The resulting structure is that of A-type Cm_2O_3.

Oxides of the transcurium elements

Whereas the oxides of the light transuranium elements can be investigated with gram, or at least milligram, amounts of the appropriate element, all oxides of the transcurium elements which have been described to date have been prepared with only microgram or nanogram quantities of the isotopes ^{249}Bk, ^{249}Cf or ^{253}Es. Consequently, only X-ray and electron microscope methods have been used for the identification of the different oxide phases. The crystallographic data for the binary oxides of berkelium, californium and einsteinium are included in Table 11.

Microgram amounts of brown $^{249}BkO_2$ have been obtained by ignition of $^{249}Bk^{3+}$, sorbed on a single ion exchange bead, in air at 1250°C for 1 hr[89]. Cubic C-Bk_2O_3 is formed by hydrogen reduction of BkO_2 at 600°C; oxidation in air at 600°C again gives BkO_2. Rapid quenching of berkelium oxides from high temperatures results in the formation of hexagonal A-Bk_2O_3[89].

Cf_2O_3 is known in three modifications: hexagonal A-Cf_2O_3, monoclinic B-Cf_2O_3, and cubic C-Cf_2O_3. Yellowish B-Cf_2O_3 is produced by igniting $^{249}Cf^{3+}$, fixed on an ion exchange bead, in air with subsequent heating in a stream of hydrogen to 600°C[91]. On the other hand, the hydrolysis of CfOF or CfOCl with water vapor at 500–600°C gives the light-colored cubic C-Cf_2O_3[92]. Hexagonal A-Cf_2O_3 is prepared by rapid quenching of the other Cf oxides from high temperatures[90]. Microgram amounts of californium dioxide, $^{249}CfO_2$, have been obtained by high-pressure oxidation ($p(O_2) = 100$ atm) of Cf_2O_3 at 300°C or by reaction of Cf_2O_3 with atomic oxygen[93]. Decomposition of CfO_2, for which the lattice constant fits well into the series of the actinide dioxides, occurs above 400°C. Besides CfO_2 and Cf_2O_3 there are indications of the existence of three intermediate oxides with the approximate compositions, $CfO_{\sim 1.56}$, $CfO_{\sim 1.70}$, and $CfO_{\sim 1.80}$.

Using nanogram amounts of the short-lived ^{253}Es, cubic C-Es_2O_3 has been identified by means of electron diffraction methods[90].

2. HYDROXIDES AND HYDROUS OXIDES

Heptavalent actinides

Black $NpO_2(OH)_3 \cdot aq$, which is the only known heptavalent hydroxide, is precipitated at

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[88a] B. G. Hyde, *Acta Cryst.* **A27** (1971) 617.
[89] R. D. Baybarz, *J. Inorg. Nucl. Chem.* **30** (1968) 1769.
[90] R. J. Haire and R. D. Baybarz, *J. Inorg Nucl. Chem.* **35** (1972) 489.
[91] J. L. Green and B. B. Cunningham, *J. Inorg. Nucl. Chem.* **30** (1969) 753.
[92] J. C. Copeland and B. B. Cunningham, *J. Inorg. Nucl. Chem.* **31** (1969) 733.
[93] R. D. Baybarz, R. G. Haire and J. A. Fahey, *J. Inorg. Nucl. Chem.* **34** (1972) 557.

pH 5–9 from an aqueous solution containing Np(VII)[94]. It dissolves in alkali hydroxide solutions according to the reaction

$$NpO_2(OH)_3 + 3OH^- \rightarrow NpO_5^{3-} + 3H_2O$$

Hexavalent actinides

Whereas few data are available on Np(VI) and Pu(VI) hydroxides, the chemistry of the uranyl hydroxides has been more extensively studied.

In the UO_3–H_2O system four different hydrates occur: $UO_2 \cdot 2H_2O$, four forms of $UO_3 \cdot H_2O$, $UO_3 \cdot 0{\cdot}8H_2O$ and $UO_3 \cdot 0{\cdot}5H_2O$[95]. An experimental phase diagram for the UO_2^{2+}–UO_3–H_2O system is given in Fig. 10[96]. This shows the temperature regions and the pH values at which the different UO_3 hydrates are formed in aqueous solution. The solid solute boundary changes to higher pH values as the UO_2^{++} concentration in solution is decreased.

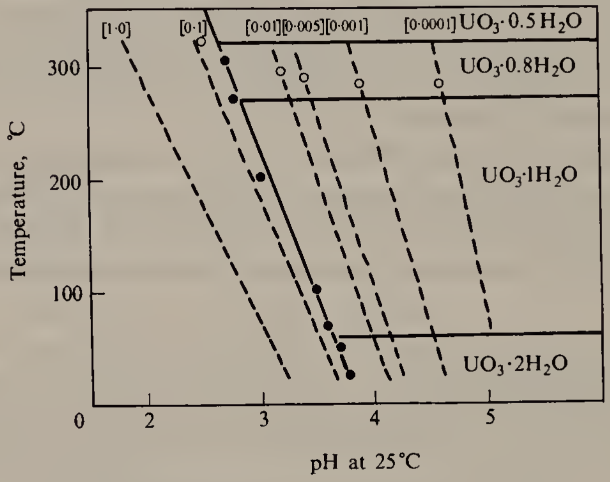

FIG. 10. Experimental phase diagram for the system UO_2^{2+}–UO_3–H_2O with molal concentrations in parentheses (● = 0·5 M solution). (Reproduced with permission from ref. 96.)

$UO_3 \cdot 2H_2O$ ($=UO_2(OH)_2 \cdot H_2O$) is formed by hydration of α- or β-UO_3 in liquid water or in water vapor at 20°C for several days. It is also produced by ion-exchange or tertiary amine hydrolysis of uranyl salt solutions[97,98]. The powder diffraction pattern of $UO_3 \cdot 2H_2O$ has been indexed on the basis of an orthorhombic cell (Table 12)[99]. Single-crystal studies of the natural form of $UO_3 \cdot (2 \pm x)H_2O$, schoepite, have shown the existence of three orthorhombic modifications with only slight differences in their lattice parameters (Table 12). Schoepite II and III are said to be formed from schoepite I by loss of some of the interlayer water, schoepite I therefore being the original mineral[100]. Polynary hydrated uranium oxide minerals are known, e.g. fourmarierite, $Pb(OH)_2 \cdot 4UO_2(OH)_2 \cdot 2H_2O$;

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[100] C. L. Christ and J. R. Clark, *Am. Mineral.* **45** (1960) 1026.

TABLE 12. CRYSTALLOGRAPHIC DATA FOR ACTINIDE HYDROXIDES

Compound	Symmetry	Space group	Lattice constants (Å)			Ref.
			a	*b*	*c*	
$UO_3 \cdot 2H_2O$	Orthorhombic		13·97	16·69	14·65	a
Schoepite I	Orthorhombic	*Pbca*	14·33	16·79	14·73	b
Schoepite II	Orthorhombic	*Pbna*	13·99	16·72	14·73	b
Schoepite III	Orthorhombic	*Pbca*	14·12	16·83	15·22	b
Roubaultite	Triclinic	*P*1	7·73	6·87	10·87†	c
α-$UO_2(OH)_2$	Orthorhombic	*Cmca* or *C2ab*	4·242	10·302	6·868	d
β-$UO_2(OH)_2$	Orthorhombic	*Pbca*	5·635	6·285	9·919	e
Becquerelite	Orthorhombic	*Pnma* or *Pm2a*	13·86	12·38	14·96	b
ϵ-$UO_2(OH)_2$	Monoclinic	*Cm*, *C*2 or *C*2/*m*	6·419	5·518	5·561‡	f
$NpO_2(OH)_2$	Orthorhombic	*Pbca*	5·607	6·270	9·956	g
$Am(OH)_3$	Hexagonal	*P*6$_3$/*m*	6·426		3·745	h

† $\alpha = 86·49°$, $\beta = 134·20°$, $\gamma = 93·17°$.
‡ $\beta = 112·77°$.
[a] V. J. Wheeler, R. M. Dell and E. Wait, *J. Inorg. Nucl. Chem.* **26** (1964) 1829.
[b] C. L. Christ and J. R. Clark, *Am. Mineral.* **45** (1960) 1026.
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[e] R. B. Roof, D. T. Cromer and A. C. Larson, *Acta Cryst.* **17** (1964) 701.
[f] E. H. P. Cordfunke and P. C. Debets, *J. Inorg. Nucl. Chem.* **26** (1964) 1671.
[g] K. W. Bagnall and J. B. Laidler, *J. Chem. Soc.* (1964) 2693.
[h] W. O. Milligan and M. L. Beasly, *Acta Cryst.* **B24** (1968) 979.

roubaultite, $2Cu(OH)_2 \cdot 3UO_2(OH)_2 \cdot 5H_2O$; becquerelite, $Ca(OH)_2 \cdot 6UO_2(OH)_2 \cdot 4H_2O$; and billiete, $Ba(OH)_2 \cdot 6UO_2(OH)_2 \cdot 4H_2O$. The crystal structure of all of these compounds consists of $UO_2(OH)_2$ layers (similar to those in UO_2F_2), with the water of hydration and cations present in interlayer positions.

Hydration of UO_3 in steam for longer than 8 hr gives α-$UO_3 \cdot H_2O$; with δ-UO_3, however, the product is a mixture of α- and β-$UO_3 \cdot H_2O$. Continued hydration results in the conversion of β- to α-$UO_3 \cdot H_2O$. β-$UO_3 \cdot H_2O$ is also prepared by the hydrolysis of uranyl acetate. ϵ-$UO_3 \cdot H_2O$ is difficult to prepare in a pure form; it is best obtained by treating an aged form of ϵ-UO_3 with water at 100°C for about 2 hr[101a]. ϵ-$UO_3 \cdot H_2O$ slowly recrystallizes to β-$UO_3 \cdot H_2O$ when heated in air above 125°C. A fourth modification is formed, mixed with other hydrates, when UO_3 is leached with hot water from $U/LiClO_4$ reaction mixtures; full details of this modification are not available.

In α-$UO_2(OH)_2$ each uranyl group (U–O distance 1·71 Å) is surrounded by six hydroxyl oxygen atoms in a puckered hexagonal configuration (U–O bond lengths: 2·51 Å (2×), 2·46 Å (4×))[101]. The hexagonal $UO_2(OH)_2$ layers are separated by about 5 Å, as compared with 7–8 Å in the hydroxide minerals. The same layer structure is also suggested for the "ammonium diuranate" compounds, with the ammonia and water molecules occupying interlayer positions. α-$UO_2(OH)_2$ begins to decompose endothermically to UO_3 at about 360°C.

The structure of β-$UO_2(OH)_2$ also consists of $UO_2(OH)_2$ layers, but there is an octahedral arrangement of oxygen atoms around the uranium atom, the bond lengths being 1·82 Å

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[101] J. C. Taylor, *Acta Cryst.* **B27** (1971) 1088.
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(2×), 2·24 Å (2×) and 2·43 Å (2×)[102]. As in the α-form the layers are hydrogen-bonded together, the hydrogen bond contacts, 2·80 Å apart, being between a hydroxyl group in one layer and the uranyl group of the adjacent layer[103]. This value is in good agreement with the value (2·72 ± 0·04) Å given for the hydrogen bond type Y–H···Z where Y–H is the donor group OH and Z is the acceptor group.

β-$UO_2(OH)_2$ transforms rapidly into α-$UO_2(OH)_2$ on application of pressure, for example, with a spatula, or on cooling with liquid nitrogen. This major structural change is associated with an increase in density from 5·73 to 6·73 g/cm³ and a decrease in cell volume from 352·6 to 300·1 Å. The transformation is similar to the martensitic transformations in metals and alloys and is normal in that the high-temperature form has the more open structure and lower coordination number.

The hemihydrate $UO_3 \cdot 0{\cdot}5H_2O$, which may be prepared hydrothermally, is also obtained by heating $UO_4 \cdot 2H_2O$ in water at 310–350°C or by the reaction between γ-UO_3 and water at 325°C in an autoclave. The product of decomposition at 550°C is α-UO_3.

Two non-stoichiometric uranium oxide hydrates, $UO_{2{\cdot}86} \cdot 1{\cdot}5H_2O$ and $UO_{2{\cdot}86} \cdot 0{\cdot}5H_2O$, have also been described[104]. The photochemical reduction of a uranyl acetate solution containing ethanol or ether yields an amorphous hydrate, which on aging under oxygen-free water yields the violet $UO_{2{\cdot}86} \cdot 1{\cdot}5H_2O$ (previously called U_3O_8 hydrate). The lower hydrate, $UO_{2{\cdot}86} \cdot 0{\cdot}5H_2O$, is formed at about 40°C in dry argon; it decomposes at about 160°C. The heats of formation of these hydrates are $\Delta H_{298°K} = -143{\cdot}8$ kcal/mol and −98·6 kcal/mol, respectively.

The so-called ammonium diuranate (ADU) is an orange–yellow precipitate which is obtained by the addition of ammonia to a U(VI) solution. It now seems clear that the precipitate does not have the previously assumed composition $(NH_4)_2U_2O_7$, but consists of several compounds of varying composition: $UO_3 \cdot 2H_2O$, $UO_3 \cdot 0{\cdot}33NH_3 \cdot 1{\cdot}67H_2O$, $UO_3 \cdot 0{\cdot}5NH_3 \cdot 1{\cdot}5H_2O$ and $UO_3 \cdot 0{\cdot}67NH_3 \cdot 1{\cdot}33H_2O$[105]. The heat of formation of these compounds continuously decreases with increasing ammonia content from $\Delta H_{298°K} = -437{\cdot}3$ kcal/mol for $UO_3 \cdot 2H_2O$ to $\Delta H_{298°K} = -406{\cdot}6$ kcal/mol for $UO_3 \cdot 0{\cdot}66NH_3 \cdot 1{\cdot}33H_2O$ as compared to $\Delta H_{298°K} = -367{\cdot}4$ kcal/mol for β-$UO_2(OH)_2$[106]. Other investigations, however, suggest that the precipitate does not comprise a mixture of distinct compounds, but is a single phase in which the $UO_3{:}NH_3$ ratio varies continuously[107].

The neptunium trioxide hydrates $NpO_3 \cdot 2H_2O$ and $NpO_3 \cdot H_2O$ are prepared by ozone oxidation of an aqueous suspension of Np(V) hydroxide at 18°C or 90°C, respectively[108]. $NpO_3 \cdot 2H_2O$ is also obtained as a brown precipitate on dissolution of a Np-containing $LiNO_3$–KNO_3 melt, after oxidation of the neptunium to Np(VI) with ozone at 150°[109]. Red–brown $NpO_3 \cdot H_2O$ is isostructural with β-$UO_3 \cdot H_2O$ and, therefore, should be formulated as $NpO_2(OH)_2$. The thermal decomposition of $NpO_3 \cdot H_2O$ yields Np_2O_5.

The yellow–red, hydrated oxide of hexavalent plutonium, $PuO_3 \cdot 0{\cdot}8H_2O$, is obtained by oxidation of a $PuO_2 \cdot aq$ suspension in water with ozone at 90°C[108]. On standing in air it readily absorbs water to the composition $PuO_3 \cdot H_2O$. This water is again lost on drying

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[102] R. B. Roof, D. T. Cromer and A. C. Larson, *Acta Cryst.* **17** (1964) 701.
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[104] E. H. P. Cordfunke, G. Prins and P. van Vlaanderen, *J. Inorg. Nucl. Chem.* **30** (1968) 1745.
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[106] E. H. P. Cordfunke, *J. Phys. Chem.* **68** (1964) 3353.
[107] W. I. Stuart and T. L. Whateley, *J. Inorg. Nucl. Chem.* **31** (1969) 1639.
[108] K. W. Bagnall and J. B. Laidler, *J. Chem. Soc.* (1964) 2693.
[109] D. Cohen, *Inorg. Chem.* **4** (1963) 866.

in a vacuum at 130°C. $PuO_3 \cdot 0{\cdot}8H_2O$ is not isostructural with any of the known UO_3-hydrates. Above 200°C it decomposes directly to PuO_2 with liberation of water and oxygen. The compound precipitated from Pu(VI) solutions by the addition of ammonia is not, as previously reported, ammonium diplutonate(VI): it is $PuO_2(OH)_2 \cdot H_2O$ (or $PuO_3 \cdot 2H_2O$)[110].

Pentavalent actinides

The precipitate obtained by the addition of ammonia or an alkali hydroxide to a Pa(V) solution is $Pa_2O_5 \cdot aq$ rather than a compound with a well-defined water:oxide ratio. $Pa_2O_5 \cdot H_2O$, however, is prepared by the thermal decomposition of the Pa-peroxide $Pa_2O_9 \cdot 3H_2O$ at 200°C[111]. $Pa(OH)_5$ has been postulated to exist in aqueous solution, despite the fact that the hydrolysis of pentavalent protactinium is extremely complicated and is by no means fully understood. For freshly prepared solutions containing no complexing agents the hydrolysis equilibria

$$PaOOH^{2+} \xrightleftharpoons{K_1} PaO(OH)_2{}^{+} \xrightleftharpoons{K_2} Pa(OH)_5$$

are postulated[112], with equilibrium constants ($\mu = 3$):

$$K_1 = \frac{[PaO(OH)_2{}^{+}][H^{+}]}{[PaO(OH)^{2+}]} = 9 \times 10^{-2} \text{ and}$$

$$K_2 = \frac{[Pa(OH)_5][H^{+}]}{[PaO(OH)_2{}^{+}]} = 3{\cdot}2 \times 10^{-5}$$

Since the Pa = O group has been shown to be relatively stable, the partially hydrolyzed products are probably present as oxohydroxy complexes and not as pure hydroxy complexes[113]. The proportions of the relevant ionic species as a function of the solution pH are shown in Fig. 11.

Neptunium(V) hydroxide, $NpO_2(OH)$, and plutonium(V) hydroxide, $PuO_2(OH)$, are obtained by the addition of ammonia to Np(V) or Pu(V) solutions. The gelatinous precipitates are sparingly soluble. The solubility product of, for example, $PuO_2(OH)$ is calculated to be 5×10^{-10}.

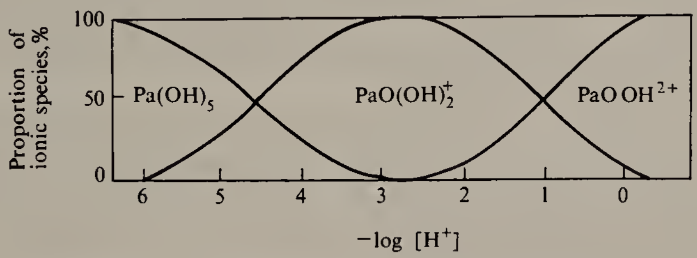

FIG. 11. Proportions of hydrolyzed species of protactinium in aqueous solutions. (Reproduced with permission from ref. 112.)

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[110] J. M. Cleveland, *Inorg. Nucl. Chem. Letters*, 6 (1970) 535.

[111] T. Stchouzkoy, H. Pézérat and R. Muxart, in *Physico-Chimie du Protactinium*, Colloques Internationaux du Centre National de la Recherche Scientifique No. 154, p. 61. Paris (1966).

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Tetravalent actinides

The precipitates which are obtained by the addition of a base to an actinide(IV) solution are hydrous oxides, $MO_2 \cdot aq$, with varying amounts of adsorbed water rather than distinct compounds such as $M(OH)_4$. On drying at room temperature the X-ray powder patterns of these precipitates show diffuse lines of the corresponding actinide dioxides.

Trivalent actinides

Crystalline $Am(OH)_3$ (Table 12) is formed at 90°C by prolonged digestion of the amorphous precipitate which forms when ammonia is added to a solution of an Am(III) salt[114]. The morphology of the precipitate changes from spherical particles (diameter *ca.* 10–20 Å) to sheets and rolls or rods[115]. Similar changes in morphology are also observed for yellow $Cm(OH)_3$, for $Bk(OH)_3$, and $Cf(OH)_3$, but these compounds have only been studied in small amounts. The time required for the transformations increases with the atomic number of the transuranium element.

3. PEROXIDES

The review by Connor and Ebsworth[116] is recommended for a comprehensive and critical discussion of the actinide peroxides.

Thorium and protactinium peroxide

A gelatinous precipitate of thorium peroxide is obtained by the addition of H_2O_2 to, or by the action of ozone or peroxidisulfate on, neutral or weakly acid solutions of thorium salts. It is a poorly characterized compound of variable composition which contains the anion from the solution. The maximum peroxide-to-thorium ratio is 1:1·75; except in the case of solutions of high sulfate concentration, where the precipitate has the composition $Th(O_2)SO_4 \cdot 3H_2O$, the anion-to-thorium ratio is a fractional value. Thorium peroxychloride, for example, is a polymeric species that is stabilized by hydration and which has an active oxygen-to-thorium ratio of 5:3 and a chloride-to-thorium ratio between 2:3 and 1:3[117]. Thorium peroxynitrate has been characterized as a hexameric thorium species $Th_6(O_2)_{10}(NO_3)_4 \cdot 10H_2O$[118]. It is assumed that in both compounds the thorium atoms are at least partially associated by peroxy bridges.

Most of these compounds, particularly those rich in peroxide oxygen, lose peroxide slowly at room temperature, and decomposition is apparently rapid at 130°C; the chlorides are particularly unstable. The only exception is $Th(O_2)SO_4 \cdot 3H_2O$, which is remarkably stable thermally, the water molecules being tenaciously held. It appears to be appreciably more crystalline than the other compounds.

Protactinium(V) peroxide precipitates on the addition of hydrogen peroxide to weakly acid solutions of protactinium(V). The product from dilute sulfuric acid solution has been

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[117] R. A. Hasty and J. E. Boggs, *J. Less-Common Metals*, 7 (1964) 447.

[118] G. L. Johnson, M. J. Kelly and D. R. Cunes, *J. Inorg. Nucl. Chem.* **27** (1965) 1787.

assigned the formula $Pa_2O_9 \cdot 3H_2O$[111]. At 200°C it decomposes to give $Pa_2O_5 \cdot H_2O$. The peroxyprotactinate(V) $NaPaO_6 \cdot aq$ is obtained from aqueous solution as a white compound.

Uranium peroxides

The peroxide chemistry of uranium is confined to the +6 oxidation state. The best characterized compound is $UO_4 \cdot xH_2O$ (where x is 2 or 4); many peroxyuranates with peroxide-to-uranium ratios between 3:1 and 1:2 are also known. In addition to these, series of mixed peroxyoxalates and peroxycarbonates have been described. If it is assumed that the uranyl group in peroxy compounds is always 6-coordinated, up to three bidentate peroxy groups may be present in these compounds. The compound with most peroxide is then $[UO_2(O_2)_3]^{4-}$, an anion which is stable above pH 14.

Yellow uranium tetroxide is formed by the action of H_2O_2 on a uranyl salt solution at pH ~ 2[119, 120]. The compound is obtained as a hydrate and contains one peroxy group per uranium atom. The air-dried material is usually a tetrahydrate, but a dihydrate is obtained if the product is dried at 90°C. An intermediate peroxide, U_2O_7, is formed in an atmosphere of oxygen between 100°C and 130°C. The decomposition at temperatures greater than 130°C, which follows first order kinetics[121], yields UO_3.

Uranium peroxide hydrates are stable for long periods at room temperature. Infrared spectra show that the bonding of the water of hydration to the uranyl group is different in the two hydrates[122]. The X-ray powder patterns of both hydrates have been indexed on the basis of body-centered lattices, e.g. $UO_4 \cdot 4H_2O$ crystallizes with monoclinic symmetry with $a = 11 \cdot 85$ Å, $b = 6 \cdot 78$ Å, $c = 4 \cdot 245$ Å, $\beta = 93 \cdot 45°$ (space group $C2$, Cm or $C2/m$), whereas orthorhombic $UO_4 \cdot 2H_2O$ has $a = 6 \cdot 502$ Å, $b = 4 \cdot 216$ Å and $c = 8 \cdot 778$ Å, the space group probably being $Immn$[122a]. Uranium peroxide is a powerful oxidizing agent, and it reacts with strong acids to liberate H_2O_2. The reaction with alkali hydroxide depends on the concentration of the alkali used. Between pH 8 and 10, sparingly soluble salts of the anions $[U_2O_5(O_2)_2H]^-$ or $[U_2O_5(O_2)_2]^{2-}$ are formed; with 10 M potassium hydroxide, the monoperoxyuranate(VI), $K_2[U(O)_3(O_2)] \cdot 4H_2O$, is precipitated. The relationship between peroxyuranium species in 0·1 to 1·0 M uranyl salt solutions is shown in Fig. 12.

Salts of general formula $M^I_4UO_8 \cdot xH_2O$ are obtained by the action of H_2O_2 on uranates or by the reaction of $UO_4 \cdot xH_2O$ with $NaOH/H_2O_2$ solutions. $Na_4[UO_2(O_2)_3] \cdot 9H_2O$, obtained as an orange–yellow crystalline precipitate on cooling followed by addition of ethanol, possesses monoclinic symmetry with $a = 6 \cdot 413$ Å, $b = 17 \cdot 292$ Å, $c = 14 \cdot 186$ Å, $\beta = 98 \cdot 87°$, space group $P2_1/c$. The uranyl triperoxide anion consists of three coplanar peroxide groups arranged equatorially around the linear uranyl group with approximately D_{3h} symmetry[124].

The $M_4UO_8 \cdot nH_2O$ salts are relatively stable thermally, e.g. the sodium salt may be dehydrated at 100°C without loss of peroxide oxygen. The decomposition in alkaline solution is very complicated and the products depend on the conditions. In solutions that are very dilute in uranium (~ 10^{-4} M), the initial product of decomposition is the mononuclear monoperoxyanion, $[UO_2(O_2)(H_2O)]^{2-}$.

[119] L. Silverman and R. A. Sallach, *J. Phys. Chem.* **65** (1961) 370.
[120] T. Sato, *Naturwissenschaften*, **48** (1961) 668.
[121] J. E. Boggs and El-Chehabi, *J. Am. Chem. Soc.* **79** (1957) 4258.
[122] T. Sato, *J. Appl. Chem.* **13** (1963) 361.
[122a] P. C. Debets, *J. Inorg. Nucl. Chem.* **25** (1963) 727.
[123] A. M. Gurevitch, *Radiochemistry*, 3 (1961) 100.
[124] N. W. Alcock, *J. Chem. Soc.* (A) (1968) 1588.

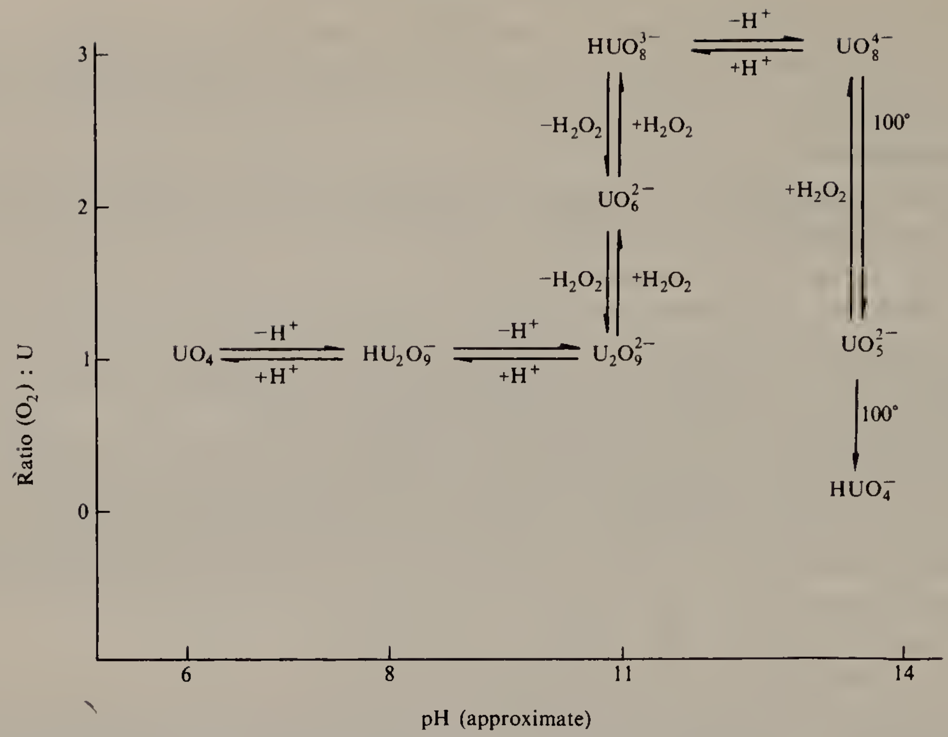

FIG. 12. Relationship between peroxyuranium species in aqueous solution at $0{\cdot}1 \leqslant [U] \leqslant 1$ M [123].

Other known peroxy-complexes include species such as $M_2UO_6{\cdot}aq$, $M_3UO_7{\cdot}aq$, $M_2UO_5{\cdot}aq$ and $M_2U_2O_{10}{\cdot}aq$, but such compounds have not been studied in detail. Complex peroxyuranates(VI), e.g. $(NH_4)_2[UO_2(O_2)CO_3]{\cdot}2H_2O$ and $(NH_4)_2[(UO_2)_2(O_2)(C_2O_4)_2]$, may be precipitated by the addition of alcohol to solutions of uranyl nitrate, oxalate or carbonate, containing hydrogen peroxide[116].

Neptunium peroxide

On the addition of hydrogen peroxide to a solution of Np(IV) in nitric acid, purple-gray Np(IV) peroxide precipitates. At low acid concentration (1 M HNO_3) the fcc modification ($a = \sim 17$ Å) is obtained with a peroxide:Np ratio of 2·9; the neptunium(IV) peroxide formed at higher acidity (~ 3 M HNO_3) gives an X-ray powder pattern similar to that of the hexagonal Pu peroxide and has a peroxide:Np ratio of about 3·3. The cubic modification can be converted into the hexagonal form by treatment with 3 M nitric acid. In 1·5 M HNO_3, with an H_2O_2 concentration of 4·6 M, neptunium peroxide has a minimum solubility of about 22 mg/l at 23°C[125].

A sparingly soluble Np(V) peroxide of unknown composition is obtained by the addition of H_2O_2 to a Np(V) solution at pH ~ 3·5, whereas in a 0·5 M sodium carbonate solution a strongly colored soluble complex is formed[126].

Plutonium peroxides

The addition of hydrogen peroxide to a solution of tetravalent plutonium in dilute acid results initially in the formation of a brown, water-soluble complex containing two plu-

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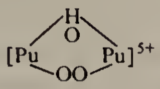
[125] E. K. Dukes and G. A. Burney, *J. Inorg. Nucl. Chem.* **24** (1962) 899.
[126] C. Musikas, *Radiochem. Radioanal. Letters*, **4** (1970) 347.

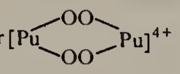
tonium atoms, one peroxide group, and at least one hydroxyl group. Its structure may be

$(Pu\text{-}OO\text{-}Pu\text{-}OH)^{5+}$ or



On further addition of H_2O_2, the brown complex is transformed into a red, water-soluble peroxide complex, which contains two plutonium atoms and two peroxide groups, and for which the structures

$(HO\text{-}Pu\text{-}OO\text{-}Pu\text{-}OOH)^{4+}$ or



have been suggested[127].

On further addition of hydrogen peroxide to the red peroxide complex a green precipitate is formed, which contains about three peroxide groups per plutonium atom and variable amounts of anions. These anions are firmly incorporated and are not merely adsorbed.

Two different modifications of the peroxide may be formed, depending on the precipitation conditions. Precipitation from slightly acidic solution gives a cubic plutonium peroxide ($a = 16{\cdot}5$ Å) with, on average, 3·03 peroxide groups per plutonium atom, whereas the hexagonal product formed from at least 2 M acid has a peroxide:Pu ratio of 3·37 in the non-dried form[128].

The designation $PuO_4{\cdot}aq$, frequently used for plutonium peroxide, is thus only an approximation. Another substantial difference between the two modifications is the content of coprecipitated anions, the cubic form containing on the average appreciably fewer anions than the hexagonal form. Nevertheless, hexagonal plutonium peroxide is the preferred form for precipitation since it is more easily filtered than the cubic modification. The best precipitation conditions are 1–2 M HNO_3 + 0·05 M SO_4^{2-} with an H_2O_2 concentration of at least 2·5 M[129]. Trivalent and hexavalent plutonium are transformed under the conditions of precipitation into Pu(IV), but as the reduction of hexavalent plutonium by H_2O_2 proceeds relatively slowly, it is advantageous to reduce the plutonium to the tetravalent state before adding the H_2O_2. Plutonium peroxide is soluble in concentrated nitric and hydrochloric acids, and also in dilute acids if a reducing agent is added.

A red, soluble Pu(V) peroxide of unknown composition may be prepared at 0°C by the addition of a Pu(V) solution to a 0·2 M H_2O_2 solution in 1 M NaOH[130]. At higher temperature the Pu(V) peroxide decomposes and Pu(IV) peroxide precipitates.

Americium peroxide

Slow addition of aqueous ammonia to a 0·1 M acid solution of Am(III) which is 0·2 M in H_2O_2 leads to the formation of a yellow–brown color at a pH of around 5[131]. On further addition of ammonium hydroxide a yellow–brown precipitate of Am(III) hydroxyperoxide of unknown composition is formed. On treatment with concentrated solutions of ammonia or with aqueous potassium hydroxide the precipitate is converted to Am(IV) oxide hydrate.

[127] R. E. Connick and W. H. McVey, *J. Am. Chem. Soc.* **71** (1949) 1534.

[128] J. A. Leary, A. N. Morgan and W. J. Maraman, *Ind. Eng. Chem.* **51**(1) (1959) 27.

[129] M. Ganivat, French Report CEA-1592 (1960); English translation see HW-tr-53.

[130] C. Musikas, *Radiochem. Radioanal. Letters*, **7** (1971) 375.

[131] K. Buijs and K. P. Louwrier, *J. Inorg. Nucl. Chem.* **28** (1966) 2463.

4. TERNARY AND POLYNARY OXIDES

Polynary oxides and oxide phases of trivalent to heptavalent actinides can be prepared by solid state or hydrothermal reactions. A detailed description of the reactions of the oxides of the transuranium elements in the solid state is given in the *Gmelin Handbuch, Transuranelemente*[2a], and a critical and very detailed summary of the reaction of actinide oxides with alkaline and alkaline earth metals is to be found in ref. 132. Other summaries of critically selected data on ternary oxides of the transuranium elements are also available[1a, 2b, 2c].

Table 13 shows the conditions of preparation of the various ternary actinide oxides. It is seen that the reactions between alkali metal and alkaline earth metal oxides and the oxides of actinides capable of occurring in a number of oxidation states usually result, under oxidizing conditions, in the formation of compounds in the higher oxidation states (an observation which also is to be found in the oxide chemistry of most other elements), e.g.

Np(VII) and Pu(VII) in $Li_5M^{VII}O_6$ and $Ba_2LiM^{VII}O_6$
Am(VI) in Li_6AmO_6 and Na_4AmO_5
Cm(IV) in Li_8CmO_6

The preparation of alkali metal oxometallates of low valency is difficult or impossible. For instance, the reaction of UO_2 with excess Na_2O proceeds according to the reaction

$$UO_2 + 2Na_2O \xrightarrow[\text{Vacuum}]{400^\circ C} Na_3UO_4 + Na$$

i.e. UO_2 reduces Na_2O to sodium metal. In contrast to U_3O_8 and UO_3, UO_2 does not react with liquid sodium even at 600°C. The first two oxides are reduced to UO_2 by liquid sodium at 400°C, and the formation of Na_3UO_4 is observed at $> 540^\circ C$[133].

Reactions involving actinide oxides and the oxides of trivalent and tetravalent elements generally yield ternary oxides that contain the actinide element in the intermediate or low oxidation states. Exceptions are the rare earth oxides which, at least with uranium and neptunium, form ternary oxides and oxide phases of very high thermal stability, containing pentavalent and hexavalent actinides.

Compounds containing heptavalent actinide elements

The following compounds have been prepared by solid state reactions: $Li_5M^{VII}O_6$ (M^{VII} = Np, Pu), $M^I_3M^{VII}O_5$ (M^I = K–Cs, M^{VII} = Np, Pu), $Ba_2M^INpO_6$ (M^I = Li, Na) and $Ba_3(NpO_5)_2$[133–136]. Most of these compounds are best prepared by reaction between the alkali metal oxide (or peroxide) and/or alkaline earth oxide and NpO_2 (or $NpO_3 \cdot H_2O$) or PuO_2 at moderate temperatures in a stream of oxygen, e.g.

$$2{\cdot}5Li_2O + NpO_2(PuO_2) \xrightarrow[400\text{–}420^\circ C]{O_2\ (1\ atm)} Li_5NpO_6(Li_5PuO_6)$$

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[132] C. Keller, *Lanthanide and Actinide Mixed Oxide Systems with Alkali and Alkaline Earth Elements*, K. W. Bagnall (Ed.), p. 47. MTP International Review of Science, Butterworth, London (1971).

[133] C. C. Addison, M. G. Barker, R. W. Lintonbon and R. J. Pulham, *J. Chem. Soc.* (A) (1969) 2457.

[134] C. Keller and H. Seiffert, *Inorg. Nucl. Chem. Letters*, **5** (1969) 51; *Angew. Chemie Int. Ed.* **8** (1969) 279.

[135] S. K. Awasthi, L. Martinot, J. Fuger and G. Duyckaerts, *Inorg. Nucl. Chem. Letters*, **7** (1971) 45.

[136] M. Pagès, F. Nectoux and W. Freundlich, *Compt. Rend.* **2726** (1971) 1968; *Radiochem. Radioanal. Letters*, **8** (1971) 147.

TABLE 13. CONDITIONS OF PREPARATION OF TERNARY OXIDES OF THE ACTINIDE ELEMENTS[a]

Element valence	Thorium	Protactinium	Uranium	Neptunium	Plutonium	Americium	Curium
+3	Unknown		No compound formation		Only possible in strongly reducing conditions $BaO \cdot Pu_2O_3$ $PuTaO_4$	Various $LiAmO_2$ in H_2 $AmNbO_4$ in air	No particular precautions necessary $CmPO_4$ $(Cm_{0.5}, Pa_{0.5})O_2$
+4	No particular precautions necessary $BaThO_3$ $Th_{0.25}NbO_3$	Only with strict exclusion of O_2 $BaPaO_3$ $PaSiO_4$	Only with strict exclusion of O_2 $UGeO_4$ $BaUO_3$	No particular precautions necessary $NpGeO_4$ $BaNpO_3$	$PuGeO_4$ $BaPuO_3$	Only possible in oxidizing atmospheres $AmGeO_4$ $BaAmO_3$	Only possible in oxidizing atmospheres Li_8CmO_6
+5	Unknown	No particular precautions necessary $LiPaO_3$ $Pa_2O_5 \cdot 3Ta_2O_5$	By symproportionation from U(VI)+U(IV) Ba_2YUO_6 Li_3UO_4	In oxidizing atmospheres Li_3NpO_4 $(RE^{III}_{0.5},Np^{V}_{0.5})O_2$	By synthesis reaction only in oxidizing atmospheres or by decomposition in inert or oxidizing atmospheres. Only compounds with alkali metals and alkaline earth metals known Li_3PuO_4	Li_3AmO_4	Unknown
+6		Unknown	In air or O_2 $UO_3 \cdot 6LaO_{1.5}$ BaU_2O_7	In oxidizing atmospheres Li_4NpO_5 $CaNpO_4$ $NpO_3 \cdot 6YO_{1.5}$	Only by synthesis reaction in oxidizing atmospheres. Only compounds with alkali metals and alkaline earth metals known Li_4PuO_5 $CaPuO_4$	Li_4AmO_5 Ba_3AmO_6	
+7				In oxidizing atmospheres Li_5NpO_6 Ba_2LiNpO_6	In oxidizing atmospheres Li_5PuO_6	Unknown	

[a] C. Keller, *The Chemistry of the Transuranium Elements*, Verlag Chemie (1971).

TABLE 14. CRYSTALLOGRAPHIC DATA FOR POLYNARY OXIDES CONTAINING HEPTAVALENT, HEXAVALENT AND PENTAVALENT ACTINIDE ELEMENTS

Valency	Compound	Symmetry	Space group	Lattice constants				Isostructural compounds	Ref.
				a (Å)	b (Å)	c (Å)	$\alpha(\beta)$ (°)		
VII	Li_5PuO_6	Hexagonal	$P3_112$	5·19		14·48		M(VII) = Np, I, Re, Tc, Os	a
	Ba_2LiNpO_6	Cubic	$Fm3m$(?)	8·092				M(VII) = Re, Tc	b
VI	Li_4AmO_5	Tetragonal	$I4/m$	6·666		4·41		M(I) = Na M(VI) = U, Np, Pu	c
	α-Na_2NpO_4	Orthorhombic	$Cmmm$	9·685	5·705	3·455		M(VI) = U	d
	β-Na_2NpO_4	Orthorhombic	$Fmmm$	5·936	5·785	11·652		M(VI) = U	d
	K_2NpO_4	Tetragonal	$I4/mmm$	4·26		13·01		M(VI) = U	e
	$BaNpO_4$	Orthorhombic	$Pbcm$	5·730	8·089	8·167		M(VI) = U	f
	$SrPuO_4$	Rhombohedral	$R\bar{3}m$	6·51			35·68	M(VI) = U, Np	g
	$MgUO_4$	Orthorhombic	$Imma$	6·520	6·595	6·924			h
	BaU_2O_7	Tetragonal	$I4_1/amd$	7·128		11·95			i
	Sr_2UO_5	Monoclinic	$P2_1/c$	8·104	5·661	11·919	108·99		j
	UV_2O_8	Orthorhombic	$Pnma$	5·70	11·78	10·42			k
	$NpO_3\cdot 6LaO_{1\cdot 5}$	Hexagonal	$R\bar{3}$	10·391		9·994		M(VI) = U, W, Mo M(III) = La–Lu	l
V	UO_2WO_4	Monoclinic	$P2_1/c$	7·205	5·482	13·57	104·58	M(VI) = Mo	m
	$LiUO_3$	Rhombohedral	$R3c$	5·901			54·60	M(V) = Nb	n
	$RbPaO_3$	Cubic	$Pm3m$	4·368				M(V) = U	o
	UVO_5	Orthorhombic	$Pbma$	12·31	7·19	4·12			p
	$FeUO_4$	Orthorhombic	$Pbcn$	4·888	11·937	5·110		M(III) = Cr	q
	$Ni_2U_2O_6$	Hexagonal	$P321$	9·015		5·103			r
	Li_7AmO_6	Hexagonal	$R\bar{3}$(?)	5·54		15·65		M(V) = Pa, U, Np, Pu	c
	$(La_{0\cdot 5},Np_{0\cdot 5})O_2$	Cubic	$Fm3m$	5·530				M(V) = Pa, U	l
	Ba_2LaPuO_6	Pseudo-cubic		8·63				M(III) = La–Lu M(V) = Pa, U, Np(?)	s
	USb_3O_{10}	Orthorhombic	$Fddd$(?)	7·352	12·631	15·306		M(V) = V, Nb, Ta	t

For notes to Table see opposite.

At higher temperatures the dark green neptunates(VII) and plutonates(VII) lose oxygen and form ternary oxides containing hexavalent transuranium elements, e.g. K_3NpO_5 yields K_2NpO_4.

The neptunates(VII) and plutonates(VII) are isostructural with the corresponding compounds of iodine, rhenium and technetium, but no single-crystal studies have been reported for any of these compounds. The lattice constants of Li_5PuO_6 and Ba_2LiNpO_6 are given in Table 14. The presence of heptavalent actinide elements in these ternary oxides has been proved unequivocally by various physicochemical methods. Whereas Np(VII) in Li_5NpO_6 is diamagnetic, Pu(VII) in Li_5PuO_6 has a very low magnetic moment of about 0·34 μ_B. The (highest ever) observed isomer shift of Np(VII) in Li_5NpO_5, nearly −70 mm/sec (Table 15), confirms the heptavalent oxidation state of neptunium[137].

TABLE 15. MÖSSBAUER DATA FOR HEPTAVALENT NEPTUNIUM COMPOUNDS[a]

Compound	Isomer shift† (mm/sec)	Quadrupole splitting 1/4 eqQ (mm/sec)	Asymmetry parameter	Half-width Γ_{exp} (mm/sec)
Li_5NpO_6	−68·7 ± 2·9	8·2 ± 0·2	0·33 ± 0·01	3·1 ± 0·2
$Ba_3(NpO_5)_2\cdot aq$	−60·2 ± 2·8	23·1 ± 0·5	0·40 ± 0·03	5·4 ± 0·4
$Ca_3(NpO_5)_2\cdot aq$	−60·7 ± 3·0	18·1 ± 0·5	0·38 ± 0·03	3·2 ± 0·3
$[Co(NH_3)_6]NpO_5\cdot aq$	−62·8 ± 0·8	3·1 (2·1)	0·83 (0·69)	
$[Coen_3]NpO_5\cdot aq$	−61·1 ± 2·6	24·5 ± 0·4	0·23 ± 0·02	2·8 ± 0·2
Ozonized $BaNp_2O_7\cdot aq$	−62 ± 1	25 ± 2	0·6 ± 0·1	
$BaNp_2O_7\cdot aq$	−40 ± 1	36 ± 2	0·8 ± 0·2	
Np(VII) in NaOH	−60 ± 1			

† Referred to NpO_2.

[a] Compilation from C. Keller, *Die Transuranoxide*, in *Gmelin Handbuch der Anorganischen Chemie, Transuran*, Band 71, Teil C, Verlag Chemie, Weinheim (1972).

[137] K. Fröhlich, P. Gütlich and C. Keller, *Angew. Chem.* **84** (1972) 26.

Notes to Table 14:

[a] C. Keller and H. Seiffert, *Angew. Chem.* **81** (1969) 294.

[b] C. Keller and H. Seiffert, *Inorg. Nucl. Chem. Letters*, **5** (1969) 51.

[c] C. Keller, *Solid State Chemistry of Americium Oxides*, in Adv. Chem. Series No. 71, p. 228. American Chemical Society, Washington D.C. (1967).

[d] C. Keller, L. Koch and K. H. Walter, *J. Inorg. Nucl. Chem.* **27** (1965) 1205.

[e] M. Pagès, F. Nectoux and W. Freundlich, *Compt. Rend.* **272C** (1971) 1968.

[f] C. Keller, *Nukleonik* **5** (1963) 89.

[g] C. Keller, *Nukleonik* **4** (1962) 271.

[h] W. H. Zachariasen, *Acta Cryst.* **7** (1954) 788.

[i] J. G. Allpress, *J. Inorg. Nucl. Chem.* **27** (1965) 1521.

[j] B. O. Loopstra and H. M. Rietvield, *Acta Cryst.* **B25** (1969) 787.

[k] P. Mahé-Pailléret, *Rev. Chim. Minérale*, **7** (1970) 807.

[l] C. Keller, H. Engerer and H. Seiffert, *J. Inorg. Nucl. Chem.* **31** (1969) 2727.

[m] E. J. Juenke and S. F. Bartram, *Acta Cryst.* **17** (1969) 618.

[n] S. Kemmler-Sack, *Z. anorg. allg. Chem.* **338** (1965) 9.

[o] C. Keller, *J. Inorg. Nucl. Chem.* **27** (1965) 321.

[p] R. Chevalier and M. Gasperin, *Bull. Soc. fr. Minéral Cristallogr.* **93** (1970) 18.

[q] M. Bacman and E. F. Bertaut, *Bull. Soc. fr. Minéral Cristallogr.* **90** (1967) 257.

[r] S. Kemmler-Sack, *Z. anorg. allg. Chem.* **358** (1968) 226.

[s] S. K. Awasthi, D. M. Chackruburtty and V. K. Tondon, *J. Inorg. Nucl. Chem.* **30** (1968) 819.

[t] K. Aykan and A. W. Sleight, *J. Am. Ceram. Soc.* **53** (1970) 427.

On the basis of the quadrupole splitting and the asymmetry parameter of the Mössbauer spectrum of Li_5NpO_6, the site symmetry of the octahedral NpO_6^{5-} anion must be lower than O_h (the latter was suggested for Li_5ReO_6 on the basis of powder diffraction data); the Np–O bonds to the apices of the octahedron are longer than required for a neptunyl group. However, a neptunyl group, NpO_2^{3+}, seems to exist in the compounds of the type $M^{II}_3(NpO_5)_2 \cdot aq$ (M = Ba, Sr, Ca) and in $[Co(en)_3]NpO_5 \cdot aq$; the Mössbauer spectra do not agree with the assumption of a NpO_5^{3-} group, postulated to exist in these compounds[138]. These compounds, as well as $[Co(NH_3)_6]NpO_5 \cdot aq$, $[Pt(NH_3)_3Cl]NpO_5 \cdot aq$ and $Ba_3(PuO_5)_2 \cdot aq$, may be obtained by precipitation from aqueous solution. They are thermally very unstable and, in contrast to the ternary oxides of the actinides prepared by thermal reactions, even decompose on prolonged storage.

Compounds containing hexavalent actinide elements

The oxometallates(VI) of the actinides can be classified into two groups[132]. The first includes compounds with the actinyl group MO_2^{2+} as a structural unit, whereas in the second group the lattice is built up of M^{6+} ions without short covalent metal–oxygen bonds.

The alkali metal and alkaline earth metal monouranates(VI) and diuranates(VI) and their isostructural Np(VI) and Pu(VI) analogues belong to the first group. The following three types of uranium–oxygen bonds are characteristic of these compounds:

(a) hexagonal or pseudohexagonal $(UO_2)O_2$ layers in $(UO_2)O_6$ arrangements joined by sharing edges (of the type $Ca(UO_2)O_2$);
(b) tetragonal or pseudotetragonal $(UO_2)O_2$ layers in $(UO_2)O_4$ octahedra joined by sharing corners (of the type $Ba(UO_2)O_2$); and
(c) infinite $(UO_2)O_2$ chains in $(UO_2)O_4$ octahedra joined by sharing edges (of the type $Mg(UO_2)O_2$).

The oxometallates(VI) of the actinides not containing a pronounced actinyl group include compounds such as $Ba(Ba_{0.5}, M_{0.5})O_3$ with an "ordered" perovskite structure (M(VI) = U–Am), UV_2O_8 with an orthorhombic structure, and the hexagonal–rhombohedral compounds $MO_3 \cdot 6REO_{1.5}$ (M = U, Np). The tetragonal compound Li_4UO_5, which is built up of infinite UO_2 chains in $(UO_4)O_2$ octahedra joined by sharing opposite corners, may be regarded as intermediate between the two groups of U(VI) oxometallates. In this type of structure, which is also known for Np(VI), Pu(VI), and Am(VI) compounds, there are four bond lengths of 2·00 Å and two longer U–O distances of 2·22 Å[139]. This structure may be considered as a NaCl-type lattice with every fifth alkali metal atom being replaced by uranium.

Compounds of the type $MO_3 \cdot 6REO_{1.5}$ are also very interesting. Structural investigations have shown that $UO_3 \cdot 6YO_{1.5}$ contains an undistorted UO_6 octahedron with a U–O distance of 2·07 Å[140]. The only other compound known to contain an undistorted UO_6 configuration is δ-UO_3.

The most extensively investigated systems of polynary oxides containing hexavalent actinide elements are those with the alkaline and alkaline earth elements[132]. No compounds with beryllium oxide have been prepared, but similar ternary oxides with other divalent

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[138] V. I. Spitsyn, A. D. Gelman, N. N. Krot, M. P. Mefod'yeva, F. A. Zakharova, Y. A. Komkov, V. P· Shilov and I. V. Smirnova, *J. Inorg. Nucl. Chem.* 31 (1969) 2733.

[139] H. Hoekstra and S. Siegel, *J. Inorg. Nucl. Chem.* **26** (1964) 693.

[140] S. F. Bartram, *Inorg. Chem.* **5** (1966) 749.

metal atoms (e.g., Pb, Co, Cu, Mn, Ni) have been described. Furthermore, in the alkali metal and alkaline earth oxide–transuranium oxide systems no compounds with M(I) : M(VI) ratios < 1 are known, comparable to the so-called polyuranates(VI). Crystallographic data of characteristic compounds are given in Table 14.

The compounds are best prepared by heating the appropriate actinide oxide with the oxide, peroxide, hydroxide or carbonate of the appropriate element at temperatures between 400°C and 1300°C, the temperature depending on the thermal stability of the compound in question. The thermal stability of the alkali metal–actinide(VI) oxides shows some very interesting features. Thus, it depends on

(a) the M(I) : M(VI) ratio, the stability decreasing in the order:

$$M_2U_6O_{19} > M_2U_3O_{10} > M_2U_2O_7 > M_2UO_4 > M_4UO_5$$

(i.e. $Na_2U_6O_{19}$ is thermally more stable than $Na_2U_3O_{10}$);

(b) the atomic number of the alkali metal; that is, upon the volatility and the polarization behavior. The following order of decreasing thermal stability is observed:

$$Li_2UO_4 > Na_2UO_4 > K_2UO_4 > Rb_2UO_4 > Cs_2UO_4$$

(c) the atomic number of the actinide element, the thermal stability decreasing in the order U > Np > Pu > Am.

The thermal stability and preparative conditions of the ternary oxides in the Li_2O–$AmO_{1.5}$–O_2 system are summarized in Fig. 13. By careful choice of reaction conditions all the compounds can be easily prepared pure.

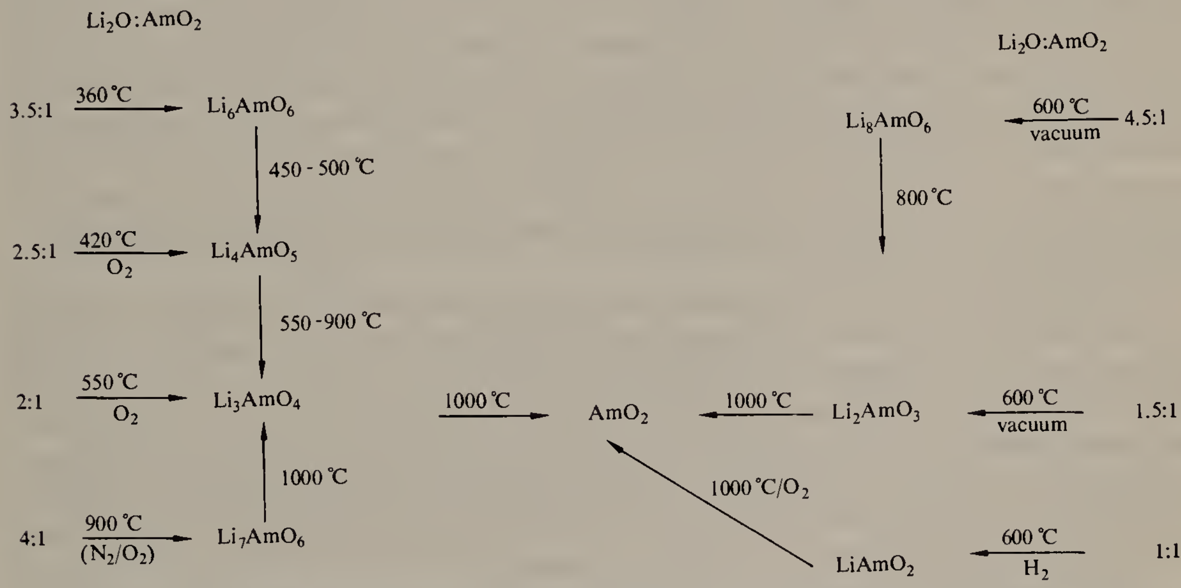

FIG. 13. Preparative conditions and thermal stability of compounds in the Li_2O–$AmO_{1.5}$–O_2 system. (Reproduced with permission from ref. 141.)

Compounds containing pentavalent actinide elements

Typical examples of oxometallates(V) of the actinide elements are compounds of the types $M^IM^VO_3$ (M^I = Li–Cs, M^V = Pa, U), $M^I_3M^VO_4$ (M^I = Li, Na; M^V = Pa–Am),

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[141] C. Keller, *The Solid State Chemistry of Americium Oxides*, in *Lanthanide/Actinide Chemistry*, Adv. Chem. Series No. 71, p. 228, American Chemical Society, Washington D.C. (1967).

$Li_7M^VO_6$ (M^V = Pa–Am) and $Ba(RE^{III}_{0\cdot5}, M^V_{0\cdot5})O_3$ (M^V = Pa–Pu)[2a, 2b, 132]. In addition to these ternary oxides, which are known for most or all pentavalent actinides, a limited number of individual compounds containing U(V) or Pa(V) have been described. This includes, for example, those of the types MUO_5 (M = Sb, V, Nb, Ta, Mo)[142], MU_2O_6 (M = Ca, Co, Ni)[143], MUO_4 (M = Cr, Fe)[144], $M_2U_2O_7$ (M = Ca, Ba) and $M'M''_3O_{10}$ (M′ = Pa, U, M″ = Sb, V, Nb)[142, 145, 146]. The only compound known to contain the UO_2^+ group is $Ca_2U_2O_7$[147].

Other ternary oxides of this valency state include the members of the actinide oxide–rare earth oxide fluorite phases with 1 : 1 stoichiometry $(M^V_{0\cdot5}, RE^{III}_{0\cdot5})O_2$ (M^V = Pa, U, Np), in which the metal atoms are randomly distributed over the calcium positions of CaF_2. These stoichiometric ternary oxides, however, should not be regarded as individual compounds but as members of corresponding oxide phases, for they take up into solid solution varying amounts of the single components. The 1 : 1 compositions are easily obtained by reactions between the appropriate oxides at 1000–1200°C:

$$Pa_2O_5 + La_2O_3 \longrightarrow 4(La_{0\cdot5}, Pa_{0\cdot5})O_2$$

$$2U_3O_8 + 3Y_2O_3 \xrightarrow{O_2} 12(Y_{0\cdot5}, U_{0\cdot5})O_2$$

$$2NpO_2 + Eu_2O_3 \xrightarrow{O_2} 4(Eu_{0\cdot5}, Np_{0\cdot5})O_2$$

Fluorite phases of pentavalent uranium are also known with divalent metals. They include, for example, CdU_2O_6 (=$(Cd_{1/3}, U_{2/3})O_2$) and MgU_2O_6 (=$(Mg_{1/3}, U_{2/3})O_2$). These ternary oxides are the M(II)-rich boundary members of the M(II)–UO_{2+x} fluorite phases.

The crystal structures of most of these ternary actinide(V) oxides are known, but few other physicochemical data are available. A summary of crystallographic data is given in Table 14. A cubic perovskite type of structure is found only for compounds of the types KMO_3 and $RbMO_3$ (M = Pa, U); the sodium compounds crystallize with the orthorhombic $CaTiO_3$ structure and $LiUO_3$ with the rhombohedral $LiNbO_3$ lattice. The $Li_3M^VO_4$ ternary oxides have a structure based on an ordering of univalent and pentavalent cations in the rocksalt lattice. The crystal structure of Li_7SbO_6 and of the isostructural actinide(V) compounds is closely related to the Li_8SnO_6-type of structure with a hexagonal close-packing of oxygen atoms.

The interesting class of III–V-ordered perovskites, $Ba_2M^VM^{III}O_6$, is obtained by replacing the +4 cations in $M^{II}M^{IV}O_3$-perovskite compounds with +3 and +5 cations. As would be expected from calculations of the Madelung energy of the lattice, all these compounds possess an ordering of the metal cations. The barium compounds are cubic or hexagonal, but most strontium compounds are orthorhombic with pseudocubic symmetry. Typical compounds are Ba_2YUO_6, Ba_2RhUO_6, Ba_2AmPaO_6 and Ba_2NdPuO_6. The compound $Ba_3PaO_{5\cdot5}$ (=$Ba(Ba^{II}_{0\cdot5}, Pa^V_{0\cdot5})O_{2\cdot75}$) also crystallizes with the ordered perovskite structure ($a = 8\cdot932$ Å), with vacancies in the anion sublattice.

Several combinations exist in which different oxidation states of the B-cations are possible. According to the results of spectroscopic and magnetic measurements, the charge distribution in, for example, Ba_2MnUO_6 is $Ba_2(Mn^{III}_{0\cdot4}, Mn^{II}_{0\cdot6})(U^V_{0\cdot4}, U^{VI}_{0\cdot6})O_6$, whilst Ba_2FeUO_6 is a III–V compound and Ba_2CoUO_6 and Ba_2NiUO_6 are II–VI compounds.

[142] R. Chevalier and M. Gaspérin, *Bull. Soc. fr. Minéral. Cristallogr.* **93** (1970) 18.
[143] S. Kemmler-Sack, *Z. anorg. allg. Chem.* **358** (1968) 226.
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[145] P. Mahé-Paillerez, *Rev. Chim. Minérale*, **7** (1970) 807.
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[147] J. M. Leroy and G. Tridot, *Compt. Rend.* **262C** (1966) 1376.

Another perovskite structure with cation ordering is found for compounds of the type $Ba_3MU_2O_9$ (M(II) = Mg, Fe, Zn, Mn, Co, Ni); the ordering corresponds to the formula $Ba_2(M_{0\cdot 67}, U_{0\cdot 33})UO_6$.

Chemical, spectroscopic and magnetic data for some of the uranium compounds have shown clearly that they contain U(V) and not a mixture of U(IV) + U(IV). The ternary oxides with a $5f^1$ electronic configuration exhibit magnetic behavior which depends strongly on the oxygen environment of the metal atom, i.e. on the ligand field and its symmetry. The magnetic moments of U(V) and other $5f^1$ ternary oxides are very low, ranging from $\mu_{eff} \sim 0 \cdot 4\, \mu_B$ to $\sim 0 \cdot 66\, \mu_B$. The spectra of KUO_3 and $RbUO_3$ have been successfully analysed on the basis of a $5f^1$ configuration for the U(V) ion in an octahedral ligand field[148].

Compounds containing tetravalent actinide elements

Besides the fluorite phases, the best known polynary oxides of tetravalent actinide elements are the alkali metal compounds of $M^I_2M^{IV}O_3$ or $M^I_8M^{IV}O_6$ stoichiometry (e.g. Na_2ThO_3 and Li_8PuO_6), the cubic or pseudocubic perovskites $M^{II}M^{IV}O_3$ (M^{II} = Ba, Sr, M^{IV} = Th-Am), the silicates and germanates of formula $M^{IV}Si(Ge)O_4$[149], which are known for the elements from thorium to americium, and the $M^{IV}Ti_2O_6$ compounds (M^{IV} = Th, U, Np) with the brannerite type of structure. Other compounds containing tetravalent actinide elements include $M^{IV}{}_{0\cdot 25}Nb(Ta)O_3$ (M = Th-Pu)[150], a transition member between the primitive cubic ReO_3 type of structure and the bcc perovskite lattice, and some vanadates, molybdates, and perrhenates, e.g. ThV_2O_7, $Np(VO_3)_4$, $NpMo_2O_8$, $Na_4Np(MoO_4)_3$ and $Np(ReO_4)_4$. Crystallographic data of characteristic polynary oxides are given in Table 16.

Perovskite compounds containing the actinide(IV) ions are known only with Ba(II) and Sr(II), and not with the light alkaline earth elements calcium, magnesium, and beryllium. These latter systems are simple eutectics, the $BeO–ThO_2$ system, for example, has a eutectic at 70 mol.% BeO (=18·1 wt.%) and 2155°C.

The germanates $M^{IV}GeO_4$ and silicates $M^{IV}SiO_4$ of the tetravalent actinide elements may be prepared either by high-temperature and/or hydrothermal methods, the structure of the product depending on the reaction method. By thermal reactions, only β-$ThSiO_4$ and β-$PaSiO_4$ which possess the monoclinic huttonite type of structure are obtained, whereas the hydrothermal preparation at 230°C yields α-$ThSiO_4$ to α-$AmSiO_4$ with the tetragonal zircon lattice. On heating to about 1000°C, β-$ThSiO_4$ and β-$PaSiO_4$ transform to the α-modification, whereas the other compounds decompose to the component oxides. α-$MGeO_4$ phases (M = Th-Am) with the scheelite structure are obtained by heating GeO_2 and the actinide dioxide to 1000–1100°C. β-$ThGeO_4$ to β-$NpGeO_4$, which crystallize with the zircon-type structure, and α-$PuGeO_4$ and α-$AmGeO_4$ are the products of hydrothermal reactions.

Uranium glasses containing up to 50 wt.% UO_2 have been described. The solubility of UO_2 is highest for glasses having a molar ratio of $Na_2O:SiO_2$ between 1:2 and 1:3[151].

Fluorite Phases of the Actinide Oxide Systems

One of the most characteristic features of actinide oxide chemistry is the formation of

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[148] S. Kemmler-Sack, *Z. anorg. allg. Chem.* **363** (1968) 295.

[149] C. Keller, *Nukleonik*, **5** (1963) 41.

[150] C. Keller, *J. Inorg. Nucl. Chem.* **27** (1965) 1233.

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TABLE 16. CRYSTALLOGRAPHIC DATA FOR POLYNARY OXIDES CONTAINING TETRAVALENT AND TRIVALENT ACTINIDE ELEMENTS

Valency	Compound	Symmetry	Space group	Lattice constants				Isostructural compounds	Ref.
				a (Å)	*b* (Å)	*c* (Å)	α(β) (°)		
IV	$Na_{11}U_5O_{16}$	Cubic	*P*4$_2$32	9·543					a
	K_2ThO_3	Monoclinic	*C*2/*c*	6·41	11·09	12·72	99·40		b
	Na_2AmO_3	Monoclinic		5·92	10·26	11·23	100·12		c
	Li_8PuO_6	Hexagonal	*R*$\bar{3}$(?)	5·64		15·96		M(IV) = Am, Ce, Pr	d
	$BaAmO_3$	Cubic	*Pm*3*m*	4·365				M(IV) = Th–Pu, Ce, Pr	c
	α-$ThMo_2O_8$	Hexagonal	*P*$\bar{6}$	17·60		6·20		M(IV) = U	e
	β-$ThMo_2O_8$	Orthorhombic	*Pcab*	9·74	10·22	14·46		M(IV) = Np	e
	$Np(VO_3)_4$	Tetragonal		11·88		28·36		M(IV) = Th	f
	$ThTi_2O_4$	Monoclinic	*C*2/*m*	9·822	3·824	7·036	118·84	M(IV) = U, Ce, Np	g
	α-$NpGeO_4$	Tetragonal	*I*4$_1$/*a*	5·061		11·16		M(IV) = Th–U, Pu, Am	h
	β-$PaGeO_4$	Tetragonal	*I*4$_1$/*amd*	7·156		6·509		M(IV) = Th, U, Np	h
	β-$ThSiO_4$	Monoclinic	*P*2$_1$/*n*	6·77	6·98	6·51	107·78	M(IV) = Pa	h
	$Pu_{0\cdot25}TaO_3$	Tetragonal		7·67		7·74		M(IV) = Th–Np	i
	$Na_2Np(MoO_4)_3$	Tetragonal	*I*4$_1$/*a*	5·224		11·420			j
	$BaTiPuO_6$	Pseudocubic		8·06					k
III	$PuAsO_4$	Monoclinic	*P*2$_1$/*n*	6·92	7·09	6·66	105·45	M(III) = Am	l
	$CmNbO_4$	Monoclinic	C2	5·42	11·22	5·13	94·66	M(III) = Am	l
	$PuVO_3$	Orthorhombic	*Pbnm*	5·48	5·61	7·78		M(III) = Am	m
	$AmBO_3$	Orthorhombic	*Pnam*	5·053	8·092	5·738			c
	$PuScO_3$	Orthorhombic	*Pbnm*	5·654	5·839	8·104		M(III) = Am	n
	$(Cm_{0\cdot5}, Pa_{0\cdot5})O_2$	Cubic	*Fm*3*m*	5·43				M(III) = Am, Pu	l
	$AmVO_4$	Tetragonal	*I*4$_1$/*amd*	7·31		6·42			c
	$AmTaTiO_6$	Orthorhombic	*Pnam*	5·33	10·95	7·49			c
	$Am_2(MoO_4)_3$	Tetragonal	*I*4$_1$/*a*	5·24		11·52			o
	$AmAlO_3$	Rhombohedral	*R*$\bar{3}$*m*	5·29			60·53		c
	$Ba(Am_{0\cdot5}, Nb_{0\cdot5})O_3$	Cubic	*Fm*3*m*(?)	8·520					c

For notes to Table see opposite.

extensive non-stoichiometric oxide phases, the structures of which are derived from the fcc fluorite lattice. The fluorite lattice of actinide and lanthanide dioxides is capable of taking into solid solution not only structurally related oxides, but also oxides with quite different types of structures and formal compositions. Furthermore, the fluorite lattice not only dissolves other oxides but also nitrides, fluorides, etc. For example, a fcc fluorite type of solid solution of U_2N_3 in UO_2 is described up to a limiting composition of $UON_{0\cdot75}$ below 1030°C, whereas UN is soluble up to 12·1 mol.% in UO_2 at 2000°C[152, 153]. ThO_2 dissolves up to 22 mol.% UF_4 at 1100°C and up to 20 mol.% ThF_4 at 1200°C to give $Th_{0\cdot78}U_{0\cdot22}O_{1\cdot56}F_{0\cdot88}$ and $ThO_{1\cdot6}F_{0\cdot8}$, respectively[154].

Fluorite structures are also obtained from reactions involving metal oxides which have non-fluorite type structures, e.g. La_2O_3 with Pa_2O_5 or Sm_2O_3 with U_3O_8. Corresponding ternary oxides are also known with the rutile or the silicon dioxide types of structure, e.g. $FeTaO_4$, $VNbO_4$ or $AlPO_4$. These compounds, however, are stoichiometric or possess only a very small range of homogeneity in contrast to the fluorite phases with their ranges of stoichiometry.

Other interesting ternary oxide phases of the actinides include the cubic uranium and thorium tungsten bronzes M_xWO_3, e.g. $U_{0\cdot10}WO_3$ ($a = 3\cdot8096$ Å) and $Th_{0\cdot07}WO_3$ ($a = 3\cdot815$ Å). These are metallic in character. The magnetic moment of uranium in the uranium tungsten bronzes U_xWO_3 ($0\cdot08 \leqslant x \leqslant 0\cdot12$) is $3\cdot1\ \mu_B$.

Fluorite Phases containing Mono- and Divalent Elements. Few data are available for fluorite phases containing monovalent elements. The thermal decomposition of Li_2UO_4 yields (Li, U)O_{2+x} with $a = 5\cdot375$ Å, this phase probably being the same as $(Li_{0\cdot33}, U_{0\cdot67})O_{1\cdot835}$ which has been described with a small, if any, homogeneity range and a superstructure with $a = 10\cdot70$ Å. In the Pa_2O_5–M_2O(Li, Na) system fcc phases with no detectable phase widths are observed at the composition $M_2O \cdot 2Pa_2O_5$ (e.g. $a = 5\cdot399$ Å for M = Na).

No compound formation has been observed in the investigated actinide dioxide/BeO (MgO, CaO) systems. These systems are of the simple eutectic type with very small terminal solubilities. In the uranium system the situation is completely changed under oxidizing conditions. Thus, the solubility of MO in UO_{2+x} markedly increases with the formation of a fluorite phase (U, M)O_{2+x} in which the anion vacancies of the fluorite lattice, obtained by

[152] P. L. Blum, J. Langier and J. M. Martin, *Compt. Rend.* **268C** (1969) 148.

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Notes to Table 16

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[b] P. Hagenmüller, M. Devalette and J. Claverie, *Bull. Soc. Chim. France* (1966) 1581.

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[g] R. Ruh and A. D. Wadsley, *Acta Cryst.* **21** (1966) 974.

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[i] C. Keller, *J. Inorg. Nucl. Chem.* **27** (1965) 1233.

[j] W. Freundlich and M. Pagès, *Compt. Rend.* **273C** (1971) 44.

[k] S. K. Awasthi, D. M. Chackruburtty and V. K. Tondon, *J. Inorg. Nucl. Chem.* **30** (1968) 819.

[l] C. Keller and K. H. Walter, *J. Inorg. Nucl. Chem.* **27** (1965) 1253.

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[n] C. Keller, U. Berndt, M. Debbabi and H. Engerer, *J. Nucl. Mat.* **42** (1972) 23.

[o] W. Freundlich and M. Pagès, *Compt. Rend.* **269C** (1969) 392.

dissolving MO in UO_2, are occupied by excess oxygen. Such fluorite phases of different thermal stability and phase widths are known for Mg, Ca, Sr, Ba, Cd, Co, Zn, Pb, and Mn, for example. The ease of formation of these oxidized fluorite phases may be illustrated by the formation of the U–Cd–O phase by the reaction between UO_2 and CdO in an argon atmosphere at >750°C[155]. The reaction

$$UO_2 + 2x\text{CdO} \rightarrow (\text{CdO})_x UO_{2+x}$$

proceeds via two steps:

(a) oxidation of UO_2 by CdO and vaporization of Cd at >750°C:

$$UO_2 + x\text{CdO} \rightarrow UO_{2+x} + x\text{Cd}$$

(b) formation of the fluorite phase by dissolution of CdO in UO_{2+x}:

$$UO_{2+x} + x\text{CdO} \rightarrow (\text{CdO})_x UO_{2+x} \, (= (\text{Cd}_x,\text{U})O_{2+2x})$$

This phase occurs up to $x = 0{\cdot}5$ which corresponds to $(\text{Cd}_{0\cdot33}, \text{U}_{0\cdot67})O_2$ or to CdU_2O_6 as the limiting composition.

Fluorite Phases containing Trivalent Elements. The actinide dioxide–lanthanide sesquioxide systems are especially characterized by their extensive formation of non-stoichiometric oxide phases, a characteristic which has no analogy in other oxide systems. Most of these phases are disordered, very few ordered phases (thermally unstable) and ternary oxides being known. In the similar $ZrO_2(HfO_2)$–RE_2O_3 systems, with the smaller ionic radius of M(IV), however, more ordered than disordered phases exist, but the ordered phases may still be derived from the fluorite structure.

The ThO_2 lattice takes up considerable amounts of $REO_{1\cdot5}$ with the formation of "massively defective crystalline solid solutions"[156]. The solubility is strongly dependent on the ionic radii of the lanthanide elements, an increase being observed from La(III) to Nd(III) and a decrease from Sm(III) to Lu(III)[157] (Fig. 14). As the $|r_{Th^{4+}} - r_{RE^{3+}}|$ difference increases, the phase widths of the $(Th, RE)O_{2-x}$ solid solution decrease. The solubility of $REO_{1\cdot5}$ in ThO_2 also increases with temperature, as shown in Fig. 15, where the phase diagrams for the ThO_2–$LaO_{1\cdot5}$, ThO_2–$EuO_{1\cdot5}$ and ThO_2–$ErO_{1\cdot5}$ systems are illustrated. The smallest solubility is observed in the ThO_2–$ScO_{1\cdot5}$ system (less than 1 mol.% at 1750°C)[158]. Density measurements indicate that the fcc $(Th_{1-x}, RE_x)O_{2-x/2}$ solid solutions have a cation sub-lattice filled with Th^{4+} and RE^{3+} and vacancies in the anion sub-lattice.

The uranium oxide–lanthanide oxide systems may be generally characterized by the following facts:

(a) A fluorite phase $(U, M^{III})O_{2\pm x}$ exists over a wide range of U:M^{III} ratios. In the case of the UO_2–UO_3–$LaO_{1\cdot5}$ system, for example, the superstoichiometric phase $(U, La)O_{2+x}$ ranges from $0 < x \leqslant 0{\cdot}25$, whereas in the substoichiometric fluorite phase $(U, La)O_{2-x}$, x never exceeds $0{\cdot}40$ (Fig. 16). The stoichiometric composition $(U, La)O_{2\cdot00}$ ranges from 0 to 66·7 mol.% $LaO_{1\cdot5}$. It includes the intermediates with pentavalent uranium $(U_{0\cdot5}, La_{0\cdot5})O_2$ and the final member with hexavalent uranium $(U_{0\cdot33}, La_{0\cdot67})O_2$[159].

(b) No solubility of $MO_{1\cdot5}$ in U_3O_8 and of uranium oxides in the hexagonal and monoclinic lanthanide oxides is observed. The solubility of UO_{2+x} in cubic lanthanide oxides is small and decreases with increasing temperatures.

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[159] H. G. Diehl and C. Keller, *J. Solid State Chem.* **3** (1971) 621.

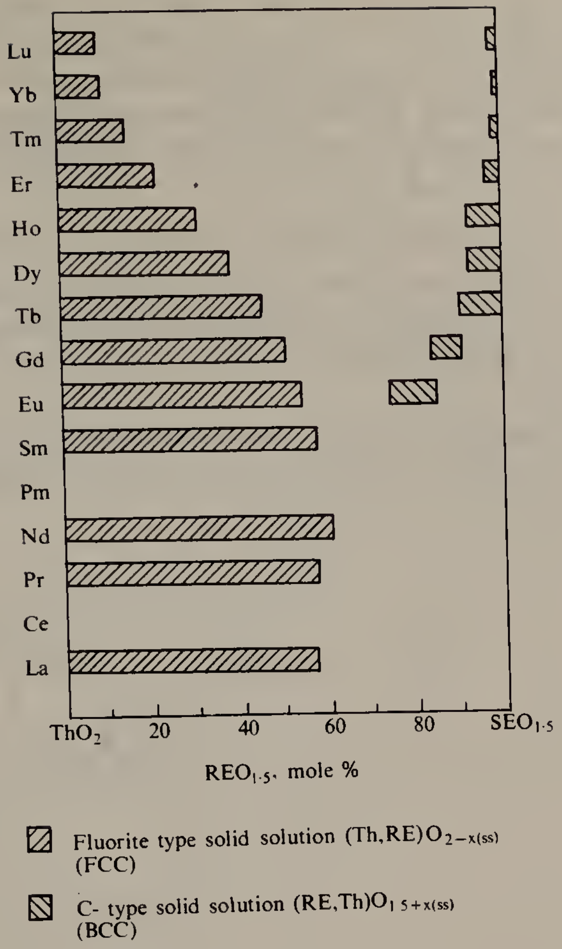

FIG. 14. Solubility of $REO_{1.5}$ in ThO_2 and of ThO_2 in $REO_{1.5}$ at 1550°C. (Reproduced with permission from ref. 157.)

(c) Several ordered phases have been detected in these systems. Their structures may be derived from the fluorite lattice and they are stable only up to moderate temperatures. $UO_3 \cdot 6MO_{1.5}$ is the only ordered compound which does not transform to the disordered state below 1600°C.

(d) On the basis of i.r. spectral results it appears that neither the ordered nor the disordered phases contain a uranyl group, UO_2^+ or UO_2^{++}.

(e) The volatility of uranium oxide is markedly depressed by the incorporation of yttrium or lanthanide oxides in the UO_2 lattice.

(f) The fcc solid solutions containing unoxidized UO_2 take up oxygen very rapidly, even at −20°C or below. This indicates the great tendency of oxygen to fill the vacant oxygen positions in fcc $(U, RE)O_{2-x}$.

The neptunium oxide–lanthanide oxide systems are intermediate between the corresponding thorium and uranium oxide systems. The phase widths of the fluorite phases are greater for the neptunium systems than for the thorium systems because of the oxidation of neptunium oxides.

The oxidized fluorite phases, however, are thermally less stable than the corresponding uranium phases, the mean valency reaching +5 in, for example, the stoichiometric fcc intermediates $(NpO_{0\cdot5}, RE_{0\cdot5})O_2$[160, 161]. In the plutonium oxide–lanthanide oxide systems the oxidation of plutonium stops at mean valencies less than five.

Protactinium pentoxide reacts with lanthanide and actinide sesquioxides (La–Lu, Y, Am, Cm) to give ternary oxides $(M^{III}_{0\cdot5}, Pa^{V}_{0\cdot5})O_2$ with the fluorite type of structure and a statistical distribution of the metal ions[162], e.g.

$$La_2O_3 + Pa_2O_5 \rightarrow 2(La_{0\cdot5}, Pa_{0\cdot5})O_2 \quad a = 5{\cdot}525\ \text{Å}$$

$(M_{0\cdot5}, Pa_{0\cdot5})O_2$ takes Pa_2O_5 into solid solution (as a binary fluorite oxide, e.g. ThO_2, PuO_2, does) as well as M_2O_3. At 1250°C, the solubility of M_2O_3 continuously increases with increasing ionic radius of M(III), from 25 mol.% $LuO_{1\cdot5}$ in $(Lu_{0\cdot5}, Pa_{0\cdot5})O_2$ to 62 mol.% $LaO_{1\cdot5}$ in $(La_{0\cdot5}, Pa_{0\cdot5})O_2$.

In their solid state chemistry the $(M_{0\cdot5}, Pa_{0\cdot5})O_2$ ternary oxides behave like a normal binary fluorite oxide. Reactions with alkaline earth oxides, for example, lead to the ordered

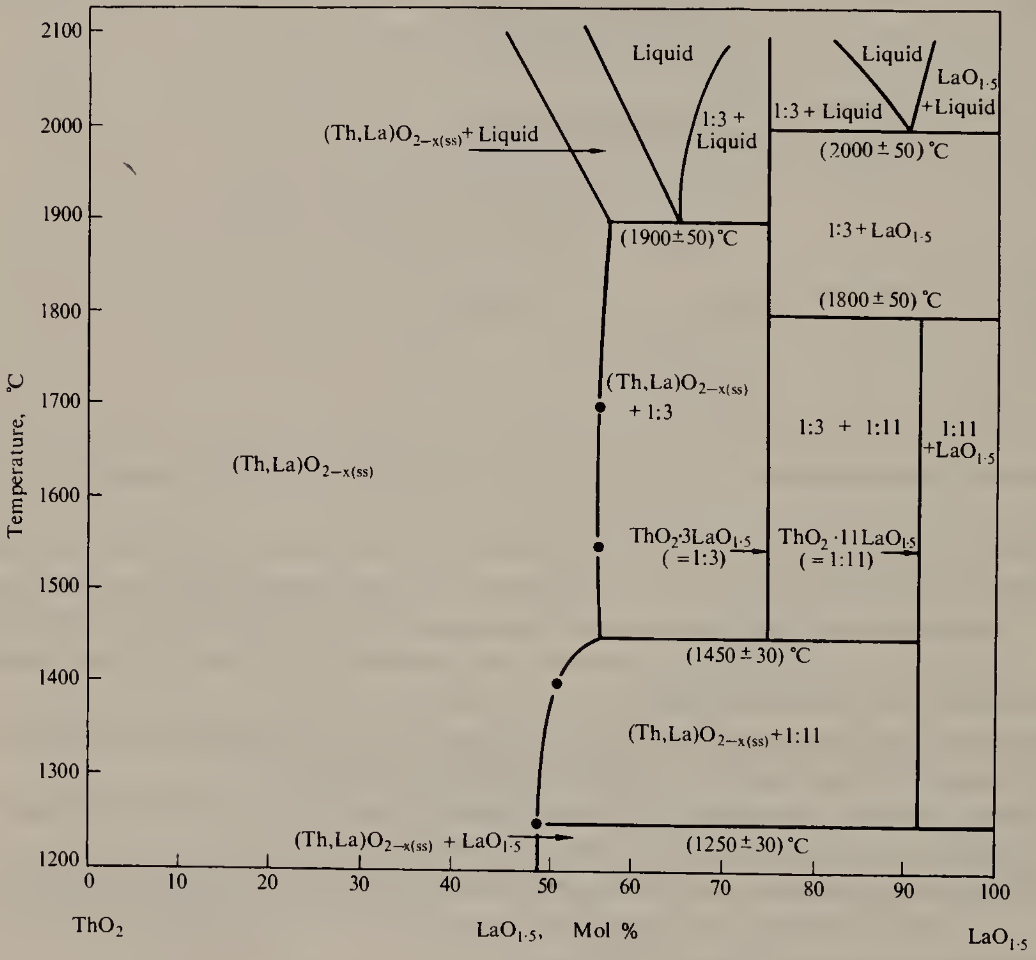

FIG. 15a.

FIG. 15. Phase diagrams of the ThO_2–$LaO_{1\cdot5}$($EuO_{1\cdot5}$, $ErO_{1\cdot5}$) systems. (Reproduced with permission from ref. 157.)

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[160] C. Keller, H. Engerer and H. Seiffert, *J. Inorg. Nucl. Chem.* **31** (1969) 3421.

[161] C. Keller, H. Engerer, L. Leitner, U. Sriyotha and U. Berndt, *J. Inorg. Nucl. Chem.* **31** (1969) 3421.

[162] C. Keller and K. H. Walter, *J. Inorg. Nucl. Chem.* **27** (1965) 1253.

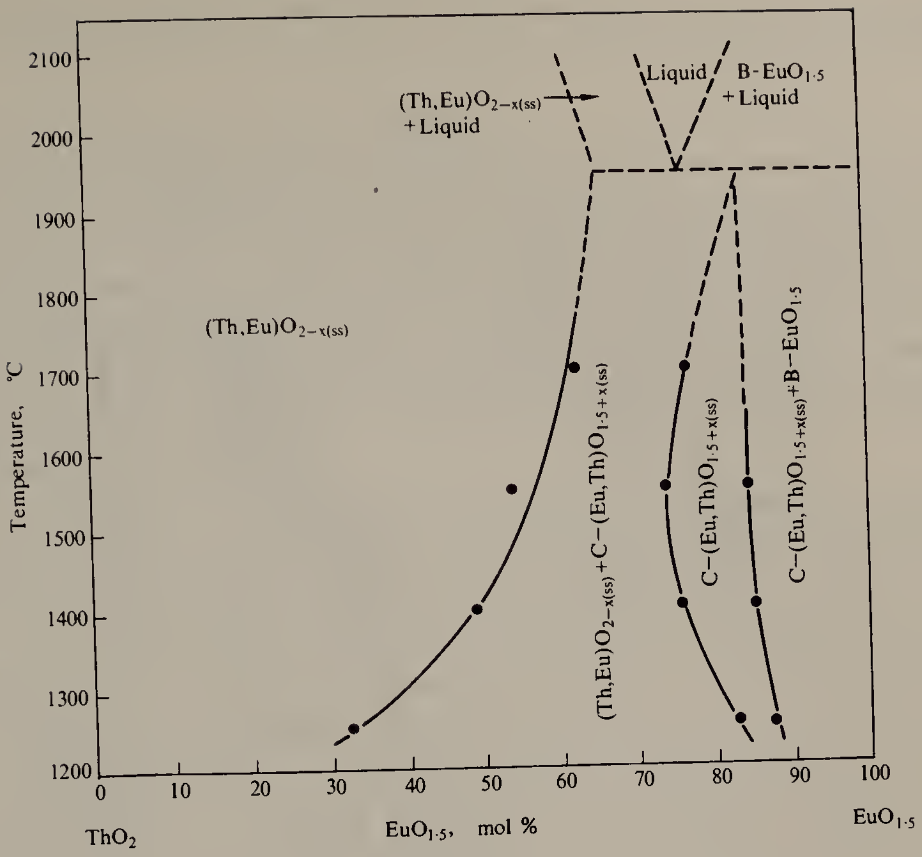

FIG. 15b

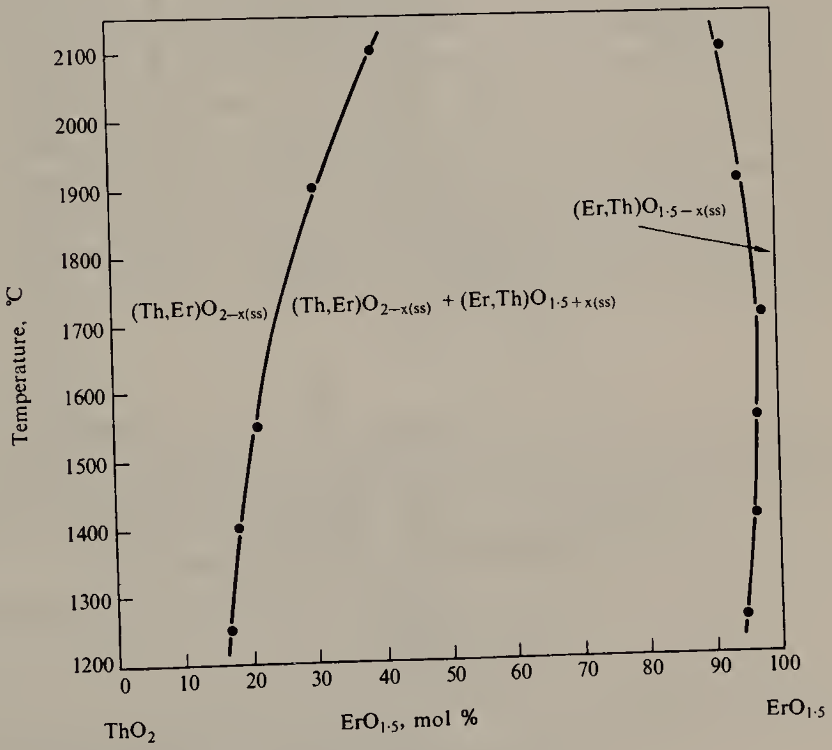

FIG. 15c

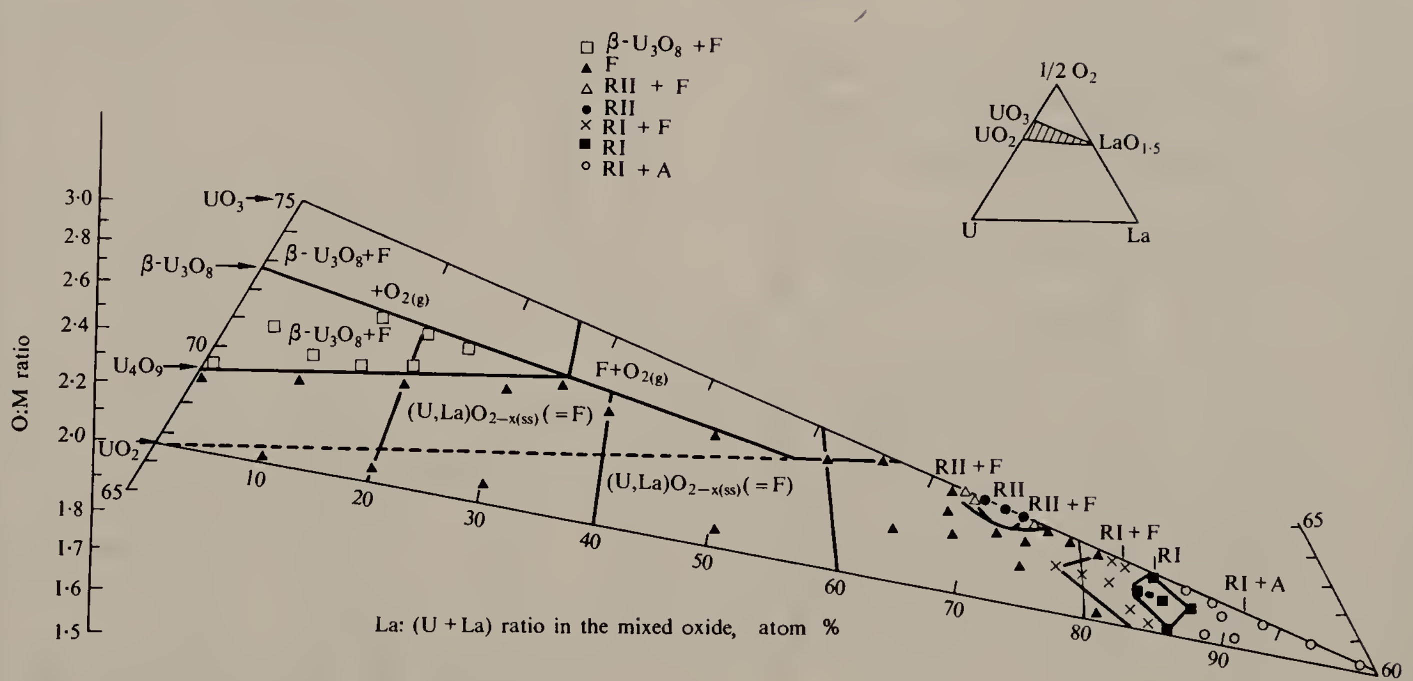

FIG. 16. The U-La-O phase diagram in the UO_3–UO_2–$LaO_{1\cdot5}$ region at 1250°C. (Reproduced with permission from ref. 159.)

perovskite compounds $Ba(M_{0\cdot5}, Pa_{0\cdot5})O_3$; in addition, PaO_2 yields $BaPaO_3$. ThO_2 takes Pa_2O_5 into solid solution to form a superstoichiometric $(Th_{1-x}, Pa_x)O_{2+x/2}$ fluorite phase.

Fluorite Phases containing Tetravalent Elements

As one would expect, because the actinide dioxides crystallize in the fluorite lattice, complete solid solutions of the binary oxides are observed. For systems like, for example, ThO_2–UO_2, UO_2–PuO_2, and NpO_2–AmO_2 the validity of Vegard's rule has been demonstrated by several authors[1a, 2a]. The solubility of higher uranium oxides (O:U > 2) in actinide dioxides depends on the solute. In the MO_2–UO_{2+x} systems at 1100°C and $p(O_2) = 1$ atm the fcc phase width increases in the sequence Th(IV) < Ce(IV) < Np(IV)[163]. No oxidation of neptunium to Np(>IV) occurs in the NpO_2–$ThO_2(CeO_2)$ and NpO_2–UO_{2+x} systems, an observation which contrasts with the behavior of Np in the fluorite phases with trivalent metal ions.

The U–Pu–O system is of great nuclear technological interest since mixed oxides $(U, Pu)O_2$ with 10 to 20% PuO_2 will be used in the fast breeder reactors. To prepare these mixed oxides one either sinters the finely powdered binary oxides in an argon or helium atmosphere or decomposes the mixed precipitate of $(NH_4)_2U_2O_7$ and $PuO_2 \cdot aq$ in a reducing atmosphere at about 1000–1200°C directly to $(U, Pu)O_2$. By these techniques, however, it is very difficult to get a completely homogenized mixed oxide, even by prolonged heating, since the reaction products generally contain different amounts of the starting materials. The phase diagram of the UO_2–$UO_{2\cdot67}$–PuO_2–$PuO_{1\cdot5}$ system is characterized by an extensive formation of fcc and bcc solid solutions[164]. At a very high temperature gradient, $dT/dx \sim 800$ deg/cm and $T \sim 2300$°C, a small uranium–plutonium segregation in the $(U, Pu)O_2$ mixed crystal is observed, the plutonium diffusing to the hot part of the system[165].

A more limited solubility, especially at moderate temperatures, is observed in the UO_2–ZrO_2 system because of the greater difference between the ionic radii of U^{4+} and Zr^{4+} (Fig. 17). In this connection it should be mentioned that monoclinic ZrO_2 is transformed to the cubic modification on contact with uranium fission products. Pure zirconia, however, does not transform under neutron irradiation; the mineral baddeleyite, and ZrO_2 containing trace impurities of uranium, transform when irradiated. This means that regions of the high-temperature cubic phase form in thermal spikes produced by the fission fragments and are frozen in because of the rapid dissipation of the heat. It is concluded that about $3\cdot4 \times 10^{16}$ fissions/cm³ are required to produce complete conversion to the cubic phase.

4.5. Compounds containing trivalent actinide elements

Unless they can be precipitated from aqueous solution like $PuAsO_4$, ternary oxides of trivalent plutonium are obtained only under reducing conditions, e.g.

$$2PuO_2 + Al_2O_3 \xrightarrow[1400°C]{H_2} 2PuAlO_3$$

or, starting with Pu_2O_3,

$$Pu_2O_3 + Ta_2O_5 \xrightarrow[1200°C]{\text{Vacuum}} 2PuTaO_4$$

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[163] M. Paul and C. Keller, *J. Nucl. Mat.* **41** (1971) 133.
[164] C. Sari, U. Benedict and H. Blank, *J. Nucl. Mat.* **35** (1970) 267.
[165] M. Bober, C. Sari and G. Schumacher, *J. Nucl. Mat.* **39** (1971) 265.

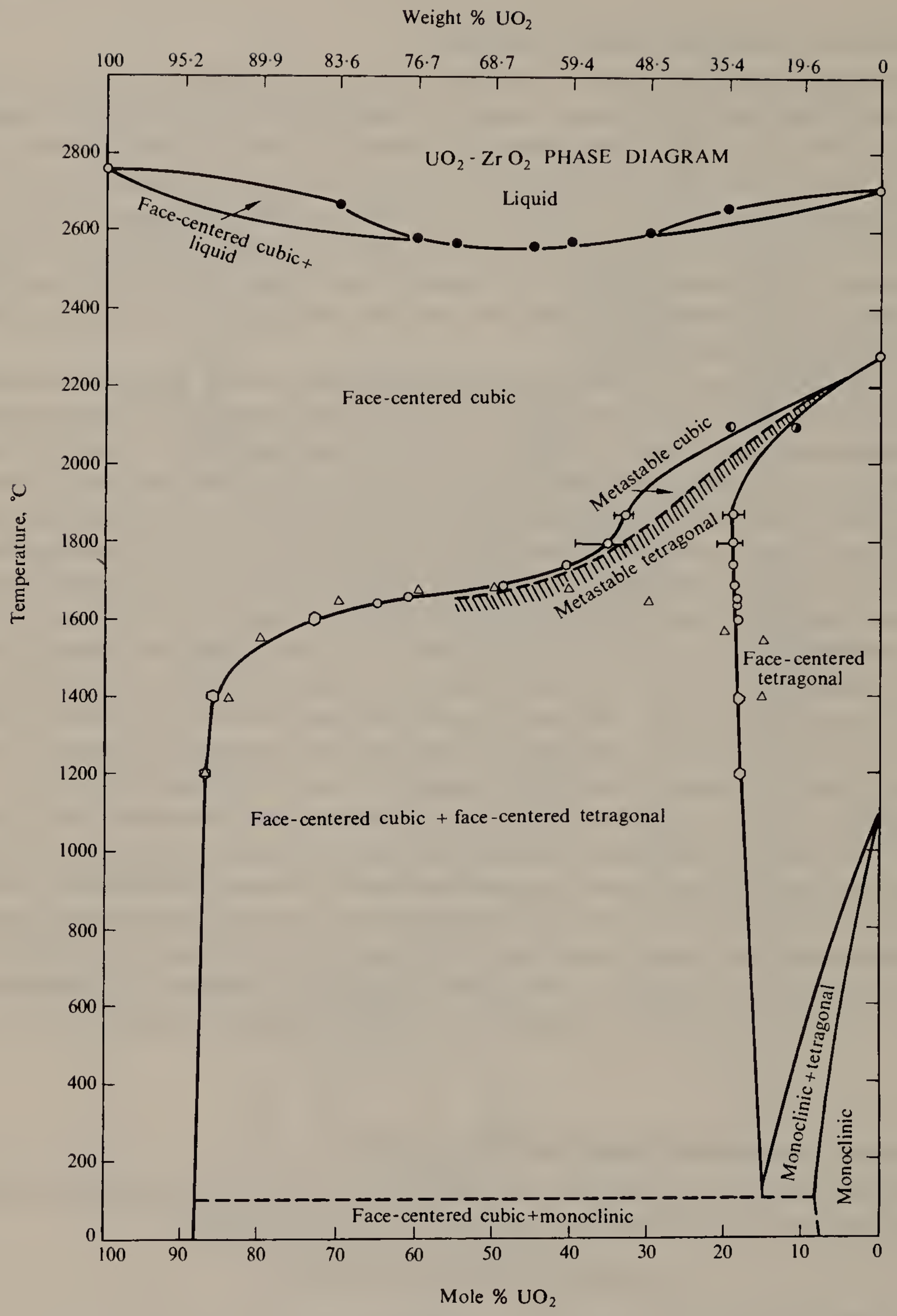

FIG. 17. The UO–ZrO_2 phase diagram. (Reproduced with permission from ref. 166.)

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[166] J. Cohen and B. E. Schaner, *J. Nucl. Mat.* 9 (1963) 18.

On the other hand, the thermal reaction of AmO_2 or CmO_2 with oxides of elements belonging to Group III or V of the periodic system leads directly to ternary oxides containing M(III), e.g.

$$2AmO_2 + V_2O_5 \xrightarrow[1000°C]{} 2AmVO_4$$

and

$$AmO_2 + H_3BO_3 \xrightarrow[900°C]{} AmBO_3$$

A characteristic difference between the behavior of PuO_2 and that of AmO_2 appears, for example, in the reaction with Nb_2O_5[150]. PuO_2 reacts to give $Pu_{0\cdot25}NbO_3$ containing Pu(IV), while an oxometallate of trivalent americium, $Am_{0\cdot33}NbO_3$, is formed by the corresponding reaction with AmO_2. Ternary oxides of trivalent actinides are very similar in their properties and structures to the corresponding compounds of trivalent lanthanides with the same ionic radii (e.g. Pu corresponds to Pr and Am to Nd)[141].

5. PHOSPHATES AND ARSENATES

The chemistry of the actinide phosphates and the related arsenates has not been extensively investigated and a reinvestigation using modern methods would be valuable. Most compounds which are described in the literature have been obtained by precipitation reactions, the precipitates very often being gelatinous and in most cases they are only characterized by the metal and phosphate content. More reliable data are available for compounds which have been prepared by solid state reactions, but even in most of these cases details of structure and/or chemical behavior are not available. Crystallographic data for the actinide phosphates and arsenates are summarized in Tables 17 and 18, respectively.

In addition to solid compounds, numerous soluble anionic, neutral, and cationic phosphate complexes of the elements actinium to curium have been described and in many instances stability constants have been established. Critically selected data are summarized in Table 19. For other data see refs. 2b, 167 and 168.

Heptavalent actinide elements

Amorphous, yellowish-brown neptunyl(VII) phosphate, $NpO_2PO_4 \cdot aq$, precipitates on the addition of phosphate ions to a 0·1–0·3 M nitric acid solution of heptavalent neptunium[169]. A pure product could not be obtained owing to the rapid reduction to Np(VI), even in the solid state.

Hexavalent actinide elements

Whereas many data are available for actinide(VI) phosphates, only few compounds have been described containing phosphorus in a lower oxidation number. Uranyl hypophosphite, $UO_2(H_2PO_2)_2$, is precipitated by the addition of a NaH_2PO_2 solution to a uranyl nitrate solution. Treatment of the precipitate with an excess of sodium hypophosphite results in the formation of $NaUO_2(H_2PO_2)_3 \cdot xH_2O$ ($x = 3\cdot5$ and 5). The uranyl hypophosphites appear to be decomposed by light. Gelatinous uranyl phosphite, UO_2HPO_3, may also be prepared by precipitation reactions.

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[167] A. E. Martell and L. G. Sillén, *Stability Constants*, Special Publication No. 17, The Chemical Society, London (1964).

[168] A. D. Gelman, A. I. Moskvin, L. M. Zaitsev and M. P. Mefod'eva, *Complex Compounds of Transuranium Elements*. English translation by Consultants Bureau, New York (1962).

[169] M. P. Mefod'eva, N. N. Krot and A. D. Gelman, *Sov. Radiochemistry*, **12** (1970) 210.

TABLE 17. CRYSTALLOGRAPHIC DATA FOR ACTINIDE PHOSPHATES

Valency	Compound	Lattice symmetry	Space group	Lattice constants				Refractive index	Ref.
				a (Å)	*b* (Å)	*c* (Å)	*β* (°)		
VI	$H_{11}(UO_2)_2(PO_4)_5$	Monoclinic	*P*2₁/*c*	11·37	13·94	7·47	113·5	1·533, 1·553, 1·583	a
	$HUO_2PO_4 \cdot 4H_2O$	Tetragonal	*P*4/*nmm*	6·99		8·72			b
	$LiUO_2PO_4 \cdot 4H_2O$†	Tetragonal	*P*4/*nmm*	6·93		9·06			b
	$Ba(UO_2PO_4)_2 \cdot 6H_2O$‡	Tetragonal	*I*4/*mmm*	6·96		16·99			b
	$HNpO_2PO_4 \cdot 4H_2O$	Tetragonal	*P*4/*nmm*	6·96		8·76			b
	$LiNpO_2PO_4 \cdot 4H_2O$†	Tetragonal	*P*4/*nmm*	6·93		9·16			b
	$Ba(NpO_2PO_4) \cdot 6H_2O$‡	Tetragonal	*I*4/*mmm*	6·98		17·31			b
IV	$Th_3(PO_4)_4$	Monoclinic	*P*2, *Pm* or *P*2/*m*	10·55	10·66	8·80	106·68		c
	ThP_2O_7	Cubic	*Pa*3	8·721					d
	$(Ca_{0.5}Th_{0.5})PO_4$	Monoclinic	*P*2₁/*n*	7·292	6·452	6·417			e
	(α-)UP_2O_7	Cubic	*Pa*3	8·6274§					f
	(β-)UP_2O_7	Orthorhombic	*Pnam* or *Pna*2₁	11·526	12·810	7·045			g
	α-$U(PO_3)_4$	Monoclinic		23·42	13·02	23·00	90	1·659, 1·684, 1·690	h
	β-$U(PO_3)_4$	Orthorhombic	*Pbca*	13·80	14·92	9·00		1·630, 1·635, 1·654	h
	NpP_2O_7	Cubic	*Pa*3	8·565					i
	PuP_2O_7	Cubic	*Pa*3	8·560				1·676	k
	$Pu(PO_3)_4$	Orthorhombic	*Pnab*	8·93	14·89	6·87		1·654, 1·661, 1·686	l
III	$PuPO_4$	Monoclinic	*P*2₁/*n*	6·73	7·00	6·42	103·8	1·855, 1·86, 1·905	k
	$AmPO_4$	Monoclinic	*P*2₁/*n*	6·73	6·93	6·41	103·83		i
	$CmPO_4$	Monoclinic	*P*2₁/*n*	6·72	6·93	6·37	104·11		m
	$AcPO_4 \cdot 0.5H_2O$	Hexagonal	*C*6₂2	7·21		6·64			n
	$PuPO_4 \cdot 0.5H_2O$	Hexagonal	*C*6₂2	7·01		6·40		1·76	k
	$AmPO_4 \cdot 0.5H_2O$	Hexagonal	*C*6₂2	6·99		6·37			i

For notes to Table see opposite.

The following uranium(VI) orthophosphates have been obtained by precipitation reactions: $UO_2(H_2PO_4)_2\cdot 3H_2O$, $UO_2HPO_4\cdot 4H_2O$ and $(UO_2)_3(PO_4)_2\cdot 6H_2O$[170, 171]. Solubility measurements have shown that these compounds are the only stable solid compounds in the UO_3–H_3PO_4–H_2O system at 25°C, the stability ranges being

$(UO_2)_3(PO_4)_2\cdot 6H_2O$	$0{\cdot}014\ \text{M} > \Sigma PO_4^{3-}$
$UO_2HPO_4\cdot 4H_2O$	$0{\cdot}014\ \text{M} < \Sigma PO_4^{3-} < 6{\cdot}1\ \text{M}$
$UO_2(H_2PO_4)_2\cdot 3H_2O$	$6{\cdot}1\ \text{M} < \Sigma PO_4^{3-}$

Another uranyl phosphate, monoclinic $H_{11}(UO_2)_2(PO_4)_5$, is reported to crystallize from hot 7 M phosphoric acid solution[172].

The most interesting compound seems to be the monohydrogen phosphate, $HUO_2PO_4\cdot 4H_2O$, the hydrogen of which may be replaced by monovalent and divalent metal ions without change of structure, e.g. Li, Na, K, Ca, Ba[171, 173]. This so-called uranium mica with its layer structure may also incorporate n-alkylammonium ions, with up to eight carbon atoms, arranged perpendicularly between the uranium phosphate layers.

Minerals which belong to this structural group are autenite, $Ca(UO_2PO_4)_2\cdot 10(6)H_2O$; tobernite, $Cu(UO_2PO_4)_2\cdot 8H_2O$; metazeunerite, $Cu(UO_2AsO_4)_2\cdot 8H_2O$; and uranocircite, $Ba(UO_2PO_4)_2\cdot 8H_2O$[174–177]. No structural details are available for any of these compounds, but it is suggested that these polynary oxides are built up of $UO_2PO_4^-$ (or $UO_2AsO_4^-$) sheets spread normal to the *c* axis and held together by the water molecules and the monovalent and divalent metal ions situated between the sheets. Such a structure resembles that found for the micas and other "plate-like" silicates[178].

The uranyl phosphates are sparingly soluble compounds, solubility products being $6{\cdot}4 \times 10^{-29}$ for $NaUO_2PO_4\cdot aq$ and $3{\cdot}6 \times 10^{-26}$ for $NH_4UO_2PO_4\cdot 3H_2O$. The thermal decomposition of ammonium uranyl phosphate at 700°C leads to the formation of uranyl pyrophosphate, $(UO_2)_2P_2O_7$, a hydrated form of which may be obtained by precipitation

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[171] A. Weiss, K. Harte and U. Hofmann, *Z. Naturforsch.* **12b** (1957) 351 and 669.

[172] E. Staritzky and D. T. Cromer, *Anal. Chem.* **28** (1956) 1354.

[173] F. Weigel, G. Hoffmann, paper presented at the Meeting of the Gesellschaft Deutscher Chemiker, Karlsruhe (1971).

[174] F. Hanic, *Czech. J. Phys.* **10** (1960) 169.

[175] E. S. Makarov and V. I. Ivanov, *Dokl. Akad. Nauk SSSR* **132** (1960) 673.

[176] Y. Takano, *Am. Mineralogist*, **46** (1961) 812.

[177] M. E. Mrose, *Am. Mineralogist*, **38** (1953) 476.

[178] R. G. Wykoff, *Crystal Structures*, 2nd ed. Vol. 3, p. 869. Interscience Publishers, New York (1965).

Notes to Table 17:

† Corresponding compounds have also been described for M(I) = Na and K.

‡ Corresponding compounds have also been described for M(II) = Mg, Ca, and Sr.

§ Probably subcell, normal cell $a = 3a'$.

[a] E. Staritzky and D. T. Cromer, *Anal. Chem.* **28** (1956) 1354.

[b] F. Weigel and G. Hoffmann, paper presented at the Meeting of the Gesellschaft Deutscher Chemiker, Karlsruhe (1971).

[c] J. Shankar and P. G. Khubchandani, *Anal. Chem.* **29** (1957) 1375.

[d] A. Burdese and M. L. Borlera, *Ann. Chim.* **53** (1963) 333.

[e] A. LaGinestra, G. Variali and M. Valigi, *Gazz. Chim. Ital.* **95** (1965) 1096.

[f] L. O. Hagman and P. Kierkegaard, *Acta Chem. Scand.* **23** (1969) 327.

[g] L. M. Douglas and E. Staritzky, *Anal. Chem.* **28** (1956) 1211.

[h] Y. Baskin, *J. Inorg. Nucl. Chem.* **29** (1967) 383.

[i] C. Keller and K. H. Walter, *J. Inorg. Nucl. Chem.* **27** (1965) 1253.

[k] C. W. Bjorklund, *J. Am. Chem. Soc.* **79** (1957) 6347.

[l] R. M. Douglass, *Acta Cryst.* **15** (1962) 505.

[m] F. Weigel and H. Haug, *J. Inorg. Nucl. Chem.* **27** (1965) 1253.

[n] S. Fried, F. Hageman and W. Zachariasen, *J. Am. Chem. Soc.* **72** (1950) 771.

TABLE 18. CRYSTALLOGRAPHIC DATA FOR ACTINIDE ARSENATES

Valency	Compound	Lattice symmetry	Space group	Lattice constants				Ref.
				a (Å)	*b* (Å)	*c* (Å)	α (β) (°)	
VI	$HUO_2AsO_4 \cdot 4H_2O$	Tetragonal	*P4/nmm*	7·12		8·77		a
	$NH_4UO_2AsO_4 \cdot 3H_2O$†	Tetragonal	*P4/nmm*	7·17		9·06		a
	$Mg(UO_2AsO_4)_2 \cdot 8H_2O$‡	Tetragonal	*I4/mmm*	7·17		17·16		a
	$HNpO_2AsO_4 \cdot 4H_2O$	Tetragonal	*P4/nmm*	7·15		8·87		a
	$NH_4NpO_2AsO_4 \cdot 3H_2O$†	Tetragonal	*P4/nmm*	7·18		9·06		a
	$Mg(NpO_2AsO_4)_2 \cdot 8H_2O$‡	Tetragonal	*I4/mmm*	7·09		17·47		a
IV	$(Ca_{0.5}, Th_{0.5})AsO_4$	Tetragonal	$P2_1/n$	7·197		6·424		b
	$(Cd_{0.5}, Th_{0.5})AsO_4$	Tetragonal	$P2_1/n$	7·150		6·420		b
III	$PuAsO_4$	Monoclinic	$P2_1/n$	6·92	7·09	6·66	105·45	c
	$AmAsO_4$	Monoclinic	$P2_1/n$	6·89	7·06	6·62	105·50	c

† Corresponding compounds have also been described for M(I) = Li, Na, and K.
‡ Corresponding compounds have also been described for M(II) = Ca, Sr, and Ba.

[a] F. Weigel and G. Hoffmann, paper presented meeting of the Gesellschaft Deutscher Chemiker, Karlsruhe (1971).

[b] H. Schwarz, *Z. anorg. allg. Chem.* 334 (1964) 175.

[c] C. Keller and K. H. Walter, *J. Inorg. Nucl. Chem.* 27 (1965) 1253.

reactions. Sodium uranyl metaphosphate, $Na_2[(UO_2)_2(PO_3)_6]$, is obtained by the reaction of uranyl ions with sodium metaphosphate (Graham's salt)[179].

Crystalline $HNpO_2PO_4 \cdot 4H_2O$, which is isostructural with the corresponding uranium compound, is prepared by the reaction between NpO_2^{2+} ions and aqueous phosphoric acid. Neutralization of this monobasic acid with alkali and alkaline earth hydroxides yields the corresponding neutral salts, e.g. light violet, tetragonal $LiNpO_2PO_4 \cdot 4H_2O$ and brown-violet $Mg(NpO_2PO_4)_2 \cdot 9H_2O$[173].

Green plutonyl(VI) monohydrogenphosphate, $PuO_2HPO_4 \cdot 4H_2O$, which would probably be better formulated as $HPuO_2PO_4 \cdot 4H_2O$, precipitates on the addition of dilute phosphoric acid to a solution of Pu(VI) in 0·1 M nitric acid[180]. Treatment of this compound with 45% H_3PO_4 at 25°C for 14 days results in the formation of $PuO_2(H_2PO_4)_2 \cdot 3H_2O$, which is stable when washed with alcohol or ether, but undergoes hydrolysis when washed with water.

Rose-colored $NH_4PuO_2PO_4 \cdot 3H_2O$, which may be regarded as the ammonium salt of the formerly mentioned plutonylphosphoric acid, is obtained by the addition of an $(NH_4)_2HPO_4$ solution to a hot solution of Pu(VI) in 0·1 M nitric acid. Thermal decomposition is reported to result in the formation of the following compounds: $NH_4PuO_2PO_4 \cdot H_2O$ at 20–180°C, $NH_4PuO_2PO_4$ at 180–200°C, PuO_2HPO_4 at 410–510°C, and $(PuO_2)_2P_2O_7$ at 625–700°C[181].

[179] R. C. Mehrotra and N. R. Dhar, *Proc. Natl. Inst. Sci. India*, 16 (1950) 59.

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[181] R. G. Denotkina and V. B. Shevchenko, *Russ. J. Inorg. Chem.* 12 (1967) 42.

TABLE 19. STABILITY CONSTANTS FOR ACTINIDE COMPLEXES IN SOLUTION WITH PHOSPHORUS-CONTAINING ANIONS

Complexing agent	Metal ion	Composition of complex ion	Method of investigation	Stability constants	Ref.
H_3PO_4(= H_3L)	Ac^{3+}	AcH_2L^+	Extraction, $\mu = 0{\cdot}5$, 25°C	log β_1 = 1·59	a
	Th^{4+}	$ThHL^{2+}$	Solubility, $\mu = 0{\cdot}35$	log β_1 = 10·8	b
		$Th(HL)_2$		log β_2 = 22·8	
		$Th(HL)_3^{2-}$		log β_3 = 31·3	
	Pa(V)	$PaO(HL)^+$	Extraction, $\mu = 3{\cdot}0$ 1–3 M H^+, < 0·5 H_3L	log $K \sim 2$†	c
		PaO(HL)L		log $K \sim 4$‡	
	UO_2^{++}	$UO_2(HL)$	Solubility, $\mu = 0{\cdot}5$	log β_1 = 7·18	d
		$UO_2(HL)_2^{2-}$		log β_2 = 17·30	
	NpO_2^+	$NpO_2(HL)^-$	Ion exchange, $\mu = 0{\cdot}2$, 20°C	log β_1 = 2·85	e
		$NpO_2(H_2L)$		log β'_1 = 0·81	
	Pu^{3+}	$Pu(H_2L)^{2+}$	Ion exchange (?), $\mu = 1{\cdot}0$	log β_1 = 1·48	f
		$Pu(H_2L)_2^+$		log β_2 = 2·20	
		$Pu(H_2L)_3$		log β_3 = 2·90	
		$Pu(H_2L)_4^-$		log β_4 = 3·5	
	Pu^{4+}	$Pu(HL)^{2+}$	Solubility, 0·012 to 2 M H_3PO_4 + 2 M HNO_3, 25°C	log β_1 = 12·92	g
		$Pu(HL)_2$		log β_2 = 23·74	
		$Pu(HL)_3^{2-}$		log β_3 = 33·43	
		$Pu(HL)_4^{4-}$		log β_4 = 43·22	
		$Pu(HL)_5^{6-}$		log β_5 = 52·04	
	PuO_2^{++}	$PuO_2(H_2L)^+$	Extraction, $\mu = 0{\cdot}5$	log β_1 = 1·66	f
	Am^{3+}	$Am(H_2L)^{2+}$	Ion exchange (?), $\mu = 1{\cdot}0$	log β_1 = 1·48	
		$Am(H_2L)_2^+$		log β_2 = 2·10	
		$Am(H_2L)_3$		log β_3 = 2·85	
		$Am(H_2L)_4^-$		log β_4 = 3·4	
	Cm^{3+}	$Cm(H_2L)^{2+}$	Ion exchange (?), $\mu = 1{\cdot}0$	log β_1 = 1·48	f
		$Cm(H_2L)_2^+$		log β_2 = 2·08	
		$Cm(H_2L)_3$		log β_3 = 2·84	
		$Cm(H_2L)_4^-$		log β_4 = 3·1	
		CmL		log β'_1 = 17·5	
		CmL_2^{3-}		log β'_2 = 34·1	
$H_4P_2O_7$(= H_4L)	Th^{4+}	ThL_2^{4-}	Solubility, 20°C	log K = 5·26§	h
$H_3P_3O_9$(= H_3L)	Am^{3+}	AmL	Ion exchange, μ = 0·2, 25°C	log β_1 = 3·48	i
	Cm^{3+}	CmL	Ion exchange, μ = 0·2, 25°C	log β_2 = 3·64	

† For the reaction $PaO(OH)^{2+} + H_3L \rightleftharpoons PaO(HL)^+ + H^+ + H_2O$.

‡ For the reaction $PaO(OH)^{2+} + 2H_3L \rightleftharpoons Pa(HL)L + 2H^+ + 2H_2O$.

§ For the reaction $ThL + L^{4+} \rightleftharpoons ThL_2^{4-}$.

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The equilibrium constants[181] for the reactions

$$NH_4^+ + PuO_2^{2+} + PO_4^{3-} \rightleftharpoons NH_4PuO_2PO_4$$

and

$$PuO_2^{++} + HPO_4^{2-} \rightleftharpoons PuO_2HPO_4$$

are, respectively,

$$K = \frac{[NH_4PuO_2PO_4]}{[NH_4^+][PuO_2^{2+}][PO_4^{3-}]} = 2{\cdot}7 \times 10^{21}$$

and

$$K = \frac{[PuO_2HPO_4]}{[PuO_2^{2+}][HPO_4^{2-}]} = 1{\cdot}5 \times 10^{8}$$

Only few data are available for uranyl(VI) arsenates. The following compounds have been described: $HUO_2AsO_4 \cdot 4H_2O$, $(UO_2)_3(AsO_4)_2 \cdot 12H_2O$ and $(UO_2)_2As_2O_7$. Substitution of hydrogen in $HUO_2AsO_4 \cdot 4H_2O$ by metal ions leads to ternary arsenates such as $KUO_2AsO_4 \cdot 4H_2O$, $Ca(UO_2AsO_4)_2 \cdot 4H_2O$ and $Cu(UO_2AsO_4)_2 \cdot 4H_2O$, which are isostructural with the corresponding phosphates[171].

Pentavalent actinide elements

Several soluble ionic phosphate complexes of pentavalent actinide elements have been described, but only two papers deal with solid compounds.

White, amorphous, basic protactinium phosphate, $PaO(OH)HPO_4 \cdot aq$, has been obtained by the addition of a dilute phosphoric acid solution to a dilute Pa(V) solution in 2·5 molar in sulfuric acid[182]:

$$PaO(SO_4)_2^- + H_2PO_4^- + H_2O \rightarrow PaO(OH)HPO_4 + 2HSO_4^-$$

The precipitate is soluble in both 2·5 M HF and 11 M HP_3O_4. Infrared studies have confirmed the presence of the PO_4^{3-} ion, but it was not possible to unambiguously identify a band due to the Pa = O group. Heating the amorphous precipitate to 800°C or 1050°C results in the formation of two different anhydrous phosphates of unknown compositions and structures.

The addition of $(NH_4)_2HPO_4$ to a solution of Pu(V) in dilute nitric acid yields a white precipitate of ammonium plutonyl(V) hydrogen phosphate tetrahydrate $(NH_4)PuO_2HPO_4 \cdot 4H_2O$[183].

Tetravalent actinide elements

Compounds of tetravalent thorium and uranium with anions containing phosphorus in a lower oxidation state are ill-defined. The preparation of gelatinous thorium hypophosphate by precipitation proceeds according to the equation

$$Th^{4+} + H_2P_2O_6^{2-} \rightarrow ThP_2O_6 + 2H^+$$

Uranium phosphite, $U(HPO_3)_2 \cdot 4H_2O$, and hypophosphite, $U(H_2PO_2)_4$, and similar compounds of thorium have been described, but preparative details are lacking.

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Thorium phosphate, $Th_3(PO_4)_4 \cdot aq$, precipitates on the addition of phosphate ions to a thorium(IV) solution. The anhydrous phosphate is one of three phosphates which have been identified by thermal studies of the ThO_2–P_2O_5 system[184], the other compounds being $Th_3P_2O_{11}$ and the pyrophosphate ThP_2O_7 which exists in two crystal modifications. Extensive solid solution on either side of $Th_3(PO_4)_4$ is observed. Studies of the ThP_2O_7–ZrP_2O_7 system have shown that a series of metastable, low-expansion, cubic solid solutions are obtained at room temperature by a process of mutual stabilization. These solid solutions are generally stable only above the inversions of ZrP_2O_7 and ThP_2O_7 at 300°C and 1294°C, respectively[185]. Phosphates of the type $(M^{II}_{0\cdot5}, Th^{IV}_{0\cdot5})PO_4$, with M = Ca, Sr, Cd and Pb, which are prepared by solid state reactions at 1000–1200°C, are isostructural with monoclinic $CePO_4$[186].

Thorium hydrogen phosphate, $Th(HPO_4)_2 \cdot 4H_2O$, and some ternary thorium phosphates such as $(NH_4)_2Th(PO_4)_2 \cdot 5H_2O$ and $KTh(OH)_2PO_4 \cdot 3 \cdot 5H_2O$ have been prepared from aqueous solutions by the reaction between thorium nitrate and phosphoric acid and alkali metal phosphates[187]. These compounds have only been characterized by their composition, thermal behavior and i.r. spectra.

Solubility measurements in the UO_2–P_2O_5–H_2O system at 25°C have proved the existence of $U(HPO_4)_2 \cdot 6H_2O$ at $< 9\cdot8$ M ΣPO_4^{3-} and $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ at $> 9\cdot8$ M ΣPO_4^{3-} as the equilibrium solid phases[188]. A mixed phosphate $U(HPO_4)(H_2PO_4)_2 \cdot 5H_2O$ also forms, especially at temperatures between 174° and 320°C for $0\cdot4$–$0\cdot5$ M U^{4+} and $17\cdot6$ M ΣPO_4^{3-}[189, 190]. In mixed phosphoric acid–perchloric acid solutions $U(H_2PO_4)(ClO_4)_2 \cdot xH_2O$ ($x = 4$ and 6) precipitates.

U(IV) pyrophosphate, UP_2O_7, and U(IV) metaphosphate, $U(PO_3)_4$, both of which exist in two crystal modifications, are prepared by solid state reactions[191–194]. Orthorhombic β-$U(PO_3)_4$, which is probably metastable, transforms endothermically and irreversibly to monoclinic α-$U(PO_3)_4$ which begins to decompose to UP_2O_7 and P_2O_5 at 1200°C[192]. $(Ca_{0\cdot5}, U_{0\cdot5})PO_4$, with the monazite-type of structure, similar to the corresponding thorium compound, is obtained by heating the co-precipitated single phosphates in a stream of nitrogen at 950°C[195]. A double pyrophosphate of composition $Na_4U(P_2O_7)_2 \cdot 8H_2O$ has also been described.

A slightly soluble, gelatinous plutonium(IV) hydrogen phosphate, $Pu(HPO_4)_2 \cdot aq$ (solubility product 2×10^{-28}), precipitates on the addition of phosphoric acid to a weakly acid Pu(IV) solution[196]. Red $Pu_2H(PO_4)_3 \cdot aq$ and rose to green–brown $Pu_3(PO_4)_4 \cdot aq$ are obtained by treating $Pu(HPO_4)_2 \cdot aq$ with HNO_3–H_3PO_4 mixtures at 110°C. Cubic plutonium pyrophosphate, PuP_2O_7, forms on the thermal decomposition (950°C) of a so-called Pu(IV) oxalatophosphate, which is precipitated from a solution containing Pu(IV), $H_2C_2O_4$ and

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H_3PO_4 in the ratio 1:5:100[197]. PuP_2O_7 is stable in air up to about 1000°C, but decomposes in a vacuum to $PuPO_4$. Orthorhombic Pu(IV) metaphosphate forms when PuO_2 is treated with metaphosphoric acid[198]. These compounds are isostructural with their thorium, uranium and neptunium analogues (Table 17) (for the Np(IV)–P_2O_5 system only NpP_2O_7 has been described[199]).

In addition to the above compounds, several amorphous, ill-defined Pu(IV) precipitates have been described, to which formulas such as $H_6Pu(HPO_4)_5 \cdot aq$ and $H_4Pu(HPO_4)_4$ have been assigned. With the exception of the Pu:PO_4^{3-} ratio and solubility data, no other details of these rose-colored products are known[200]. No reliable data on actinide(IV) arsenates have yet been published.

Trivalent actinide elements

Actinide(III) phosphate hemihydrates $MPO_4 \cdot 0{\cdot}5H_2O$ (M = Ac, Pu, Am, Cm) are obtained by the addition of phosphate ions to weakly acidic solutions[197,199–201] of M^{3+}. To obtain well-crystallized products it is necessary to digest the precipitates under the mother liquor for some hours at elevated temperatures. The actinide(III) phosphate hemihydrates crystallize with hexagonal symmetry (Table 17). The water of crystallization is removed at temperatures in excess of 300°C; the anhydrous phosphates, MPO_4, possess monoclinic symmetry. They are isostructural with the minerals huttonite ($ThSiO_4$) and monazite ($CePO_4$); crystallographic data are listed in Table 17. The anhydrous phosphates, which are insoluble in dilute acids, exhibit remarkable thermal stability, e.g. blue $PuPO_4$ decomposes only at 1400–1500°C in a high vacuum. Thus, it is also possible to prepare these compounds by thermal reactions, e.g. by heating a mixture of AmO_2 and $(NH_4)_2HPO_4$ to temperatures above 600°C[199].

Blue plutonium and rose americium arsenates, $PuAsO_4$ and $AmAsO_4$, are prepared by precipitation reactions, e.g. the addition of an ammonium hydrogen arsenate solution to weakly acidic Pu^{3+} or Am^{3+} solutions[199]. They crystallize with the monoclinic $CePO_4$-type of structure (Table 18). The actinide(III) arsenates are thermally less stable than the phosphates; $AmAsO_4$, however, may also be obtained by the reaction between AmO_2 and $(NH_4)_2HAsO_4$ at 600–700°C.

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CARBONATES, NITRATES, SULPHATES, SULPHITES, SELENATES, SELENITES, TELLURATES AND TELLURITES

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1. CARBONATES

Introduction

Of the information available on the actinide carbonates the great majority pertains to thorium and uranium compounds. Few simple carbonates have been characterized to date. Thus, no tetravalent or pentavalent carbonates have been prepared directly, although there is evidence for the formation of $Pu(CO_3)_2$ during the thermal decomposition of $Pu(C_2O_4)_2 \cdot 3H_2O$ in nitrogen, and the only trivalent compounds characterized to date are $Am_2(CO_3)_3$ (and its hydrates) and $Cm_2(CO_3)_3$. The hexavalent oxycarbonates UO_2CO_3 and PuO_2CO_3 are known and the tetravalent americium compound $AmOCO_3$ has been identified during the thermal decomposition of $Am_2(CO_3)_3$ in oxygen. The thorium(IV) and plutonium(IV) compounds reported as $ThOCO_3 \cdot xH_2O$ ($x = 1$, 2 or 8) and $PuOCO_3 \cdot 2H_2O$, respectively, may be hydroxycarbonates of the type $M^{IV}(OH)_2CO_3 \cdot xH_2O$. Trivalent oxycarbonates of the types $M^{III}{}_2O(CO_3)_2$ and $M^{III}{}_2O_2CO_3$ appear to form when americium and curium sesquicarbonates are heated *in vacuo*, but they have not been prepared by other methods. The majority of the reports on actinide carbonate chemistry deal with the formation of carbonato-complexes and a wide range of such compounds is known for both tetra- and hexavalent elements; in addition, a few tri- and pentavalent complexes have been characterized. Neither solid carbonates nor carbonato-complexes are yet known for the elements protactinium and berkelium to lawrencium inclusive.

Although the carbonates of individual actinide elements have been briefly reviewed, e.g. thorium[1], uranium[2], neptunium[3,4] and plutonium[5,6], the carbonate chemistry of this series of elements has not previously been discussed in a single article. The present review covers the literature to the end of 1970. As will become apparent to the reader, few chemical properties have been recorded for the presently known compounds, few structural data are available, and magnetic and thermodynamic properties do not appear to have been recorded. The majority of the articles on actinide carbonate chemistry have appeared in the Russian literature.

Trivalent carbonates and carbonato-complexes

Preparation and Properties of Carbonates and Oxycarbonates

$Am_2(CO_3)_3 \cdot 2H_2O$, identified crystallographically (Table 1), is reported to precipitate as a pink solid when a solution of americium(III) hydroxide in $Cl_3C \cdot COOH$ is heated at

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50°C[7]. A tetrahydrate, $Am_2(CO_3)_3 \cdot 4H_2O$, has subsequently been isolated from sodium bicarbonate solution saturated with carbon dioxide[8]. Thermal decomposition of both hydrates leads to the formation of $Am_2(CO_3)_3$[8, 9]; the oxalate hydrate $Am_2(C_2O_4)_3 \cdot 10H_2O$ is also converted to $Am_2(CO_3)_3$ (via the anhydrous oxalate) above 390°C[9]. The latter technique has been employed for the preparation of $Cm_2(CO_3)_3$[10], which is a white solid; the decomposition is believed to involve the intermediate formation of $Cm_2(CO_3)_{1\cdot5}(C_2O_4)_{1\cdot5}$. Although many lanthanide carbonates have been identified during the vacuum thermal decomposition of lanthanide oxalates (for example, see ref. 11), there appears to be no evidence for the formation of $Pu_2(CO_3)_3$ during the decomposition of the trivalent oxalate hydrate[12]. This may be a reflection of the easier oxidation of plutonium(III) since the product, both in air and an inert atmosphere, is plutonium dioxide. Decomposition of americium(III) oxalate hydrate under the influence of the α-particles emitted by the americium atoms (Am-241) is reported[13] to result in the formation of the hemihydrate, $Am_2(CO_3)_3 \cdot 0{\cdot}5H_2O$.

TABLE 1. CRYSTALLOGRAPHIC DATA FOR ACTINIDE CARBONATES AND CARBONATO-COMPLEXES

Compound	Symmetry/Space group†	Lattice parameters				Ref.
		a_0 (Å)	b_0 (Å)	c_0 (Å)	β°	
$Am_2(CO_3)_3 \cdot 2H_2O$	C; —	14·09	—	—	—	a
$KNpO_2CO_3$	H; D^4_{6h}–$C6mmc$	5·120	—	9·971	—	b
*$KPuO_2CO_3$	,, ,,	5·093	—	9·815	—	b, c
$KAmO_2CO_3$	,, ,,	5·112	—	9·740	—	b
*$NH_4PuO_2CO_3$	,, ,,	5·09	—	10·39	—	c
$RbAmO_2CO_3$	,, ,,	5·12	—	10·46	—	c
*UO_2CO_3	O; D^{13}_{2h}–$Pmmn$	4·85	9·22	4·30	—	d, j
$Na_4UO_2(CO_3)_3$	H; —	4·324	—	12·802	—	i
$K_4UO_2(CO_3)_3$	M; C^6_{2h}–$C2/c$	10·22	9·18	12·18	94·78	e
$(NH_4)_4UO_2(CO_3)_3$	M; ,,	10·65	9·36	12·845	96·4	f
*$K_3NaUO_2(CO_3)_3$	H; D^4_{3h}–$P\bar{6}2c$	9·29	—	8·26	—	g
$K_2Ca_3(UO_2)_2(CO_3)_6 \cdot 9H_2O$	O; —	17·98	18·29	16·95	—	h

* Full structural information is given in the reference cited.
† C, cubic; H, hexagonal; O, orthorhombic; M, monoclinic.

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When heated at elevated temperatures in a vacuum $Am_2(CO_3)_3$[9] and $Cm_2(CO_3)_3$[10] decompose to their respective sesquioxides with the successive, intermediate formation of oxycarbonates of the types $M^{III}{}_2O(CO_3)_2$ and $M^{III}{}_2O_2CO_3$ (M^{III} = Am and Cm); $Am_2O_2CO_3$ has also been observed[9] to form during the thermal decomposition of the trivalent formate hydrate, $Am_2(HCOO)_3 \cdot 0 \cdot 2H_2O$.

The thermal decomposition of $Am_2(CO_3)_3$ in oxygen also results in the formation of $Am_2O(CO_3)_2$ which subsequently reacts with oxygen to form[8] the tetravalent oxycarbonate $AmOCO_3$ at *ca.* 300°C; at higher temperatures this decomposes to yield AmO_2.

Preparation and Properties of Trivalent Carbonato-complexes

Trivalent complexes have scarcely been studied; the only report appears to be that dealing with the americium(III) complexes $Na[Am(CO_3)_2] \cdot 4H_2O$ and $Na_3[Am(CO_3)_3] \cdot 3H_2O$ which precipitate from aqueous sodium bicarbonate (0·5 M) and aqueous sodium carbonate (1·5 M) solution, respectively[8]. Analogous trivalent lanthanide compounds are also known[14]. Thermal decomposition of the americium(III) complexes proceeds via the intermediate formation of the anhydrous carbonato-complexes to mixtures of AmO_2 and sodium carbonate[8]. Trivalent curium is known to precipitate from solution on the addition of potassium carbonate, but the white solid, presumably a carbonato-complex, has not been characterized[15].

Tetravalent carbonates and carbonato-complexes

The only dicarbonate known at present is $Pu(CO_3)_2$ and the evidence for the existence of this compound has only been obtained during studies of the thermal decomposition of plutonium(IV) oxalate hydrates. Decomposition in nitrogen results in the formation of $Pu(CO_3)_2$ at *ca.* 300°C whilst decomposition in air is believed to yield PuO_2–$Pu(CO_3)_2$ mixtures[16,17].

Thorium[18–20] and plutonium[21,22] are reported to form tetravalent compounds of the type $M^{IV}OCO_3 \cdot xH_2O$ and the isolation of a tetravalent uranium oxycarbonate of undetermined water content has been briefly mentioned[23]. In the absence of reliable structural information it is quite possible that these compounds are hydroxy- rather than oxycarbonates, viz. $M^{IV}(OH)_2CO_3 \cdot xH_2O$. Thorium compounds are obtained as white precipitates under a variety of conditions. For example, treatment of thorium(IV) hydroxide with carbon dioxide under pressure[18], and the controlled addition of sodium or ammonium carbonate to aqueous thorium nitrate solutions[19] are reported to yield the dihydrate $ThOCO_3 \cdot 2H_2O$ (or $Th(OH)_2CO_3 \cdot H_2O$) and monohydrate, respectively. A trihydrate[20] and a heptahydrate[18] have also been isolated by the addition of alkali metal carbonates to aqueous thorium(IV) solutions; the latter is converted to the dihydrate[18] at 120°C in air.

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Decomposition of $[NH_4]_4[Pu(CO_3)_4]\cdot 4H_2O$ in air at room temperature is stated[21] to slowly result in the formation of $PuOCO_3\cdot 2H_2O$ (or $Pu(OH)_2\cdot CO_3\cdot H_2O$) and the same product is apparently formed[22] as a result of the internal α-radiation decomposition of either $Pu(C_2O_4)_2\cdot 6H_2O$ or $[NH_4]_6[Pu(C_2O_4)_5]\cdot xH_2O$. The existence of basic carbonates such as $ThO_2\cdot ThOCO_3\cdot 0{\cdot}5H_2O$, and $PuO_2\cdot PuOCO_3$ has also been suggested[18,21], but the evidence that these are individual compounds and not mixtures is far from conclusive.

The formation of $AmOCO_3$ during the thermal decomposition of the trivalent carbonate in oxygen is discussed above (p. 279).

Preparation and Properties of Tetravalent Carbonato-complexes

The elements thorium, uranium and plutonium form a wide range of tetravalent carbonato-complexes, but analogous compounds have not yet been characterized for other actinide elements. Numerous complexes have been characterized for the $[M(CO_3)_5]^{6-}$, $[M(CO_3)_4]^{4-}$ and $[M(CO_3)_3]^{2-}$ anions and in many instances a range of different hydrates is known for a given cation, e.g. $Na_6[Th(CO_3)_5]\cdot xH_2O$ with $x = 20$, 12, 3, 1 and 0. Information on the various complexes is summarized in Table 2. Full preparative details will be found in the references cited. In general the complexes have been isolated by the addition of the appropriate carbonate or bicarbonate to the tetravalent hydroxide or to solutions of the actinide(IV) sulphate, nitrate, or oxalate, by metatheses involving ammonium carbonate solutions of the tetravalent actinide and the appropriate bicarbonate, and by dehydration of higher hydrates. Additional plutonium(IV) complexes, $K_8[Pu(CO_3)_6]\cdot xH_2O$ and $K_{12}[Pu(CO_3)_8]\cdot xH_2O$, are reported to precipitate from high concentrations of potassium carbonate[24]; the analogous thorium and uranium complexes have not been characterized. This is surprising, if the plutonium complexes are genuine, since the ionic radii of thorium(IV) and uranium(IV) are greater than that of plutonium(IV) (p. 153).

Although many complexes have been isolated, little work appears to have been done on their chemical and physical properties. The ammonium complexes are the least stable, $[NH_4]_6[Th(CO_3)_5]\cdot 3H_2O$, for example, decomposing quickly when exposed to the atmosphere. They all appear to undergo rapid hydrolysis in water, are decomposed by the addition of aqueous acids and are insoluble in organic solvents.

No structural data are available for the tetravalent carbonato-complexes, but recent infrared studies[20] have indicated the presence of bidentate, or both bi- and monodentate, carbonate groups in several of the thorium(IV) complexes. The results of this investigation (Table 3) contradict earlier deductions[25] that the sodium and potassium pentacarbonato-complexes contain ionic carbonate and should be represented as $M^{I}_{4}[Th(CO_3)_4]\cdot nH_2O\cdot M^{I}_{2}CO_3$. The recent interpretation[26] of the mode of thermal decomposition of $Tl_6[Th(CO_3)_5]\cdot 2H_2O$, stated to indicate the composition $[Th(CO_3)_2\cdot 2H_2O]\cdot 3Tl_2CO_3$, is as surprising as the author's opinion that 6-coordination can be expected for thorium(IV) since, in fact, this coordination is relatively rare for the large Th(IV) cation.

It would obviously be valuable to have structural data obtained by X-ray or neutron diffraction techniques on certain of the tetravalent complexes, many of which have potentially high coordination numbers.

In addition to the complexes listed in Table 2, mixed carbonato–oxalato-complexes are

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TABLE 2. EXAMPLES OF TETRAVALENT ACTINIDE CARBONATO-COMPLEXES

Complex type*†	Values of n for M =		
	Th	U	Pu
$Na_6[M(CO_3)_5]\cdot nH_2O$	$20^{a,b,c}$; 12^{a-e}; $3^{a,b}$; 1^a; 0^a	11^k	4^n; 2^n
$K_6[M(CO_3)_5]\cdot nH_2O$	$10^{a,f}$	6^l	3–4^o
$Tl_6[M(CO_3)_5]\cdot nH_2O$	2^g; 1^a; 0^f		
$[CN_3H_6]_o[M(CO_3)_5]\cdot nH_2O$	$4^{a,b,h}$; $3^{a,h}$; 0^h	5^l; 4^m	
$[NH_4]_6[M(CO_3)_5]\cdot nH_2O$	$3^{a,l}$		$?^p$
$[NH_4]_2[CN_3H_6]_4[M(CO_3)_5]\cdot nH_2O$		$?^k$	
$Ba_3[M(CO_3)_5]\cdot nH_2O$	7^a		
$Ca_3[M(CO_3)_5]\cdot nH_2O$	7^a		
$[Co(NH_3)_6]_2[M(CO_3)_5]\cdot nH_2O$	$?^a$; $9^{b,i}$; 6^i; $4^{b,l}$	4^l; 5^l; $?^k$	
$[NH_4]_4[M(CO_3)_4]\cdot nH_2O$		6^q	4^p
$[Na]_4[M(CO_3)_4]\cdot nH_2O$			3^n
$[CN_3H_6]_4[M(CO_3)_4]\cdot nH_2O$		4^k; 10^q	
$[NH_4]_3[CN_3H_6]_3[M(CO_3)_5]\cdot nH_2O$	3^a	2^l	
$[NH_4]_2[M(CO_3)_3]\cdot nH_2O$	$6^{a,f}$		
$[C_2H_4(NH_2)_2H_2]\,[M(CO_3)_3]\cdot nH_2O$		4^l	

* In view of the lack of structural data the formulae are represented with water molecules outside the sphere of coordination for convenience.

† The range of hydrates reported for certain cations probably merely reflects different drying conditions.

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[n] A. D. Gel'man and L. M. Zaitseva, *Zhur. Neorg. Khim.* 3 (1958) 1551.

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[p] A. D. Gel'man and L. M. Zaitseva, *Russ. J. Inorg. Chem.* 4 (1959) 1243.

[q] A. Menes, ref. 5 in ref. o above.

known for tetravalent thorium and plutonium (see refs. 27 to 31) and a few hydroxycarbonato-complexes (described in references cited with Table 2) have also been characterized.

Pentavalent carbonates and carbonato-complexes

Neither pentavalent carbonates nor oxycarbonates have been characterized to date, but several carbonato-complexes are known.

Preparation and Properties of Pentavalent Carbonato-complexes

Pentavalent oxycarbonato-complexes of the type $M^IM^VO_2CO_3$ are known for neptunium[32] (M^I = K), plutonium[32-34] (M^I = K and NH_4) and americium[32-35] (M^I=K, NH_4 and Rb); additional complexes of the type $M^I_5[M^VO_2(CO_3)_3]$ (M^I = K and Cs; M^V = Np[36,37] and Am[38,39]) and the dicarbonato-complex $K_3[AmO_2(CO_3)_2]$ have also been characterized[40], but the analogous plutonium compounds are unknown.

TABLE 3. CARBONATE GROUP VIBRATIONAL FREQUENCIES FOR CERTAIN THORIUM(IV) CARBONATO-COMPLEXES WITH AN INDICATION OF THE TYPE OF GROUP PRESENT[a]

Compound	Bidentate carbonato-group					Unidentate carbonato-group ν_5 (CO)
	ν_1 (CO)	ν_5 (CO)	ν_2 (CO)	ν_3	$\nu_3[\delta(CO) + \delta(MO_2C)]$	
$Na_6[Th(CO_3)_5]\cdot 12H_2O$	1535	1340 1378	1050 1054 1067	867	725 735	
$Na_6[Th(CO_3)_5]\cdot xH_2O$*	1570	1350 1372	1048 1063	858	713 718	
$Na_6[Th(CO_3)_5]\cdot 3H_2O$	1570	1350 1375	1046	856	718	
$(CN_3H_6)_6[Th(CO_3)_5]\cdot 4H_2O$	1600?	1370	1048 1056	862	723	1480
$(CN_3H_6)_6[Th(CO_3)_5]$	1590?	1350	1047 1059	859	723	1485
$[Co(NH_3)_6]_2[Th(CO_3)_5]\cdot 4H_2O$†	1641 1665	1345	1053	870	778 782	1441
$[Co(NH_3)_6]_2[Th(CO_3)_5]\cdot 9H_2O$†	1500	1370	1051	860	726	
$Th(OH)_2CO_3\cdot 2H_2O$	1535	1380	1070	840	730	(1460?)

* Sorbed moisture.

† Superposition of absorption bands of degenerate vibrations of coordinated ammonia is possible.

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$KNpO_2CO_3$ is obtained[32] by the addition of potassium bicarbonate to a solution of Np(V) in dilute nitric acid (final solution, pH = 7, 0·1 M bicarbonate) followed by heating at *ca.* 90°C, whereas the tricarbonato-complexes $K_5[NpO_2(CO_3)_3]$ and $Cs_5[NpO_2(CO_3)_3]$ are formed on the addition of an excess of a 50% solution of the appropriate alkali metal carbonate to neptunium(V) hydroxide[36]. Similarly, the americyl(V) complexes $KAmO_2CO_3$[32,35], $K_3[AmO_2(CO_3)_2]$[40] and $K_5[AmO_2(CO_3)_3]$[38,39] precipitate from solutions containing increasing amounts of carbonate. $KPuO_2CO_3$[32,33] and $NH_4PuO_2CO_3$[33] are obtained in a similar manner to $KNpO_2CO_3$.

Available crystallographic data are shown in Table 1. Ellinger and Zachariasen[34] have deduced the structures of the isostructural complexes $KPuO_2CO_3$, $NH_4PuO_2CO_3$ and $RbAmO_2CO_3$ from powder data and suggest that the pentavalent actinide metal is bonded to six carbonate oxygens (M^V–O, 2·55 Å (Pu); 2·56 Å (Am)) in a plane normal to the linear $O=M^V=O$ group. Approximate Pu=O and Am=O distances in the latter groups are 1·94 Å and 1·93 Å respectively. The only infrared data available are those for the tricarbonato-complexes of neptunium(V) for which $\nu_{Np=O}$ is observed at 780 and 775 cm^{-1} for the potassium and caesium salts, respectively[36,37]. The neptunium–oxygen bond length in the NpO_2^+ group is estimated as 1·8 Å on the basis of these results; the carbonate groups appear to be bidentate.

Hexavalent carbonates and carbonato-complexes

Preparation and Properties of the Actinyl(VI) Carbonates

The preparation and properties of uranyl carbonate, UO_2CO_3, which exists naturally as the mineral rutherfordite, have been reviewed by Čejka[41]. It is conveniently obtained by a variety of methods, the best of which appears to be the reaction between an aqueous suspension of UO_3 and carbon dioxide under pressure[42–48] at *ca.* 100°C. Alternative routes include treatment of alcoholic uranyl nitrate solutions with carbon dioxide under pressure[49], the reaction between carbon dioxide and hydrated uranium trioxide followed by dehydration of the initial product at 50°C[50], and dehydration of $UO_2CO_3 \cdot 2{\cdot}5H_2O$ at 160°C *in vacuo*[23].

Plutonyl carbonate, a pink solid, is conveniently prepared[51] by the thermal decomposition of $[NH_4]_4[PuO_2(CO_3)_3]$ at 120–130°C. Although the analogous neptunyl(VI) carbonate is unknown, it is likely that high-pressure reactions involving $NpO_3 \cdot H_2O$ and carbon dioxide (cf. UO_2CO_3 above) will result in the formation of this compound.

Although little is known concerning the chemistry of PuO_2CO_3 the properties of UO_2CO_3 have been briefly studied. The structure of rutherfordite has been examined by Christ *et al.*[52] and that of synthetic UO_2CO_3 by Cromer and Harper[46]. The uranyl–oxygen distance

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in the linear O=U=O group is 1·67 Å[46]; the associated asymmetric stretching vibration occurs at 965 cm^{-1}[44]. UO_2CO_3 decomposes in a single step between 500° and 600°C to yield UO_3 and CO_2[43,47]; in contrast to this stability it is reported that PuO_2CO_3 decomposes at 140°C to form PuO_2[51]. Uranyl carbonate, which is only moderately soluble in water, can be converted directly to UO_2 by high-temperature reduction with formaldehyde sulphoxylates and formaldehyde–ammonium bisulphite mixtures[45].

Preparation and Properties of Hexavalent Carbonato-complexes

A wide range of uranyl(VI) carbonato-complexes has been prepared, but few analogous complexes are known for neptunyl(VI) and plutonyl(VI) at present. Examples of compounds containing anions of the types $[M^{VI}O_2(CO_3)_2]^{2-}$, $[M^{VI}O_2(CO_3)_3]^{4-}$ and $[(M^{VI}O_2)_2(CO_3)_5]^{6-}$ are shown in Table 4. General preparative methods include the addition of an excess of, or the stoichiometric amount of, the appropriate carbonate to an actinyl(VI) solution, hydroxide or oxide, the addition of the appropriate quantity of uranyl nitrate to an aqueous solution of $[NH_4]_4[UO_2(CO_3)_3]$ and metatheses involving solutions of ammonium uranyl(VI) carbonates and alkaline earth element compounds. Full preparative details for individual complexes will be found in the references cited with Table 4; Čejka[53] has reviewed the earlier work on uranyl(VI) carbonato-complexes. The addition of barium, calcium and sodium salts to solutions of americium(VI) in carbonate media results in the precipitation of complexes, but their compositions are unknown[54]. Mixed complexes such as $[NH_4]_2[Na]_2[UO_2(CO_3)_3]\cdot H_2O$[55], $CaMg[UO_2(CO_3)_3]\cdot 12H_2O$[56] (swartzite), $KNa_3[UO_2(CO_3)_3]$[57] and $K_2Ca_3[(UO_2)_2(CO_3)_5]\cdot 9H_2O$[58] have also been characterized and a few hydroxy-carbonato-[59–62], peroxy-carbonato-[63], oxalato-carbonato-[55,64] and fluoro-carbonato-[65] complexes are reported to form in aqueous media.

Available crystallographic data are presented in Table 1. Metal–oxygen stretching vibrations associated with the actinyl(VI) group have been recorded around 880 cm^{-1} (UO_2^{2+})[37,66–68] and 873 cm^{-1} (NpO_2^{2+})[37,67]; the calculated Np–O bond length in $K_4[NpO_2(CO_3)_3]$ is 1·75 Å.[67] Bands observed around 898 cm^{-1} in the infrared spectra of the unidentified americium(VI) complexes are believed to be associated with the AmO_2^{2+} group[54].

Thermal decomposition of $[NH_4]_4[UO_2(CO_3)_3]$ results in the formation of uranium

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TABLE 4. EXAMPLES OF ACTINIDE(VI) CARBONATO-COMPLEXES

Element	Complex type*	M	*n*	Reference
Uranium	$M_2^I[UO_2(CO_3)_2]\cdot nH_2O$	Li, Rb, Cs	0	a
		Na	0	a, l
		Na	2	f
		NH_4	1	b
		NH_4	2	c
	$M_4^I[UO_2(CO_3)_3]\cdot nH_2O$	Li, Rb, Cs	0	a
		Na	0	a, e, g, h, k, l
		K	0	a, g, u
		NH_4	0	b, c, d, e, g, u
		NH_4	3	e
	$M^{II}[UO_2(CO_3)_2]\cdot nH_2O$	Ba	4	c
	$M_2^{II}[UO_2(CO_3)_3]\cdot nH_2O$	Ca	0	m
		Ca	4	j
		Ca	9	b
		Ca	10	m
		Ba	5	b
		Ba	6	c, m
		Sr	0	b
		Sr	9	m
		Cu	1	b
		Ni	6	b
		Co	2	b
		Mn	0	i
		Mg	20	j
		Mg	18	o
	$M_4^{III}[UO_2(CO_3)_3]_3\cdot nH_2O$	La	0	n
	$M_6^I[(UO_2)_2(CO_3)_5]\cdot nH_2O$	Li, Na	0	a
		NH_4	2	c
		NH_4	3	b, c
	$M_3^{II}[(UO_2)_2(CO_3)_5]\cdot nH_2O$	Ba	10	c
Neptunium	$M_4^I[NpO_2(CO_3)_3]\cdot nH_2O$	K	0	q
Plutonium	$M_4^I[PuO_2(CO_3)_3]\cdot nH_2O$	K	0	s, q, r
		NH_4	0	p
	$M_6^I[(PuO_2)_2(CO_3)_5]\cdot nH_2O$	NH_4	2	t
	$M^{II}[PuO_2(CO_3)_2]\cdot nH_2O$	Ba	3	t
	$M_3^{II}[(PuO_2)_2(CO_3)_5]\cdot nH_2O$	Ba	10	t

* In view of the lack of structural information the formulae are shown with the water outside the sphere of coordination for convenience.

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[h] K. B. Brown and J. B. Schmitt, U.S. Report AECD 3229 (1950).

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[j] A. Chambionnot, *Compt. Rend.* **251** (1960) 2377.

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dioxide[69,70] whilst alkali metal and alkaline-earth metal uranyl carbonato-complexes yield metal uranates when heated to high temperatures (for example, see refs. 47, 71 and 72). As mentioned earlier, the controlled thermal decomposition of $[NH_4]_4[PuO_2(CO_3)_3]$ results in the formation of PuO_2CO_3[51].

2. NITRATES

Introduction

Few simple nitrates are known for the actinide elements. The only anhydrous compounds characterized to date are $ThO(NO_3)_2$, $Th(NO_3)_4$, $UO_2(NO_3)_2$ and $PuO_2(NO_3)_2$. Hydrated nitrates are known for thorium(IV) and uranium(VI) and for the elements protactinium, neptunium and plutonium in various valence states; these compounds are listed in Table 5. Nitrate complexes with a variety of donor ligands have been prepared for all these elements and nitrato-complexes of the types $M^I_2M^{IV}(NO_3)_6$ (M^I = univalent cation; M^{IV} = Th, U, Np and Pu), $M^{II}M^{IV}(NO_3)_6 \cdot 8H_2O$ (M^{II} = a divalent cation; M^{IV} = Th, U and Pu), $M^IPa(NO_3)_6$, $M^IM^{VI}O_2(NO_3)_3$ (M^{VI} = U, Np and Pu) and $M^I_2M^{VI}O_2(NO_3)_4$ (M^{VI} = U) are known. Solid nitrates do not appear to have been characterized for the elements beyond plutonium and, in fact, there are very few publications which deal with protactinium, neptunium and plutonium nitrates, the vast majority of the published information pertaining to thorium(IV) and uranium(VI) compounds. The present article covers work published to the end of 1970; the extensive literature on solvent extraction of actinide nitrates is not discussed. The earlier work on thorium(IV) nitrate compounds has been summarized by Flahaut[1] and that on uranium(VI) compounds by Huré[2] and by Tsapkina[73].

Tetravalent Nitrates

Preparation

Although a large number of different thorium tetranitrate hydrates have been reported at various times (see refs. 1 and 74 for summaries) a detailed investigation of the thorium nitrate–nitric acid–water system has revealed[74] that only $Th(NO_3)_4 \cdot 5H_2O$ and $Th(NO_3)_4 \cdot 4H_2O$ can be isolated as stable phases at room temperature. $Pu(NO_3)_4 \cdot 5H_2O$ crystallizes[75] from nitric acid solutions when they are allowed to evaporate slowly at room temperature whereas a dihydrate, $Np(NO_3)_4 \cdot 2H_2O$, is obtained[76] on vacuum evaporation of dilute nitric acid solutions containing neptunium(IV). Analogous uranium tetranitrate hydrates are unknown and attempts[77] to repeat earlier preparations of the basic nitrates $UO(NO_3)_2$ and $UO(NO_3)_2 \cdot 4H_2O$ have been unsuccessful. In view of the ready oxidation of protactinium(IV) it is unlikely that a tetranitrate or tetranitrate hydrates will be capable of existence.

Anhydrous thorium tetranitrate is obtained by vacuum thermal decomposition of either

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Table 5. Actinide Nitrates and Nitrate Hydrates

Valence state	Compounds known for: Th	Pa	U	Np	Pu
IV	$ThO(NO_3)_2$	—	—	—	—
	$Th(NO_3)_4$	—	—	—	—
	$Th(NO_3)_4 \cdot 2H_2O$(?)	—	—	$Np(NO_3)_4 \cdot 2H_2O$	—
	$Th(NO_3)_4 \cdot 4H_2O$	—	—	—	—
	$Th(NO_3)_4 \cdot 5H_2O$	—	—	—	$Pu(NO_3)_4 \cdot 5H_2O$
V		$PaO(NO_3)_3 \cdot xH_2O$	—	$NpO(NO)_3 \cdot 3H_2O$	—
		—	—	$NpO_2(NO_3) \cdot$	—
		—	—	$NpO_2(NO_3) \cdot H_2O$	—
VI			$UO_2(NO_3)_2$	—	$PuO_2(NO_3)_2$
			$UO_2(NO_3)_2 \cdot H_2O$	—	—
			$UO_2(NO_3)_2 \cdot 2H_2O$	—	$PuO_2(NO_3)_2 \cdot 2H_2O$
			$UO_2(NO_3)_2 \cdot 3H_2O$	—	$PuO_2(NO_3)_2 \cdot 3H_2O$
			$UO_2(NO_3)_2 \cdot 6H_2O$	$NpO_2(NO_3)_2 \cdot 6H_2O$	$PuO_2(NO_3)_2 \cdot 6H_2O$

$(NO_2)_2[Th(NO_3)_6]$[78] at 150°C, or $(NO)_2[Th(NO_3)_6]$[79] at 90°C. At higher temperatures the former complex decomposes to yield $ThO(NO_3)_2$[79]. No other anhydrous actinide(IV) nitrates are known; attempts to dehydrate $Th(NO_3)_4 \cdot 5H_2O$, $Np(NO_3)_4 \cdot 2H_2O$ and $Pu(NO_3)_4 \cdot 5H_2O$ have resulted in the ultimate formation of the dioxides (p. 288).

Structures and Properties

Determinations of the structure of $Th(NO_3)_4 \cdot 5H_2O$ by X-ray[80] and by neutron[81] diffraction are in excellent agreement. The four nitrate groups are each bidentate and three of the five water molecules are coordinated resulting in an 11-coordinate thorium atom. The structure derived by the neutron investigation[81] is illustrated in Fig. 1; Th–O (nitrate) distances range from 2·528 to 2·618 Å and Th–O (water) distances range from 2·438 to 2·473 Å. Two different types of hydrogen bonding are present, water–water and water–nitrate, with respective bond distances of 2·70 Å, and 2·90–2·95 Å. Unit cell dimensions for $Th(NO_3)_4 \cdot 5H_2O$ and the isostructural plutonium(IV) analogue are given in Table 6. Deductions based on infrared[82,83,85–87] and Raman[84,87,88] results that two types of water molecules are present and that all the nitrate groups are covalently bonded, are consistent with the above structure. Typical infrared data for thorium tetranitrate hydrates are given in Table 7 together with those for $Th(NO_3)_4$ and $Np(NO_3)_4 \cdot 2H_2O$. Th–O stretch-

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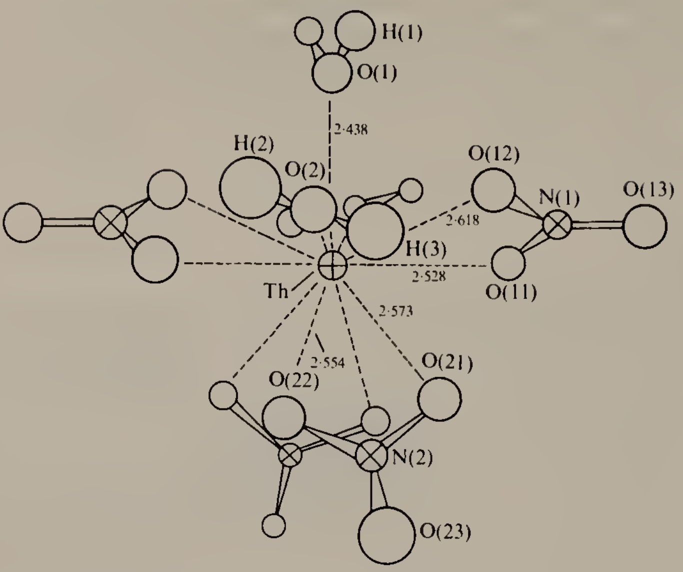

FIG. 1. Oxygen arrangement around the thorium atom in $Th(NO_3)_4 \cdot 5H_2O$ as viewed in the *b* direction. (Reproduced by permission from J. C. Taylor *et al.*, *Acta Cryst.* **20** (1966) 842.)

ing vibrations have been tentatively assigned at 244 cm^{-1} ($Th(NO_3)_4$), 249 and 218 cm^{-1} ($Th(NO_3)_4 \cdot 4H_2O$) and 244 and 211 cm^{-1} ($Th(NO_3)_4 \cdot 5H_2O$).

Thermal decomposition of thorium[86,89], neptunium[76], and plutonium[75,90] tetranitrate hydrates results in the ultimate formation of the respective dioxide. Anhydrous nitrates are not formed during such decompositions, but there is some evidence (see refs. 1 and 86) that lower thorium hydrates can be isolated by controlled decomposition of $Th(NO_3)_4 \cdot 5H_2O$ at 80°C; such products, however, are generally deficient in nitrate, e.g. $ThO_{0.15}(NO_3)_{3.7} \cdot 1 \cdot 1H_2O$[86]. The basic nitrate $ThO(NO_3)_2 \cdot H_2O$ is reported to form when the pentahydrate is heated at 140° and it is suggested, on the basis of infrared data, that Th–O–Th groups are present in this compound. An earlier report[91] that ionic nitrate is present in the lower hydrates produced by thermal decomposition of $Th(NO_3)_4 \cdot 4H_2O$ appears to be incorrect[85,86].

Addition of hydrogen peroxide to thorium in aqueous nitric acid results in the formation[92] of a polymeric peroxynitrate, $Th_6(OO)_{10}(NO_3)_4 \cdot 10H_2O$ whilst hydrolysis of thorium tetranitrate hydrates in aqueous solution yields hydroxy compounds[93] such as $Th_2(OH)_4(NO_3)_4 \cdot xH_2O$ and $Th_2(OH)_2(NO_3)_6 \cdot 8H_2O$. Unit cell dimensions for the last two compounds are given in Table 6 and the structure of $Th_2(OH)_2(NO_3)_6 \cdot 8H_2O$ is illustrated in Fig. 2. Thorium atoms[94] are linked by bridging oxygen atoms (O_{14} and O_{15}) the Th–Th separation in the discrete dinuclear groups being 3·988 Å. Three bidentate nitrate groups are coordinated to each thorium atom and a coordination number of 11 (cf. $Th(NO_3)_4 \cdot 5H_2O$) is achieved by coordination of three water molecules (O_{10}, O_{11} and O_{12}). Bond

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[89] W. W. Wendlandt, *Anal. Chim. Acta*, **15** (1956) 435.
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[93] G. Johansson, *Svensk. Kem. Tidskr.* **78** (1966) 486.
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TABLE 6. CRYSTALLOGRAPHIC DATA FOR ACTINIDE NITRATES AND NITRATO-COMPLEXES

Compound	Colour	Symmetry; Space group	Lattice parameters				Ref.
			a_0 (Å)	b_0 (Å)	c_0 (Å)	β°	
†$Th(NO_3)_4 \cdot 5H_2O$	White	O; $C_{2v}^{19}–Fdd2$	11·191	22·889	10·579	—	a, b
$Pu(NO_3)_4 \cdot 5H_2O$	Green	O; $C_{2v}^{19}–Fdd2$	11·14	22·55	10·51	—	c
†$Th_2(OH)_2(NO_3)_6 \cdot 8H_2O$	White	M; $C_{2h}^{5}–P2_1/c$	6·772	11·693	13·769	102·63	d
$Th(OH)_2(NO_3)_2 \cdot xH_2O$	White	M; $C_{2h}^{6}–C2/c$	14·25	8·95	6·11	98·0	e
*†$MgTh(NO_3)_6 \cdot 8H_2O$	White	M; $C_{2h}^{5}–P2_1/c$	9·08	8·75	13·61	97·0	f
†$UO_2(NO_3)_2 \cdot 6H_2O$	Yellow	O; $C_{2v}^{12}–Cmc2_1$	13·197	8·035	11·467	—	g
$NpO_2(NO_3)_2 \cdot 6H_2O$		O; $C_{2v}^{12}–Cmc2_1$	13·25	8·00	11·40	—	h
†$UO_2(NO_3)_2 \cdot 2H_2O$	Yellow	M; $C_{2h}^{5}–P2_1/c$	14·124	8·432	7·028	108·0	i
†$UO_2(NO_3)_2 \cdot 2(C_2H_5O)_3PO$	,,	T; $C_1^{1}–P1$	9·12	8·65	9·06	98·93‡	j
$UO_2(NO_3)_2 \cdot 2Ph_3PO$	,,	M; $C_{2h}^{5}–P2_1/c$	11·01	19·02	10·93	128·16	k, l
†$UO_2(NO_3)_2 \cdot 2Ph_2AsO$	,,	M; $C_{2h}^{5}–P2_1/c$	11·09	19·28	10·88	128·16	k, l
†$RbUO_2(NO_3)_3$	,,	H; $D_{3d}^{6}–R\bar{3}c$	9·36	—	18·18	—	m
†$CsUO_2(NO_3)_3$	,,	H; $D_{3d}^{6}–R\bar{3}c$	9·64	—	19·51	—	n
$Rb_2UO_2(NO_3)_4$	,,	M; $C_{2h}^{5}–P2_1/c$	6·47	7·90	12·89	108·2	o
†$[UO_2(CO(NH_2)_2)_4 \cdot H_2O] \cdot [NO_3]_2$	,,	M; $C_{2h}^{5}–P2_1/c$	9·99	14·99	13·18	100·08	p

* The analogous Mn, Co, Ni and Zn complexes are isostructural.
† Full structural data are provided in reference cited.
‡ α and $\gamma = 102 \cdot 5°$ and $97 \cdot 91°$, respectively.
[a] T. Ueki, A. Zalkin and D. H. Templeton, *Acta Cryst.* **20** (1966) 836.
[b] J. C. Taylor, M. H. Mueller and R. L. Hitterman, *Acta Cryst.* **20** (1966) 842.
[c] E. Staritzky, *Anal. Chem.* **28** (1956) 2021.
[d] G. Johansson, *Acta Chem. Scand.* **22** (1968) 389.
[e] G. Johansson, *Svensk. Kem. Tidskr.* **78** (1966) 486.
[f] S. Šćavničar and B. Prodić, *Acta Cryst.* **18** (1964) 698.
[g] J. C. Taylor and M. H. Mueller, *Acta Cryst.* **19** (1965) 536.
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lengths are shown in Fig. 2. Short O–O contacts (2·77–2·96 Å) for the oxygen atoms of the water molecules indicate the presence of hydrogen bonding.

Thorium and plutonium tetranitrate hydrates are soluble in a variety of organic solvents and several complexes with oxygen donor ligands have been characterized for the actinide tetranitrates of thorium and of uranium to plutonium inclusive. These are generally prepared by direct reaction between the appropriate tetranitrate hydrate and the organic ligand or by metatheses involving the tetrachloride complex and silver nitrate in a suitable non-aqueous solvent. A selection of the known complexes is shown in Table 8 and the recently characterized complexes with sulphoxides are listed in Table 9 together with infrared data; full preparative details will be found in the references cited. The complexes identified during solvent extraction studies but not isolated as solids are not included in this article.

TABLE 7. INFRARED DATA (cm^{-1}) FOR TETRAVALENT ACTINIDE NITRATES AND NITRATO-COMPLEXES

Compound	Colour	Infrared bands*						Ref.
		ν_1	ν_4	ν_2	ν_6	ν_5/ν_3	ν_{M-O}	
$Th(NO_3)_4$	White	1620 1560	1328 1240	1010	800	740	244	a
$Th(NO_3)_4 \cdot 5H_2O$	White	1550 1510 1420	1350 1325 1293	1040 1030	875 815 808	760 745	244 211	a
$Th(NO_3)_4 \cdot 4H_2O$	White	1550 1500	1320 1290	1040 1030	812 805	759 743	249 218	a
$Np(NO_3)_4 \cdot 2H_2O$	Green	1524	1287	1034	804	765 749	—	b
$Cs_2Th(NO_3)_6$	White	1550 1527	1276	1026	805	738 702	—	c
$Cs_2Np(NO_3)_6$	Green	1523	1280	1028	802	742 702	—	c
$MgTh(NO_3)_6 \cdot 8H_2O$	White	1520†	1313 1293 1280	1037	813	750 727	—	d

* Where necessary, assignments have been modified to agree with those recommended for bidentate nitrate groups (R. W. Hester and W. L. Grossman, *Inorg. Chem.* **5** (1966) 1308; J. I. Bullock, *J. Inorg. Nucl. Chem.* **29** (1967) 2257).

† Complex band.

[a] J. Ferraro and A. Walker, *J. Chem. Phys.* **45** (1966) 550.

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TABLE 8. EXAMPLES OF ACTINIDE TETRANITRATE COMPLEXES WITH OXYGEN DONOR LIGANDS

Ligand	Stoichiometry
N,N-dimethylacetamide	1:2·5 (Th,[a] U[b] and Np[k]); 1:3 (Th,[c] as trihydrate)
Triphenylphosphine oxide	1:2 (Th[d,j] and Pu[e])
Triphenylarsine oxide	1:2 (Pu[e])
Phenanthroline	1:2 (Th[d])
N-phenylsalicylideneimine	1:2 (Th[f])
2-dimethylaminomethyl-4-methyl phenol	1:4 (Th[g])
2,4,6-tris(dimethylaminomethyl) phenol	1:1 (Th[g])
Urea	1:2 (Th[h]; $6H_2O$); 1:4 (Th[h]; $4H_2O$); 1:5 (Th[h]; $3H_2O$); 1:6 (Th[h]; $2H_2O$); 1:10 (Th[h]); 1:11 (Th[h]; $2 \cdot 5H_2O$)

[a] K. W. Bagnall, D. Brown, P. J. Jones and P. S. Robinson, *J. Chem. Soc.* (1964) 2531.

[b] K. W. Bagnall, P. S. Robinson and M. A. A. Stewart, *J. Chem. Soc.* (1961) 4060.

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[i] K. I. Petrov, A. K. Molodkin, O. M. Ivanova and O. D. Saralidze, *Sov. Radiochem.* **14** (1969) 215.

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[k] J. B. Laidler, *J. Chem. Soc.* (A) (1966) 780.

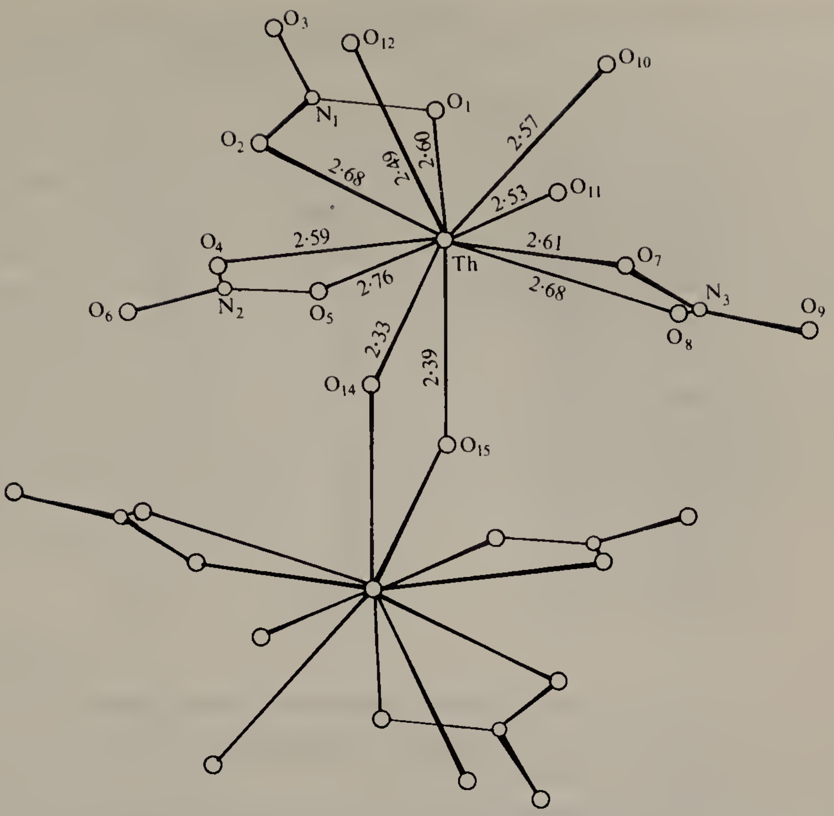

FIG. 2. The atomic arrangement in $Th_2(OH)_2(NO_3)_6(H_2O)_6$ viewed down [100] with [010] vertical. (Reproduced by permission from G. Johansson, *Acta Chem. Scand.* **22** (1968) 389.)

Coordination of the ligand in those complexes listed is via the oxygen atom (cf. $\Delta\nu_{S=O}$ values, Table 9) and, in general, infrared studies have demonstrated the presence of only covalent nitrate groups. However, both covalent and ionic nitrate are believed to be present in the thorium tetranitrate–urea complexes containing four or more molecules of ligand[95], and in the complexes of the type $M(NO_3)_4 \cdot 6DMSO$[96] (DMSO, dimethylsulphoxide). The preparation of protactinium(IV) complexes has not been attempted.

Tetravalent nitrato-complexes

Preparation and Properties

Hexanitrato-complexes of the type $M^I_2M^{IV}(NO_3)_6$ (M^I = univalent cation; M^{IV} = actinide element) are known for thorium(IV)[1,87,97–100], uranium(IV)[77,101,102], neptunium(IV)[96,97,101] and plutonium(IV)[97,100,101,103]; there appears to have been no attempt

[95] K. I. Petrov, A. K. Molodkin, O. M. Ivanova and O. D. Saralidze, *Russ. J. Inorg. Chem.* **14** (1969) 215.

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TABLE 9. EXAMPLES OF ACTINIDE TETRANITRATE COMPLEXES WITH DIALKYL- AND DIARYL-SULPHOXIDES[a]

Compound*†‡	$\nu_{S=O}$	$\Delta\nu_{S=O}$
$Th(NO_3)_4\cdot 6DMSO$	960,945	96,111
$Np(NO_3)_4\cdot 6DMSO$	951,933	105,123
$Pu(NO_3)_4\cdot 6DMSO$	950,928	106,128
α-$Th(NO_3)_4\cdot 3DMSO$	951	105
β-$Th(NO_3)_4\cdot 3DMSO$	956	100
γ-$Th(NO_3)_4\cdot 3DMSO$	950	106
$Np(NO_3)_4\cdot 3DMSO$	939	117
$Pu(NO_3)_4\cdot 3DMSO$	937	119
$Th(NO_3)_4\cdot 3DESO$	951	108
$Np(NO_3)_4\cdot 3DESO$	—	—
$Th(NO_3)_4\cdot 4DPSO$	967	72
$Np(NO_3)_4\cdot 4DPSO$	945	94
$Pu(NO_3)_4\cdot 4DPSO$	945	94
$Th(NO_3)_4\cdot 3DPSO$	967	72
$Np(NO_3)_4\cdot 3DPSO$	948	91
$Th(NO_3)_4\cdot 3DNSO$	977,946	65,96
$Th(NO_3)_4\cdot 3DNSO\cdot EA$	979,949	63,93

* Infrared results indicate the presence of both ionic and covalent nitrate groups in compounds of the type $M(NO_3)_4\cdot 6DMSO$ and of only covalent nitrate groups in the rest of the compounds listed.

† DMSO, dimethylsulphoxide; DESO, diethylsulphoxide; DPSO, diphenylsulphoxide; DNSO, di-α-naphthylsulphoxide; EA, ethyl acetate.

‡ Analogous uranium compounds apart from $U(NO_3)_4\cdot 3DMSO$ have not been characterized.

[a] K. W. Bagnall, D. Brown and P. J. Alvey, *J. Chem. Soc.* (A), in press (1973).

to prepare analogous protactinium(IV) complexes. The above compounds and those of type $M^{II}M^{IV}(NO_3)_6\cdot 8H_2O$ (M = variously, Mg, Zn, Co, Ni and Mn; M^{IV} = thorium[1,87,100], uranium[102] and plutonium[100]) are all conveniently obtained by mixing the appropriate tetravalent actinide and the uni- or divalent cation nitrate in nitric acid solution. $Cs_2Th(NO_3)_6$ has also been prepared by the reaction[79] between $CsNO_3$ and $(NO_2)_2[Th(NO_3)_6]$. The latter complex, which is formulated as a hexanitratothorate(IV) (rather than $Th(NO_3)_4\cdot 2N_2O_5$) on the basis of infrared results (NO_2^+ at 2360 cm^{-1}), is conveniently obtained[79] by the addition of chlorine nitrate to anhydrous thorium tetrachloride or by the addition of dinitrogen pentoxide to thorium tetranitrate tetrahydrate in anhydrous nitric acid[78]. Treatment with dinitrogen tetroxide results in the formation of $(NO)_2[Th(NO_3)_6]$ for which the NO^+ vibration is observed at 2270 cm^{-1} [79].

Hydrated pentanitratothorates(IV) $M^ITh(NO_3)_5\cdot xH_2O$ (M = Na and K) also appear[1,87] to exist but although the older literature (see ref. 1) contains reports of the existence of complexes of the type $M^I[Th_2(NO_3)_7]\cdot xH_2O$, these results have not been confirmed.

Thermal decomposition of $(NO)_2[Th(NO_3)_6]$ at 90° in a vacuum results in the formation of anhydrous thorium tetranitrate; at 190° *in vacuo* $(NO_2)_2[Th(NO_3)_6]$ decomposes to yield the oxynitrate, $ThO(NO_3)_2$[79], the tetranitrate being obtained at lower temperature[78]. Uranium(IV) hexanitrato-complexes undergo oxidation when heated in air[102] decomposing at around 100°C to yield either uranyl(VI) trinitrato-complexes, $M^IUO_2(NO_3)_3$ ($M^I = NH_4$)

or uranyl(VI) tetranitrato-complexes, $M^I_2UO_2(NO_3)_4$ (M^I = Rb, Cs, PyH, QuinH) and $M^{II}UO_2(NO_3)_4$ (M^{II} = Mg and Zn).

Although it is likely that the hexanitrato-complexes contain bidentate nitrato-groups this has only been confirmed for the hydrated complexes of the type $M^{II}M^{IV}(NO_3)_6 \cdot 8H_2O$ which, on the basis of X-ray structural data[104], are better formulated as $[M^{II}(H_2O)_6]$ $[M^{IV}(NO_3)_6] \cdot 2H_2O$. Thus, in the magnesium complex, each thorium atom is surrounded by twelve oxygen atoms from six nitrate groups, the average Th–O distance being 2·63 Å. The oxygen atoms are at the corners of an irregular icosahedron (Fig. 3 (a)). A schematic representation of the structure is shown in Fig. 3 (b). $[Mg(H_2O)_6]^{2+}$ and $[Th(NO_3)_6]^{2-}$ polyhedra are linked by weak hydrogen bonding.

Few infrared[87,96] or Raman[87] data are available for the actinide(IV) hexanitrato-complexes; selected values are shown in Table 7. The assignments are based on the presence of bidentate nitrato-groups. Magnetic studies have been reported[105] only for $Cs_2U(NO_3)_6$ and $(NEt_4)_2U(NO_3)_6$, the recorded magnetic moments being 3·16 B.M. ($\theta = -226°$) and 3·07 B.M. ($\theta = -192°$), respectively.

Pentavalent nitrates

Preparation and Properties

Simple nitrates of the type $M^V(NO_3)_5$ are unknown, but the hydrated protactinium(V) compound $PaO(NO_3)_3 \cdot xH_2O$ ($1 < x < 4$) precipitates[106] on evaporation of fuming nitric acid containing protactinium pentahalides, and the methyl cyanide complex $Pa_2O(NO_3)_8 \cdot 2CH_3CN$ is obtained by vacuum evaporation of methyl cyanide containing protactinium pentachloride and dinitrogen tetroxide. The neptunium(V) oxynitrate hydrates $NpO_2(NO_3) \cdot H_2O$ and $NpO(NO_3)_3 \cdot 3H_2O$ have both been isolated[76] by vacuum evaporation of aqueous nitric acid containing neptunium(V).

Structural data are not available for these compounds, but infrared results (Table 10) indicate the presence of covalent nitrate groups only. The Np–O stretching vibrations associated with the Np=O and O=Np=O groups, respectively, are observed at 961 cm^{-1} and 759 cm^{-1}. The positions of the Pa–O vibrations (Table 10) suggest the presence of Pa–O–Pa groups in both compounds.

Thermal decomposition of the protactinium(V) compounds failed[106] to yield the corresponding anhydrous complexes or other stable oxynitrates of compositions between those of the starting materials and Pa_2O_5. In contrast to this behaviour, $NpO_2NO_3 \cdot H_2O$ loses the water of crystallization at *ca.* 80°C *in vacuo* and the anhydrous compound NpO_2NO_3, which is extremely moisture-sensitive, appears to be stable over the temperature range 140–220°C[76].

Pentavalent nitrato-complexes

Preparation and Properties

Only protactinium is known to form pentavalent nitrato-complexes[106]. Thus, products of the type $M^IPa(NO_3)_6$ (M^I = Cs, NEt_4 and NMe_4) are obtained by treatment of the

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[104] S. Šćavničar and B. Prodič, *Acta Cryst.* 18 (1965) 698.
[105] K. W. Bagnall, D. Brown and R. Colton, *J. Chem. Soc.* (1964) 2527.
[106] D. Brown and P. J. Jones, *J. Chem. Soc.* (A) (1966) 733.

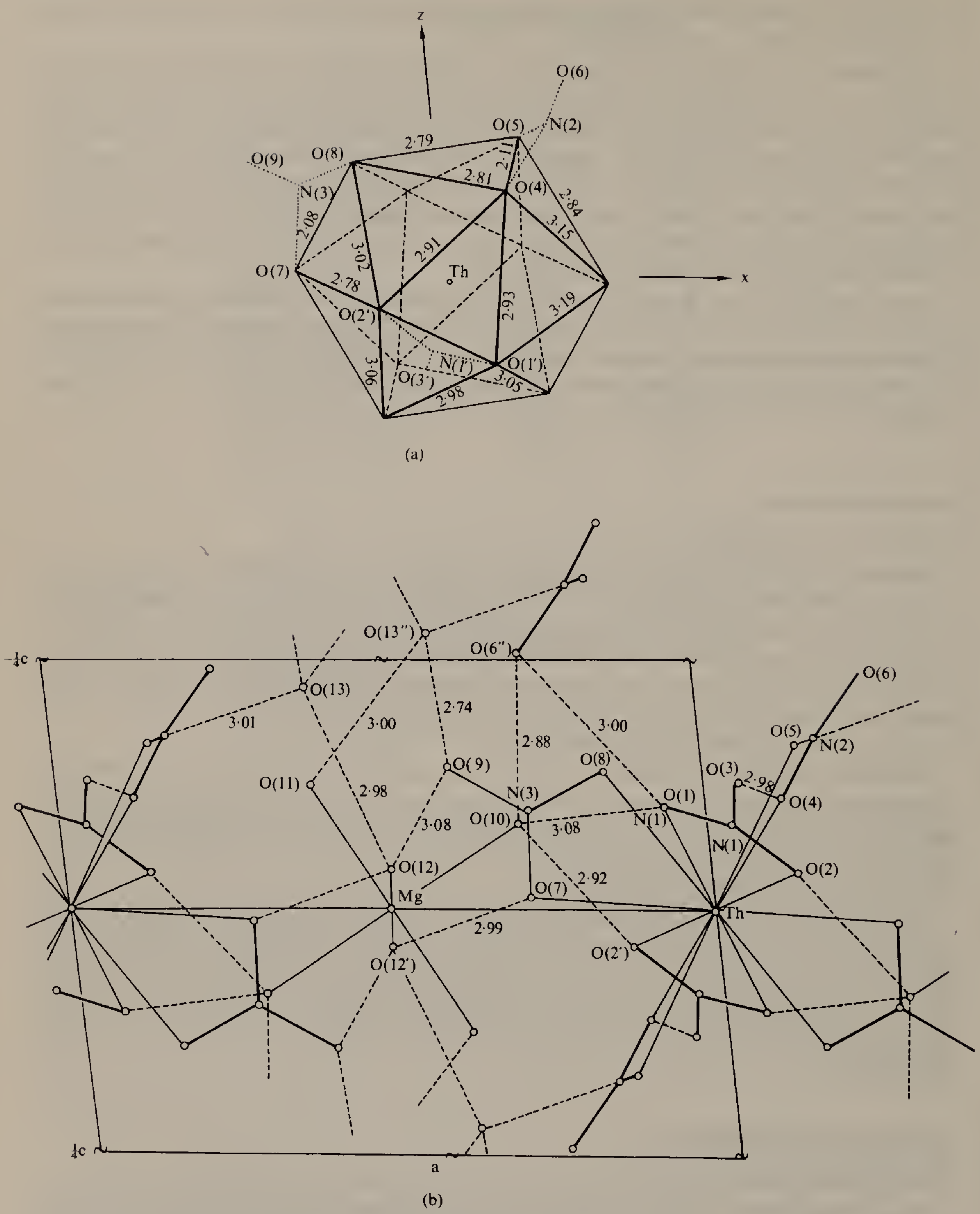

FIG. 3. (a) Icosahedron around the thorium atom in $Mg[Th(NO_3)_6]\cdot 8H_2O$ as seen along (010). (b) Schematic representation of the structure of $Mg[Th(NO_3)_6]\cdot 8H_2O$ in the (010) projection. Nitrate ions are shown by heavy lines; Th–O and Mg–O bonds are shown by thin lines. Dashed lines connect atoms of different polyhedra and isolated water molecules; only distances of less than 3·1 Å are taken into account. (Reproduced by permission from S. Šćavničar and B. Prodič, *Acta Cryst.* **18** (1965) 698.)

TABLE 10. INFRARED DATA FOR PENTAVALENT OXYNITRATES AND HEXANITRATOPROTACTINATES(V)

Compound	Colour	Infrared bands* (cm^{-1})						Ref.
		ν_1	ν_4	ν_2	ν_6	ν_5/ν_3	ν_{M-O}	
$PaO(NO_3)_3 \cdot xH_2O$	White	1524	1269	1021	804	746	773	a
$Pa_2O(NO_3)_8 \cdot 2CH_3CN$	White	1603 1558	1299 1256	1016	803 798	749	721	a
$NpO(NO_3)_3 \cdot 3H_2O$	Pink	1495	1292 1277	1040 1022	803	750 739	961	b
$NpO_2(NO_3) \cdot H_2O$	Green	1517	1308	1044	813	752	759	b
$HPa(NO_3)_6$	White	1600 1563 1536	1299 1265	1018	803 796	746	—	a
$CsPa(NO_3)_6$	White	1594 1558 1527	1290 1262 1220	1015	799 792 786	751 744	—	a
$NEt_4Pa(NO_3)_6$	White	1597 1567 1541	1277 1255	1023	810 803 799	750 747	—	a

* Assignments have been modified where necessary to agree with those recommended for bidentate nitrate groups (R. W. Hester and W. L. Grossman, *Inorg. Chem.* **5** (1966) 1308; J. I. Bullock, *J. Inorg. Nucl. Chem.* **29** (1967) 2257).

[a] D. Brown and P. J. Jones, *J. Chem. Soc.* (A) (1966) 733.

[b] J. B. Laidler, *J. Chem. Soc.* (A) (1966) 780.

appropriate hexachloroprotactinate(V) with liquid dinitrogen pentoxide at room temperature. The soluble, air-sensitive complexes are isolated by removal of excess reagent *in vacuo*. An unusual compound believed to be $HPa(NO_3)_6$ is formed when protactinium(V) hydroxide is treated with dinitrogen pentoxide. These compounds are unique in that hexanitratometallates(V) are not known for any other element. Analogous reactions involving hexachloroniobates(V) or hexachlorotantalates(V), for example, result in the formation of oxynitrato-complexes[106], $M^IM^VO(NO_3)_4$, possibly as a consequence of the smaller ionic radii of the *d*-transition elements relative to that of Pa(V). No structural information is available for the hexanitratoprotactinates(V), but infrared results (Table 10) indicate the presence of only covalent nitrate groups.

Hexavalent nitrates

Simple actinide(VI) nitrates are unknown, but both uranium and plutonium form hexavalent nitrates of the type, $MO_2(NO_3)_2$ (M = U and Pu) and several hydrates (Table 5) are also known for each compound. The analogous neptunium system has barely been investigated and only the hexahydrate, $NpO_2(NO_3)_2 \cdot 6H_2O$, is known at present, but it is likely that under the correct conditions other hydrates and $NpO_2(NO_3)_2$ will exist. The interested reader is referred to summaries by Huré[2] and Tsapkina[73] for details of the earlier literature on uranyl nitrate and its hydrates; in contrast to the extensive amount of work done on the uranium compounds relatively little effort has been expended on the chemistry of the neptunium and plutonium analogues.

Preparation

A variety of methods have been reported for the preparation of anhydrous uranyl nitrate[2]. Easily the most satisfactory is the thermal decomposition of the dinitrogen tetroxide adduct, $UO_2(NO_3)_2 \cdot N_2O_4$[107–110], (or, as it is alternatively formulated[111], $(NO)[UO_2(NO_3)_3]$) which is obtained from reactions involving dinitrogen tetroxide and uranium metal, uranium oxides or uranium halides. The temperature of decomposition appears to be critical, pure uranyl nitrate being obtained at 163–165°C[108–110]. The dinitrogen pentoxide adduct, $UO_2(NO_3)_2 \cdot N_2O_5$, provides an alternative starting material; it is somewhat less stable than the dinitrogen tetroxide adduct, decomposing at 125–130°C[112].

Anhydrous uranyl(VI) nitrate has also been reported to form as an intermediate in the thermal decomposition of the various uranyl(VI) nitrate hydrates (see, for example, refs. 89 and 113–116), but this type of reaction is inferior to those mentioned above on account of

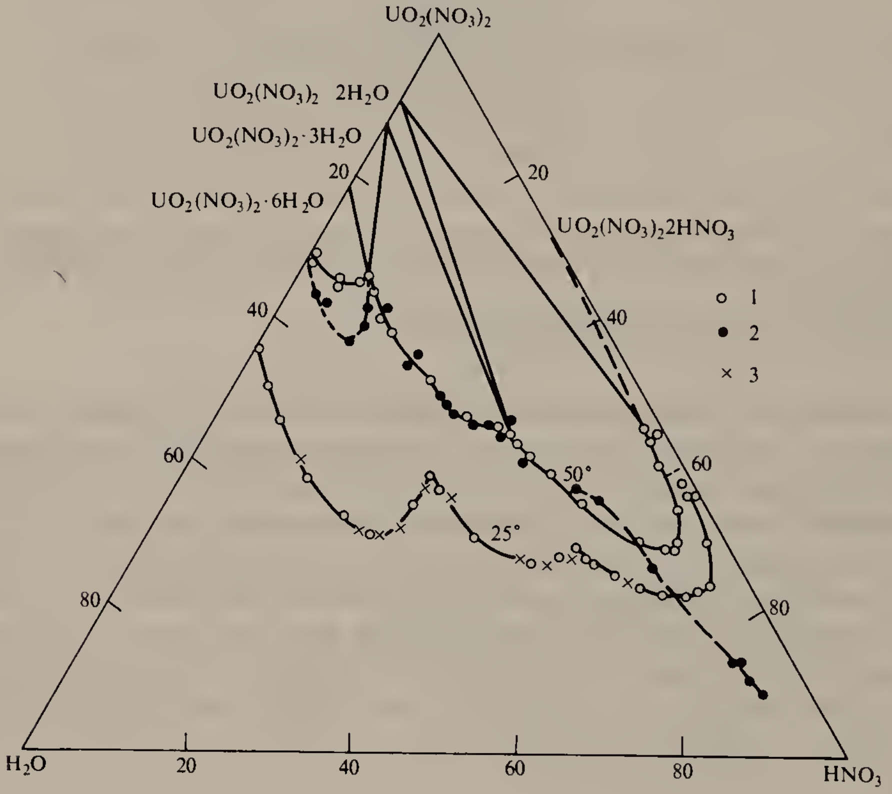

FIG. 4. Solubility isotherms in the system $UO_2(NO_3)_2$–HNO_3–H_2O at 25°C and 50°C. Compositions are expressed as wt. %. (Reproduced by permission from M. A. Yakimov and V. Ya. Mishin, *Sov. Radiochem.* **6** (1964) 437.)

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[107] E. Späth, *Monatsh.* **33** (1912) 853.

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[110] C. C. Addison, H. A. J. Champ, N. Hodge and A. H. Norbury, *J. Chem. Soc.* (1964) 2354.

[111] V. M. Vdovenko, D. N. Suglobova and G. A. Romanov, *Dokl. Akad. Nauk. SSSR*, **146** (1962) 1078; *Sov. Radiochem.* **5** (1963) 281.

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[113] R. S. Ondrejcin and T. P. Garrett, *J. Phys. Chem.* **65** (1961) 470.

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[116] R. S. Ondrejcin, *J. Chem. Eng. Data*, **11** (1966) 130.

the possibility of hydrolysis occurring. Contamination of the anhydrous nitrate with UO_3 has, in fact, been mentioned[115]. However, it is claimed[117] that controlled thermal dehydration of $PuO_2(NO_3)_3 \cdot 6H_2O$ (150°C for 76 hr) yields anhydrous plutonyl(VI) nitrate and, although it has not been isolated, $NpO_2(NO_3)_2$ appears to be formed[76] at 190°C during the vacuum thermal decomposition of $Np(NO_3)_4 \cdot xN_2O_5$. The product rapidly adsorbed water to yield $NpO_2(NO_3)_2 \cdot 6H_2O$.

Conditions for the preparation of uranyl(VI) hexa-, tri- and dihydrate are well established (see, for example, refs. 2, 73, 85, 118–121). The hexahydrate is obtained by crystallization from aqueous nitric acid followed by desiccation over 35–40% sulphuric acid or by evaporation of ethereal extracts of uranium(VI). Crystallization from concentrated nitric acid or vacuum dehydration (1 cm Hg) of the hexahydrate over 60–65% sulphuric acid results in the formation of $UO_2(NO_3)_2 \cdot 3H_2O$, whilst dehydration over 95% sulphuric acid yields the dihydrate. The last is also formed by the thermal decomposition of $UO_2(NO_3)_2 \cdot N_2O_5 \cdot 2H_2O$. Both the tri- and dihydrate have also been identified (for example, ref. 115) as intermediate products during the thermal decomposition of $UO_2(NO_3)_2 \cdot 6H_2O$, a procedure which, under controlled conditions[122,123], can also yield the monohydrate, $UO_2(NO_3)_2 \cdot H_2O$. The thermal decomposition of uranyl nitrate hydrates has been widely investigated in view of its industrial application in the preparation of uranium trioxide and the reader is referred to the articles by Huré[2] for other references to the original literature.

An investigation of the heterogeneous equilibria in the ternary system $UO_2(NO_3)_2$–HNO_3–H_2O[124] has yielded the results shown schematically in Fig. 4; in addition to the hexa-, tri- and dihydrates, a phase believed to be $UO_2(NO_3)_2 \cdot 2HNO_3$ was identified at high concentrations of nitric acid.

The only neptunyl(VI) hydrate known at present, $NpO_2(NO_3)_2 \cdot 6H_2O$, is conveniently obtained[76,125] by crystallization from aqueous nitric acid, whilst the pink plutonyl(VI) analogue results[117] when nitric acid solutions containing plutonium(VI) are evaporated over phosphorus pentoxide at room temperature. When the latter compound is heated under controlled conditions, water is lost with the successive formation of a tetra-, tri-, and dihydrate, the ultimate product being $PuO_2(NO_3)_2$.

Properties

Results of earlier infrared[126] and X-ray investigations[127] were reported to be consistent with the presence of ionic nitrate groups in the uranyl(VI) nitrate hydrates. However, more recent infrared studies[85,110,120,128–132] have clearly indicated the presence of only covalent

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[121] B. Kedzia and B. J. Trzebiatowska, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.* **12** (1964) 251.

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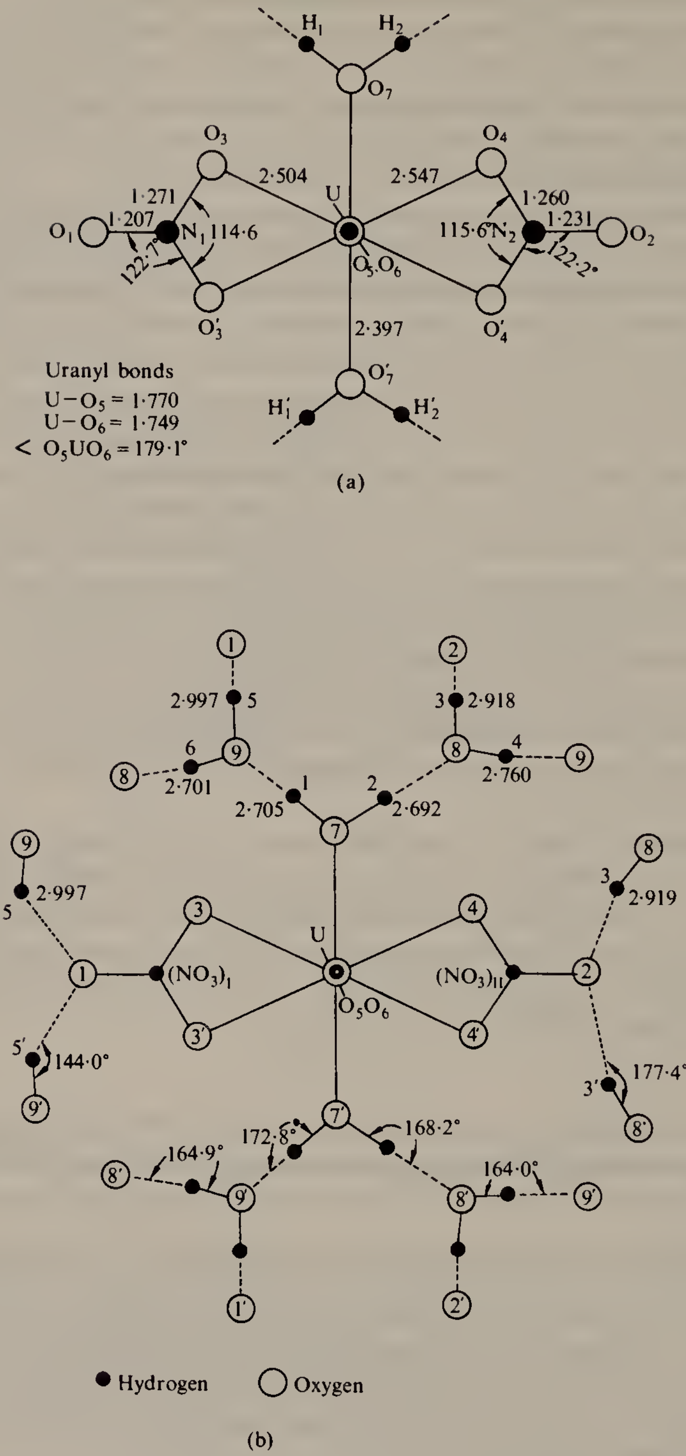

FIG. 5. (a) Configuration of the uranium atom and nitrate groups in the $UO_2(NO_3)_2 \cdot 2H_2O$ molecule. (b) Hydrogen bonding in $UO_2(NO_3)_2 \cdot 6H_2O$. (Reproduced by permission from J. C. Taylor and M. H. Mueller, *Acta Cryst.* **19** (1965) 536.)

nitrate groups and both X-ray[133–135] and neutron diffraction[136,137] investigations have confirmed such interpretations.

In the hexahydrate[134, 136] the virtually linear uranyl group is surrounded by an almost planar hexagon of four oxygen atoms from two bidentate nitrate groups and two oxygen atoms from two equivalent water molecules. This hexagonal bipyramidal arrangement is illustrated schematically in Fig. 5 (a). As shown by the neutron diffraction study[136], the oxygens in the uranyl group are not equivalent and, in addition, the two bidentate nitrate groups are also non-equivalent, although each itself is symmetrically bonded to the uranium atom. The structural units are linked, as indicated in Fig. 5 (b), by hydrogen bonds associated with both the water molecules (2·68–2·75 Å) and the nitrate groups (2·93–2·99 Å).

X-ray diffraction studies have indicated that two bidentate nitrate groups and two of the three water molecules are coordinated to the uranyl group in the trihydrate[135] and a recent neutron diffraction investigation[137] has demonstrated that the basic stereochemistry around the uranium atom in $UO_2(NO_3)_2 \cdot 2H_2O$ is virtually identical with that of the hexahydrate. In contrast to the arrangement in the hexahydrate, however, both nitrate groups are equivalent in the dihydrate. The structural units are bound together by hydrogen bonds between the oxygen of the water molecules and the uncoordinated oxygen of the nitrate group and the oxygens of the uranyl group. Unit cell dimensions of the hexa- and dihydrate are listed in Table 6 together with those for $NpO_2(NO_3)_2 \cdot 6H_2O$, which is isostructural with the uranyl(VI) analogue. $UO_2(NO_3)_2 \cdot 3H_2O$[135] possesses triclinic symmetry, space group C_1^1–$P1$ with $a_0 = 5{\cdot}73$ Å, $b_0 = 6{\cdot}99$ Å, $c_0 = 7{\cdot}21$ Å, $\alpha = 115°$, $\beta = 119{\cdot}5°$ and $\gamma = 82°$.

As mentioned above, infrared data for the uranyl(VI) nitrate hydrates have been interpreted on the basis of coordinated nitrate groups. There have been numerous infrared spectral studies[85,110,120,128–132] and some typical results are listed in Table 11 together with data for $NpO_2(NO_3)_2 \cdot 6H_2O$. The spectrum of anhydrous uranyl nitrate is somewhat unusual[85,110,121,132] and it will obviously be of value to have X-ray or neutron diffraction results for this compound. Ferraro and Walker[85] have assigned bands in the range 249–260 cm^{-1} to the U–O (nitrate) vibration and have assigned $\nu_2 UO_2^{2+}$ (O–U–O, bending mode) to bands observed below 152 cm^{-1}. However, these assignments appear to be in error since, on the basis of the comparison of spectra of a wide range of uranyl(VI) halogeno-, perchlorato-, nitrato- and carbonato-complexes, Vdovenko *et al.*[138] and Bullock and Parrett[139] assign the bands in the range 248–260 cm^{-1} to $\nu_2 UO_2^{2+}$ with U–O (nitrate) vibrations at lower frequencies (219 and 223 cm^{-1}). Interpretation of the nitrogen-14 NMR[140] and PMR[141] spectral results for the hexahydrate are in agreement with the structure described above. The excellent book by Rabinowitch and Belford[142] is recommended for an authoritative discussion of the fluorescence and absorption spectra of uranyl(VI) compounds, including the nitrates.

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TABLE 11. TYPICAL INFRARED VIBRATIONS FOR ACTINIDE(VI) OXYNITRATES AND OXYNITRATO-COMPLEXES

Compound	Observed bands (cm^{-1})						Ref.
	ν_1	ν_4	ν_2	ν_6	ν_5/ν_3	$\nu_3MO_2^{2+}$	
$UO_2(NO_3)_2 \cdot 6H_2O$	1530 1480 1452	1337 1303	1050 1038	806	748	959	a
$NpO_2(NO_3)_2 \cdot 6H_2O$	1520 1489	1308 1282	1045 1031	799	746 741	952	b
$UO_2(NO_3)_2 \cdot 3H_2O$	1535 1501	1303 1277	1041 1028	800	743	952	a
$UO_2(NO_3)_2 \cdot 2H_2O$	1536 1505	1263	1023	801	751 708	949	a
$UO_2(NO_3)_2 \cdot H_2O$	1618 1540	1270 1240	1028 1008	802 787	755 698	960,945	c
$UO_2(NO_3)_2 \cdot 2CO(NH_2)_2$	1525	1290	1032	809	750 722	938	d
$UO_2(NO_3)_2 \cdot 2C_5H_5N$	1500	1282	1028	812	741 725	921,911	d

[a] G. Chottard, J. Fraissard and B. Imelik, *Bull. Soc. Chim. Fr.* (1967) 4331; similar results with minor differences are given in the references quoted in the text (p. 299).
[b] J. B. Laidler, *J. Chem. Soc.* (A) (1966) 780.
[c] G. Chottard, *Compt. Rend.* **267C** (1968) 147.
[d] J. I. Bullock, *J. Inorg. Nucl. Chem.* **29** (1967) 2257.

Rand and Kubaschewski[143] have assessed the earlier thermodynamic data on uranyl nitrate and the various hydrates. Recommended values are: ΔH_f and S_{298} $\langle UO_2(NO_3)_2 \rangle$, 332 kcal mole^{-1} and 50 eu, respectively; ΔH_f and S_{298} $\langle UO_2(NO_3)_2 \cdot 2H_2O \rangle$, 475 kcal mole^{-1} and 77 eu, respectively; ΔH_f and S_{298} $\langle UO_2(NO_3)_2 \cdot 3H_2O \rangle$, 547 kcal mole^{-1} and 88 eu, respectively; ΔH_f and S_{298} $\langle UO_2(NO_3)_2 \cdot 6H_2O \rangle$, 759 kcal mole^{-1} and 120·9 eu, respectively. Following determinations of the heats of solution of γ-UO_3 and $UO_2(NO_3)_2 \cdot 6H_2O$ in 6 M nitric acid solution together with measurements of the water vapour pressure of the equilibria,

$$UO_2(NO_3)_2 \cdot 6H_2O(s) \rightleftharpoons UO_2(NO_3)_2 \cdot 3H_2O(s) + 3H_2O(g)$$

and

$$UO_2(NO_3)_2 \cdot 3H_2O(s) \rightleftharpoons UO_2(NO_3)_2 \cdot 2H_2O(s) + H_2O(g)$$

Cordfunke[144,145] has more recently reported slightly higher values for the heats of formation of the various compounds.

The free energy expressions given by Rand and Kubaschewski[143] for the above transformations and for conversion of the dihydrate to anhydrous uranyl nitrate

$$UO_2(NO_3)_2 \cdot 2H_2O(s) \rightleftharpoons UO_2(NO_3)_2(s) + 2H_2O(g)$$

are, respectively, $\Delta G = 38{,}600 - 102{\cdot}3\,T$ cal, $\Delta G = 13{,}900 - 34{\cdot}1\,T$ cal, and $\Delta G = 27{,}800 - 62{\cdot}8\,T$ cal.

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[143] M. H. Rand and O. Kubaschewski, *The Thermochemical Properties of Uranium Compounds*, Oliver & Boyd, London (1963).
[144] E. H. P. Cordfunke, *J. Phys. Chem.* **68** (1964) 3357.
[145] E. H. P. Cordfunke, *Proc. Therm. Proc. Symp. Vienna*, **2** (1965) 483.

Although no heat of formation is available for $NpO_2(NO_3)_2 \cdot 6H_2O$ the free energy and heat of solution in water are reported to be −2·94 kcal and 5·06 kcal mole^{-1}, respectively, the estimated entropy being 123·4 eu[125].

Complexes with Donor Ligands

In addition to the hydrates discussed earlier, uranyl nitrate forms a wide range of complexes with numerous other donor ligands. Comyns[146] has reviewed the complexes formed with oxygen and nitrogen donors, covering the literature to *ca.* 1960. A selection of typical 1:1 and 1:2 complexes is provided in Table 12 together with references (mainly 1960 onwards) to their modes of preparation, which usually involve reaction between a uranyl nitrate hydrate and the appropriate ligand in a suitable organic solvent. Complexes identified during solvent extraction studies but not isolated as solids are not included. Infrared and X-ray crystallographic data (discussed below) indicate that the complexes listed contain only covalently bonded nitrate groups; some typical infrared results are provided in Table 11 and other data will be found in the various references cited in Table 12. However, in addition to the 1:2 complex with urea, $UO_2(NO_3)_2 \cdot 2CO(NH_2)_2$, complexes are known which contain a larger number of ligand molecules, e.g. $UO_2(NO_3)_2 \cdot 3CO(NH_2)_2$, $UO_2(NO_3)_2 \cdot 4CO(NH_2)_2 \cdot H_2O$, $UO_2(NO_3)_2 \cdot 5CO(NH_2)_2$ and $UO_2(NO_3)_2 \cdot 6CO(NH_2)_2$, and these contain ionic nitrate groups[147,148]. It has been shown by neutron diffraction studies[149,150] that in $UO_2(NO_3)_2 \cdot 4CO(NH_2)_2 \cdot H_2O$ the four urea molecules and the water are coordinated, both nitrates being ionic. A similar displacement of nitrate is observed for thorium tetranitrate–urea complexes (p. 291) and for mixed nitrato-halogeno-complexes[151] of the types $UO_2X_a(NO_3)_{2-a} \cdot 4CO(NH_2)_2 \cdot H_2O$ ($X = Br$ and I; $a = 0$ to 1) and $UO_2X_a(NO_3)_{2-a} \cdot 5CO(NH_2)_2$. The infrared active uranyl deformation mode (ν_2) occurs in the range 248 to 274 cm^{-1} [139,152].

Few structural studies have been reported for the uranyl nitrate complexes with donor ligands. As mentioned above, ionic nitrate groups are present in the urea complex $UO_2(NO_3)_2 \cdot 4CO(NH_2)_2 \cdot H_2O$ which, therefore, is more correctly formulated as $[UO_2(CO(NH_2)_2)_4H_2O][NO_3]_2$. In contrast to this, bidentate nitrate groups are found in the 1:2 complexes $UO_2(NO_3)_2 \cdot 2(C_2H_5O)_3PO$[153], $UO_2(NO_3)_2 \cdot 2Ph_3PO$[154,155] and $UO_2(NO_3)_2 \cdot 2Ph_3AsO$[154,155]. In each of these compounds six oxygen atoms are coordinated to the uranyl(VI) group, the stereochemistry around the uranium atom being hexagonal bipyramidal. Unit cell dimensions are listed in Table 6.

Although it has been suggested on the basis of infrared results[111] that the dinitrogen tetroxide adduct $UO_2(NO_3)_2 \cdot N_2O_4$ is better formulated as the complex $NO[UO_2(NO_3)_3]$ the evidence is not conclusive[156,157].

[146] A. E. Comyns, *Chem. Rev.* 60 (1960) 115.

[147] V. P. Markov and I. V. Tsapkina, *Russ. J. Inorg. Chem.* 7 (1962) 1057.

[148] P. S. Gentile and L. S. Campari, *J. Inorg. Nucl. Chem.* 27 (1965) 2291.

[149] M. H. Mueller and N. K. Dalley, *Nat. Bur. Stand. Spec. Pub.* No. 301 (1969) 253.

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[151] V. G. Kuznetsov, G. V. Ellert, I. V. Tsapkina and Yu. N. Mikhailov, *Russ. J. Inorg. Chem.* **15** (1970) 1280.

[152] F. A. Hart and J. E. Newberry, *J. Inorg. Nucl. Chem.* **30** (1968) 318.

[153] J. E. Fleming and H. Lynton, *Chem. and Ind.* (1960) 1415.

[154] R. Grazziani, B. Zarli and G. Bandoli, *Ric. Sci.* 37 (1967) 984.

[155] C. Panattoni, R. Grazziani, U. Croatto, B. Zarli and G. Bombieri, *Inorg. Chim. Acta*, **2** (1968) 43.

[156] C. C. Addison and D. Sutton, Chapter 4 in *Progress in Inorganic Chemistry*, Vol. 8. F. A. Cotton (Ed.) (1967).

[157] C. C. Addison and N. Hodge, *J. Chem. Soc.* (1961) 2490.

TABLE 12. EXAMPLES* OF URANYL NITRATE COMPLEXES WITH DONOR LIGANDS

Complex type	Ligand (L)
$UO_2(NO_3)_2 \cdot L$	1,10-phenanthroline[a, b, c], 2,2^1-bipyridyl[a, b, c, v], pyridine[a, c, d], (as monohydrate), α-picoline[c] (as monohydrate), α-benzylpyridine[c] (as monohydrate), di-ethyl ether[e] (as dihydrate), biphosphine oxides of the types $R_2POCH_2POR_2$ and $(RO)_2POCH_2PO(OR)_2$ where R is an alkyl group[y], bisdiphenylphosphinoethane oxide[u], bisdiphenylphosphinobutane oxide[u].
$UO_2(NO_3)_2 \cdot 2L$	Triphenylphosphine oxide[a, f, g], phosphine oxides[y] of the types (2-propyl-O)$_2$ RPO (R = alkyl or aryl group) and $(RO)_3PO$ (R = alkyl group), triethylphosphate[i], triphenylarsine oxide[a, g, h], methyldiphenylphosphate,[j] pyridine[a, c, d], bipyridyl[c], phenanthroline[c], diphenylsulphoxide[o], dimethylsulphoxide[v], dimethylformamide[n], urea and its alkyl derivatives[k, l, m, t], thiourea[w], di-ethyl ether[d], di-isopropyl ether[p], methyl cyanide[d, q], methyl acetate[q], ethyl acetate[q], pyridine-N-oxide and derivatives[r, s], β and γ-picoline-N-oxide[r, s], quinoline-N-oxide[x].

* This list is not intended to be exhaustive; details of other complexes will be found in the articles by Huré[2] and by Comyns[146]. Complexes identified during solvent extraction studies but not isolated as solids are not included.

[a] J. L. Bullock, *J. Inorg. Nuclear Chem.* **29** (1967) 2257.

[b] V. P. Markov and V. V. Tsapkin, *Zhur. Neorg. Khim.* **7** (1962) 490.

[c] I. M. Kopashova, I. K. Skutov, D. S. Umreiko and R. I. Shamanovskaya, *Russ. J. Inorg. Chem.* **12** (1967) 1748.

[d] V. M. Vdovenko, D. N. Suglobov and V. A. Krasil'nikov, *Sov. Radiochem.* **5** (1963) 311.

[e] V. M. Vdovenko, M. P. Koval'skaya and T. V. Kovalek, *Zhur. Neorg. Khim.* **2** (1957) 1677.

[f] C. Panattoni, R. Graziani, U. Croatto, B. Zarli and G. Bombieri, *Inorg. Chim. Acta* **2** (1968) 43.

[g] F. A. Hart and J. E. Newberry, *J. Inorg. Nucl. Chem.* **28** (1966) 1334; **30** (1968) 318.

[h] B. Zarli and G. Panattoni, *Inorg. Nucl. Chem. Letters* **3** (1967) 111.

[i] J. E. Fleming and H. Lynton, *Chem. and Ind.* (1960) 1415.

[j] A. Apelblat and R. Levin, *Chem. Commun.* (1970) 514.

[k] P. S. Gentile and L. H. Talley, *J. Amer. Chem. Soc.* **79** (1957) 4296.

[l] V. P. Markov and I. V. Tsapkin, *Russ. J. Inorg. Chem.* **7** (1962) 1057.

[m] P. S. Gentile and L. S. Campisi, *J. Inorg. Nucl. Chem.* **27** (1965) 2291.

[n] A. S. Solokin, K. A. Rybakov and A. M. Panteleeva, *Russ. J. Inorg. Chem.* **14** (1969) 1362.

[o] V. V. Savant and C. C. Patel, *J. Inorg. Nucl. Chem.* **31** (1969) 2319.

[p] V. M. Vdovenko, I. G. Suglobova and M. Mezei, *Sov. Radiochem.* **4** (1962) 342.

[q] C. C. Addison, H. A. J. Champ, N. Hodge and A. H. Norbury, *J. Chem. Soc.* (1964) 2354.

[r] A. V. Nikolaev, V. G. Torgov, V. K. Roman, V. A. Mikhailov and I. L. Kotlyarevskii, *Sov. Radiochem.* **4** (1962) 266.

[s] V. G. Torgov, A. V. Nikolaev, V. E. Mikhailov, L. N. Korolenok, L. G. Stadnikova and I. L. Kotlyarevskii, *Izv. Sibirsk. Otd. Akad. Nauk. SSSR Ser. Khim. Nauk.* (1964) 95; according to *C.A.* **63**, 5004 d.

[t] A. Deptula, *Nukleonika* **10** (1965) 765.

[u] S. S. Sandhu and S. S. Sandu, *Chem. and Ind.* **33** (1967) 1405.

[v] P. V. Balakrishnan, S. K. Patil, H. D. Sharma and H. V. Venkatasetty, *Can. J. Chem.* **43** (1965) 2052.

[w] V. P. Markov and N. N. Knyazeva, *Russ. J. Inorg. Chem.* **6** (1961) 782.

[x] A. K. Majumdar and R. G. Battacharyya, *Sci. Culture* (*Calcutta*) **35** (1969) 271.

Hexavalent oxynitrato-complexes

Preparation and Properties

It is well established that oxynitrato ions of uranyl(VI) play an important role both in the anion exchange of uranium(VI) and in its extraction from aqueous nitrate media by, for example, trialkylamines, and solid uranyl(VI) complexes of the types $M^IUO_2(NO_3)_3$

(M^I = for example[2,101,126,138,139,152,158–161], K, NH_4, Rb, Cs, NEt_4, NEt_2H_2, NMe_4, $N(C_{10}H_{21})_4$) and $M^I{}_2UO_2(NO_3)_4$ (M^I = for example[2,100,158–164], NH_4, $NEtH_3$, Rb and Cs) are obtained by reactions in either aqueous nitric acid or dinitrogen tetroxide. Analogous neptunyl(VI)[101,161,165] and plutonyl(VI)[100,101,161] trinitrato-complexes are known, although they have not been so extensively studied, but tetranitrato-complexes appear not to have been characterized. Uranyl(VI) tetranitrato-complexes of the types $M^I{}_2UO_2(NO_3)_4$ (M^I = Rb, Cs, PyH and QuinH) and $M^{II}UO_2(NO_3)_4$ (M^{II} = Mg and Zn) are also formed during the thermal decomposition of hexanitratouranates(IV)[102].

X-ray and neutron diffraction studies have demonstrated the presence of bidentate nitrate groups in $RbUO_2(NO_3)_3$[166] and $CsUO_2(NO_3)_3$[167,168]. As in the uranyl nitrate hydrates (p. 299) and certain complexes with oxygen donor ligands (p. 301) there are six oxygen atoms (in this case from three bidentate nitrate groups) arranged equitorially around a virtually linear uranyl(VI) group. The three nitrate groups are symmetrically distributed around the uranium atom, the U–O (nitrate) distances being 2·48 Å in $RbUO_2(NO_3)_3$[166] and 2·50 Å in the isostructural caesium salt[167]. Unit cell dimensions are given in Table 6 together with those for $Rb_2UO_2(NO_3)_4$ and the structure of $RbUO_2(NO_3)_3$ is shown schematically in Fig. 6.

Infrared data are consistent with the presence of only covalent nitrate groups in the

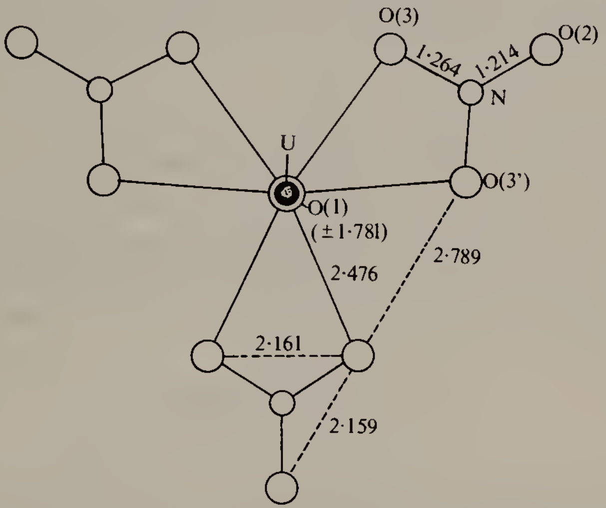

FIG. 6. Configuration of the oxygen atoms about the uranium atom and bond distances (Å) in the nitrate group for $RbUO_2(NO_3)_3$. (Reproduced by permission from G. A. Barclay *et al.*, *Acta Cryst.* **19** (1965) 205.)

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[158] C. C. Addison and N. Hodge, *J. Chem. Soc.* (1961) 2987, and references therein.

[159] M. A. Yakimov, N. F. Nosova and A. Ya. Degtyarev, *Sov. Radiochem.* **5** (1963) 60.

[160] L. V. Volod'ko, A. I. Komyak, M. R. Posledovich and A. I. Serafimovich, *Zur. Prikl. Spektrosk.* **8** (1968) 990, according to *C.A.* **69**, 81932e.

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[162] A. A. Lipovskii and M. G. Kuzina, *Sov. Radiochem.* **5** (1963) 628.

[163] V. M. Vdovenko, A. A. Lipovskii and M. G. Kuzina, *Zhur. Neorg. Khim.* **2** (1957) 970.

[164] E. Staritzky and D. I. Walker, *Anal. Chem.* **29** (1957) 164.

[165] C. C. Waggener, *J. Amer. Chem. Soc.* **80** (1958) 3167.

[166] G. A. Barclay, T. M. Sabine and J. C. Taylor, *Acta Cryst.* **19** (1965) 205.

[167] M. S. Zivadinovic, *Bull. Inst. Nucl. Sci. Phys. Boris Kidric* **18** (1967) 1.

[168] S. S. Malcic and L. M. Manojlovic, *Bull. Inst. Nucl. Sci. Boris Kidric* **11** (1961) 135.

trinitrato-complexes (see, for example, refs. 126, 131, 139, 156, 160, 169, 170), but there is a controversy over the existence of discrete $UO_2(NO_3)_4^{2-}$ ions. It appears from the results obtained by Addison and Hodge[158] that such species do not exist in appreciable concentrations in non-aqueous media and earlier infrared studies[160, 162] are stated to indicate the presence of ionic nitrate in the solids. However, on the basis of spectral studies Ryan[161] considers that discrete $UO_2(NO_3)_4^{2-}$ ions do exist in nitromethane solution in the presence of high concentrations of NEt_4NO_3 and some recent polarized infrared studies[170] are interpreted on the basis of the presence of this ion with both mono- and bidentate nitrate groups in certain solid complexes. Obviously this question will be settled only by reliable X-ray or neutron diffraction studies.

The asymmetric uranyl stretching frequency, ν_3, occurs in the region of 950 cm^{-1} (see, for example, refs. 126, 131, 160, 169–171) in the above types of complex and ν_2 (the bending deformation) has been identified[138,139,152] in the range 260–268 cm^{-1}; bands at 219 and 223 cm^{-1} are believed to be associated with U–O (nitrate) vibrations[138]. The infrared inactive symmetric stretching frequency, ν_1, is observed[172] in the Raman spectra of the complexes between 870 and 880 cm^{-1}, close to the position recorded for uranyl nitrate complexes with oxygen donor ligands.

Spectral results obtained during the Manhattan Project are discussed by Dieke and Duncan[173] and the extensive literature on the absorption and fluorescence spectra of uranyl(VI) nitrato-complexes has been authoritatively reviewed by Rabinowitch and Bedford[142]. More recent publications[97,101,158] contain spectral data for uranium, neptunium and plutonium complexes in non-aqueous media such as nitromethane and dinitrogen tetroxide and Komyak and co-workers[174,175] have reported solid state spectral data for a variety of uranyl(VI) trinitrato- and tetranitrato-complexes.

The PMR spectrum[176] of NpO_2^{2+} doped $RbUO_2(NO_3)_3$ and the optical absorption spectrum[177] of NpO_2^{2+} doped $CsUO_2(NO_3)_3$ have been reported. The latter results lead to the assignment of four pure electronic excitations within the $5f^1$ configuration (6458, 9420, 17,841, and 20,815 cm^{-1}) and the assignment of five electronic levels (13,914, 16,071, 16,093, 17,968 and 21,021 cm^{-1}) to excitations of a bonding electron into the $5f$ shell.

3. SULPHATES

Introduction

As indicated by the anhydrous complexes listed in Table 13, surprisingly few actinide sulphates are known. This appears to stem from lack of research, since it is very likely that

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[170] L. V. Volod'ko, A. I. Komyak and M. R. Posledovich, *Zhur. Prikl. Spektrosk.* **11** (1969) 1097, according to *C.A.* **72**, 94796a.

[171] L. V. Volod'ko, A. I. Komyak and M. R. Posledovich, *Zhur. Prikl. Spektrosk.* **9** (1968) 436, according to *C.A.* **70**, 52611.

[172] J. I. Bullock, *J. Chem. Soc.* (A) (1969) 781.

[173] G. H. Dieke and A. B. F. Duncan, *The Spectroscopic Properties of Uranium Compounds*, Nat. Nucl. En. Series Div. III, Vol. 2, McGraw-Hill, N.Y. (1949).

[174] A. I. Komyak and L. V. Volod'ko, *Vestsi Navuk Belaruss SSR Ser. Fiz.-Mat. Navuk* (1969) 115, according to *C.A.* **71**, 17311r.

[175] A. I. Komyak, A. N. Serchenko and E. V. Ditsh, *Dokl. Akad. Nauk. Beloruss. SSR* **12** (1968) 769, according to *C.A.* **70**, 42531z.

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[177] A. F. Leung and E. Y. Wong, *Phys. Rev.* **187** (1969) 504.

stable sulphates or sulphate hydrates will exist for neptunium(III), protactinium(IV), neptunium(IV), neptunium(VI) and plutonium(VI). The situation with respect to uranium(V), neptunium(V) and plutonium(V) is somewhat different and, for example, in view of the ready disproportionation of uranium(V) in most aqueous media it appears unlikely that stable sulphates will form in other than non-aqueous systems. Numerous hydrates, not always well characterized, are formed by most of the compounds listed in Table 13 and examples of trivalent (U, Pu and Am), tetravalent (Th, U and Pu) and hexavalent (U) sulphato-complexes are known.

Previous summaries of the actinide sulphates have been limited to articles on individual elements. Many references to earlier publications will be found in the articles on thorium[178], uranium[179–181], and plutonium[182,183]. In contrast to many other fields of actinide chemistry, little work has been reported on sulphates during recent years.

Trivalent sulphates and sulphato-complexes

Preparation and Properties

Although anhydrous uranium(III) sulphate is unknown, the olive-green octahydrate $U_2(SO_4)_3 \cdot 8H_2O$ has been obtained[184] by the addition of ethanol to a uranium(III) solution prepared by the electrolytic reduction of uranium(VI) at a mercury cathode. The solid compound is moderately stable in dry air, but oxidation to uranium(IV) occurs on dissolution in water and in aqueous sulphuric or hydrochloric acids. Trivalent neptunium sulphates

TABLE 13. ACTINIDE SULPHATES*

Valence state	Element					
	Th	Pa	U	Np	Pu	Am
III	†	†	‡	§	$Pu_2(SO_4)_3$	$Am_2(SO_4)_3$
IV	$Th(SO_4)_2$	§	$U(SO_4)_2$	§	$Pu(SO_4)_2$	§
V		$H_3PaO(SO_4)_3$ $HPaO(SO_4)_2$ $HPaO_2(SO_4)$	§	§	§	§
VI			UO_2SO_4	§	§	§

* Hydrates are formed by all the compounds listed apart from those of protactinium.

† Trivalent compounds are unlikely to be capable of existence for Th and Pa.

‡ The hydrated compound $U_2(SO_4)_3 \cdot 8H_2O$ is known.

§ The preparation of compounds for these valence states appears not to have been studied or products obtained (e.g. Np(IV)) have not been analysed.

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[178] J. Flahaut, ref. 1, p. 1103.

[179] J. Huré, ref. 2, Vol. XV(2) pp. 395 and 449; Vol. XV(4) pp. 742 and 773.

[180] R. N. Shchelokov, Chapter 8 in *Complex Compounds of Uranium*, I. I. Chernyaev (Ed.), Israel Prog. Scien. Transl., Jerusalem (1966): IPST Cat. No. 2173.

[181] G. T. Bolotova and V. A. Golovnya, Chapter 20 in *Complex Compounds of Uranium*, I. I. Chernyaev (Ed.), Israel Prog. Scien. Transl., Jerusalem (1966): IPST Cat. No. 2173.

[182] P. Faugeras and M. Heunenberger, ref. 5, Vol. XV(3), p. 774; P. Faugeras and E. Poulin, ref. 5, Vol. XV(5), p. 473.

[183] M. Cleveland, ref. 6, p. 430.

[184] R. Barnard, J. I. Bullock and L. F. Larkworthy, *Chem. Commun.* (1967) 1270.

are unknown, but $Pu_2(SO_4)_3$[185] and $Am_2(SO_4)_3$[186,187] are both readily obtained by dehydration of hydrated sulphates ($Pu_2(SO_4)_3 \cdot 7H_2O$[185], $Pu_2(SO_4)_3 \cdot 5H_2O$[100], $Am_2(SO_4)_3 \cdot 5H_2O$[187] and $Am_2(SO_4)_3 \cdot H_2O$[186] are known) at elevated temperatures.

Little is known concerning the chemical and physical properties of these compounds and apart from the hydrates, complexes with donor ligands appear to be unknown. The magnetic moment of $U_2(SO_4)_3 \cdot 8H_2O$ varies with temperature[184] ($\mu_{eff} = 3{\cdot}22$ B.M. at 302°K and 2·67 B.M. at 87°K); solid state spectra have been recorded for this compound[184] and for $Am_2(SO_4)_3 \cdot 5H_2O$[187]. The anhydrous compound, $Am_2(SO_4)_3$, decomposes to yield AmO_2 at temperatures above 800°C[186].

A variety of trivalent sulphato-complexes of uranium, plutonium and americium can be obtained by crystallization from aqueous sulphate media. These include hydrated complexes of general types $M^IM^{III}(SO_4)_2 \cdot 4H_2O$ (M^I = Rb for U[188], M^I = Na, NH_4, Rb, Cs and Tl for Pu[189,190], M^I = Rb, Cs and Tl for Am[187]) and $M^IM^{III}(SO_4)_2 \cdot 2H_2O$ (M^I = Na for U[188], M^I = K for Pu[100] and Am[187]) and anhydrous compounds of the type $M^I_8M^{III}_2(SO_4)_7$ (M^I = K for Pu[100], M^I = K, Cs and Tl for Am[187]). The magnetic moments of these and other uranium complexes (e.g. $K_3U(SO_4)_3$, $Cs_2U_2(SO_4)_4 \cdot 11H_2O$ and $(NH_4)_2U_2(SO_4)_4 \cdot 9H_2O$) vary with temperature[188] (cf. $U_2(SO_4)_3 \cdot 8H_2O$ mentioned above). Little else appears to be known concerning the properties of the various complexes and it would obviously be interesting to have structural data on certain of the compounds which have potentially high coordination numbers.

Tetravalent sulphates and sulphato-complexes

Preparation and Properties of Tetravalent Sulphates

Thorium[178,191,192], uranium[179,181,193,194] and plutonium[182,183] disulphates form a variety of hydrates of which the most stable appear to be those of the types $M(SO_4)_2 \cdot 8H_2O$ and $M(SO_4)_2 \cdot 4H_2O$. Details of the conditions under which the different hydrates form and summaries of their properties will be found in the references cited. Probably the most important compound is $Pu(SO_4)_2 \cdot 4H_2O$ which is recommended[195,196] as a primary analytical standard.

The octahydrates lose water readily and are converted to the tetrahydrates at approximately 70°C. Anhydrous thorium[178,191], uranium[179,181,197–199] and plutonium disul-

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[188] R. Barnard, J. I. Bullock and L. F. Larkworthy, *Chem. Commun.* (1968) 960.

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[190] H. H. Anderson, ref. 189, Chapter 6.19.

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phate[182,183,200–202] are obtained by heating the appropriate disulphate tetrahydrate in air at temperatures between 400° and 500°C or by evaporating aqueous solutions containing an excess of sulphuric acid and heating at 450–600°C to remove the excess acid. At temperatures in excess of 600°C $Th(SO_4)_2$ and $Pu(SO_4)_2$ decompose to yield their respective dioxides, whereas $U(SO_4)_2$ undergoes oxidation with the formation of UO_2SO_4. The energy of conversion of $U(SO_4)_2$ to UO_2SO_4[197,198] is 33 kcal $mole^{-1}$. Selected thermodynamic data for the anhydrous actinide disulphates are given in Table 14. The heat of hydration, $<U(SO_4)_2\cdot 4H_2O> + (4H_2O) \rightarrow <U(SO_4)_2\cdot 8H_2O>$, is $-8\cdot42$ kcal $mole^{-1}$ [203].

Although Np(IV) is known to form an insoluble disulphate hydrate, the composition of the product has not determined[204] and $Np(SO_4)_2$ appears to be unknown. Protactinium (IV)[205], like uranium(IV)[206], is known to form mixed fluoro-sulphate hydrates, e.g. $MF_2SO_4\cdot 2H_2O$ (M = Pa and U), but simple tetravalent sulphates have not yet been prepared. Basic sulphates of the type $M(OH)_2SO_4$ (M = Th[178,207,208] and U[179,181,209])

TABLE 14. SELECTED THERMODYNAMIC DATA FOR ACTINIDE SULPHATES

Compound	Colour	$-\Delta H_{f_{289}}$ kcal $mole^{-1}$	S_{298} eu	Heat capacity			Ref.
				$C_p = A+B\times10^{-3}T$ cal $mole^{-1}$ °K		Temp. range °K	
				A	B		
$^*U_2(SO_4)_3$	—	911±30	—				a
$^*Np_2(SO_4)_3$	—	911±15	—				a
$Pu_2(SO_4)_3$	Blue-grey	942±20	—				a
$Th(SO_4)_2$	White	607	35·4	25·0	55·2	623–897	b
$U(SO_4)_2$	Green	540±10	38·4				c
$^*Np(SO_4)_2$	—	546±15	—				a
$Pu(SO_4)_2$	Pink	526±5	39·0	†	†	†	d
$UO_2(SO_4)$	Yellow	449±7	—				c
$UO_2(SO_4)\cdot H_2O$	Yellow	519±6	—				c
$UO_2(SO_4)\cdot 3H_2O$	Yellow	661±5	—				c
$UO_2(SO_4)\cdot 2\cdot 5H_2O$	Yellow	624·4	—				e

* Compound unknown.

† C_p values in the temperature range 298–1500°K are given in ref. d.

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are known and the existence of a variety of other, less well-characterized uranium(IV) basic sulphates has been claimed[181], but the evidence is not conclusive.

Although no structural data are yet available for anhydrous actinide(IV) disulphates, X-ray studies have shown[210] that there is a square antiprismatic arrangement of eight oxygen atoms around each uranium atom in $U(SO_4)_2 \cdot 4H_2O$. Uranium atoms are linked by bridging sulphate groups and each is bonded to four water molecules. Non-bonded sulphate oxygen atoms appear to hydrogen bond to water molecules in adjacent layers. A square antiprismatic arrangement of oxygen atoms around the metal atom is also found for $Th(OH)_2SO_4$[207] and $U(OH)_2SO_4$[209]. Unit cell dimensions for tetravalent actinide sulphate hydrates are given in Table 15. The magnetic susceptibilities of both $U(SO_4)_2 \cdot 4H_2O$[184, 211, 212] and $Pu(SO_4)_2 \cdot 4H_2O$[213] exhibit marked, positive deviations from Curie–Weiss behaviour at low temperature. Extrapolation over the linear regions yields effective magnetic moments of 3·58 ($\theta = -113°$) and 2·96 B.M. ($\theta = -290°$), respectively. Solid state spectra have been recorded for both compounds[184,214,215] but no energy level assignments have been made.

Apart from the hydrates described above complexes with oxygen donor ligands known at present appear to be limited to those formed with urea, $Th(SO_4)_2 \cdot xCO(NH_2)_2$ ($x = 4$, 6 and 8[216,217]), $U(SO_4)_2 \cdot 4CO(NH_2)_2$[193,194] and $U(SO_4)_2 \cdot 4CO(NH_2)_2 \cdot 4H_2O$[193], and with acetamide $U(SO_4)_2 \cdot 4CH_3CONH_2$ [193].

Tetravalent Sulphato-complexes

A large number of hydrated sulphato-complexes of thorium(IV), uranium(IV) and plutonium(IV) have been isolated from aqueous acidic media. A selection is listed in Table 16 and full preparative details will be found in the references cited with this table. The majority of the complexes lose water when heated in air to yield the corresponding anhydrous compounds, which in general are hygroscopic; $(NH_4)_2Th(SO_4)_3$[218] and $(NH_4)_4Th(SO_4)_4$[219] decompose at *ca.* 500°C to form $Th(SO_4)_2$. Uranium disulphate is obtained in a similar manner from $(NH_4)_2U(SO_4)_3$[181]. In certain instances anhydrous complexes have been isolated directly from aqueous solution, e.g. $Rb_2U(SO_4)_3$[181], $Rb_2Th(SO_4)_3$[218], $(NH_4)_2U(SO_4)_3$[181] and $(NH_4)_4U(SO_4)_4$[181], or by washing the hydrated complex with methanol, e.g. $K_4Th(SO_4)_4$[219]. Preparative details for many of the uranium(IV) complexes are summarized by Bolotova and Golovnya[181].

Apart from infrared studies on the thorium complexes[220], solid state spectral studies on the plutonium complexes[215] and the determination of the structure of $K_4Th(SO_4)_4 \cdot 2H_2O$[221]

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[216] A. K. Molodkin, O. M. Ivanova and L. E. Kozina, *Russ. J. Inorg. Chem.* **13** (1968) 1192.

[217] K. I. Petrov, A. K. Molodkin, O. D. Saralidze and O. M. Ivanova, *Russ. J. Inorg. Chem.* **14** (1969) 643.

[218] A. K. Molodkin, G. A. Skotnikova and O. M. Ivanova, *Russ. J. Inorg. Chem.* **10** (1965) 1220, and references therein.

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[221] E. G. Arutyunyan, M. A. Porai-Koshits and A. K. Molodkin, *J. Struct. Chem.* **7** (1966) 683.

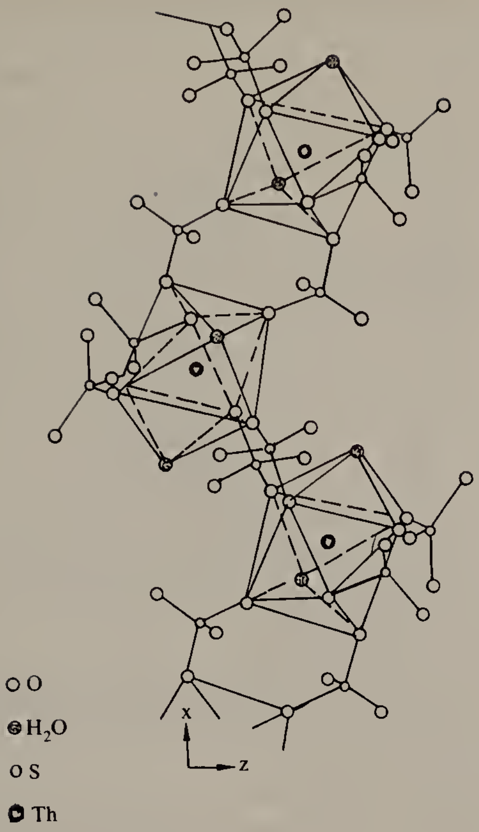

FIG. 7. Projection of the structure of $K_4[Th(SO_4)_4]\cdot 2H_2O$ on the (010) plane. (Reproduced by permission from E. G. Arutyunyan *et al.*, *J. Struct. Chem.* 7 (1966) 683.)

the chemical and physical properties of these complexes have scarcely been investigated. $K_4Th(SO_4)_4\cdot 2H_2O$ possesses triclinic symmetry with $a_0 = 10\cdot096$ Å, $b_0 = 16\cdot752$ Å, $c_0 = 9\cdot762$ Å, $\alpha = 95\cdot15°$, $\beta = 95\cdot21°$ and $\gamma = 91\cdot00°$, space group $P\bar{1}$; the structure, which is illustrated in Fig. 7, comprises chains of thorium atoms linked by pairs of bridging sulphate groups. There are nine oxygen atoms arranged around each thorium atom, the coordination polyhedron being a trigonal prism with additional vertices over the square side faces. Monodentate, bidentate and bridging sulphate groups are present with Th–O distances of 2·34 Å, 2·46–2·49 Å and 2·30–2·57 Å, respectively. Thorium–oxygen distances to the coordinated water molecules are 2·54 and 2·58 Å, respectively.

Uranium(IV) mixed sulphato–oxalato-complexes, e.g. $Rb_4U_2(SO_4)_3(C_2O_4)_3\cdot 4H_2O$, $Rb_6U_2(SO_4)_4(C_2O_4)_3\cdot 4H_2O$ and $(NH_4)_6U_2(SO_4)_4(C_2O_4)_3\cdot 4H_2O$, are also known[222,223].

Pentavalent sulphates

Preparation and Properties

The white crystalline solid $H_3PaO(SO_4)_3$ is obtained by high-temperature evaporation of sulphuric–hydrofluoric acid mixtures containing protactinium(V)[224]. Vacuum thermal

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TABLE 15. CRYSTALLOGRAPHIC DATA FOR ACTINIDE SULPHATES AND SULPHATO-COMPLEXES

Compound	Colour	Symmetry/ Space group	Lattice parameters				Ref.
			a_0 (Å)	b_0 (Å)	c_0 (Å)	$\beta°$	
$^*U(SO_4)_2 \cdot 4H_2O$	Green	O; D_{2h}^{16}–$Pnma$	14·674	11·093	5·688	—	a
$^*Th(OH)_2 \cdot SO_4$	White	O; D_{2h}^{16}–$Pnma$	11·733	6·040	7·059	—	b
$^*U(OH)_2 \cdot SO_4$	Green	O; D_{2h}^{16}–$Pnma$	11·572	5·926	6·969	—	c
$H_3PaO(SO_4)_3$	White	H; —	9·439	—	5·506	—	d
$UO_2SO_4 \cdot 3H_2O$	Yellow	O; D_{2h}^{16}–$Pbmn$	12·58	17·00	6·73	—	e
α-UO_2SO_4	Yellow	M; C_{2h}^{5}–$P2_1/c$	6·75	5·70	12·80	103·0	f
$(UO_2)_3(SO_4)_2(OH)_2 \cdot 8H_2O$	Yellow	M; C_{2h}^{3}–$C2/m$	8·81	14·13	8·85	104·25	e
$^*U_6O_4(SO_4)_6(OH)_4$	Yellow	T; C_{4h}^{5}–$I4/m$	10·741	—	10·377	—	g
$(NH_4)_2[(UO_2)_2 \cdot (SO_4)_3] \cdot 5H_2O$	Yellow	O; D_{2h}^{16}–$Pnma$	11·54	12·86	12·99	—	h
$^*Cs_2[(UO_2)_2(SO_4)_3]$	Yellow	T; D_{2d}^{3}–$P\bar{4}2_1m$	9·62	—	8·31	—	i
$K_2[UO_2(SO_4)_2] \cdot 2H_2O$	Yellow	O; D_{2h}^{7}–$Pnmb$	11·55	13·78	7·28	—	e
$Rb_2[UO_2(SO_4)_2] \cdot 2H_2O$	Yellow	O; D_{2h}^{7}–$Pnmb$	11·50	13·48	7·42	—	i
$H_2[(UO_2)_2(SO_4)_3] \cdot 5H_2O$	Yellow	O; D_{2h}^{12}–$Pmnn$	12·86	12·99	11·57	—	e

* Full structural data are given in reference cited.

[a] P. Kierkegard, *Acta Chem. Scand.* **10** (1956) 599.

[b] G. Lundgren, *Arkiv. Kemi*, **2** (1950) 535; *Svensk. Kem. Tidskr.* **71** (1959) 200.

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[e] R. J. Traill, *Amer. Mineralogist* **37** (1952) 394.

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[h] E. Staritsky, D. T. Cromer, and D. I. Walker, *Anal. Chem.* **28** (1956) 1634.

[i] M. Ross and H. T. Evans, *J. Inorg. Nucl. Chem.* **15** (1960) 338.

decomposition is believed to lead to the successive formation of $HPaO(SO_4)_2$ (375–400°C), $HPaO_2SO_4$ (*ca.* 500°C) and Pa_2O_5 (> 600°C). $H_3PaO(SO_4)_3$ possesses hexagonal symmetry (Table 15), but no structural results are available. However, the infrared spectrum of this compound and that of $HPaO(SO_4)_2$ indicate the presence of bidentate sulphato-groups. Although a potassium sulphato-protactinate(V) complex appears to exist, the product has not been satisfactorily characterized.

Pentavalent sulphates and sulphato-complexes have not been reported for other actinide elements.

Hexavalent sulphates and sulphato-complexes

Preparation and Properties of Uranyl Sulphate and Basic Uranium(VI) Sulphates

It has been accepted for many years (see, for example, refs. 179, 180, 199, 225–228) that crystallization of uranium(VI) from aqueous sulphuric acid results in the formation of the yellow trihydrate $UO_2SO_4 \cdot 3H_2O$ for which X-ray (Table 15) and thermodynamic data (Table 14) are available. It is also claimed[199,227] that thermal decomposition of the trihydrate in air results in the successive formation of a dihydrate, a monohydrate and anhydrous

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[227] K. J. Notz and H. H. Jaffe, *J. Inorg. Nucl. Chem.* **25** (1963) 851.

[228] B. B. Owens and S. W. Mayer, *J. Inorg. Nucl. Chem.* **26** (1964) 501.

TABLE 16. HYDRATED SULPHATO-COMPLEXES

Complex type*	M^I with x in parentheses	Ref.
$M^I_2[Th(SO_4)_3]\cdot xH_2O$	Na (6), NH_4 (5), K (4), Rb (2), Cs (2), Tl (4)	a, b
$M^I_2[U(SO_4)_3]\cdot xH_2O$	K (2), Cs (2)	c, d
$M^I_4[Th(SO_4)_4]\cdot xH_2O$	Na (4), K (2), NH_4 (2), Cs (1)	b, e
$M^I_4[U(SO_4)_4]\cdot xH_2O$	Na (6), K (2), NH_4 (3), Rb (2), enH (2)	c, d
$M^I_4[Pu(SO_4)_4]\cdot xH_2O$	K (2), NH_4 (2), Rb (2 and 1)	f, g, h, i
$M^I_6[Th(SO_4)_5]\cdot xH_2O$	NH_4 (3), Cs (3)	e, j
$M^I_6[U(SO_4)_5]\cdot xH_2O$	NH_4 (4)	c, d
$M^I_6[Pu(SO_4)_5]\cdot xH_2O$	Na (1), NH_4 (3–4), K (?)	g
$M^I_8[Th(SO_4)_6]\cdot xH_2O$	NH_4 (2)	e, j
$M^I_8[U(SO_4)_6]\cdot xH_2O$	NH_4 (3)	c, d
$M^I_6[U_2(SO_4)_7]\cdot xH_2O$	Na (4)	d

* The water of hydration is shown outside the coordination sphere for convenience since structural data are available only for $K_4[Th(SO_4)_4]\cdot 2H_2O$.

[a] A. K. Molodkin, G. A. Skotnikova and O. M. Ivanova, *Russ. J. Inorg. Chem.* **10** (1965) 1220, and references therein.

[b] O. N. Evstaf'eva, A. K. Molodkin, G. G. Dvoryantseva, O. M. Ivanova and M. I. Struchkova, *Russ. J. Inorg. Chem.* **11** (1966) 697.

[c] V. A. Golovnya, L. A. Pospelova and G. T. Bolotova, *Russ. J. Inorg. Chem.* **5** (1960) 1069, and references therein.

[d] V. A. Golovnya and G. T. Bolotova, *Russ. J. Inorg. Chem.* **6** (1961) 288, and references therein.

[e] A. K. Molodkin, G. A. Skotnikova and O. M. Ivanova, *Russ. J. Inorg. Chem.* **10** (1965) 1329, and references therein.

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[h] W. B. Lewis and N. Elliott, *J. Chem. Phys.* **27** (1957) 904.

[i] W. H. Brown and D. R. Rogers, U.S. Reports MLM-1163 (1963) and MLM-1212 (1964).

[j] A. K. Molodkin, G. A. Skotnikova and O. M. Ivanova, *Russ. J. Inorg. Chem.* **10** (1965) 1453, and references therein.

uranyl sulphate; an alternative decomposition[226] involving $UO_2SO_4\cdot 1{\cdot}5H_2O$ and UO_2SO_4 has also been proposed. The existence of the trihydrate as the stable phase obtained on crystallization from water, and other reports concerning the existence of $UO_2SO_4\cdot 4H_2O$[198,229,230] and $UO_2SO_4\cdot 3{\cdot}5H_2O$[229–232] have, however, recently been queried by Cordfunke[233] who obtained $UO_2SO_4\cdot 2{\cdot}5H_2O$ by drying the initial product of crystallization at 50°C or, alternatively, by allowing anhydrous uranyl sulphate to hydrate over saturated sodium chloride solution. Wet crystals in equilibrium with saturated aqueous uranyl sulphate solutions apparently give the same X-ray powder diffraction pattern as $UO_2SO_4\cdot 2{\cdot}5H_2O$, this pattern being somewhat different from that previously reported for $UO_2SO_4\cdot 3H_2O$. Cordfunke also reports[233] that $UO_2SO_4\cdot 2{\cdot}5H_2O$ decomposes directly to UO_2SO_4 without the formation of intermediate hydrates, although it must be recognized

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[229] J. M. Leroy, J. Trudo and G. Tridot, *Compt. Rend.* **260** (1965) 5802.

[230] J. M. Leroy, *Rev. Chim. Miner.* **4** (1967) 129.

[231] H. W. Dunn, U.S. Report ORNL-2092 (1956).

[232] T. Urbanski, Polish Acad. Sci. Inst. Nucl. Res. Rept. 118/IV (1959).

[233] E. H. P. Cordfunke, *J. Inorg. Nucl. Chem.* **31** (1969) 1327.

that the rate of heating during these experiments, 8°/min, was appreciably faster than the rate, 3°/min, employed by certain earlier workers[227]. However, the existence of $UO_2SO_4 \cdot 2H_2O$ as a metastable phase[225] in the UO_2SO_4–H_2O–H_2SO_4 phase system is confirmed by Cordfunke[233] who also reports the formation of $UO_2SO_4 \cdot H_2SO_4 \cdot 2{\cdot}5H_2O$ at 26°C. It appears that the most satisfactory route to the monohydrate involves[228,233] heating together stoichiometric amounts of UO_2SO_4 and $UO_2SO_4 \cdot 2{\cdot}5H_2O$ (or $UO_2SO_4 \cdot 3H_2O$) in a sealed quartz vessel at 200°C for several hours. This compound is unstable when stored at room temperature[233].

Thermal decomposition of uranyl sulphate hydrates yields the yellow, anhydrous compound above 300°C[179,180,198,199,226–230,233]; an $\alpha \rightarrow \beta$ transformation is believed to occur at *ca.* 755°C[198,227,230]. Unit cell dimensions for the low-temperature (α) form are given in Table 15; no structural data are available. On the basis of Raman studies in non-aqueous solvents the ν_1 and ν_2 modes of the uranyl group in UO_2SO_4 have been assigned[234] at 751–757 cm^{-1} and *ca.* 200 cm^{-1}, respectively. The asymmetrical stretching vibration (ν_3) occurs[235] at 939 cm^{-1} in $UO_2SO_4 \cdot 3H_2O$, the position of ν_2 being estimated as 192 cm^{-1}. Absorption and fluorescence spectral data for uranyl sulphate and its hydrates are discussed in the excellent review by Rabinowitch and Bedford[142] and in a more recent publication by Pant and Pande[236]. Thermodynamic data are listed in Table 14.

Anhydrous uranyl sulphate decomposes when heated in air to yield U_3O_8 at elevated temperatures. In the presence of hydrogen or hydrogen sulphide–hydrogen mixtures the

TABLE 17. EXAMPLES* OF URANYL SULPHATE COMPLEXES WITH DONOR LIGANDS

Complex type	Ligand (L)
$UO_2SO_4 \cdot L$	Acetamide[c], (as dihydrate), thiourea[d], thiourea dioxide[h] (as monohydrate), 1,10 phenanthroline[f] (as pentahydrate), 2,2′ bipyridyl[f] (as tetrahydrate)
$UO_2SO_4 \cdot 2L$	Urea[a], urea[b] (as monohydrate), methylurea[b], tetramethylurea[b], 1,3 diethylurea[b], thiourea[d], acetamide[c], pyridine-N-oxide[e], α-picoline oxide[e]
$UO_2SO_4 \cdot 3L$	Urea[a,b], 1,3 dimethylurea[b], ethylurea[b], 1,3 diethylurea[b], acetamide[c] (as monohydrate), tributylphosphine oxide[g]
$UO_2SO_4 \cdot 4L$	Urea[a], 1,3 dimethylurea[b]

* This list is not intended to be exhaustive.

[a] V. P. Markov and I. V. Tsapkina, *Russ. J. Inorg. Chem.* 4 (1959) 1028; 7 (1962) 620.

[b] A. Deptula, *Nukleonika*, 10 (1965) 765.

[c] V. P. Markov and I. V. Tsapkina, *Russ. J. Inorg. Chem.* 7 (1962) 1057.

[d] V. P. Markov and N. N. Knyazeva, *Russ. J. Inorg. Chem.* 6 (1961) 782.

[e] A. V. Nikolaev, V. G. Torgev, V. K. Roman, V. A. Mikhailov and I. L. Kotlyarevskii, *Soviet Radiochem.* 4 (1962) 266.

[f] V. P. Markov and I. V. Tsapkina, *Russ. J. Inorg. Chem.* 4 (1959) 1030.

[g] S. M. Sinitsyna and N. M. Sinitsyn, *Dokl. Akad. Nauk. SSSR*, **168** (1966) 110.

[h] V. A. Golovnya and G. T. Bolotova, *Russ. J. Inorg. Chem.* 6 (1961) 288.

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[234] L. V. Volod'ko and K. V. Sabilo, *Zhur. Prikl. Spekt. Akad. Nauk Beloruss. SSR* 4 (1966) 52.

[235] K. Ohwada, *Spect. Chim. Acta*, **24A** (1968) 595.

[236] D. D. Pant and D. N. Pande, *Ind. J. Pure App. Phys.* 4 (1966) 471.

dioxide is formed at 580°C and 300°C, respectively[237]. Publications dealing with solubility data and the physical and chemical properties of aqueous uranyl sulphate solutions are discussed in previous reviews[179,180].

In addition to the hydrates discussed above, uranyl sulphate is known to form complexes with a number of donor ligands. Typical examples are listed in Table 17 together with references to their modes of preparation. The chemistry of these complexes has not been studied.

Basic uranium(VI) sulphates have also been recorded but many of the compounds have not been satisfactorily characterized (see refs. 179 and 180 for a survey of the literature on basic compounds). The compound $(UO_2)_3(SO_4)_2(OH)_2 \cdot 8H_2O$, however, exists naturally as the mineral zippeite; it possesses monoclinic symmetry, space group C^3_{2h}–$C2/m$ (Table 15). In addition, $U_6O_4(OH)_4(SO_4)_6$ has been characterized crystallographically; the structure consists of $U_6O_4(OH)_4$ cations and sulphate anions[238]. Each cation comprises an octahedron of uranium atoms between which are placed oxygens and hydroxyls at the approximate corners of a cube. Thus each uranium has three (O, OH) neighbours (U–O = 2·3 Å) and each (O, OH) has four uranium neighbours. The U–U distances are 3·84 and 3·85 Å. The analogous cerium compound is isostructural.

Preparation and Properties of Uranyl Sulphato-complexes

Complex sulphates of uranyl(VI) have been known for many years (for summaries of earlier work see refs. 179 and 180) and numerous compounds have been characterized. Examples of different classes of compound are given in Table 18. It is not possible in the space available to discuss preparative procedures which, in general, involve precipitation from aqueous media under controlled conditions or dehydration of a hydrated complex, and the interested reader is referred to the references cited with Table 18 and to the discussion by Shchelokov[180]. Very little recent work has been published on the uranyl(VI) sulphato-complexes and few of their properties have been recorded.

In contrast to complexes containing $U:SO_4$ ratios up to 1:2·0, those of the types $M^I_6[(UO_2)_2(SO_4)_5] \cdot 2H_2O$ and $M^I_4[UO_2(SO_4)_3] \cdot 2H_2O$ are appreciably unstable in aqueous media and relatively difficult to isolate. The anhydrous sodium salt $Na_4[UO_2(SO_4)_3]$, which melts congruently at 562°C, has been identified during an investigation of the Na_2SO_4–UO_2SO_4 phase system[239]; $Na_2[UO_2(SO_4)_2]$ and $Na_2[(UO_2)_3(SO_4)_4]$ were also characterized during this investigation. Another example of the uranyl(VI) trisulphato series, the tridecylammonium salt, was recently isolated during extraction studies[240].

Acid complexes such as $H_2[(UO_2)_2(SO_4)_3] \cdot 5H_2O$ (cf. analogous complexes listed in Table 18), $H_2[(UO_2)_2(SO_4)_3] \cdot 3H_2O$ and $H_2[UO_2(SO_4)_2] \cdot 2H_2O$ are reported to have been characterized during UO_2SO_4–H_2SO_4–H_2O studies[241–244] and it is claimed[245,246] that the anhydrous compound $H_2[UO_2(SO_4)_2]$ also exists. The last apparently forms the dihydrate on exposure to the atmosphere. More recently, however, Cordfunke[233] reported the isola-

[237] G. Tridot and J. M. Leroy, *Bull. Soc. Chim. Fr.* (1964) 1178.
[238] G. Lundgren, *Arkiv. Kemi*, **34** (1953) 349; *Svensk. Kem. Tidskr.* **71** (1959) 200.
[239] P. I. Federov, *Russ. J. Inorg. Chem.* **11** (1966) 1167.
[240] A. A. Lipovskii and M. G. Kuzina, *Russ. J. Inorg. Chem.* **10** (1965) 740.
[241] G. Wyroubuff, *Bull. Soc. Min.* **32** (1909) 340.
[242] J. Meyer and E. Kasper, *Z. anorg. Chem.* **155** (1926) 49.
[243] A. Colani, *Compt. Rend.* **185** (1927) 274; *Bull. Soc. Chim. Fr.* **43** (1928) 754.
[244] R. I. Traill, *Amer. Mineral.* **37** (1952) 394.
[245] E. Peligot, *Ann. Chim. Phys.* **12** (1844) 558.
[246] C. Schultz-Sellack, *Ber.* **4** (1871) 12.

tion of only $UO_2SO_4 \cdot 2{\cdot}5H_2O$, $UO_2SO_4 \cdot 2H_2O$ (metastable) and $UO_2SO_4 \cdot H_2SO_4 \cdot 2{\cdot}5H_2O$ during an investigation of the UO_2SO_4–H_2SO_4–H_2O system; he observed no evidence for the existence of the above acid sulphato-uranates(VI). If the latter observation is correct it does, of course, cast doubt on the validity of the X-ray data reported by Traill[244] for $H_2[(UO_2)_2(SO_4)_3] \cdot 5H_2O$.

TABLE 18. EXAMPLES OF THE DIFFERENT CLASSES OF URANYL(VI) SULPHATO-COMPLEXES

Complex type	U:SO₄	M^{I}
$M^{I}_2[(UO_2)_2(SO_4)_3] \cdot 5H_2O$	1:1·5	NH_4[a,b], K[a], NH_3OH[c]
$M^{I}_2[(UO_2)_2 \cdot (SO_4)_3]$	1:1·5	NH_4[d], Cs[e]
$M^{I}_2[UO_2(SO_4)_2] \cdot 2H_2O$	1:2·0	NH_4[a,b,e,f–l], K[a,c,g–j], Rb[b,c,e] Cs[h,j], Na[a] ($3H_2O$), Tl[k] ($3H_2O$)
$M^{I}_2[UO_2(SO_4)_2]$	1:2·0	NH_4[d,n], K[j], Rb[j], $C_7H_{10}N$[l]*, $C_6H_{13}N_4$[m]†
$M^{I}_6[(UO_2)_2(SO_4)_5] \cdot 2H_2O$	1:2·5	NH_4[n], K[n]
$M^{I}_4[UO_2(SO_4)_3] \cdot 2H_2O$	1:3·0	K[c], Na[a] ($3H_2O$)

* $C_7H_{10}N$, dimethylpyridinium.

† $C_6H_{13}N_4$, hexamethylenetetramine.

[a] A. Colani, *Bull. Soc. Chim. Fr.* **43** (1928) 754; *Compt. Rend.* **185** (1927) 274.

[b] E. Staritsky, D. T. Cromer and D. I. Walker, *Anal. Chem.* **28** (1956) 1634.

[c] E. Rimbach, *Ber.* **37** (1904) 461.

[d] H. Morton, and H. C. Bolton, *Chem. N.* **28** (1873) 50.

[e] M. Ross and H. T. Evans, *J. Inorg. Nucl. Chem.* **15** (1960) 338.

[f] I. A. Arfvedson, *Pogg. Ann.* **1** (1824) 262.

[g] E. Peligot, *Ann. Chim. Phys.* **5** (1842) 43.

[h] F. W. O. De Connick, *Bull. Belg. Acad.* (1905) 94.

[i] R. J. Traill, *Amer. Mineral.* **37** (1952) 394.

[j] I. I. Chernyaev, V. A. Golovnya and R. N. Shchelokov, *Russ. J. Inorg. Chem.* **5** (1960) 1454.

[k] M. Kohn, *Z. anorg. Chem.* **59** (1908) 111.

[l] C. G. Williams, *Chem. N.* **44** (1881) 307.

[m] J. Foucry, *J. Pharm. Chim.* **20** (1934) 168.

[n] R. N. Shchelokov, Chapter 8 in *Complex Compounds of Uranium*, (Ed.) I. I. Chernyaev, Eng. Transl. from Russian, Israel Prog. for Scien. Transl., Jerusalem (1966), Oldbourne Press, London.

Of the various hydroxy-sulphato-complexes believed to exist (see ref. 180 for details of the original literature) the most important is the copper complex, $Cu[(UO_2)_2(SO_4)_2(OH)_2] \cdot 6H_2O$, which exists naturally as the mineral johannite. Numerous fluoro-sulphato, oxalato-sulphato, and thiocyanato-sulphato complexes have also been characterized, but these will not be discussed; the interested reader is referred to the comprehensive review by Shchelokov and Shubochkin[247].

Few physical data are available for the known uranyl(VI) sulphato-complexes. Infrared vibrations of the uranyl group have been recorded at 918 cm^{-1} and 836 cm^{-1} for $K_2[UO_2(SO_4)_2] \cdot 2H_2O$[248] and at 911 cm^{-1} for the tridecylammonium complex[240]. Other spectral results (absorption and fluorescence) for solid complexes are summarized by

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[247] R. N. Shchelokov and L. K. Shubochkin, Chapter 9 in *Complex Compounds of Uranium*, I. I. Chernyaev (Ed.), Israel Prog. Scien. Transl., Jerusalem (1966) IPST Cat. No. 2173.

[248] L. V. Volod'ko, A. I. Komyak and L. E. Sleptsova, *Russ. J. Inorg. Chem.* **12** (1967) 1604.

Rabinowitch and Bedford[142]. Unit cell dimensions are available for several complexes (Table 15), but full structural details are available only for $Cs_2[(UO_2)_2(SO_4)_3]$[249] and for $Cu[(UO_2)_2(SO_4)_2(OH)_2]\cdot 6H_2O$[250]. The former compound, which crystallizes with tetragonal symmetry (Table 15), possesses a layer structure comprising $[(UO_2)_2(SO_4)_3]_n^{2n-}$ sheets parallel to (001), tied together by caesium ions. Each uranyl group is coordinated by five sulphate oxygens arranged as an almost planar pentagon approximately normal to the linear uranyl group. The uranium–oxygen distances in the uranyl group are 1·74 Å and the uranium bond lengths to the five oxygens from five different sulphate groups are 2·37 (×2), 2·46 and 2·47 (×2) Å[249]. There is also a pentagonal bipyramidal array of seven oxygen atoms around the uranium atoms in johannite ($Cu[UO_2SO_4(OH)]\cdot 3H_2O$)[250].

4. SULPHITES

Introduction

Actinide sulphites have not been extensively studied and only a few tetravalent thorium and uranium compounds and some hexavalent uranium compounds are known at present.

Tetravalent sulphites and sulphito-complexes

Preparation and Properties

Thorium disulphite tetrahydrate, $Th(SO_3)_2\cdot 4H_2O$, is a white, air-sensitive solid which precipitates on the addition of either sulphur dioxide or sodium sulphite to an aqueous nitrate solution containing thorium(IV)[251–253]. It was originally reported[251] that this compound lost water at 75–150°C with the formation of the anhydrous disulphite, but more recent studies[253] have shown that partial oxidation to thorium disulphate also occurs during the dehydration; the anhydrous disulphite appears never to have been obtained in a pure state.

Disulphite hydrates are not known for other actinide elements although an incompletely characterized green solid has been obtained by precipitation of plutonium(IV) in sulphite media[254].

The estimated heats of formation[255] for solid $Th(SO_3)_2$ and $U(SO_3)_2$ are −490·2 and −455·8 kcal mole⁻¹, respectively, and it is calculated[256] that the dissociation pressures of the two compounds are given, respectively, by the equations

$$\log P_{\mathrm{mm}}\,(SO_2) = -\frac{6140}{T} + 11{\cdot}154$$

and

$$\log P_{\mathrm{mm}}\,(SO_2) = -\frac{4796}{T} + 11{\cdot}231$$

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[249] M. Ross and H. T. Evans Jnr., *J. Inorg. Nucl. Chem.* **15** (1960) 338.
[250] D. E. Appleman, *Bull. Geol. Soc. Amer.* **68** (1957) 1696.
[251] V. A. Golovnya, A. K. Molodkin and V. N. Tverdokhlebov, *Russ. J. Inorg. Chem.* **9** (1964) 1097.
[252] V. A. Golovnya, A. K. Molodkin and V. N. Tverdokhlebov, *Russ. J. Inorg. Chem.* **12** (1967) 1254.
[253] V. A. Golovnya, A. K. Molodkin and V. N. Tverdokhlebov, *Russ. J. Inorg. Chem.* **12** (1967) 1092.
[254] B. B. Cunningham, Chapter 10 in *The Actinide Elements*, G. T. Seaborg, and J. J. Katz (Eds.), Nat. Nucl. Energy Series Div. IV, Vol. 14A, McGraw-Hill, N.Y. (1954).
[255] E. Erdos, *Coll. Czech. Chem. Comm.* **27** (1962) 1428.
[256] E. Erdos, *Coll. Czech. Chem. Comm.* **27** (1962) 2273.

Thorium(IV) sulphito-complexes are obtained by precipitation from aqueous media in the presence of sulphur dioxide[252,253,257,258]; analogous complexes are unknown for the remaining actinide elements, although there is spectrophotometric evidence[259] that tetravalent plutonium sulphito-complexes exist in aqueous solution. The characterized thorium(IV) complexes are of the types $M^I_2[Th(SO_3)_3]\cdot xH_2O$ (M^I = Na with $x = 5$, K with $x = 7{\cdot}5$, NH_4 with $x = 4$, and CN_3H_6 with $x = 12$) and $M^I_4[Th(SO_3)_4]\cdot xH_2O$ (M^I = Na with $x = 6$ or 3, and NH_4 with $x = 5$). Infrared data have been recorded for these complexes and for some unusual oxy- or hydroxy-sulphitothorates(IV)[253]. Thermal dehydration, as in the case of $Th(SO_3)_2\cdot 4H_2O$, is accompanied by simultaneous oxidation, the ammonium complexes, for example, yielding $Th(SO_4)_2$ above *ca.* 250°C[253].

The compositions reported for the only examples of sulphito-uranates(IV)[260], $Na_{2x}[U(SO_3)_{x+2}]\cdot zH_2O$ ($x = 3$, 4, 5 and 6), and for the range of mixed oxalato-sulphitothorates(IV)[258,260] and uranates(IV)[260], $Na_{2x}[M^{IV}(C_2O_4)_2(SO_3)_x]\cdot zH_2O$ ($x = 2$ to 7 inclusive, and 9 for Th and 2 to 6 inclusive for U), suggest that confirmatory evidence is required before the existence of such species is accepted.

Hexavalent sulphites and sulphito-complexes

Preparation and Properties

Uranyl sulphite hydrates precipitate when an aqueous suspension of UO_3 or a solution of uranyl nitrate or acetate is treated with gaseous sulphur dioxide[261–263]. The degree of hydration of the product varies with the temperature of precipitation, for example $UO_2SO_3\cdot 3H_2O$ is obtained at 80°C, and with the drying conditions, for example $UO_2SO_3\cdot 4{\cdot}5H_2O$ is obtained by drying the ethanol washed precipitate in air at room temperature whilst lower hydrates form over concentrated sulphuric acid in a vacuum. Complete thermal dehydration cannot be achieved without decomposition occurring and anhydrous uranyl sulphite is unknown. The orange precipitate obtained on the addition of a 0·2 M nitric acid solution containing Pu(VI) to aqueous ammonium sulphite has not been characterized[254] and there appears to have been no attempt to prepare neptunyl(VI) sulphites.

Anhydrous uranyl(VI) sulphito-complexes, for example, those of the types $M^I_2UO_2(SO_3)_3$ and $M^I_2(UO_2)_2(SO_3)_3$ (M^I = Na, K and NH_4[263,264]), and mixed oxalato-sulphito-uranates(VI)[265], $M^I_2[UO_2(C_2O_4)(SO_3)]$ (M^I = Na, K, NH_4 and CN_3H_6), are obtained from reactions in aqueous media. The properties of these complexes do not appear to have been investigated.

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[257] V. A. Golovnya, A. K. Molodkin and V. M. Tverdokhlebov, *Russ. J. Inorg. Chem.* **10** (1965) 1195

[258] L. N. Essen, D. P. Alekseeva and A. D. Gel'man, *Russ. J. Inorg. Chem.* **11** (1966) 853.

[259] P. H. Goeckerman and G. W. Watt, U.S. Report CN-3278 (1945).

[260] A. D. Gel'man, L. N. Essen, F. A. Zakharov, D. P. Alekseeva and M. M. Orlova, *Dokl. Akad. Nauk SSSR*, **149** (1963) 1071.

[261] A. E. Klygin and N. S. Kolyada, *Russ. J. Inorg. Chem.* 4 (1959) 101.

[262] G. A. Polonikova and K. F. Kudinova, *Russ. J. Inorg. Chem.* **6** (1961) 781.

[263] V. Kohlschütter, *Ann.* **311** (1900) 1.

[264] F. A. Zakharova and M. M. Orlova, *Russ. J. Inorg. Chem.* **12** (1967) 1699.

[265] F. A. Zakharova and M. M. Orlova, *Russ. J. Inorg. Chem.* **12** (1967) 1384.

5. SELENATES AND SELENITES

Introduction

Actinide selenates and selenites have not been extensively studied and very few compounds are known. Thus, the only selenates reported are hydrated thorium diselenate, the pentavalent protactinium compound $H_3PaO(SeO_4)_3$, and a few uranyl(VI) complexes, whilst selenites have been characterized only for thorium(IV), uranium(IV) and uranyl(VI).

Selenates

Preparation and Properties

White, crystalline thorium diselenate hydrate, $Th(SeO_4)_2 \cdot 9H_2O$, forms when thoria is heated with selenic acid; at 250°C in air it appears to form the monohydrate. The only investigations of the preparation and properties of these compounds were reported prior to 1910[266] and it would be interesting to have further information on the thorium–selenic acid system; the elements protactinium to plutonium inclusive should also form tetravalent selenates.

Evaporation of hydrofluoric–selenic acid solutions containing protactinium(V) results[224] in the crystallization of $H_3PaO(SeO_4)_3$ which is isostructural with $H_3PaO(SO_4)_3$, possessing hexagonal symmetry with $a_0 = 9{\cdot}743$ Å and $c_0 = 5{\cdot}679$ Å. Vacuum thermal decomposition yields Pa_2O_5 above 600°C without evidence for the formation of intermediate selenates (cf. $H_3PaO(SO_4)_3$, p. 309). No other pentavalent selenates are known.

Uranyl(VI) selenate is unknown, but there is one report[242] in the older literature concerning the preparation of some unusual selenato-complexes. Further information is required before the existence of many of these compounds is accepted.

Selenites

Preparation and Properties

Thorium diselenite hydrates are formed by precipitation from aqueous media[267–269] and it is reported that $U(SeO_3)_2$, a blue–green solid, is obtained by the addition of selenious acid to a solution of uranium tetrachloride in acetic acid followed by vacuum drying of the precipitate over potassium metal[270]. Uranium diselenite is stable in air at room temperature.

Uranyl selenite, UO_2SeO_3, is conveniently obtained by thermal decomposition of either $U(SeO_3)_2$[270], at *ca.* 600°C *in vacuo*, or the acid selenite[271] $H_2UO_2(SeO_3)_2$ above 290°C in air. The latter is formed by the addition of selenious acid to uranium trioxide, the thermal decomposition apparently involving the intermediate formation, 150–200°C, of the pyroselenite $UO_2Se_2O_5$. These reactions, and direct combination of selenium dioxide and uranium trioxide under controlled conditions[271], are superior to the older techniques[272] involving precipitation from aqueous uranyl sulphate, acetate or nitrate.

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[266] J. Flahaut, ref. 1, p. 1111.

[267] J. Flahaut, ref. 1, p. 1110.

[268] V. D. Anand, B. Srinivasa Achar and G. S. Deshmukh, *Z. anorg. Chem.* **315** (1962) 309.

[269] Jen-Yin Yen, Kuang-Hua Djao and Feng-Chiao Hsiau, *Pei Ching Ta Hsuëh Hsuëh Pao-Tza Ko Hsuëh*, **4** (1958) 195, according to *C.A.* **53**, 8937f.

[270] P. Khodadad, *Compt. Rend.* **250** (1960) 1273.

[271] R. Claude, *Compt. Rend.* **242** (1956) 643.

[272] J. Huré, ref. 2, Vol. XV (2) 463.

UO_2SeO_3 is a yellow solid which is water insoluble and stable in air to *ca.* 550°C. Above this temperature it decomposes with the formation of triuranium octaoxide, selenium dioxide and oxygen.

6. TELLURATES AND TELLURITES

Preparation and Properties

Very little is known concerning the chemistry of actinide tellurates and tellurites. In fact, simple tellurates appear to be unknown, although basic thorium compounds of composition $ThO(TeO_4) \cdot 8H_2O$ and $ThO(TeO_4) \cdot 4H_2O$ appear to exist[273], the only reported complex is $Na_4[UO_2(TeO_4)_3] \cdot 4H_2O$ which forms on the addition of sodium tellurate to a solution of uranyl nitrate[274].

Only two actinide tellurites are known at present. Thus, $U(TeO_3)_2$, a blue–green solid, is obtained[275] from the reaction between tellurium dioxide and uranium tetrachloride in aqueous hydrochloric acid and this is converted to the uranyl compound UO_2TeO_3 when heated at 300°C in a vacuum and when treated with oxygen-free, boiling water for several hours. Uranyl tellurite, which is a yellow solid, is alternatively prepared[276] by drying the precipitate obtained by the addition of tellurous acid to uranyl acetate, at 110°C in air. It decomposes to form U_3O_8 above 800°C in air.

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[273] E. Montigniè, *Bull. Soc. Chim.* **5** (1938) 197; **6** (1939) 672.

[274] E. Montigniè, *Bull. Soc. Chim.* **2** (1935) 864.

[275] P. Khodadad, *Compt. Rend.* **254** (1962) 1079.

[276] P. Khodadad, *Compt. Rend.* **255** (1962) 1617.

COMPOUNDS WITH GROUPS Vb AND VIb ELEMENTS

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1. INTRODUCTION

This section is concerned with the binary compounds formed between the actinides and the elements of Group VIb ("chalcogenides") and Group Vb ("pnictides"). The oxides are discussed separately in another section. Ternary systems, both compounds and solid solutions, in which there are two non-metallic elements and one actinide, or two actinides and a non-metal, are also considered briefly.

The systematic study of these compounds has been carried out almost entirely since 1945. An interest in their preparation and crystal chemistry arose in the 1950s and attention was later directed towards determining their physical and chemical behaviour, in particular magnetic, electrical and thermodynamic properties. Several hundred papers were published during the decade 1960–70, many of which were concerned with the elucidation of the chemical bonding and electronic structure in a class of compounds whose electrical behaviour ranges from that of poor semiconductors to good metallic conductors. Altogether, some seventy binary chalcogenides and forty pnictides have been reported, as well as numerous ternary compounds. By far the major amount of work has been concerned with compounds of thorium and uranium, which present no handling hazards, and plutonium, which is readily available as a by-product of the atomic energy industry and is technologically important as a fissile material. Relatively few papers have been published on neptunium and higher actinide compounds.

2. SULPHIDES, SELENIDES AND TELLURIDES

Preparation of chalcogenides

The thermochemical stability of the actinide oxides makes them unsuitable as starting materials from which to prepare the chalcogenides, except possibly at very high temperatures in the presence of carbon. The pure compounds are best prepared by reacting the finely divided metals with sulphur, selenium or tellurium or with their gaseous hydrides. Considerable care must be taken to exclude all traces of air and water vapour, since oxygen, once present, cannot be removed and results in the formation of the metal oxide or the oxychalcogenide.

Generally the pure metal in the massive form is converted to a powder by taking it through a hydriding/dehydriding cycle[1-4]. This yields a reactive form of metal, free of oxygen, which must be handled under an inert atmosphere. Either of two procedures is then employed:

(1) The powdered metal is reacted with excess H_2S or H_2Se to form the dichalcogenide,

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[1] M. Allbutt, A. R. Junkison and R. F. Carney, *Proc. Brit. Ceram. Soc.* **7** (1967) 111.

[2] M. Allbutt and R. M. Dell, *J. Nucl. Mat.* **24** (1967) 1.

[3] M. Allbutt, R. M. Dell and A. R. Junkison, *The Chemistry of Extended Defects in Non-Metallic Solids*, p. 124, North Holland (1970).

[4] P. D. Shalek, *J. Amer. Ceramic Soc.* **46** (1963) 155.

e.g. ThS_2, $ThSe_2$, US_2, USe_2. This method is not well suited to plutonium because of the greater stability of plutonium hydride, which is formed and inhibits further reaction. Tellurides have not generally been prepared in this fashion.

(2) The metal powder and an appropriate quantity of the chalcogen element are placed at opposite ends of a silica ampoule which is evacuated, sealed and heated in a two-zone furnace. The non-metal volatilizes and reacts with the metal powder to form the higher chalcogenide (e.g. ThX_2, UX_2, PuX_2 where X = S, Se, Te). This technique, known as the Faraday Method, is adopted to avoid the excessive liberation of heat which occurs when the elements are premixed.

At normal temperatures of preparation (400–700°C) each of these methods generally yields the dichalcogenide. Higher (poly) chalcogenides (e.g. MX_3, M_2X_5) are prepared by controlled heating of the dichalcogenide with an excess of the non-metal under pressure in a sealed tube. Lower (sub) chalcogenides are prepared by thermal degradation *in vacuo* or in flowing hydrogen. The monochalcogenides (MX) cannot normally be produced by thermal degradation, because of the low dissociation pressure of the next higher phase. Rather, the primary dichalcogenide is mixed with the appropriate quantity of the actinide metal powder, pelleted and homogenized by heating for an extended period at 1600–1800°C in argon or a vacuum. Alternatively, the mixture can be "reaction-melted" under an argon arc.

Alternative preparative methods include:

(1) Reaction of an actinide halide with H_2S or H_2Se at ~600°C

$$UCl_4 + 2H_2S \xrightarrow{600^\circ C} \beta\text{-}US_2 + 4HCl$$

The same reaction may conveniently be carried out by bubbling H_2S through a solution of UCl_4 in fused, anhydrous NaCl/KCl eutectic mixtures, when β-US_2 precipitates[2]. These reactions are particularly advantageous when the actinide metal is not readily available.

(2) Monochalcogenides may be prepared by reacting finely divided metal (U or Th) with the chalcogenide of a volatile metal such as mercury, zinc, cadmium, magnesium, calcium, barium or strontium, e.g.

$$U + ZnSe \rightarrow USe + Zn\uparrow^{5}$$

This method is simpler than the conventional route, although the product is not so pure.

(3) Small single crystals of the higher chalcogenides may be grown from the polycrystalline powder by vapour phase transport using a halogen (I_2 or Br_2) carrier. The compound is sealed in an evacuated silica tube containing a small amount of halogen and the tube is heated in a temperature gradient[6].

(4) Larger single crystals of the monochalcogenides may be prepared by zone-melting techniques or crystallized from a melt of composition MX_{1+x} which is slowly losing its excess chalcogen by volatilization. For example, single crystals of US have been obtained at 1700°C from a melt of composition $US_{1\cdot10}$[7].

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TABLE 1. CRYSTALLOGRAPHIC DATA FOR THE ACTINIDE CHALCOGENIDES

Compound	Range of homogeneity	Symmetry	Structure type	Lattice parameters				Ref.	Remarks
				a (Å)	b (Å)	c (Å)	β°		
Ac_2S_3		Bcc	Th_3P_4	8·99	—	—	—	a	
ThS		Fcc	NaCl	5·68	—	—	—	b, z	Metallic lustre
Th_2S_3		Orthorhombic	Sb_2S_3	10·99	10·85	3·96	—	c, z	
Th_7S_{12}	$ThS_{1\cdot71-1\cdot76}$	Hexagonal	—	11·06	—	3·99	—	c, z	
ThS_2		Orthorhombic	$PbCl_2$	4·28	7·27	8·62	—	d, z	
Th_2S_5		Tetragonal	—	5·43	—	10·15	—	d	Uncertainty concerning *a* parameter (ref. d)
ThSe		Fcc	NaCl	5·88	—	—	—	f	
Th_2Se_3		Orthorhombic	Sb_2S_3	11·34	11·57	4·27	—	f	Possibly oxygen stabilized phases
Th_7Se_{12}		Hexagonal	Th_7S_{12}	11·57	—	4·23	—	f, g	
$ThSe_2$		Orthorhombic	$PbCl_2$	4·42	7·61	9·07	—	g	
Th_2Se_5		Tetragonal	Th_2S_5	5·63	—	10·76	—	d	
ThTe		Bcc	CsCl	3·83	—	—	—	h	
Th_2Te_3		Hexagonal		12·49	—	4·35	—	d	
$ThTe_2$		Hexagonal?		8·49	—	9·01	—	d, h	
$ThTe_3$		Monoclinic	$ZrSe_3$	6·14	4·31	10·44	98·4	d	Cf, $ZrTe_3$, $HfTe_3$
US	$US_{0\cdot96-1\cdot01}$	Fcc	NaCl	5·49	—	—		b	Metallic grey
U_2S_3		Orthorhombic	Sb_2S_3	10·36	10·60	3·86		j	
U_3S_5		Orthorhombic	U_3S_5	7·43	8·11	11·76		j, k	
"α-US_2"	$US_{1\cdot80-1\cdot93}$	Tetragonal	Fe_2B	10·30	—	6·36		l	$US_{1\cdot80}$
				10·26	—	6·34		l	$US_{1\cdot93}$
β-US_2		Orthorhombic	$PbCl_2$	4·12	7·12	8·48		l	
γ-US_2		Hexagonal		7·25	—	4·07		j	
U_2S_5		Tetragonal	Th_2S_5					m	
US_3		Monoclinic	$ZrSe_3$	5·37	3·96	9·06	97·2	l	
USe		Fcc	NaCl	5·66 –5·76	—	—	—	n	
U_3Se_4		Bcc	Th_3P_4	8·80	—	—	—	n	
U_2Se_3		Orthorhombic	Sb_2S_3	11·33	10·94	4·06	—	n	
U_3Se_5		Orthorhombic	U_3S_5	7·76	8·44	12·26	—	n, u	Single-crystal study (u)
$USe_{1\cdot9}$	$USe_{1\cdot80-2\cdot00}$	Tetragonal	$US_{1\cdot9}$	10·77	—	6·67	—	l	$USe_{1\cdot80}$
				10·70	—	6·61	—	l	$USe_{2\cdot00}$

TABLE 1 (*cont.*)

Compound	Range of homogeneity	Symmetry	Structure type	Lattice parameters				Ref.	Remarks
				a (Å)	b (Å)	c (Å)	$\beta°$		
$\beta\text{-USe}_2$		Orthorhombic	PbCl_2	4·26	7·46	8·98	—	n	
$\gamma\text{-USe}_2$		Hexagonal		7·68	—	4·21	—	n	
USe_3		Monoclinic	ZrSe_3	5·65	4·06	9·55	97·5	l	
UTe		Fcc	NaCl	6·16	—	—	—	o, p	
U_3Te_4	$\text{UTe}_{1\cdot33-1\cdot50}$	Bcc	Th_3P_4	9·42	—	—	—	p	U_3Te_4
				9·41	—	—	—	p	U_2Te_3
U_3Te_5		—	—	—	—	—	—	q	
U_7Te_{12}		Hexagonal	Th_7S_{12}	12·31	—	4·24	—	p	
UTe_{2-x}	$\text{UTe}_2\text{–UTe}_{1\cdot78}$	Orthorhombic	—	4·16	6·13	13·97	—	p, r	
UTe_3		Monoclinic	ZrSe_3	6·09	4·23	10·30	98·0	p	
$\text{UTe}_{3\cdot38}$		Tetragonal	—	8·70	—	13·08	—	p	
UTe_5		—	—	—	—	—	—	q	
NpS		Fcc	NaCl	5·53	—	—	—	e, m	
$\alpha\text{-Np}_2\text{S}_3$		Orthorhombic	$\alpha\text{-Ce}_2\text{S}_3$	3·98	7·39	15·50		e, m	
$\beta\text{-Np}_2\text{S}_3$		Tetragonal						e, m	
$\gamma\text{-Np}_2\text{S}_3$	$\text{NpS}_{1\cdot33-1\cdot5}$	Bcc	Th_3P_4	8·44	—	—	—	e, m	Np_3S_4
Np_3S_5		Orthorhombic	U_3S_5	8·42	8·07	11·71	—	e, m	
Np_2S_5		Tetragonal	Th_2S_5	10·48	—	9·84	—	e, m	
NpS_3		Monoclinic	ZrSe_3	5·36	3·87	18·10	99·5	e, m	
Np_3Se_4		Bcc	Th_3P_4	8·83	—	—	—	y	
Np_3Te_4		Bcc	Th_3P_4	9·40	—	—	—	y	
PuS	$\text{PuS}_{0\cdot95-1\cdot00}$	Fcc	NaCl	5·54	—	—	—	e, s	
Pu_3S_4	$\text{PuS}_{1\cdot33-1\cdot50}$	Bcc	Th_3P_4	8·40	—	—	—	e, s	Pu_3S_4
$\gamma\text{-Pu}_2\text{S}_3$				8·46	—	—	—	e, s	Pu_2S_3
$\beta\text{-Pu}_2\text{Se}_{3-x}$	$\text{PuS}_{1\cdot4-1\cdot5}$	Tetragonal	Ce_5S_7	14·90	—	19·78	—	e	
$\alpha\text{-Pu}_2\text{S}_3$		Orthorhombic	$\alpha\text{-Ce}_2\text{S}_3$	7·39	15·32	3·98	—	s	
PuS_{2-x}	$\text{PuS}_{1\cdot8-1\cdot9}$	Tetragonal	Fe_2As	3·94	—	7·96		t	
PuS_2		Monoclinic	CeSe_2	7·96	7·96	3·98	90·0	t	Pseudotetragonal
PuSe		Fcc	NaCl	5·77	—	—	—	e, s	
Pu_3Se_4	$\text{PuSe}_{1\cdot33-1\cdot50}$	Bcc	Th_3P_4	8·77	—	—	—	s	
$\gamma\text{-Pu}_2\text{Se}_3$				8·80	—	—	—	s	
$\eta\text{-Pu}_2\text{Se}_3$		Orthorhombic	Sb_2S_3	4·10	11·10	11·32	—	v	
$\text{PuSe}_{1\cdot8}$		Tetragonal	Fe_2As	4·09	—	8·36	—	s	
$\text{PuSe}_{2\cdot0}$		Pseudotetragonal		4·13	—	8·34	—	s	

PuTe		Fcc	NaCl	6·15	—	—	—	s
Pu_2Te_3(?)		Bcc	Th_3P_4	9·36	—	—	—	s
$PuTe_{1 \cdot 8}$		Tetragonal	Fe_2As	4·33	—	8·98	—	s
$PuTe_2$		Pseudotetragonal		4·39	—	8·94	—	s
Am_2S_3		Bcc	Th_3P_4	8·45	—	—	—	a
Am_3Se_4		Bcc	Th_3P_4	8·78	—	—	—	y
Am_3Te_4		Bcc	Th_3P_4	9·39	—	—	—	y
Cm_2S_3		Bcc	Th_3P_4	8·44	—	—	—	w
Bk_2S_3		Bcc	Th_3P_4	8·44	—	—	—	w
Cf_2S_3		Bcc	Th_3P_4	8·39	—	—	—	x

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Thorium compounds

Rather surprisingly, the thorium chalcogenides have not been extensively investigated. This is presumably because of the greater technological interest in uranium and plutonium compounds as potential nuclear fuels.

Thorium Sulphides

Thorium forms a polysulphide, Th_2S_5, when reacted with excess sulphur at 400°C[8]. It has tetragonal symmetry (Table 1) although there is some dispute over whether the *a* parameter should be multiplied by $\sqrt{2}$[9]. On heating in a vacuum this degrades first to ThS_2 at 950°C and subsequently to Th_7S_{12} at 1950°C. The lower sulphides Th_7S_{12}, Th_2S_3 and ThS are most conveniently prepared from pellets of the desired composition (ThS_2 + Th mixtures) by homogenization at ~ 1800°C *in vacuo*.

The monosulphide ThS has a metallic lustre; it may be melted in an argon arc without decomposition at 2335°C[4]. The range of stoichiometry of ThS_{1+x} has not been established, although the reported lattice parameter varies from 5·673 to 5·690 Å. Vacuum sintering of ThS pellets takes place at 1900–2000°C; in the presence of oxygen impurity, which forms ThOS, sintering is facilitated by a eutectic ThOS–ThS liquid at the grain boundaries. Dense ThS shows metallic conductivity, with a specific resistance in the range 16–70 μ ohm cm at 293K. By contrast, $ThS_{2\cdot5}$ and ThS_2 are electrical insulators ($5\text{–}10 \times 10^9$ ohm cm) and exhibit a non-metallic, reddish-brown or purple colour[10].

All the thorium sulphides were first reported to be diamagnetic, indicating an oxidation state for thorium of +4. Later investigation of ThS revealed a small, temperature-independent paramagnetism associated with the conduction electrons[11]. Little thermodynamic information is available on the thorium sulphides (Table 2), the most reliable being that of Aronson[12]. Preliminary vapour pressure measurements[13] for ThS over the temperature range 1935–2464K give an estimated total effective pressure of $\log p_e\,(\text{atm}) \simeq 7{\cdot}7 - \dfrac{3{\cdot}366 \times 10^4}{T}$.

Thorium Selenides

The thorium selenides are isostructural with the corresponding sulphides (Table 1). They have been investigated only superficially and there is little information available beyond their preparation and crystal chemistry. No reliable thermodynamic data have been reported, although tentative estimates of their entropies have been made[14]. $ThSe_{2\cdot5}$ is prepared by reacting thorium with excess selenium at 600°C, followed by sublimation of the surplus chalcogen at 350°C[15]. It is degraded to $ThSe_2$ by heating at 900°C *in vacuo*; lower selenides are prepared by reacting the appropriate quantities of the elements together and annealing.

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Table 2. Thermodynamic Functions for the Actinide Chalcogenides at 298·15K
(Units: cal, g formula wt, K)

Compound*	C_p	$S°$	$H°-H°_0$	$-(G°-H°_0)/T$	$-\Delta H_f°$ ($\times 10^{-3}$)	$-\Delta G_f°$ ($\times 10^{-3}$)	$\Delta S_f°$	Ref.
ThS		16·9(e)			109†			c,d
$ThS_{1·5}$		20·0(e)			—			b
$ThS_{1·71}$		21·0(e)			165			c,b
ThS_2	16·80	23·0			175			a,c
US	12·08	18·64	2667	9·70	74, 79	73		f,g,j,k
$US_{1·9}$	17·68	25·91	3605	13·82				f,l
β-US_2	17·86	26·39	3698	13·98	124			e,g
US_3	22·85	33·09	4663	17·46	125			e,h
USe	13·10	23·07	3097	12·68	66			f,g,m
$USe_{1·33}$					78			g
USe_2	18·92	31·98	4209	17·86	102(e)			f,g,l
UTe					44			g
$UTe_{1·33}$					55			g
UTe_2					76(e)			g
PuS	14·6	18·7(e)			105(e)		18·7(e)	n,o
$PuS_{1·5}$		23·0(e)			237(e)		46(e)	n

* Fractional formulae are employed in this table in order to facilitate comparison of numerical values on a common basis.

e = estimated.

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ThSe is a gold-coloured, metallic compound of melting point 1880°C. An outline phase diagram has been presented[16]. $ThSe_2$ and $ThSe_{2·5}$ are both semiconductors, their colours being dark grey and dark purple, respectively[10].

Thorium Tellurides

The thorium tellurides do not seem to be isostructural with the sulphides and selenides (Table 1). The highest telluride, $ThTe_3$, is monoclinic, with marked structural similarities to the trichalcogenides of Ti, Zr and Hf; here thorium is behaving more as a Group IV element than as an actinide. $ThTe_3$ degrades to $ThTe_2$ above 600°C. The latter compound is a semiconductor, of much higher conductivity than $ThSe_2$. Th_2Te_3 and ThTe may both be synthesized from the elements; the former compound is an hexagonal phase whose

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structural analogy to Th_7Se_{12} and U_7Te_{12} suggests that its formula may be Th_7Te_{12}. The monocompound is remarkable in having the bcc CsCl structure rather than the usual fcc NaCl structure. In contrast to ThS and ThSe, which both melt above 1800°C, ThTe is degraded *in vacuo* below 1000°C. There is scope for further investigation of the differences between the tellurides and the other chalcogenides of thorium.

Uranium compounds

The three uranium–chalcogen systems have been investigated in some detail and measurements made of their thermodynamic, chemical and physical properties. Particular interest has centred upon the monocompounds US, USe and UTe.

Uranium Sulphides

Although numerous authors have studied the U–S system, no single paper reports all eight phases which are now believed to exist (Table 1); Picon and Flahaut[17], however, prepared seven of the compounds. Structurally, there will be seen to be points of similarity and points of difference between the Th–S and U–S systems, with the phases M_2S_5, MS_2, M_2S_3 and MS being isostructural for each system.

The starting material for the preparation of various uranium sulphides is generally β-US_2, produced by one of the methods described above. US_3 is formed by heating β-US_2 with sulphur in a sealed tube at 600–800°C. In a vacuum at ~500°C it decomposes to U_2S_5 and at higher temperature to β-US_2. Of the two other so-called "polymorphs of US_2", the α-phase has a composition range from $US_{1\cdot80}$ to $US_{1\cdot93}$ approximately, while the exact composition of the lower temperature γ-phase remains in doubt[18]. The transition of γ-US_2 to β-US_2 takes place irreversibly on heating and the latter transforms to the α-phase at 1350°C with loss of sulphur.

$$\gamma\text{-}US_2 \xrightarrow[\substack{425^\circ C \\ (700^\circ C?)}]{} \beta\text{-}US_2 \xrightarrow[1350^\circ C]{} \text{“}\alpha\text{-}US_2\text{”}\ (US_{1\cdot8-1\cdot93})$$

Further degradation of $US_{1\cdot8}$ occurs only in a vacuum at $\geqslant$1500°C to yield successively U_3S_5 and U_2S_3. US cannot conveniently be prepared by decomposition and is usually produced by annealing mixtures of $US_2 + U$ at ~1800°C. The powder so produced may be consolidated by pressing and sintering or by arc-casting under argon. When fabricated, US is a silvery, metallic compound of density $10\cdot87$ g cm^{-3} and melting point 2462 ± 30°C, with a small but finite range of composition ($US_{0\cdot96}$–$US_{1\cdot01}$). A tentative phase diagram for the U–S system has been proposed[19].

Thermodynamic Properties Low-temperature heat capacity measurements have been reported for US_3, β-US_2, $US_{1\cdot9}$ and US. From these the standard thermodynamic functions are calculated (Table 2). From the heat capacity curves (Fig. 1) it will be seen that US undergoes a λ-type transition at 180K. This transition, for which $\Delta H_t = 231 \pm 20$ cal mole^{-1} and $\Delta S_t = 1\cdot62 \pm 0\cdot2$ cal mole^{-1} deg^{-1}, is associated with ferromagnetic ordering of the unpaired spins (see below). At low temperatures the heat capacity may be resolved into lattice, magnetic and electronic components. No C_p anomaly is observed for US_2 or US_3.

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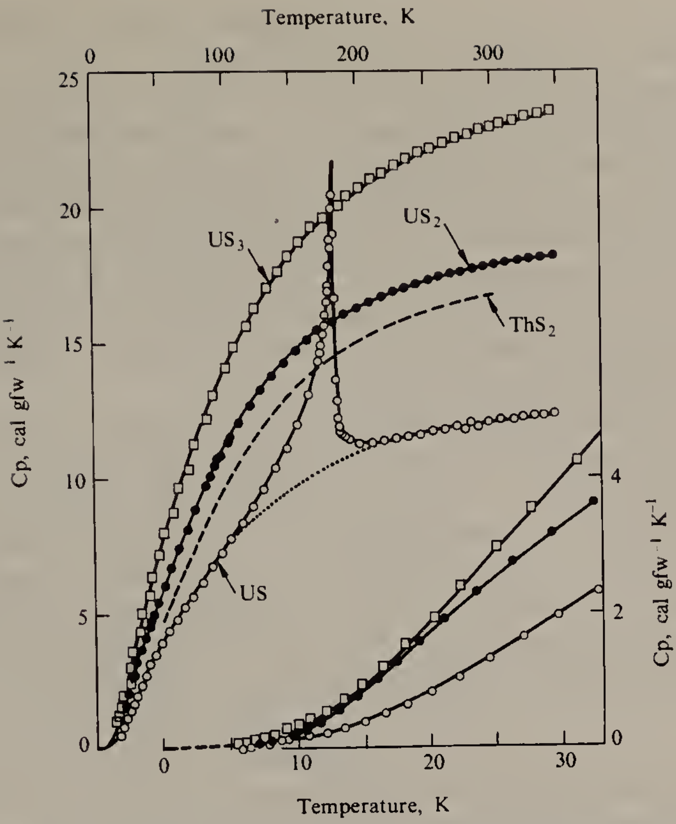

FIG. 1. Molar heat capacity curves for US_3, US_2, US and ThS_2.[14] (Reprinted by permission of the International Atomic Energy Agency.)

At high temperatures the enthalpy of US has been measured by adiabatic drop calorimetry[20] with the following results

$$H_T - H_{298} = -4139 + 12{\cdot}633T + 7{\cdot}7865 \times 10^{-4}T^2 + 9{\cdot}0413 \times 10^4 T^{-1} \text{ cal mole}^{-1} \text{ (298–1400K)}$$

Heat capacities have also been measured to 873K by a transient laser pulse technique[21]; there is a 10% disagreement at 1000K. The vaporization of US has been studied using an effusion cell and a mass spectrometer[22,23]. Above 2000K the compound vaporizes congruently, but the vapour consists of a mixture of $US_{(g)}$, $U_{(g)}$ and $S_{2(g)}$. The free energies of formation of solid and gaseous US between 2100 and 2400K are expressed by

$$\Delta G_f(US_{(s)}) = 64{\cdot}0T - 268{,}000 \text{ cal mole}^{-1}$$
$$\Delta G_f(US_{(g)}) = 38{\cdot}8T - 152{,}000 \text{ cal mole}^{-1}$$

The heat of formation of US has been measured by fluorine bomb calorimetry and by direct reaction calorimetry (Table 2). The latter method was used also for β-US_2.

Chemical and Physical Properties Oxidation studies have been carried out on uranium monosulphide which is stable in air at room temperature, even when finely divided. A surface oxide film protects it from oxidation and hydrolysis. On heating in air US reacts in several steps[24]: (1) US → UOS + γ-US_2, (2) γ-US_2 → UOS + UO_2, (3) UO_2 → UO_{2+x},

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(4) UOS → UO_2SO_4, (5) UO_{2+x} → U_3O_8, (6) UO_2SO_4 → U_3O_8. The first step begins at ~350°C, but oxidation is complete only above 800°C.

β-US_2 and UOS are often present as impurities in US, possibly as a result of partial oxidation. By means of electron microscopy it has been shown that these impurity phases precipitate in a definite orientation relationship with respect to the US crystal[25].

The electrical properties of β-US_2 (single crystals) and of US have been measured. β-US_2 is a semiconductor of resistivity ~25 ohm cm: this contrasts with ThS_2 which is an insulator. Evidently the latter compound has a simple ionic structure, whereas US_2 has a conduction band. US is a semi-metal of resistivity $\sim 290 \times 10^{-6}$ ohm cm with little temperature dependence over the range 20–900°C[4,26]. It exhibits a positive thermoelectric power coefficient, indicating positive hole conduction.

Magnetic Properties and Bonding The nature of the chemical bonding in the uranium sulphides can be inferred from magnetic and allied measurements. All the sulphides exhibit paramagnetism, with μ_{eff} varying between 2·2 B.M. (for US) and 3·1 B.M. (for US_2 and US_3) (Table 3)[18]. The paramagnetism of US_3 indicates that this compound is not derived from U^{VI}; rather it is to be regarded as a polysulphide. Since the paramagnetic moments of US_2 and US_3 are closely similar, we may write the latter as $U^{4+}(S\text{–}S)^{=}S^{=}$. Some indirect support for this conclusion stems from the observation that US_3 (also USe_3) crystallizes in the $ZrSe_3$ structure, which is known only for tetravalent cations (Ti, Zr, Hf, Th).

The magnetic moment of β-US_2 is somewhat uncertain (Table 3) though close to the value expected for an ionic structure with two unpaired *f* electrons. However, US_2, unlike ThS_2, is a semiconductor and it seems probable that a fractional electron charge is transferred from the ions into the conduction band. A resulting non-integral charge on the U ions (or a mixture of U^{4+} and U^{5+} ions) would lead to a non-typical value for the magnetic moment. By analogy with Np_3S_5 (p. 332) orthorhombic U_3S_5 is believed to contain *trivalent* uranium ions and may be represented as $U^{4+}(U^{3+})_2(S^{=})_5$.

Uranium monosulphide (US) crystallizes in the rocksalt structure and exhibits a smaller paramagnetic moment (2·2 B.M.). The question of whether US has a $5f^2$ (U^{4+}) configuration with part of the spin moment quenched, or a different electronic structure (e.g. $5f^3$) has been debated at length, but remains unresolved[26a]. Photoelectric emission measurements on US[27] indicate a narrow *f–d* conduction band near the Fermi surface.

On cooling, US orders ferromagnetically at 180K. Associated with this ordering is the C_p anomaly and a transformation from cubic symmetry to rhombohedral symmetry. The interaxial angle changes from 90° above T_c to 89·6° at 4K[28] (Fig. 2). Neutron diffraction measurements on a single crystal of US have shown that in the ferromagnetic state the direction of easy magnetization is along the (111) axis, which explains the rhombohedral distortion of the cubic lattice associated with the ordering process[29]. The ferromagnetic moment determined from the neutron measurements at 4·2K (1·70 B.M.) is considerably smaller than the paramagnetic moment, but larger than the saturation moment determined from ferromagnetic measurements on powders (Table 3).

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TABLE 3. MAGNETIC PROPERTIES OF THE ACTINIDE CHALCOGENIDES

Compound	Paramagnetic moment μ_{eff} (B.M.)	Weiss constant θ_p(°)	Curie temperature T_c (K)	Ferromagnetic moment μ_{ferro} (B.M.)	Ref.
US	2·25, 2·22	+173°, +190°	178°, 180°	1·1, 1·05, 1·55	a, b, c, d, e, f, g
U_2S_3	2·53	+27°			c
U_3S_5	3·42, 3·10	−20°, 0°, −16°			c, d, h
α-$US_{1.9}$	1·83, 3·07	−30°, −50°			c, h
β-US_2	2·83, 3·14	−30°			c, h
US_3	3·42, 3·0	−150°, −100°			c, h
USe	1·8, 2·51	+182°, +188°	180°, 185°	0·7, 1·0, 1·3	d, j, k
U_3Se_4	2·45, 3·06	+164°	160°, 130°	0·5	d, j
U_2Se_3	3·2	−10°	180°		d
USe_2	3·05, 3·2	−40°, −10°			d, h, k
USe_3	3·05	−40°, −120°			h, k
UTe	2·36, 2·84	+104°	103°	1·10	l, m
U_3Te_4	3·12		105°, 120°	0·44	j, l
U_2Te_3		+123°	122°		l
UTe_2	3·12, 3·35	−54°, −80°			n, o
UTe_3	3·16	−56°			o
PuS	Non-Curie–Weiss behaviour. Small paramagnetic susceptibility, almost independent of temperature above 300K				b, p
Pu_3S_4					p
α-Pu_2S_3					p
PuS_2					p
PuSe					b, p
PuTe					b, p

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Uranium Selenides

The known uranium selenides crystallize in phases which are generally isostructural with the corresponding uranium sulphides; U_2Se_5 (the analogue of U_2S_5) has not been reported, and there exists a U_3Se_4 phase for which no corresponding U_3S_4 has been observed (Table 1). The close structural similarity of the two systems suggests that U_3S_4 and U_2Se_5 may yet be discovered.

Preparation The uranium selenides are generally prepared by reacting together the

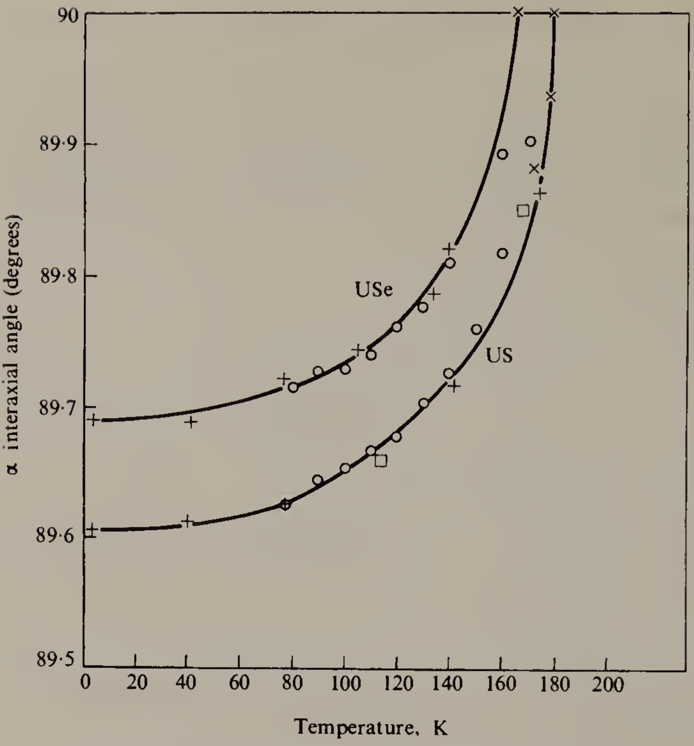

FIG. 2. Variation of interaxial angle with temperature for ferromagnetic US and USe[28]. (Reprinted by permission of *J. Phys. Chem. Solids.*)

elements in sealed tubes; for example, USe_3 is obtained as a single phase after annealing a stoichiometric mixture for 9 days at 740°C[18]. Progressively higher homogenization temperatures are required for the lower selenides. Other methods of preparing the uranium selenides include the tetrahalide/H_2Se reaction[30] (p. 320) and the metathesis:

$$US_2 + 2H_2Se \xrightarrow{600°C} USe_2 + 2H_2S.$$

The lower selenides USe_2, $USe_{1\cdot9}$, U_3Se_5, U_2Se_3 may also be prepared by decomposing USe_3 *in vacuo* at increasing temperatures to 1500°C. USe is best prepared by mixing USe_2 with uranium powder and homogenizing at ~1800°C. USe can be cast under argon (m.p. 2080°C) and the ingot so formed may be a single crystal[31]. Single crystals of U_3Se_5, USe_2 and USe_3 have been grown by halogen vapour transport techniques[32].

Properties Thermodynamic data for the uranium selenides are listed in Table 2. Low-temperature C_p data have been measured for both USe and USe_2. USe shows a λ-type anomaly associated with ferromagnetic ordering at 160·5K. The heat of the transition is $\Delta H_t = 154$ cal mole^{-1} and the entropy $\Delta S_t = 1\cdot05$ cal mole^{-1} deg^{-1}. As observed for US, the ordering process is associated with a rhombohedral distortion, with the angle α deviating from 90° below 160K (Fig. 2). It is curious that the ordering temperature as determined from the C_p measurements and X-ray measurements is 160K, whereas magnetic measurements have given 180–185° for the paramagnetic Curie temperature[33,34]. USe_2, unlike US_2,

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also exhibits a λ anomaly in the C_p curve, although for this compound the transition temperature is 13·1K. The associated heat change is very small, while the entropy change ΔS_t is only 0·19 cal mole^{-1} deg^{-1}. This anomaly is tentatively attributed to antiferromagnetic ordering of the uranium spins in USe_2.

The magnetic properties of the uranium selenides are listed in Table 3. USe_3 and USe_2 are both paramagnetic down to at least 78K. USe_3 is isostructural with US_3 and is presumably a polyselenide $U^{4+}(Se{-}Se)^{=}Se^{=}$. Some support for this view stems from the observation that when USe_3 reacts with water at 20°C, one of the three Se atoms is recovered as elemental selenium[30],

$$USe_3 + 2H_2O \rightarrow UO_2 + 2H_2Se + Se$$

USe_2 is very similar to US_2 as regards both its paramagnetic moment and Weiss constant. Magnetic measurements have not been reported to 13K where the λ anomaly exists in the C_p curve. The compound has an electrical resistivity of $\sim 10^{-2}$ ohm cm, substantially below that of US_2. The monoselenide, USe, orders ferromagnetically below ~160K. Its ferromagnetic moment is considerably smaller than the Curie–Weiss paramagnetic moment (Table 3). However, the ferromagnetic moment determined from neutron diffraction measurements at 4·2K is as high as 2·0 B.M.[29] It seems that saturation magnetization measurements give a low value for the ferromagnetic moment on account of a negative contribution from the conduction band electrons. A similar behaviour was observed for US (p. 328). Further information on uranium selenides is available in other reviews[19,34a].

Uranium Tellurides

Although there have been comparatively few studies of the U–Te system, many different phases have been reported; the most reliable of these are listed in Table 1 together with available crystallographic data. The highest telluride, UTe_5, decomposes peritectically at 490°C. The next lower compound, a tetragonal phase reported as $UTe_{3.38}$, also has no analogue among the other chalcogenides. UTe_3 (monoclinic) is isostructural with US_3 and USe_3, but UTe_{2-x}, an orthorhombic phase of wide composition range, is quite unlike US_2 and USe_2; its structure has been determined provisionally and shown to be of a new type (space group *Immm*)[35]. The next compound U_7Te_{12} also has no analogue in the sulphides or selenides of uranium, but is isostructural with Th_7S_{12} and Th_7Se_{12}. Little is known concerning U_3Te_5, but U_3Te_4 has the well-recognized bcc structure of Th_3P_4 (cf. U_3Se_4). Finally UTe, unlike ThTe, has the fcc NaCl structure; it has been reported to possess a wide homogeneity range.

Preparation and Properties The tellurides are invariably prepared from the elements. Single crystals of UTe_3 and UTe_2 have been grown by halogen vapour transport reactions[36]. Because of the occurrence of peritectic decomposition reactions it can be quite difficult to obtain polycrystalline tellurides as pure, single phases. For instance, UTe is formed by reacting finely divided UTe_2 or U_3Te_4 with U powder; at temperatures below 1300°C the reaction is very slow, while above 1400°C UTe decomposes peritectically to U_3Te_4. It is therefore difficult to prepare UTe free of contamination by U_3Te_4.

No low-temperature heat capacity measurements have been reported for the uranium

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tellurides. Estimated heats of formation, based upon direct reaction calorimetry, are listed in Table 2.

The magnetic properties of the uranium tellurides have been investigated only briefly (Table 3). The higher tellurides (UTe_5, UTe_3 and UTe_2) are paramagnetic down to 78K, while the lower tellurides (U_2Te_3, U_3Te_4 and UTe) order ferromagnetically. As with the sulphides and selenides, the ferromagnetic moment is considerably smaller than the paramagnetic moment. Once again the ferromagnetic moment determined by neutron diffraction at 4·2K is much larger (2·2 B.M.) and it seems that this is the correct value to employ in theoretical calculations[29]. UTe_2, U_2Te_3 and UTe are all semi-metallic compounds with specific resistivities in the range 10^{-3} to 10^{-2} ohm^{-1} cm^{-1} [32]. The sign of the Hall coefficients indicates hole conduction in U_2Te_3 and UTe and free electron conduction in UTe_2.

Neptunium compounds

Seven different neptunium sulphides have been described (Table 1). Two of these are polysulphides, NpS_3 and Np_2S_5. NpS_3 appears to be isostructural with US_3 and USe_3, although the *c* parameter quoted is twice the expected value; there appears to be some uncertainty over this point. Similarly with Np_2S_5 (tetragonal Th_2S_5 structure) the *a* parameter is twice the expected value. These structures probably contain pseudo-cells. They may be represented as polysulphides $Np^{4+}(S–S)^{=}S^{=}$ and $2Np^{4+}(S–S)^{=}\cdot 3S^{=}$, respectively.

NpS_3 is relatively unstable and on heating to 500°C decomposes directly to Np_3S_5. Attempts to prepare a disulphide have failed; when Np_3S_5 was heated in a sealed tube at 500°C with a limited quantity of sulphur the product was a mixture of Np_2S_5 and unchanged Np_3S_5. The latter compound, having the U_3S_5 structure, may be represented as an ionic compound containing both tri- and quadrivalent ions $Np^{4+}(Np^{3+})_2(S^{=})_5$. Np_3S_5 decomposes above 900°C *in vacuo*, to α-Np_2S_3; $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$-Np_2S_3 transformations occur at 1200°C and 1500°C, respectively. These three phases are isostructural with the plutonium sesquisulphides rather than with Sb_2S_3 (cf. Th_2S_3 or U_2S_3, Table 1). It seems that in the sesquisulphides, neptunium is present as Np^{3+} ions, corresponding to the Pu^{3+} ions in Pu_2S_3. Np_2S_3 reacts with neptunium metal to yield the monosulphide NpS.

Thus the higher sulphides of neptunium resemble those of uranium and thorium, containing quadrivalent (Np^{4+}) ions, while the lower sulphides resemble those of plutonium, containing trivalent (Np^{3+}) ions. In this respect the behaviour of neptunium reflects its position in the Periodic Table between uranium and plutonium.

The only other neptunium chalcogenides prepared to date are Np_3Se_4 and Np_3Te_4. These both crystallize in the bcc Th_3P_4 structure (Table 1).

Plutonium compounds

The chemistry of plutonium resembles that of cerium in many respects, the similarity being most marked in the crystal chemistry of the chalcogenides. This was first noted by Zachariasen[37], who drew attention to the close structural relationship between the sulphides and oxysulphides of cerium and plutonium. More recent studies have extended this observation and explained it in terms of the similar relative stabilities of the Ce^{3+}, Ce^{4+} ions and the Pu^{3+}, Pu^{4+} ions in chalcogenide crystals. Plutonium therefore behaves analogously to a light rare-earth with variable (III–IV) valence.

[37] W. H. Zachariasen, *Acta Crystallog.* **2** (1949) 57, 60.

Plutonium Sulphides and Selenides

These systems have been studied in reasonable detail and are closely analogous to each other[3,38,39]. When plutonium metal is heated with an excess of sulphur or selenium in an evacuated and sealed tube, the highest compounds formed are PuS_2 and $PuSe_2$, respectively. The symmetry of these phases has been difficult to assign. The X-ray powder pattern of PuS_2 may be indexed according to a simple cubic cell. $PuSe_2$, however, shows a tetragonal distortion with $c/a = 2{\cdot}019$. By analogy with $CeSe_2$, for which a single-crystal study has been reported, it now seems likely that both PuS_2 and $PuSe_2$ possess monoclinic symmetry with β fortuitously equal to 90° and, in the case of PuS_2, $c/a = 2{\cdot}00$.

Support for this view stems from the fact that upon heating the dichalcogenides, metalloid is lost progressively down to $PuS_{1\cdot8}$ ($PuSe_{1\cdot8}$) with increasing tetragonal distortion of the lattice.

Continued vacuum degradation of PuS_{2-x} above 600°C produces a sesquisulphide, α-Pu_2S_3, stable to 1100°C. At higher temperatures a β-phase ($PuS_{1\cdot4-1\cdot5}$, tetragonal) and a γ-phase ($PuS_{1\cdot33-1\cdot5}$, bcc) exist. The latter phase melts at 1725 ± 10°C and sublimes congruently at a composition near $PuS_{1\cdot38}$. It crystallizes in the bcc Th_3P_4 structure with metal atom vacancies to accommodate the non-stoichiometry.

In the selenide system, a phase η-Pu_2Se_3 with the orthorhombic Sb_2S_3 structure has been found, as well as γ-Pu_2Se_3 ($PuSe_{1\cdot33-1\cdot50}$) with the bcc structure. No phases corresponding to the α- or β-sesquisulphide were found.

The monocompounds PuS and PuSe are both prepared by the usual method of mixing higher chalcogenides with finely divided metal and homogenizing at 1500–1800°C. PuS has a composition range from $PuS_{0\cdot95}$ to $PuS_{1\cdot00}$. It is a metallic, golden-coloured compound of m.p. 2350 ± 30°C. PuSe is reported to melt at 2075 ± 30°C in flowing argon at 3 atm pressure.

Few thermodynamic data have been reported for these compounds. Some estimated values are given in Table 2, but these should be viewed with caution.

Magnetic measurements have been made on PuS, Pu_3S_4, α-Pu_2S_3, PuS_2 and PuSe between 4K and 1000K[3,40]. Surprisingly, all of these compounds are only weakly paramagnetic at ambient temperatures ($\chi_{\text{mole}} = 250 - 700 \times 10^{-6}$ emu), with little temperature dependence up to 1000K (Table 3). At lower temperatures, the susceptibility does increase, reaching a value in the range $(1000\text{–}4000) \times 10^{-6}$ emu at 4K, depending upon the compound. The experimental magnetic moment is smaller than expected for Pu^{3+} ions which, on the basis of crystallographic data, are thought to be present in both Pu_2S_3 and PuS_2. It appears likely that crystal-field quenching is incomplete in the sulphides.

Electrical resistivity measurements have shown both Pu_3S_4 and PuS to be semiconductors; specific resistances of $0{\cdot}3$ ohm cm and $2{\cdot}6 \times 10^{-3}$ ohm cm, respectively, at 25°C were measured. Thermoelectric power measurements indicate PuS to be an *n*-type semiconductor.

Plutonium Tellurides

Very little work has been carried out on the plutonium tellurides[3]. The highest telluride, $PuTe_2$, is apparently isostructural with PuS_2 and $PuSe_2$ (Table 1). Loss of tellurium on heating gives a non-stoichiometric tetragonal phase in the range $PuTe_{1\cdot8-2\cdot0}$. Further

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[38] J. P. Marcon and R. Pascard, *J. Inorg. Nucl. Chem.* **28** (1966) 2551.
[39] J. P. Marcon and R. Pascard, *Rev. Int. Hautes Temper. Refract.* **5** (1968) 51.
[40] G. Raphael and C. de Novion, *J. Physique*, **30** (1969) 261.

degradation led to a bcc Th_3P_4-type phase (Pu_2Te_3?) and a further complex phase which was not indexed. PuTe is obtained by reacting $PuTe_2$ with PuH_x above 1200°C. The paramagnetic susceptibility of PuTe is small, with slight temperature dependence between 150K and 300K.

Transplutonium elements

The transplutonium chalcogenides have been little investigated. All the phases prepared so far possess the bcc Th_3P_4 structure (Table 1). Am_2S_3 was prepared as long ago as 1949. Am_3Se_4 and Am_3Te_4 were identified recently in the product formed when americium was reacted with equiatomic proportions of Se or Te respectively. No evidence for AmSe or AmTe was obtained.

The sesquisulphides, Cm_2S_3, Bk_2S_3, Cf_2S_3, were prepared in microgram amounts by reacting a mixture of H_2S and CS_2 vapour with the appropriate oxide at 1100°C, e.g.

$$Bk_2O_3 + CS_2 + H_2S \rightarrow Bk_2S_3 + CO_2 + H_2O$$

Micro-X-ray techniques were employed in their identification.

3. NITRIDES

The nitrides of uranium, plutonium and, to a lesser degree, thorium have been investigated extensively in recent years under the stimulus of a technological interest in these compounds as possible nuclear fuels. For this reason, and also because the nitrides differ significantly from the remaining pnictides in structural and other properties, it is convenient to consider them separately.

Nitrides which exhibit metal-like properties are often regarded, along with carbides, as "interstitial compounds" in which the small nitrogen or carbon atom is incorporated within the interstices of the metal lattice. While this may be a valid approximation for certain *d*-transition element carbides and nitrides, the nitrides of the rare earth and actinide metals are not of this type. Rather, they resemble the mononitrides of the Group IIIA elements. These compounds, although exhibiting semi-metallic behaviour, are often closely stoichiometric (e.g. CeN, UN). The mononitrides crystallize in the rocksalt structure and, from a consideration of the lattice parameters of these compounds, the radius of the nitrogen atom may be shown to be $\sim 1{\cdot}55$ Å[41]. This is much too large for an uncharged interstitial nitrogen atom and approaches the size of an N^{3-} ion (Pauling radius $1{\cdot}71$ Å).

The mononitrides are brittle, refractory compounds of high melting point (usually >2000°C). These properties are not those expected of a covalently-bonded structure and, taken together with the lattice dimensions, suggest a high degree of ionicity. Nevertheless, it is not correct to represent the nitrides as purely ionic compounds $M^{3+}N^{3-}$, since in the case of ScN, YN, LaN, there would then be no electrons remaining to enter a non-localized conduction band. While the precise nature of the chemical bonding in the rare earth and actinide nitrides is still a matter of debate, it seems clear that the compounds are highly ionic, that there are localized *d* or *f* electrons on the cations and that there is a delocalized conduction band superimposed upon the ionic structure in a manner not clearly understood. This description does not preclude the possibility of some covalent contribution to the bonding scheme, but any such contribution is believed to be small.

[41] M. Allbutt, and R. M. Dell, *J. Inorg. Nucl. Chem.* 30 (1968) 705.

Thorium nitrides

Thorium forms only two well-characterized nitride phases, α-Th_3N_4 and ThN (Table 4). A compound reported earlier as Th_2N_3 is, in fact, an oxynitride Th_2N_2O. Recently, a nitride-imide $Th_2N_2(NH)$ has been prepared by reacting thorium metal with ammonia gas at high pressure (2500–5500 atm) and at temperatures of 400–500°C. This is said to degrade thermally above 270°C to yield a second crystallographic modification of Th_3N_4 (β-phase, Table 4). Further confirmation of this phase is required.

α-Th_3N_4 is prepared by reacting finely divided thorium metal with nitrogen at 500–1000°C. It is a diamagnetic, maroon-coloured powder and, contrasting with most other nitrides, is an electrical insulator. These properties are consistent with a purely ionic structure $(Th^{4+})_3(N^{3-})_4$, which, in turn, explains why it is not possible to exceed a N/Th ratio of 1·33. The principal Th–N distance in the structure (2·70 Å) is exactly equal to the sum of the Pauling ionic radii for Th^{4+} (0·99 Å) and N^{3-} (1·71 Å). The phase diagram of the Th–N system[42] indicates that α-Th_3N_4 has no finite range of composition below 1500°C, but that the metal-rich boundary widens to $ThN_{1\cdot 29}$ at 1960°C.

On being heated in a vacuum above 1400°C, Th_3N_4 decomposes to ThN. This is a greenish–yellow powder, which melts congruently at 2820 ± 30°C under 2 atm nitrogen pressure. The Th-rich boundary of the ThN phase extends from the N/Th ratio 0·97 ± 0·03 at 1576°C to 0·87 at 2000°C, while the N-rich boundary extends from N/Th ratio 1·03 ± 0·03 at 1615°C to 1·08 at 2065°C[42]. Below 1500°C ThN is essentially a line compound. Fabricated pellets of ThN may be densified, with some difficulty, by high-temperature sintering. Ingots of ThN have also been prepared by induction melting of crystal-bar thorium in a tungsten crucible under 2 atm nitrogen pressure.

ThN is a good metallic conductor ($\rho = 2 \times 10^{-5}$ ohm cm at 293K) with electrons as charge carriers. Its resistivity increases linearly with temperature over the range 4–850K[43]. From the measurements of the Hall coefficient, the density of charge carriers is estimated at 1·47 electrons per thorium atom. ThN may therefore be represented notionally as $Th^{4+}N^{2\cdot 53-}$ $1\cdot 47\epsilon$). This representation is in line with the observed weak, temperature-independent paramagnetism associated with the conduction electrons, and also accords with the lattice parameter of ThN[41].

ThN resembles PuN rather more than UN in its ease of hydrolysis. It reacts readily at room temperature with moist air or argon to give hydrated oxide. In *dry* oxygen, however, ThN is rather more resistant to oxidation than UN, the measured ignition temperature for ThN powder being above 500°C[43a].

Thermodynamic Properties

The heat capacities of ThN and Th_3N_4 over the temperature range 10–300K have been measured recently (Table 5). The C_p vs. T plots are smooth curves, as expected for essentially diamagnetic materials. From measurements of the nitrogen equilibrium pressure above the two phase system ThN/Th_3N_4 at 1723–2073K, the heat change and entropy change associated with the reaction $6ThN_{(s)} + N_{2(g)} \rightarrow 2Th_3N_{4(s)}$ have been calculated[44]. Correcting to 298K, and combining with older data for the heat and entropy of formation of Th_3N_4, the

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TABLE 4. CRYSTALLOGRAPHIC DATA FOR THE ACTINIDE PNICTIDES

Compound	Range of homogeneity	Symmetry	Structure type	Lattice parameters				Ref.	Remarks
				a(Å)	b(Å)	c(Å)	β^0		
ThN		Fcc	NaCl	5·16	—	—	—	a, b, c	
α-Th_3N_4		Hexagonal	Th_3N_4	3·87	—	27·39	—	a, b, c, d	
β-Th_3N_4		Monoclinic	—	6·95	3·83	6·20	90·7	e	Requiring confirmation
UN		Fcc	NaCl	4·89	—	—	—	f	
α-U_2N_3	$UN_{1.59-1.86}$	Bcc	Mn_2O_3	10·68 10·57	— —	— —	— —	f f	$UN_{1.59}$ $UN_{1.86}$
β-U_2N_3	$UN_{1.44-1.45}$	Hexagonal	La_2O_3	3·70	—	5·84	—	g	$UN_{1.45}$
NpN		Fcc	NaCl	4·90	—	—	—	h	
PuN		Fcc	NaCl	4·90	—	—	—	j	
AmN		Fcc	NaCl	5·00	—	—	—	k	
ThP		Fcc	NaCl	5·83	—	—	—	l	
Th_3P_4		Bcc	Th_3P_4	8·65	—	—	—	m	
ThAs		Fcc	NaCl	5·97	—	—	—	n	
Th_3As_4		Bcc	Th_3P_4	8·85	—	—	—	n	
β-$ThAs_2$		Tetragonal	Fe_2As	4·09	—	8·57	—	n	
α-$ThAs_2$		Orthorhombic	$ZrAs_2$	7·29	9·78	4·00	—	y	
ThSb		Fcc	NaCl	6·32	—	—	—	o	
Th_3Sb_4		Bcc	Th_3P_4	9·37	—	—	—	o	
$ThSb_2$		Tetragonal	Fe_2As	4·35	—	9·17	—	o	
Th_3Bi_4		Bcc	Th_3P_4	9·56	—	—	—	p	
$ThBi_2$		Tetragonal	Fe_2As	4·49	—	9·30	—	p	
UP		Fcc	NaCl	5·59	—	—	—	q	
U_3P_4		Bcc	Th_3P_4	8·21	—	—	—	q	
UP_2		Tetragonal	Fe_2As	3·81	—	7·78	—	q	
UAs		Fcc	NaCl	5·78	—	—	—	r	
U_3As_4		Bcc	Th_3P_4	8·51	—	—	—	r	
UAs_2		Tetragonal	Fe_2As	3·95	—	8·12	—	r	
USb		Fcc	NaCl	6·18	—	—	—	r	
U_3Sb_4		Bcc	Th_3P_4	9·11	—	—	—	r	
USb_2		Tetragonal	Fe_2As	4·27	—	8·75	—	r	
UBi		Fcc	NaCl	6·36 6·40	—	—	—	s	
U_3Bi_4		Bcc	Th_3P_4	9·36	—	—	—	s	
UBi_2		Tetragonal	Fe_2As	4·45	—	8·92	—	s	
NpSb		Fcc	NaCl	6·25	—	—	—	t	
PuP		Fcc	NaCl	5·66	—	—	—	u	
PuAs		Fcc	NaCl	5·86	—	—	—	v	
PuSb		Fcc	NaCl	6·24	—	—	—	v, t	
PuBi		Fcc	NaCl	6·35	—	—	—	w	
AmSb		Fcc	NaCl	6·24	—	—	—	x	

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corresponding values for ThN are deduced (Table 5). It is notable that ΔH_f ($ThN_{(s)}$, 298K) is ~20 kcal more negative than the value for UN. This may reflect differences in the lattice parameters and chemical bonding in the two mononitrides.

The dissociation pressure of ThN has been measured directly over the temperature range 2689–3063K[45] (Fig. 3). For the reaction

$$ThN_{(s)} \rightarrow Th_{(l)} + \tfrac{1}{2}N_{2(g)}$$

the decomposition pressure is given by

$$\log P\,(\text{atm}) = 8{\cdot}086 - (33{\cdot}22 \times 10^{3})T^{-1} + (0{\cdot}958 \times 10^{-17})T^{5}\ (T \text{ in } ^{\circ}\text{K})$$

This equation cannot be used to calculate the heat of formation of ThN directly, as the activity of the metal is less than unity on account of dissolved nitrogen.

Uranium nitrides

Uranium forms a mononitride, UN, and two higher nitride phases, generally referred to as α- and β-sesquinitride (Table 4). Reaction of finely divided uranium powder with nitrogen or ammonia above 400°C yields α-U_2N_3. This is a non-stoichiometric phase, of composition generally in the range $UN_{1{\cdot}60-1{\cdot}70}$. The lower limit of this phase lies at $UN_{1{\cdot}55 \pm 0{\cdot}02}$ at 950–1000°C and $UN_{1{\cdot}57 \pm 0{\cdot}02}$ at 700°C[46]. Stoichiometric $UN_{1{\cdot}50}$ does not exist, as the bcc phase decomposes to UN before this composition is reached. The upper limit of the α-phase is less certain. Even at >100 atm N_2 pressure the composition attained is not likely to exceed $UN_{1{\cdot}70}$. However, $UN_{1{\cdot}80-1{\cdot}86}$ has been prepared starting from uranium hydride rather than uranium metal. In early papers UN_2 (fluorite structure) was reported, but this is now discredited and $UN_{1{\cdot}86}$ is the highest phase prepared to date. The bcc structure of α-U_2N_3 may be regarded as derived from eight unit cells of UN_2 (2 × 2 × 2) with loss of one-quarter of the anions and a resulting crystallographic rearrangement. Addition of excess nitrogen atoms results in a contraction of the cubic lattice parameter.

β-U_2N_3 possesses hexagonal symmetry. Originally this was believed to be a metastable, high-temperature phase, but later work[47] showed that β-U_2N_3 is, in fact, a phase of almost fixed composition, $UN_{1{\cdot}44-1{\cdot}45}$. Although this phase is not normally formed below ~1100°C, once formed it is stable at lower temperatures under the appropriate nitrogen pressures. It is prepared from α-U_2N_3 by heating at ~1350°C under 1 atm N_2 pressure. The temperature/pressure conditions necessary to prepare single phase β-U_2N_3 are rather critical and the specimen must be quenched to prevent it reverting to the α-phase by reaction with nitrogen during cooling.

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TABLE 5. THERMODYNAMIC FUNCTIONS FOR THE ACTINIDE PNICTIDES AT 298·15K
(Units: cal, formula wt, K)

Compound	C_p	S°	$H^\circ - H_0^\circ$	$-(G^\circ - H_0^\circ)/T$	$-\Delta H_f^\circ$ ($\times 10^{-3}$)	$-\Delta G_f^\circ$ ($\times 10^{-3}$)	$-\Delta S_f^\circ$	Ref.
ThN	10·77	13·69	2066	6·764	90·6	83·59	23·5	a, b
$ThN_{1\cdot33}$	11·77	14·59	2185	7·261	103·2	94·31	29·8	a, b
UN	11·31	14·87	2167	7·600	69–73			c, b
$UN_{1\cdot59}$	12·95	15·54	2354	7·650	86·5			c, b
$UN_{1\cdot73}$	13·77	15·74	2410	7·660				c
PuN					71·5			d
ThP		12·1(e)			106†	71·5†	29·5†	b
$ThP_{1\cdot33}$		16·6(e)			120†	77†	36·3†	b
UP	11·86	18·71	2579	10·06	75·5			e, g
$UP_{1\cdot35}$	13·95	20·61	2958	10·69				e
UP_2	19·12	24·34	3679	12·00				f
PuP	16·0							h

e = estimated.
† 1173K

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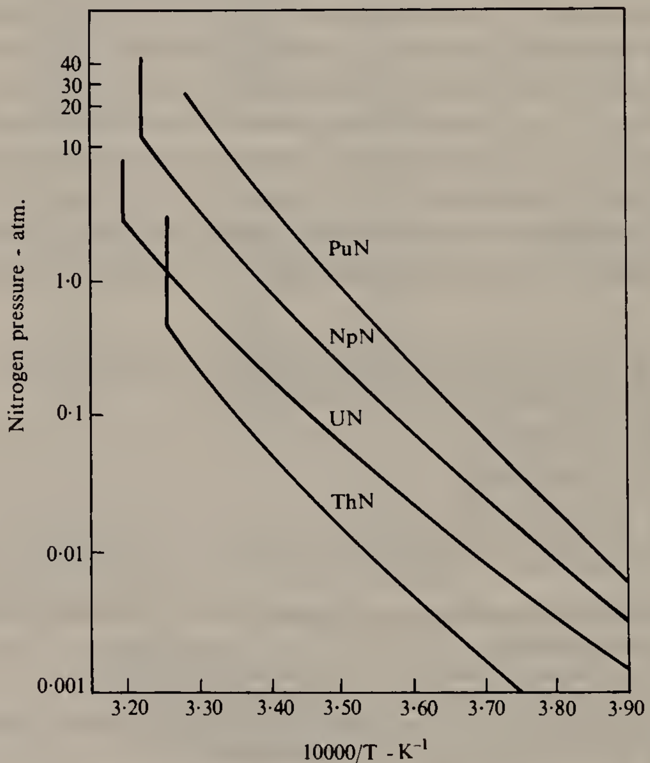

FIG. 3. Decomposition pressure curves for ThN, UN, NpN and PuN.

Above ~ 1100°C in vacuum, α-U_2N_3 decomposes to stoichiometric UN (NaCl structure). This is a line compound below 1200°C, but at high temperatures the situation is less certain. In one phase study of the U–N system[48] it was reported that the metal-rich phase boundary widens to $UN_{0\cdot96}$ at 1500°C and $UN_{0\cdot80}$ at 2000°C. However, a recent reinvestigation indicates that UN has a very narrow composition limit ($UN_{0\cdot995-0\cdot997}$) up to at least 2200°C[49].

UN melts at 2850°C, the dissociation pressure of nitrogen at this temperature being 2·5 atm. The compound may be arc-cast without dissociation under 5 atm N_2 pressure and large single crystals of UN have been extracted from the castings. The powder is densified only with difficulty by conventional cold pressing and sintering, but dense compacts may readily be prepared by hot pressing at 1500–1700°C.

Thermodynamic Properties

The thermodynamic properties of the uranium nitrides have been investigated extensively. Low-temperature (10–320K) heat capacity measurements have been made on UN, $UN_{1\cdot59}$ (α-phase) and $UN_{1\cdot73}$ (α-phase)[46] (Table 5). The C_p vs. T curve for UN shows a small anomaly at 52K, corresponding to the antiferromagnetic Néel temperature. The entropy increment associated with this anomaly is only 0·15 cal mole^{-1} deg^{-1}, a surprisingly low value corresponding to the disordering of only 0·08 unpaired spins. The α-phase nitrides were found to exhibit even smaller magnetic entropy changes, at 94K for $UN_{1\cdot59}$ and 33K for $UN_{1\cdot73}$.

The specific heat of UN at high temperatures has been derived from heat measurements made with a drop calorimeter:

$$C_p = 13\cdot32 + (1\cdot19 \times 10^{-3})T - (2\cdot10 \times 10^{5})T^{-2} \text{ cal mole}^{-1} \text{ deg}^{-1} \text{ (273–1423K)}$$

This equation gives a value for C_p (298K) of 11·31 cal mole^{-1} deg^{-1}, in good agreement with low temperature results (Table 5). However, recent specific heat measurements by Joule heating up to 2000K yield the relationship:[50]

$$C_p = 10\cdot2 + (4\cdot2 \times 10^{-3})T \text{ cal mole}^{-1} \text{ deg}^{-1} \text{ (1000–2000K)}$$

which gives values of C_p some 8 % higher. The latter equation is probably to be preferred in the high-temperature range.

The standard heat of formation of UN ($\Delta H_f{}^{\circ}{}_{298}$) has been determined by a number of different techniques. Fuger[51] discusses the various results and recommends the calorimetric value −71 ± 1 kcal mole^{-1}. The nitrogen dissociation pressure over UN varies from 5×10^{-7} atm at 1970K to 3×10^{-5} atm at 2230K.[52]

The dissociation pressure of α-U_2N_3 as a function of composition and temperature has been determined on several occasions[53–55]. Results in the two phase region (UN + α-U_2N_3) are in reasonable agreement, but in the single phase region the agreement is poor. This may be due to the presence of β-U_2N_3 and the difficulty of reaching equilibrium between the α- and β-phases.

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Chemical Properties

UN differs from ThN and PuN in being much less susceptible to reaction with water vapour. The powder may be handled in moist air without fear of hydrolysis and, indeed, does not react with boiling water at 100°C. However, because of the high heat of oxidation, finely powdered UN is pyrophoric even at room temperature. When the powder has been sintered to ~1450°C in argon it does not ignite in air below ~ 290°C.

The mechanism of oxidation and hydrolysis of UN has been investigated in detail[56,57]. Isothermal oxidation of UN at 230–270°C (below the ignition temperature) yields nitrogen gas and a product of composition $UO_3N_{0 \cdot 2-0 \cdot 4}$ in which the nitrogen is tightly bound within the structure. On dissolving this product in dilute mineral acids, nitrogen gas is released. Experiments with single crystals of UN have shown that during oxidation (or hydrolysis) a duplex layer of U_2N_3 and UO_2 is formed on the crystal surface, with the U_2N_3 sandwiched between the UN crystal and the outer layer of UO_2. Both of the product phases are found to be epitaxially oriented with respect to the underlying UN crystal, from which it is concluded that reaction involves chemisorption of the oxidant at the outer oxide surface, followed by solid state diffusion and reaction at solid/solid interfaces. The oriented layer of U_2N_3, formed on the UN surface by reaction with liberated N atoms, is responsible for the marked stability of UN towards hydrolysis. At temperatures above 300°C UN reacts with water vapour according to the overall reaction $UN + 2H_2O \rightarrow UO_2 + NH_3 + \frac{1}{2}H_2$. At 20°C UN is inert to dilute hydrochloric and sulphuric acids, but is oxidized by nitric acid to uranyl nitrate.

Physical Properties

The physical properties of the uranium nitrides have been studied in some detail. A number of these properties exhibit a discontinuity at the Néel temperature (52K). For example, the expansion coefficient, as determined by low-temperature X-ray diffraction measurements, changes sign at 52K, there being a small lattice expansion on cooling from 52 to 4K[58]. This is attributed to a stabilization of the 5*f* band in the antiferromagnetic state, with consequent electron transfer from the valence to the 5*f* band. Similarly, the curve of thermoelectric power versus temperature shows an abrupt change of slope at 52K[59]. The electrical resistivity of UN shows a metallic-type temperature dependence with a resistivity of 150 μohm cm at 20°C[59].

The thermal conductivity of UN is given by[60]

$$K = 0 \cdot 0294 + (0 \cdot 306 \times 10^{-4})T \; (K \text{ in cal cm}^{-1}\text{ sec}^{-1}\text{ deg}^{-1}, T \text{ in °C})$$

This increase in thermal conductivity with increasing temperature is unusual and is significant for a potential nuclear fuel.

The self-diffusion coefficient of nitrogen (as N^{15}) in UN is[61] reported as,

$$D = 2 \cdot 6 \times 10^{-4} \exp(-55{,}000/RT) \; (1500\text{–}1900\text{°C})$$

Magnetic Properties and Bonding

The magnetic properties of the uranium nitrides are listed in Table 6. At low temperatures UN and α-U_2N_3 order antiferromagnetically, while β-U_2N_3 orders ferromagnetically. The

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magnetic structure of UN in the antiferromagnetic state, determined by neutron diffraction at 4K, is shown in Fig. 4. In this structure (which is assumed also by UP, UAs, USb and UBi in the ordered state) the magnetic unit cell is identical to the crystallographic cell, although the symmetry of the structure is reduced from cubic to tetragonal. From the intensities of the neutron magnetic peaks, the moment associated with the uranium atom in antiferromagnetic UN is 0·75 Bohr Magnetons. This is substantially less than the paramagnetic moment (3·11 B.M.).

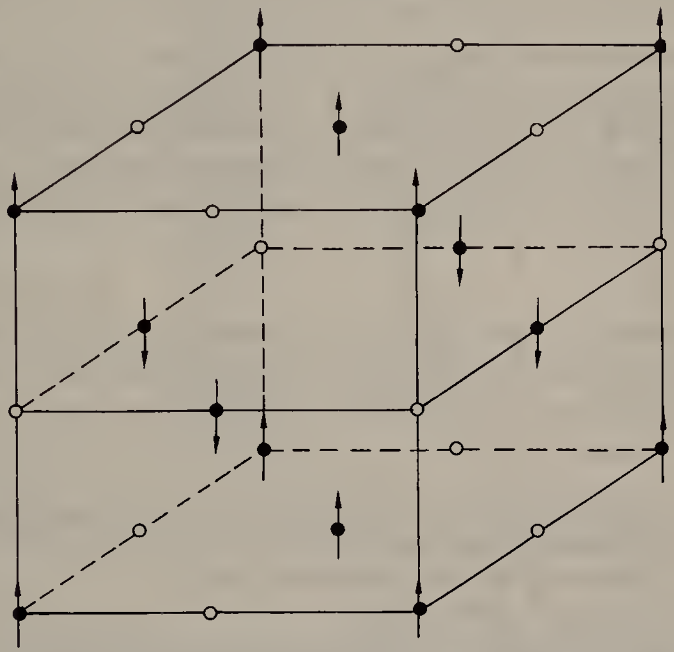

FIG. 4. Antiferromagnetic structure of uranium monopnictides[63]. (Reprinted by permission of The Physical Society.)

The magnetic properties of the α-U_2N_3 phase change progressively with composition. $UN_{1 \cdot 5}$ shows a characteristic maximum of susceptibility, associated with antiferromagnetic coupling, at 96°K. Addition of nitrogen leads to progressively lower Weiss constants, reduced susceptibilities and lower Néel temperatures[62]. Extrapolation to the composition $UN_{2 \cdot 0}$ leads to zero susceptibility, suggesting that this (hypothetical) compound would contain U^{6+} ions and be of structure $U^{6+}2N^{3-}$. This is in marked contrast to the other dipnictides and dichalcogenides which contain U^{4+} ions and polyanions. Presumably the usual α-phase compositions ($UN_{1 \cdot 55-1 \cdot 70}$) contain a mixture of U^{4+} and U^{5+} or U^{6+} ions.

The precise nature of the bonding in UN and the reason for the narrow range of stoichiometry are still far from clear. The neutron diffraction magnetic form factor points to the presence of $5f$ electrons[63]. The small value for the ordered magnetic moment implies that there are few unpaired electrons. This may be understood if the ground energy level is assumed to be split in the cubic crystal field and tetragonal uranium exchange field so that at low temperatures most of the electrons are paired in the lower energy state, thereby reducing the effective magnetic moment.

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TABLE 6. MAGNETIC PROPERTIES OF THE ACTINIDE PNICTIDES

Compound	Paramagnetic moment μ_{eff} (B.M.)	Weiss constant θ_p(°)	Néel (T_N) or Curie (T_C) temperature (°K)	Ordered moment (B.M.)	Ref.
UN	3·11 2·06	−325 −160	52 (T_N)	0·75	a,c b
α-U_2N_3	1·92	+42	96 (T_N)		d
β-U_2N_3	1·84	+162	235 (T_C) 186 (T_C)		a
NpN	2·13		82 (T_C)		e
PuN	1·08	−200	13 (T_N)		b
UP	3·17–3·56	+3, +36	121–130 (T_N)	1·7 (78K); 1·9 (4K)	f,g
U_3P_4	2·61–2·77	+134, +151	134–165 (T_C)	1·5	g
UP_2	2·24–2·30	+77, +86	199–206 (T_N)	1·0	g
UAs	3·54	+32	128 (T_N)	1·9 (78K); 2·2 (4K)	g,h
U_3As_4	2·81	+200	198 (T_C)	1·71	g,h
UAs_2	2·94	+34	283 (T_N)	1·61	g,h
USb	3·85	+95	213 (T_N)	2·1–2·8	g,h
U_3Sb_4	3·01	+148	146 (T_C)	1·29	g,h
USb_2	3·04	+18	206 (T_N)	0·94	g,h
UBi	4·06	+105	285 (T_N)	3·0	g,j
U_3Bi_4	3·14	+110	108 (T_C)		g,j
UBi_2	3·40	−53	183 (T_N)	2·1	g,j
PuP	1·06		126 (T_C)	0·42	k

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[b] G. Raphael and C. de Novion, *Solid State Commun.* **7** (1969) 791.
[c] N. A. Curry, *Proc. Phys. Soc.* **86** (1965) 1193.
[d] W. Trzebiatowski and R. Troc. *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **12** (1964) 681.
[e] C. H. de Novion and R. Lorenzelli, *J. Phys. Chem. Solids*, 29 (1968) 1901.
[f] M. Allbutt, R. M. Dell, A. R. Junkison and J. A. Marples, *J. Inorg. Nucl. Chem.* **32** (1970) 2159.
[g] R. M. Dell and N. J. Bridger, *Int. Rev. Sci.*, Inorganic Chemistry, Series 1, Vol. 7 (1972).
[h] W. Trzebiatowski, A. Sepichowska and A. Zymunt, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **12** (1964) 687.
[j] W. Trzebiatowski and A. Zymunt, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **14** (1966) 495.
[k] D. J. Lam, F. Y. Fradin and O. L. Kruger, *Phys. Rev.* **187** (1969) 606.

Neptunium nitride

Only one nitride of neptunium, NpN, has been reported (Table 4). Dissociation pressure measurements have been made over the temperature range 2483–3103K[64] (Fig. 3) leading to the relation

$$\log P\,(\mathrm{atm}) = 8{\cdot}193 - (29{\cdot}54 \times 10^{3})T^{-1} + (7{\cdot}87 \times 10^{-18})T^{5}\ (T \text{ in °K})$$

The melting point of NpN is reported as 3103 ± 30K under ~12 atm nitrogen pressure.

Magnetic studies have shown that, surprisingly, the compound orders ferromagnetically below a Curie temperature of 82K[65]. The paramagnetic susceptibility contains a temperature-independent component, χ_0, and may be written in the form $\chi = \chi_0 + C/(T - 82)$ where $\chi_0 = 400 \times 10^{-6}$ emu mole^{-1} (Table 6). The electrical resistivity of NpN shows a pronounced anomaly at the Curie temperature.

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[64] W. M. Olsen and R. N. R. Mulford, *J. Phys. Chem.* **70** (1966) 2932.
[65] C. H. de Novion and R. Lorenzelli, *J. Phys. Chem. Solids*, **29** (1968) 1901.

Plutonium nitride[66]

Plutonium forms only a mononitride, PuN (Table 4). It is best prepared by heating plutonium hydride in nitrogen at 400°C. The direct reaction between plutonium metal and nitrogen is sluggish, even above the m.p. of plutonium (639°C). However, the addition of a small quantity of hydrogen catalyses the nitridation by forming a surface layer of plutonium hydride which successively reacts and reforms in a cyclic process. The reaction then proceeds rapidly to completion to give PuN powder which is sintered in argon at 800–1000°C to reduce its reactivity.

PuN is a stoichiometric phase which shows a greater tendency than UN to substitute oxygen ions for part of the nitrogen. Up to 10 at.% of the nitrogen may be replaced by oxygen, the lattice parameter increasing concomitantly from 4·903 to 4·909 Å. Excess oxygen is present as hexagonal Pu_2O_3 rather than as PuO_2. The lattice parameter of PuN also expands gradually on long standing as a result of self-irradiation damage.

Thermodynamic Properties

No heat capacity measurements on PuN have been reported. The decomposition pressure of PuN has been determined by measuring its apparent m.p. as a function of nitrogen pressure[67]. Over the temperature range 2563–3043K the dissociation pressure is given by

$$\log P\,(\text{atm}) = 8{\cdot}193 - (29{\cdot}54 \times 10^{3})T^{-1} + (11{\cdot}28 \times 10^{-18})T^{5}\ (T \text{ in } ^{\circ}\text{K})$$

Congruent melting is not observed up to 25 atm (Fig. 3). From a consideration of the congruent m.p.s of ThN, UN and NpN, that of PuN is estimated to be 3103 ± 50K under a nitrogen pressure of 50 ± 20 atm. The observed "m.p." under 1 atm of nitrogen is 2857 ± 30K.

Direct vapour pressure measurements of PuN have been made by several groups using Knudsen effusion cell techniques[51,66]. Expressions for the free energy of the reaction $PuN_{(s)} \rightarrow Pu_{(g)} + \frac{1}{2}N_{2(g)}$ have been derived and from these the heat of formation of PuN at 298K has been calculated. The volatilization of PuN on heating *in vacuo* first becomes appreciable above 1800K. Although congruent vaporization occurs, there is no evidence for PuN molecules in the gas phase.

Thermodynamic values have also been calculated from emf measurements on cells of the type $Pu_{(s,l)}|(PuCl_3,\ LiCl\text{–}KCl)|N_{2(g)},\ PuN_{(s)}$ over the temperature range 714–1032K, and also from direct heat of combustion measurements of PuN in oxygen. All of these various techniques give values for $\Delta H_{f(298)}$ (PuN_s) in the range − 70 to − 73 kcal $mole^{-1}$ [51].

Chemical Properties

The chemical reactivity of plutonium nitride has been investigated in some depth[68]. PuN powder reacts with dry oxygen below 280°C and ignites at ~300°C, forming PuO_2 with liberation of nitrogen. The reaction kinetics of oxidation are highly sensitive to trace quantities of water vapour which catalyse the reaction. For instance, the ignition temperature in oxygen may fall from 300°C to <100°C in the presence of water vapour.

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[66] J. M. Cleveland, *The Chemistry of Plutonium*, Chapter 14, p. 413. Gordon & Breach (1970).

[67] W. M. Olsen and R. N. R. Mulford, *J. Phys. Chem.* **68** (1964) 1048.

[68] N. J. Bridger, R. M. Dell and V. J. Wheeler, *Reactivity of Solids*, 6th International Symposium, p. 389, J. Wiley (1969).

The vapour phase hydrolysis of PuN powder in the absence of oxygen takes place according to the equation:

$$PuN + (2+x)H_2O \rightarrow PuO_2 \cdot xH_2O + NH_3 + \tfrac{1}{2}H_2$$

The value of x is independent of the partial pressure of water (using A/H_2O mixtures) and depends solely on the temperature: x decreases from 2·0 at 20°C to 0·45 at 50°C and then to 0·11 at 250°C. The rate of hydrolysis is limited only by the rate of gas diffusion through the pores of the product oxide and the activation energy is only 1–2 kcal $mole^{-1}$ in the temperature range 100–300°C. Clearly, the hydrolysis of PuN is very much easier than that of UN and the mechanism is entirely different. This difference is attributed to the absence of a higher plutonium nitride capable of forming epitaxially on the surface of PuN.

In liquid water, dense PuN is hydrolysed slowly when cold and rapidly when hot to form a bulky black mass of hydrated oxide. PuN is also attacked by the common mineral acids. It dissolves readily in 3M HCl or H_2SO_4 to yield a blue Pu(III) solution. This observation provides indirect support for the view that PuN contains Pu^{3+} ions.

PuN reduces PuO_2 to β-Pu_2O_3 with liberation of nitrogen, the reaction beginning below 1200°C.

Physical Properties

The electrical resistivity of PuN is metal-like, increasing from $\sim 10\ \mu$ohm cm at 4K to $\sim 650\ \mu$ohm cm at 300K, with a change of slope near 120K. The thermoelectric power of PuN is negative and passes through a maximum at 120K[69]. The explanation for these discontinuities at 120K is not known. Magnetic susceptibility measurements provide no evidence for magnetic ordering at this temperature[70]. The molar susceptibility of PuN rises from $\sim 600 \times 10^{-6}$ emu at 300K to a maximum of $\sim 750 \times 10^{-6}$ emu at 13K and then falls abruptly. This may indicate antiferromagnetic ordering with a Néel temperature of 13K. The susceptibility in the paramagnetic region may be analysed according to the modified Curie–Weiss relationship ($\chi = \chi_0 + C/(T - \theta)$) giving $\mu = 1 \cdot 08$ B.M. and $\theta = 200$K (Table 6).

Other actinide nitrides

Protactinium nitride, PaN, is said to be formed by reacting $PaCl_4$ or $PaCl_5$ with ammonia at 800°C[70a], but no supporting X-ray data have been presented.

Americium nitride (AmN, $a = 5 \cdot 00$ Å) has been prepared by reacting ammonia with americium hydride at 800°C[71].

4. PHOSPHIDES, ARSENIDES, ANTIMONIDES AND BISMUTHIDES

The remaining pnictide compounds, from phosphides to bismuthides, are closely analogous as regards their crystal, chemical and other properties and it is therefore appropriate to discuss them together, considering each actinide element in turn.

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[69] P. Costa, R. Lallemont, F. Anselin and D. Rossignol, *Compounds of Interest in Nuclear Reactor Technology A.I.M.E. Symposium*, Nuclear Metallurgy, Vol. 10, p. 83 (1964).

[70] G. Raphael and C. H. de Novion, *Solid State Commun.* 7 (1969) 791.

[70a] P. A. Sellars, S. Fried, R. E. Elson and W. H. Zachariasen, *J. Amer. Chem. Soc.* 76 (1954) 5935.

[71] Y. Akimoto, *J. Inorg. Nucl. Chem.* 29 (1967) 2650.

Preparation of pnictide compounds

The key factor influencing the preparative procedure adopted is the volatility of the Group Vb element, which decreases progressively along the series P, As, Sb, Bi. The higher bismuthides, MBi_2, and antimonides, MSb_2, are generally prepared by mixing the powdered elements in stoichiometric proportions in evacuated, sealed tubes and annealing in a furnace. The reactions are not quite as straightforward as often depicted; for example, attention needs to be paid to compatibility with the container material, while moderately high temperatures may be required to secure completion of the reaction. Intermediate compounds, M_3Bi_4 and M_3Sb_4, may be prepared by the same route or by thermal degradation of the higher compounds.

The volatility of arsenic is such that pre-mixing of the metal and arsenic powders may result in high arsenic vapour pressures on account of the exothermicity of the reaction giving locally high temperatures. This may lead to tube breakage. For this reason, the higher arsenides are preferably prepared by the Faraday method in which the reactants are at opposite ends of an evacuated sealed tube held in a temperature gradient and the arsenic is sublimed on to the metal in a controlled fashion. However, some authors appear to have had success with the pre-mixing technique and in one case AsH_3 has been employed in the preparation of UAs.

The volatility of phosphorus is such that pre-mixing is dangerous and unreliable and the Faraday method is generally employed for phosphide. Because of the difficulty in obtaining pure phosphorus free of oxide impurity, some workers have used PH_3 gas to prepare the phosphides, although this too can be hazardous on the large scale[72] and is not recommended for highly radioactive elements where the consequences of an explosion could be serious.

The monopnictides are generally prepared by homogenizing stoichiometric mixtures of higher pnictides and the metal powder pressed into pellets. The temperatures required for homogenization are significantly lower than with the monochalcogenides. The monophosphides can also be prepared by simple thermal decomposition of higher phosphides, while at the other end of the series the monobismuthides (and to a lesser extent the monoantimonides) may be produced directly from the elements by arc-melting them together.

Thorium compounds

The thorium and uranium pnictides generally form three isostructural series of compounds, MX_2, M_3X_4 and MX (see Table 4). The formation of dipnictides of thorium is surprising, in view of the constant +4 valence of this element, and is best understood in terms of a polyanion structure $Th^{4+}(X\text{–}X)^{4-}$. It is notable that ThP_2 has not been reported although $ThAs_2$, $ThSb_2$ and $ThBi_2$ are stable.

Thorium Phosphides

The higher thorium phosphide, Th_3P_4, is a stoichiometric compound which may be prepared by reacting thorium powder with phosphine at 550°C[73]. It decomposes *in vacuo* at ~1500°C to yield the monophosphide, a deep blue compound. The compositional range of the monophosphide has been the subject of considerable disagreement. It was originally

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[72] H. A. C. McKay, *Chemy. Ind. (London)* (1964) 1978.

[73] Y. Baskin, *J. Amer. Ceram. Soc.* **52** (1969) 54.

considered to be a substoichiometric phase of wide homogeneity range, e.g. $ThP_{0\cdot96}$–$ThP_{0\cdot55}$[74]. However, later studies of phase equilibria in the Th–ThP system[75] indicate that there is a minimum P/Th ratio of 0·98 at all temperatures. The compound melts congruently (P/Th ratio $0\cdot99 \pm 0\cdot02$) at 3263K.

Thermodynamic information on the Th–P system has been obtained from e.m.f. measurements on solid-state electrochemical cells of the type $(Th, ThF_4)|CaF_2|(ThF_4, ThP, Th_3P_4)$ to study the equilibrium $Th_{(s)} + Th_3P_{4(s)} = 4ThP_{(s)}$. Combining these data with data for the dissociation pressure of Th_3P_4 ($Th_3P_4 \rightarrow 3ThP + \frac{1}{2}P_2$), the free energy, heat and entropies of formation shown in Table 5 were calculated.

ThP is comparatively stable in air, only beginning to oxidize rapidly above 400°C[73]. No phosphorus is lost during oxidation, even after heating to 950°C. It seems that a non-volatile, vitreous thorium phosphate phase is formed. ThP itself is an exceptionally good metallic conductor, the resistivity at 300K being $\sim 30\ \mu$ohm cm even for specimens of only moderate purity and density. The resistivity exhibits little temperature dependence between 100 and 500K.

Thorium Arsenides, Antimonides and Bismuthides

Little has been reported on these compounds apart from their crystallographic properties (Table 4). It is notable that alone among the dipnictides $ThAs_2$ occurs in two polymorphic forms. Orthorhombic α-$ThAs_2$ reverts to tetragonal β-$ThAs_2$ on heating above 1100°C. A detailed phase study of the Th–ThAs system has been reported[76] and some measurements of the thermoelectric properties of Th_3As_4 and Th_3As_4/Th_3Sb_4 solid solutions have been undertaken[77].

Only two bismuthides, $ThBi_2$ and Th_3Bi_4 are known for certain. During attempts to prepare ThBi, X-ray evidence was obtained for two phases, neither of which had the NaCl or CsCl structures. Dissociation pressure measurements of bismuth vapour suggested a single phase region of wide homogeneity around ThBi[78] which disproportionates to Th_3Bi_4 and excess Th on cooling.

Uranium compounds

In each of the binary systems U–P, U–As, U–Sb and U–Bi three phases are formed, UX_2, U_3X_4 and UX, which are isostructural with each other and with the corresponding thorium compounds where known (Table 4).

Uranium Phosphides

The uranium phosphides have been extensively studied, particularly uranium monophosphide which exhibits some interesting physical properties. UP_2 is best prepared by reacting powdered uranium or uranium hydride with phosphine gas at 400°C, gradually raising the temperature to complete the reaction. It decomposes to U_3P_4 in a vacuum at 700–800°C. The latter decomposes further to UP at 1350–1400°C. Both of these compounds are reasonably stable in air at room temperature. UP possesses no measurable range of stoichiometry at 20°C and generally exhibits a particularly well-crystalline X-ray powder

[74] K. A. Gingerich and D. W. Wilson, *Inorg. Chem.* 4 (1965) 987.
[75] C. A. Javorsky and R. Benz, *J. Nucl. Mat.* 23 (1967) 192.
[76] R. Benz, *J. Nucl. Mat.* 25 (1968) 233.
[77] I. H. Warren and C. E. Price, *Adv. Energy Conversion*, 4 (1964) 169.
[78] O. Dahlke, W. Gans, O. Knacke and F. Müller, *Z. Metallk.* 60 (1969) 465.

pattern. It is a grey powder which may be compacted by cold pressing and sintering at 1400–1800°C, or, preferably, by hot pressing when ingots of high density are formed[2]. After metallographic polishing, UP has a bright metallic lustre and does not tarnish on standing in air. Sintering *in vacuo* above 1800°C leads to loss of phosphorus by decomposition, with the formation of liquid uranium at grain boundaries. The melting point of UP under high phosphorus vapour pressure is 2883 ± 20K[79]. Single crystals of U_3P_4 and UP_2 have been grown successfully by iodine vapour transport.

Thermodynamic Properties

The low temperature heat capacities of UP, U_3P_4 and UP_2 have been determined up to 320K (Table 5). All three compounds show anomalies associated with magnetic ordering, UP at 121K, U_3P_4 at 136·5K and UP_2 at 203K. Values for the heat and entropy of ordering for each compound are:

	UP	$UP_{1\cdot35}$	UP_2	
ΔH_t	87·3	64·1	204·5	cal mole^{-1}
ΔS_t	0·74	0·51	1·31	cal mole^{-1} deg^{-1}

In addition, the C_p curve for UP has a second, exceedingly sharp anomaly at 22·5K, spreading over less than one degree, for which $\Delta H_t = 10\cdot2$ cal mole^{-1} and $\Delta S_t = 0\cdot45$ cal mole^{-1} deg^{-1}. Neutron diffraction studies give no evidence for a further change in magnetic order at this temperature.

The heat of formation of UP was determined by fluorine bomb calorimetry (Table 5). Values obtained by direct reaction calorimetry[80] were some 20% lower and should be regarded as suspect.

Chemical and Physical Properties

Most work has been carried out on uranium monophosphide, which is comparatively resistant to both oxidation and hydrolysis. This is attributed to the presence of a surface film of uranyl phosphate which is vitreous and so excludes gases. On heating in oxygen UP does not ignite, in marked contrast to UN and US[81]. Rather, oxidation takes place in several consecutive steps to yield ultimately $(UO_2)_2P_2O_7$.

UP is compatible with molybdenum and tantalum up to its dissociation temperature. Under high phosphorus pressure it does not attack tungsten below its melting point.

Electrical properties (resistivity, thermoelectric power, Hall coefficient) have been determined for single crystal and polycrystalline specimens of UP_2[82] and U_3P_4[83]. UP_2, being tetragonal, shows a pronounced anisotropy of the transport properties. All three phosphides are metallic conductors with specific resistances in the range 10^{-4} to 10^{-3} ohm cm. The resistivity of UP passes through a maximum at its Néel temperature (121K). The thermal conductivity of UP has also been determined[21].

[79] Y. Baskin, *Nucl. Sci. Eng.* **24** (1966) 332.

[80] Y. Baskin and S. D. Smith, *J. Nucl. Mat.* **37** (1970) 209.

[81] Y. Baskin, *J. Amer. Ceram. Soc.* **48** (1965) 153.

[82] Z. Henkie and W. Trzebiatowski, *Phys. Stat. Sol.* **35** (1969) 827.

[83] Z. Henkie and C. Bazon, *Phys. Stat. Sol.* (in press).

Magnetic Properties

The magnetic properties of the three uranium phosphides are given in Table 6. On cooling, UP and UP_2 order antiferromagnetically and U_3P_4 orders ferromagnetically[84]. There is some considerable spread in the paramagnetic data recorded in the literature, particularly for UP, and this has been attributed to sample variability[85]. UP, like UN, assumes type I antiferromagnetic ordering below T_N (Fig. 4)[86]. The magnetic moment of the uranium atoms in the ordered state, deduced from the intensity of the magnetic peaks, is 1·7 B.M. On cooling below 22K, where the anomalous C_p transition occurs, the magnetic ordering remains unchanged, but the magnitude of the ordered moment increases to 1·9 B.M. Other physical effects have also been observed at 22K and it seems likely that a change in the electronic ground state of UP takes place at this temperature.

Neutron diffraction studies have also been carried out on ferromagnetic U_3P_4[87] and antiferromagnetic UP_2[88]. The magnetic unit cell of UP_2 (tetragonal) is twice the chemical cell in the *c*-axis direction and the ferromagnetic sheets of U atoms perpendicular to the *c*-axis are stacked in the sequence $+--+$. The magnetic moments of the uranium atoms are pointing in the direction of the *c*-axis and are of magnitude 1·0 ± 0·1 B.M.

Uranium Arsenides, Antimonides and Bismuthides

Uranium forms with arsenic, antimony and bismuth compounds of similar structure to those formed with phosphorus. Thus UAs, U_3As_4, UAs_2; USb, U_3Sb_4, USb_2; UBi, U_3Bi_4 and UBi_2 have been prepared and their crystallographic parameters determined (Table 4). The compounds are generally produced by the Faraday method, although UAs has been formed by the reaction of uranium powder with AsH_3 gas, followed by homogenization in a vacuum at 1200–1400°C[89]. Single crystals of UAs_2 and U_3As_4 have been grown from the powders by iodine transport.

Limited phase studies have been made of all three systems. In the U–UAs portion of the U–As system the solubility of U in UAs does not exceed 0·15 % up to 2200°C[90]. UAs decomposes before melting; the highest melting point observed being 2978K. A study of the U–Sb system[91] has revealed that USb_2 and U_3Sb_4 decompose peritectically at 1628K and 1968K, respectively. A subantimonide, U_4Sb_3, of hexagonal structure was also reported. Similarly, UBi_2 and U_3Bi_4 were found[92] to decompose peritectically at 1283K and 1423K, respectively, while UBi was said to decompose to two liquid phases between 1673K and 1723K. Uranium is soluble to an appreciable extent in liquid bismuth and the activity of dilute solutions has been measured[19].

Magnetic Properties

There has been considerable interest in the magnetic properties of these compounds (Table 6). In each of the series UX, U_3X_4, UX_2, there is a tendency for the paramagnetic moment to increase with increasing atomic number from P through As, Sb to Bi. On

[84] W. Trzebiatowski and R. Troc, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **11** (1963) 661.
[85] M. Allbutt, R. M. Dell, A. R. Junkison and J. A. C. Marples, *J. Inorg. Nucl. Chem.* **32** (1970) 2159.
[86] N. A. Curry, *Proc. Phys. Soc.* **89** (1966) 427.
[87] R. Ciszewski, A. Murasik and R. Troc, *Phys. Stat. Sol.* **10** (1965) K85.
[88] R. Troc, J. Leciejewiez and R. Ciszewski, *Phys. Stat. Sol.* **15** (1966) 515.
[89] Y. Baskin, *J. Inorg. Nucl. Chem.* **29** (1967) 2480.
[90] R. Benz and M. C. Tinkle, *J. Electrochem. Soc.* **115** (1968) 322.
[91] B. J. Beaudry and A. H. Daane, *Trans. A.I.M.E.* **215** (1959) 199.
[92] R. J. Teitel, *J. Metals*, **9** (1957) 131.

cooling, the magnetic ordering processes are analogous to those in the phosphides with UX and UX_2 ordering antiferromagnetically and U_3X_4 ferromagnetically. UAs differs strikingly from all the other uranium monopnictides in that it undergoes a change in magnetic ordering on cooling further. At 78K it has the type I antiferromagnetic structure (Fig. 4), as also do UN, UP, USb and UBi. On cooling to 4K, UAs alone reverts to a new antiferromagnetic structure containing a tetragonal magnetic cell in which the moments are aligned along the unique tetragonal axis[93]. The sequence of ferromagnetic sheets perpendicular to the tetragonal axis is $+--+$. The precise transformation temperature has not been determined. In USb_2 the magnetic cell is again tetragonal and twice the size of the chemical cell along the *c*-axis (ferromagnetic sheet sequence $+--+$) whereas for UBi_2 the magnetic and chemical units cells are identical ($+-$). The ordered magnetic moments determined by neutron diffraction (antiferromagnetic structures) or saturation magnetization measurements (ferromagnetic structures) are given in Table 6.

Transuranium compounds

Plutonium reacts with phosphorus, arsenic, antimony and bismuth to form monocompounds of the type PuX. No higher pnictides of plutonium are known. The monocompounds all crystallize in the fcc rocksalt structure with the lattice parameters shown in Table 4.

Plutonium phosphide is also prepared by reacting phosphine with plutonium powder at 400°C[94]. However, due to plutonium hydride formation, this reaction is less satisfactory than direct union of the elements provided that phosphorus of adequate purity is available. PuP melts with decomposition at 2870K in argon at 2 atm pressure. The sintering behaviour of PuP powder has been described[95]. and its physical properties measured in some detail[96]. It is a metallic-type electrical conductor of resistivity ~850 μohm cm at 300K. From the sign of the Seebeck coefficient it is deduced that the current carriers are positive holes. The heat capacity at 298K (Table 5) was deduced from heat pulse measurements in which the value of the thermal diffusivity for PuP was also determined. The magnetic properties of PuP are of considerable interest and have been explored in detail (Table 6). Unlike PuS, PuSe, PuTe and PuN, all of which show a small paramagnetic susceptibility which has little temperature dependence, PuP has a characteristically large susceptibility which obeys the Curie–Weiss law after correction for temperature-independent orbital paramagnetism. The paramagnetic moment (1·06 B.M.) is similar to that of PuN. On cooling, PuP orders *ferromagnetically*, at a Curie temperature of 126K, and in the ordered state has a magnetic moment of 0·42 B.M. per plutonium atom. Results of NMR measurements on PuP are discussed in terms of the coupling of conduction electrons and localized 5*f* electrons.

Plutonium arsenide has been made by reactions involving elemental arsenic or arsine[97]. It melts with decomposition at 2693 ± 30K in a flow of argon at 3 atm pressure. PuSb was prepared by arc-melting the elements together and was found to melt at 2253 ± 30K under similar conditions[97]. PuBi was also prepared by melting the elements together.

The only other actinide compounds which have been reported, apart from those of plutonium, are NpSb and AmSb (Table 4). Both were prepared by arc-melting equiatomic

[93] J. Leciejewiez, A. Murasik and R. Troc, *Phys. Stat. Sol.* **30** (1968) 157.

[94] O. L. Kruger and J. B. Moser, *J. Inorg. Nucl. Chem.* **28** (1966) 825.

[95] O. L. Kruger and J. B. Moser, *J. Amer. Ceram. Soc.* **49** (1966) 661.

[96] O. L. Kruger and J. B. Moser, *J. Chem. Phys.* **46** (1967) 891.

[97] O. L. Kruger and J. B. Moser, *J. Phys. Chem. Solids*, **28** (1967) 2321.

proportions of the elements together; it is not known whether other phases of differing composition exist.

5. TERNARY COMPOUNDS AND SOLID SOLUTIONS

Ternary chalcogenides and pnictides are of two general types:

(1) Compounds of definite composition.
(2) Solid solutions of two binary compounds, either with two metals and a common anion, or two anions and a common metal.

Ternary compounds

Oxycompounds

The best known of the ternary compounds are the oxychalcogenides which are often present as impurities, particularly in the monochalcogenides. When compacts of powdered ThS, US or PuS are sintered at $\geqslant 1600$°C the corresponding oxysulphides (ThOS, UOS, Pu_2O_2S) segregate at the grain boundaries, where they tend to form liquid eutectics with the monosulphides and so facilitate sintering.

The oxychalcogenides are readily prepared in a pure state by heating a chalcogenide with the appropriate amount of oxide, e.g. $PuSe + PuO_2 \rightarrow Pu_2O_2Se$. Single crystals of certain compounds have been grown by halogen transport (e.g. UOS)[98]. The common oxychalcogenides of thorium and uranium are all of type MOX, crystallizing in the tetragonal PbFCl structure with two molecules per unit cell (Table 7). Similarly, the oxysulphides, PaOS, NpOS and PuOS, are known with this structure. These compounds are thought to contain M^{4+} ions.

Neptunium and plutonium form stable M^{3+} ions and so it might be expected that oxychalcogenides containing trivalent ions would exist. This is indeed so; both Np_2O_2S (Table 8) and $Np_4O_4S_3$ (Table 9) have been reported, the latter in a mixed valence sulphide, viz. $(Np^{4+})_2(Np^{3+})_2(O^=)_4(S^=)_3$. In the case of plutonium, the most stable oxychalcogenides of formula Pu_2O_2X are based on Pu^{3+} ions. Pu_2O_2S and Pu_2O_2Se crystallize in the hexagonal La_2O_3 structure (cf. Ce_2O_2S) while Pu_2O_2Te is tetragonal. Other plutonium oxysulphides which have been reported (Table 9) are $Pu_2O_2S_3$, which is said to be a polysulphide, $(Pu^{4+})_2(O^=)_2(S^=)(S{-}S)^=$, and the mixed valence $Pu_4O_4S_3$ (cf. $Np_4O_4S_3$) prepared by decomposing PuOS above 700°C. The analogous quaternary compound $U_2^{4+}Pu_2^{3+}O_4^=S_3^=$ has also been reported.

For the pnictides the situation is quite different. Oxygen impurity in the rock-salt monocompounds is invariably present as the corresponding dioxide. The solubility of oxygen in pnictides of higher X/M ratio is generally quite limited. There is some small solubility of oxygen in the α-U_2N_3 phase. The only oxypnictide compound which has been well characterized is thorium oxynitride Th_2N_2O (Table 8).

Nitrogen Compounds

Ternary actinide compounds containing nitrogen are of several structural types. Both thorium and uranium form compounds of general formula M_2N_2X (where X = P, As, S or Se) which crystallize in the hexagonal La_2O_3 structure and are therefore isostructural with Pu_2O_2S and Ce_2O_2S (Table 8). The uranium compounds may be regarded formally as

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[98] H. Boelsterli and F. Hulliger, *J. Mat. Sci.* 3 (1968) 664.

TABLE 7. TETRAGONAL TERNARY COMPOUNDS (MXY COMPOSITION)

Compound	Structure type	a_0	c_0	c/a	Ref.
ThOS	PbFCl	3·96	6·75	1·70	a
ThOSe	PbFCl	4·04	7·02	1·74	a
ThOTe	PbFCl	4·12	7·56	1·84	a
PaOS	PbFCl	3·83	6·70	1·75	a
UOS	PbFCl	3·84	6·68	1·74	a
UOSe	PbFCl	3·90	6·98	1·79	a
UOTe	PbFCl	4·00	7·49	1·87	a
NpOS	PbFCl	3·83	6·65	1·73	a
PuOS	PbFCl	3·80	6·59	1·73	a
ThPS	ZrSiS	3·98	8·18	2·06	b
ThPSe	ZrSiS	4·07	8·27	2·04	b
UPS	ZrSiS	3·81	7·98	2·10	c
UPSe	ZrSiS	3·96	8·18	2·07	c
ThAsS	ZrSiS	4·01	8·46	2·11	b
ThAsSe	ZrSiS	4·08	8·56	2·10	b
ThAsTe	ZrSiS	4·26	8·81	2·07	b
UAsS	ZrSiS	3·87	8·16	2·11	c
UAsSe	ZrSiS	3·99	8·38	2·10	c
UAsTe	ZrSiS	4·17	8·76	2·10	c
ThSbSe	ZrSiS	4·27	8·90	2·09	b
ThSbTe	ZrSiS	4·37	9·14	2·09	b
USbS	ZrSiS	3·94	8·53	2·16	c, d
USbSe	ZrSiS	4·12	8·68	2·11	c, d
USbTe	ZrSiS	4·32	9·06	2·10	c, d
ThBiTe	ZrSiS	4·47	9·17	2·06	b
UBiTe	ZrSiS	4·43	9·16	2·07	c
ThNCl	PbFCl	4·10	6·90	1·68	e
ThNBr	PbFCl	4·11	7·47	1·82	e
ThNI	PbFCl	4·11	9·24	2·25	e
UNCl	PbFCl	3·97	6·81	1·71	f
UNBr	PbFCl	3·94	7·95	2·02	f
UNI	PbFCl	3·99	9·20	2·31	f
USiS	ZrSiS	3·77	8·29	2·20	d
USiSe	UGeTe	3·90	16·77	4·30	d
UGeS	ZrSiS	3·81	8·31	2·18	d
UGeSe	UGeTe	3·93	16·97	4·32	d
UGeTe	UGeTe	4·11	17·60	4·29	d
USnTe	ZrSiS	4·26	9·13	2·14	d
ThSiS	UGeTe	3·91	17·06	4·36	g
ThSiSe	UGeTe	4·01	17·50	4·36	g
ThSiTe	UGeTe	4·19	18·18	4·34	g
ThGeS	UGeTe	3·93	17·12	4·36	g
ThGeSe	UGeTe	4·03	17·57	4·36	g
ThGeTe	UGeTe	4·19	18·22	4·34	g

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[a] R. M. Dell and N. J. Bridger, *Int. Rev. Sci.*, Inorganic Chemistry, Ser. 1, Vol. 7 (1972).

[b] F. Hulliger, U.S. Patent 3,510,274 (1970).

[c] F. Hulliger, U.S. Patent 3,506,410 (1970).

[d] A. J. Klein Haneveld and F. Jellinek, *J. Less Common Metals*, 18 (1969) 123.

[e] R. Juza and R. Sievers, *Z. anorg. allg. Chem.* 363 (1968) 258.

[f] R. Juza and W. Meyer, *Z. anorg. allg. Chem.* 366 (1969) 43.

[g] H. Hahn and K. Stocks, *Naturwiss.* 55 (1968) 389.

TABLE 8. HEXAGONAL TERNARY COMPOUNDS (La_2O_3 Structure)

Compound	a_0	c_0	c/a	Ref.
Np_2O_2S	3·95	6·80	1·72	a
Pu_2O_2S	3·92	6·76	1·72	b
Pu_2O_2Se	3·96	6·98	1·76	b
Th_2N_2O	3·88	6·19	1·60	c
Th_2N_2S	4·00	6·92	1·73	d, e
Th_2N_2P	4·01	6·85	1·71	d, e
Th_2N_2Se	4·03	7·16	1·78	e
U_2N_2S	3·83	6·59	1·72	d, e
U_2N_2P	3·80	6·55	1·72	d, e
U_2N_2Se	3·86	6·86	1·78	e
U_2N_2As	3·83	6·74	1·76	e

[a] J. P. Marcon, *Compt. Rendu*, **C265** (1967) 235.

[b] M. Allbutt, R. M. Dell and A. R. Junkison, *Chemistry of Extended Defects in Non-Metallic Solids*, p. 124, North Holland (1970).

[c] R. Benz and W. H. Zachariasen, *Acta Cryst.* **21** (1966) 838.

[d] M. Allbutt and R. M. Dell, *J. Nucl. Mat.* **24** (1967) 1.

[e] R. Benz and W. H. Zachariasen, *Acta Cryst.* **B25** (1969) 294.

derived from hexagonal β-U_2N_3 by substituting a P, As, S or Se atom for one of the nitrogens. They are prepared by heating UP, UAs, US or USe, respectively, in flowing nitrogen above 900°C. Attempts to prepare U_2N_2S by the converse reaction, that is between UN and excess of H_2S gas, led only to β-US_2 with elimination of nitrogen.

A second class of nitrogen-containing compound comprises the nitrihalides of thorium and uranium. These have the general formula MNZ (where Z is a halogen). The nitrichlorides, bromides and iodides all have the tetragonal PbFCl structure (Table 7), while the nitrifluoride ThNF is rhombohedral (Table 9). These compounds are formed by reacting the actinide tetrahalide with ammonia. If we assume these compounds to have the ionic structure $M^{4+}N^{3-}Z^{-}$, then it is clear why actinide oxyhalides and nitrichalcogenides do not form in this structure. No attempts to prepare corresponding Np^{4+} or Pu^{4+} nitrihalides have been reported.

A third class of nitrogen compounds are the mixed metal nitrides. In this category are Th_2CrN_3, Th_2MnN_3, U_2CrN_3 and U_2MnN_3 (Table 9).

Actinide Vb–VIb Compounds

The heavier elements in Groups Vb and VIb (above N and O) show little tendency to form ternary actinide compounds containing two different Vb elements or two different VIb elements. However, a series of mixed Vb–VIb compounds of general formula MXY is known, where X = S, Se, Te and Y = P, As, Sb, Bi. Many, but not all, of the possible thorium and uranium compounds have been prepared (Table 7). These compounds crystallize in the ZrSiS structure, which is closely related to PbFCl structure of the oxychalcogenides. They are prepared by mixing the constituent elements in stoichiometric proportions and sintering in a vacuum at 600–1100°C. Single crystals of many of the compounds were

TABLE 9. OTHER TERNARY COMPOUNDS*

Compound	Symmetry	Structure type	Lattice parameters				Ref.	Remarks
			a (Å)	b (Å)	c (Å)	β°		
U_2O_2Te	Tetragonal		3·96	—	12·50		a	
$Np_4O_4S_3$	Monoclinic	$Np_4O_4S_3$	4·07	6·76	3·89	118	b	Np^{3+} and Np^{4+} ions
$Pu_2O_2S_3$	Tetragonal	$PuS_{1\cdot9}$	3·95	—	7·95	—	b	Polysulphide
$Pu_4O_4S_3$	Monoclinic	$Np_4O_4S_3$	4·07	6·73	3·87	118	b	Pu^{3+} and Pu^{4+} ions
Pu_2O_2Te	Tetragonal		6·33	—	11·66		c	
ThNF	Rhombohedral	LaOF	7·13			$\alpha = 32\cdot66$	d	
UCe_2S_5	Orthorhombic	U_3S_5	7·48	8·14	11·81		e	
UGd_2S_5	Orthorhombic	U_3S_5	7·36	8·01	11·62		e	
$ThPu_2S_5$	Orthorhombic	U_3S_5						
UPu_2S_5	Orthorhombic	U_3S_5	7·38	8·03	11·65		e	
CaU_2S_5	Orthorhombic	U_3S_5					f	
SrU_2S_5	Orthorhombic	U_3S_5					f	
BaU_2S_5	Orthorhombic	U_3S_5					f	
Th_2CrN_3	Orthorhombic		3·87	3·52	12·84		g	Space group *Immm* (D^{25}_{2h})
Th_2MnN_3	Orthorhombic		3·79	3·55	12·83		g	
U_2CrN_3	Orthorhombic		3·74	3·31	12·33		g	
U_2MnN_3	Orthorhombic		3·72	3·33	12·21		g	

* Incomplete list.

[a] E. W. Breeze and N. H. Brett, *J. Nucl. Mat.* **40** (1971) 113.

[b] R. M. Dell and N. J. Bridger, *Int. Rev. Sci., Inorganic Chemistry*, Series 1, Vol. 7 (1972).

[c] M. Allbutt, R. M. Dell and A. R. Junkison, *Chemistry of Extended Defects in Non-Metallic Solids*, p. 124, North Holland (1970).

[d] R. Juza and R. Sievers, *Z. anorg. allg. Chem.* **363** (1968) 258.

[e] J. P. Marcon and R. Pascard, *Rev. Int. Hautes Temper. et Refract.* **5** (1968) 52.

[f] R. Brochu, J. Padiou and J. Prigent, *Compt. Rendu*, **C270** (1970) 809.

[g] R. Benz and W. H. Zachariasen, *J. Nucl. Mat.* **37** (1970) 109.

obtained by iodine transport reactions. The uranium compounds all order ferromagnetically on cooling, with Curie temperatures from 90 to 150K.

Actinide IVb–VIb Compounds

Compounds of general type MM^IX are known where M = Th, U; M^I = Si, Ge, Sn; X = S, Se, Te (Table 7). These all possess tetragonal symmetry; some crystallize in the ZrSiS structure and some in the related, but new, UGeTe structure[99]. Attempts to prepare USnS and USiTe were not successful.

Other Ternary Compounds

Among other ternary compounds are mixed metal sulphides with the M_3S_5 structure in which the trivalent cations are Ce^{3+}, Gd^{3+} or Pu^{3+}. Examples are UCe_2S_5, UGd_2S_5, $ThPu_2S_5$ and UPu_2S_5 (Table 9). These all possess the ionic configuration $M^{4+}M_2^{3+}S_5^{=}$. Another series, based upon the same crystal structure, has the ionic configuration $M^{2+}U_2^{4+}S_5^{=}$ where M = Ca, Sr, Ba (Table 9).

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[99] A. J. Klein Haneveld and F. Jellinek, *J. Less Common Metals*, **18** (1969) 123.

Solid solutions

Most work on ternary solid solutions has been confined to the monocompounds of rock-salt structure. Exceptions include studies of the magnetic properties of UP_2–ThP_2[100], UP_2–UAs_2[101], U_3P_4–U_3As_4[102] and USb_2–$ThSb_2$[103].

The extent of mutual solubility of two binary compounds of rock-salt structure is determined by their difference in lattice parameters; the nearer these approach each other, the greater is the degree of miscibility. Since the radii of the actinide metal cations do not differ greatly, binary compounds with a common anion generally exhibit complete miscibility to give homogeneous solid solutions $(M_{1-x}M^I_x)X$, where M and M^I are both actinides. The binary systems $(U_{1-x}Th_x)X$ and $(U_{1-x}Pu_x)X$ have been particularly well studied because of their technological interest as potential nuclear fuels. There has also been considerable interest in the magnetic properties of thorium based ternaries, for example $(Th_{1-x}U_x)P$[100], $(Th_{1-x}, U_x)S$[11], as it is possible to measure the magnetic moment of the isolated uranium ion surrounded by diamagnetic Th^{4+} ions.

Ternary compositions based upon a common anion are not easy to prepare as homogeneous phases. Inter-diffusion of the binary compounds into each other is slow and annealing temperatures of 1800–2000°C are generally required to ensure homogeneity. Various expedients have been employed to reduce the temperature, for instance preparing $(U_{1-x}Pu_x)S$ by blending an appropriate mixture of US_2, UH_3, PuS_2 and PuH_2 powders, pelleting and reaction sintering at 1600°C. By contrast, the mixed-anion ternary phases $M(X_{1-x}Y_x)$ may be prepared homogeneously from the corresponding binary compounds at lower temperatures. For example, mixtures of UP and US powder fabricated into a pellet will homogenize readily at 1500–1600°C to $U(P_{1-x}S_x)$. This is a result of the considerably higher diffusion coefficients of non-metals than metals in these rock-salt phases.

As the anionic radii of the various Vb and VIb elements spread over a wide range, the extent of mutual solubility of the binary rock-salt compounds is very variable. Generally, pairs of compounds in which the two non-metals are taken from different periods of the Periodic Table show restricted mutual solubilities e.g. UN–UP, US–UTe. However, binary mixtures based upon Vb and VIb elements from the same period have sufficiently close lattice parameters that solid solution is complete, e.g. UP–US, UAs–USe, USb–UTe.

These homogeneous ternary phases have stimulated considerable interest among physicists studying long-range magnetic ordering effects in solids[104,105]. On cooling, the uranium monopnictides order antiferromagnetically, while uranium monochalcogenides order ferromagnetically. A study of the ordering behaviour of the solid solutions as a function of composition has been of importance in understanding the electronic structure and magnetic interactions in these compounds. Most research to date has concentrated on the $U(P_{1-x}S_x)$ system, whose magnetic ordering behaviour in passing from UP to US has been shown to be extremely complex[106]. Although there is, as yet, no general agreement on the electronic band structure and chemical bonding in these metallic rock-salt compounds,

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[100] V. I. Chechernikov, T. M. Shavishvili, V. A. Pletyushkin and V. K. Slovyanskikh, *Soviet Physics JETP* **28** (1969) 81.

[101] W. Trzebiatowski and A. Misiuk, *Roczniki Chemii*, **42** (1968)163.

[102] W. Trzebiatowski and A. Misiuk, *Roczniki Chemii*, **44** (1970) 695.

[103] V. I. Chechernikov, *et al.*, *Soviet Physics JETP* **30** (1970) 73.

[104] J. Grunzweig-Genossar, M. Kuznietz and F. Friedman, *Phys. Rev.* **173** (1968) 562.

[105] M. Kuznietz, *Proc. Conf. Rare Earths and Actinides*, p. 162, Physical Society, Durham (1971).

[106] M. Kuznietz, G. H. Lander and Y. Baskin, *J. Appl. Phys.* **40** (1969) 1130.

the evidence for US suggests that the conduction band is a narrow *f–d* band and that magnetic ordering is determined by long-range interactions via the conduction electrons.

6. CONCLUSIONS

A very substantial amount of research has been carried out since 1960 on the actinide-Vb and VIb compounds, particularly those of uranium and plutonium. Looking ahead, three major areas for new work may be discerned:

(i) Investigations on protactinium, neptunium and americium compounds, to permit a comparison of behaviour along the actinide series.
(ii) Physical property measurements on binary and ternary phases of X/M ratio > 1 to parallel the extensive series of measurements made on the rock-salt phases.
(iii) The use of more sophisticated physical techniques, for example photoelectric emission measurements[107], hyperfine field determinations by NMR[107], variation of physical properties with applied pressure, to assist in understanding the electronic structure of the rock-salt compounds.

The ultimate goal of all this work is to derive a quantitative understanding of these actinide compounds which will satisfy the inorganic chemist, the crystallographer and the solid state physicist.

[107] F. Friedman and J. Grunzweig-Genossar, *Phys. Rev.* **B4** (1971) 180.

CARBIDES, SILICIDES AND BORIDES

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1. INTRODUCTION

The carbides, silicides and borides of the actinide elements are refractory compounds, and their stoichiometries are very varied. The borides are relatively stable to atmospheric attack, as are the silicides, whilst the carbides are readily attacked by water vapour. There are not at present enough data to make adequate comparisons of the various properties of the compounds. It will be seen that there is a relatively larger amount of information on the thorium, uranium and plutonium compounds than the other elements; these studies have, of course, received stimulation from the possible application of many of the compounds as nuclear fuel materials, and of the other actinide elements only protactinium, neptunium and americium compounds have been studied. These compounds for the actinides with higher atomic numbers than americium have not yet been reported.

2. CARBIDES

2.1. Introduction

Because of their significance in nuclear technology, much attention has been focused on obtaining a detailed knowledge of the chemical and physical properties of the uranium–carbon and plutonium–carbon systems; a solid solution of uranium monocarbide and plutonium monocarbide is a possible fuel for a fast breeder nuclear reactor, and studies of the thorium–carbon system have also been stimulated by interest in possible utilizations of the uranium–thorium and plutonium–thorium fuel cycles for nuclear reactor applications.

The carbide phases which have been reported are listed using their ideal formulae in Table 1.

TABLE 1. IDEAL FORMULAE OF THE ACTINIDE CARBIDE PHASES

				Pu_3C_2	
ThC	PaC	UC	NpC	PuC	
Th_2C_3*		U_2C_3	Np_2C_3	Pu_2C_3	Am_2C_3
ThC_2	PaC_2	UC_2	NpC_2	PuC_2	

* Not stable at ambient pressure.

The reported carbides have a silver metallic appearance with the exception of thorium dicarbide which is pale yellow when a new surface is cleaved.

2.2. Preparative methods

The methods which have been used for the preparation of the carbides can be classified as follows:

(a) The reaction of carbon with the metal or metal hydride.
(b) The reaction of hydrocarbons with the metal or hydride.

(c) The precipitation of carbides from solutions of uranium and plutonium in a molten metal.
(d) The carbothermic reduction of the oxides *in vacuo* or inert atmospheres (i.e. flowing argon).
(e) The reduction of halides.

When considering these different preparative methods a distinction must be made between those that are suitable for the laboratory scale preparation of pure materials and those for larger scale industrial applications where certain levels of impurities such as nitrogen and oxygen may be tolerated. The methods used for the larger scale manufacture of the carbides of technological interest will be considered in a later section.

A convenient method for the preparation of laboratory samples of the actinide carbides is directly from the elements by arc-melting them together. The metal and carbon in the form of graphite are usually melted together under an inert atmosphere of helium or argon on a water-cooled copper hearth with a graphite electrode, although tungsten electrodes have been employed for some preparations[1]. Oxygen and nitrogen contamination is kept to a minimum (< 100 ppm) by gettering the argon or helium atmosphere with molten zirconium before melting the actinide element and graphite together. In the later discussion of the individual phase diagrams it will be seen that the rapidly quenched molten alloy will not be in equilibrium at ambient temperatures and will require annealing at a temperature where equilibrium will be attained in reasonable times. Because of the different volatilities of the actinide elements, changes in composition can occur during the arc-melting process and it is always necessary to determine the composition of the product and to determine the oxygen and nitrogen contamination levels.

A suitable method for the determination of carbon[2] involves burning the sample in oxygen at 1400°C, and determining the CO_2 formed manometrically. The accuracy of the method is better than 5%.

For the determination of oxygen impurity concentrations in the actinide carbides both vacuum fusion and inert gas fusion have been employed[3,4]. Using inert gas fusion, oxygen and also nitrogen can be determined in amounts varying from 10 μg to 10 mg, that is from impurity level concentrations to those occurring in stoichiometric oxides and nitrides. In addition to the vacuum and inert gas fusion techniques, the methods of Kjeldahl and Dumas have been applied to these materials[5].

A modification of the preparation from the elements is to use the metal in a hydrided form. The metal is initially hydrided and then the hydrides, which in the case of uranium and plutonium are unstable at temperatures in excess of 500°C, decomposed to give metals in a finely divided form which are then mixed with carbon and the mixtures are reacted together at temperatures less than 1500°C. For example, for the preparation of uranium monocarbide and plutonium monocarbide[6] massive uranium metal was hydrided at 1500°C

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[1] S. Rosen, M. V. Nevitt and A. W. Mitchell, *J. Nucl. Mat.* **9** (1963) 137; S. Rosen, M. V. Nevitt and J. J. Barker, *ibid.* **9** (1963) 128.

[2] G. W. C. Milner, G. Phillips, I. G. Jones, D. Crossley and D. H. Rowe, *Carbides in Nuclear Energy*, p. 162, L. E. Russell *et al.* (Eds.), Macmillan, London (1964).

[3] B. L. Taylor, G. W. C. Milner, F. T. Birks and H. A. Prior, *ibid.*, p. 447.

[4] B. L. Taylor, G. Phillips and G. W. C. Milber. Conference on Analytical Methods in the Nuclear Fuel Cycle, Paper SM.149/22, IAEA, Vienna (1971).

[5] K. H. Neeb and W. Gebauhr, *Fortschritte der Chemischen Forschung*, **12** (1969) 622.

[6] R. Pascard, *Powder Metallurgy in the Nuclear Age*, p. 387, F. Benesovsky (Ed.), Reute, Tyrol, Metallwerke Plansee A.G. (1962).

under 3 atm pressure of hydrogen; the UH_3 formed was then mixed with graphite powder, while plutonium hydride was prepared at much lower temperatures (<300°C) with 1 atm pressure of hydrogen, and then mixed with graphite powder in the required proportions. The mixtures were then pressed into pellets which were heated slowly *in vacuo*, initially at a low rate to enable all the hydrogen to be pumped off and then more rapidly up to 1400°C. The release of hydrogen was complete at 200°C for UH_3 but continued up to 500°C for plutonium hydride. Usually 1200°C was a sufficiently high temperature for carburization, but the use of 1400°C guaranteed complete freedom from any trace of metal, although temperatures as low as 900°C have been successfully employed[7].

The carbides of uranium and plutonium have also been prepared by the reaction of finely divided metals with both methane and propane[8] using a fluidized bed process. The principle of the method is to equilibrate the finely divided metal with a mixture, for example, of hydrogen and methane; the ratio of the proportions and the temperature will determine the carbon potential which should be that of the carbide which it is desired to prepare. The equilibrium is

$$\text{C (in the carbide phase)} + 2\text{H}_2\text{ (gas)} \rightleftharpoons \text{CH}_4\text{ (gas)}$$

and at any temperature (T°K)

$$\Delta G_f{}^{\circ}{}_{(\text{CH}_4)} = RT \ln \frac{P_{\text{H}_2}}{P_{\text{CH}_4}} + RT \ln a_\text{C}$$

where $\Delta G_f{}^{\circ}{}_{(\text{CH}_4)}$ is the standard free energy of formation of methane gas, P_{H_2} and P_{CH_4} are the pressure of hydrogen and methane, a_C is the activity of carbon, ln is $\log_e$ and R is the gas constant.

Some uranium and plutonium carbides have been prepared by the reaction of the actinide element dissolved in liquid zinc–magnesium alloy with finely divided carbon suspended in the liquid metal solution at *ca.* 800°C[9]. Uranium carbides have also been prepared by the reaction of uranium halides with calcium, magnesium, or aluminium in the presence of carbon or as the carbides[10]. The reactions were carried out *in vacuo* at 700°C, and in the case of magnesium the final heat treatment at 1200°C removed the $MgCl_2$.

As will be described later, much of the recent attention to the fabrication of dense pellets of monocarbides of uranium and of the solid solutions of uranium–plutonium monocarbides has been based on the development of the carbothermic reduction route to produce the carbides[11].

Whilst many methods have been used and the development of many processes for the technological applications has been considered, and certain levels of impurities may be acceptable for nuclear applications, for the determination of chemical and physical properties of all the actinide carbides carefully characterized specimens are required and the arc-melting route is the most suitable for the preparation of pure materials. The preparations should always be characterized by complete chemical analyses, metallography and lattice parameter determinations.

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[7] F. Anselin, G. Dean, R. Lorenzelli and R. Pascard, *Carbides in Nuclear Energy*, p. 113, L. E. Russell *et al.* (Eds.), Macmillan, London (1964).

[8] E. J. Petkus and P. W. Krause, USAEC Report, ANL-7325 (1966).

[9] E. J. Petkus, T. R. Johnson and R. K. Streunenberg, USAEC Report ANL-7301 (1966).

[10] P. Beucherie, M. Payrissat and J. G. Wurm, Euratom Report EUR-3170f (1966).

[11] J. D. L. Harrison and J. W. Isaacs, *Carbides in Nuclear Energy*, p. 569, L. E. Russell *et al.* (Eds.), Macmillan, London (1964).

2.3. Physical properties

Crystal Structures

Pu_3C_2. This has no analogues amongst the other actinide elements. The crystal structure has not been determined although the X-ray powder pattern has been given[12,13].

Monocarbides. The monocarbides all have the NaCl structure (space group *Fm*3*m*), and can have variable stoichiometry; carbon can be removed from the lattice and the width of the stoichiometric range depends on the temperature. Examination of the phase diagrams in section 2.4, p. 371, shows the magnitude of these variations in stoichiometry with temperature for the Th–C, U–C, and Pu–C systems. The lattice parameters of the monocarbides decrease with removal of carbon atoms, and where there is an appreciable stoichiometry range, for example with Th and Pu, there is an almost linear relationship between the number of carbon vacancies and the lattice parameter. This relationship for thorium monocarbide is shown in Fig. 1 from the data reviewed by Storms[14]; the marked deviations from a linear relationship for some alloys are due to the presence of dissolved oxygen in the thorium monocarbide lattice[15]. The variation of lattice parameter with stoichiometry for plutonium monocarbide[16] is shown in Fig. 2.

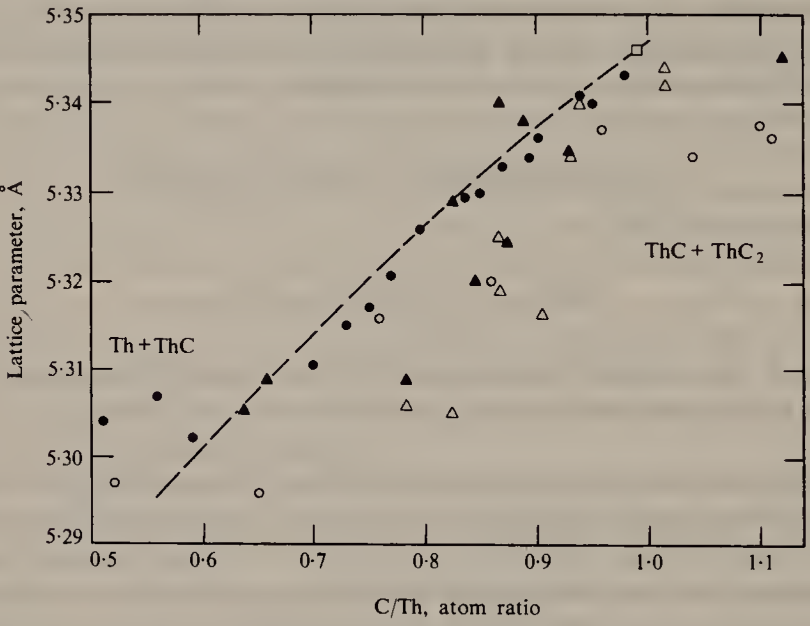

FIG. 1. The variation of lattice parameter with stoichiometry for thorium monocarbide (after Storms[14]).

The lattice parameters of the actinide monocarbides are given in Table 2.

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[12] R. N. R. Mulford, F. G. Ellinger, G. S. Hendrix and E. D. Albrecht, *Plutonium 1960*, p. 301, E. Grison, W. B. H. Lord, R. D. Fowler (Eds.), London, Cleaver-Hume Press, London (1961).

[13] S. Rosen, USAEC Report ANL-6435 (1964).

[14] E. K. Storms, *The Refractory Carbides*, p. 157, Academic Press, New York and London (1967).

[15] P. E. Potter, *J. Inorg. and Nuclear Chem.* **31** (1969) 1821.

[16] S. Rosen, M. V. Nevitt and A. W. Mitchell, *J. Nucl. Mat.* **10** (1963) 90.

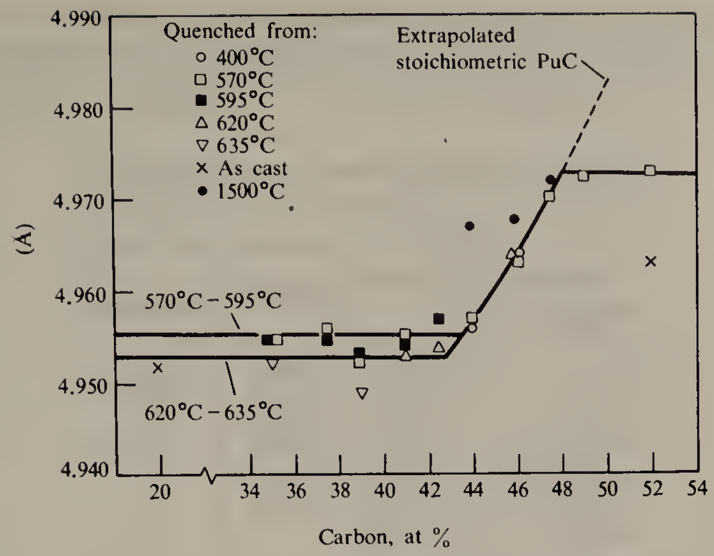

FIG. 2. The variation of lattice parameter with stoichiometry for plutonium monocarbide.

TABLE 2. LATTICE PARAMETERS OF THE ACTINIDE MONOCARBIDES

Phases in equilibrium	Composition of monocarbide	Lattice parameter (Å)	Reference
Th + ThC	$ThC_{0.62}$	5·303 ± 0·002	a
ThC + ThC_2	$ThC_{0.99}$	5·346 ± 0·002	b
PaC		5·0608 ± 0·0002	c
U + UC	$UC_{0.93}$	4·9563 ± 0·0007	d
UC + UC_2	$UC_{1.0}$	4·9605 ± 0·0002	e
NpC		5·003 ± 0·003	f
PuC + Pu_3C_2	$PuC_{0.74}$	4·954	g
Pu_2C_3 + PuC	$PuC_{0.87}$	4·9730 ± 0·0001	g

[a] E. K. Storms, *Refractory Carbides*, p. 160, Academic Press, New York and London (1967).

[b] C. P. Kempter and N. H. Krikorian, *J. Less-Common Metals*, **4** (1962) 244.

[c] R. Lorentz, H. L. Scherff and N. Toussaint, *J. Inorg. and Nuclear Chem.* **31** (1969) 2381.

[d] P. Magnier and A. Accary, *Carbides in Nuclear Energy*, p. 22, L. E. Russell *et al.* (Eds.), Macmillan, London (1964).

[e] E. K. Storms, *Refractory Carbides*, p. 184.

[f] W. H. Zachariasen and H. A. Plettinger, USAEC Report ANL-4798 (1952) 38.

[g] O. L. Kruger, *J. Nucl. Mat.* **7** (1962) 142.

Sesquicarbides. The actinide sesquicarbides are all isomorphous, with a body-centred cubic (space group $I\bar{4}3d$) structure. Thorium sesquicarbide has been prepared only at high pressures[17].

The lattice parameters of the sesquicarbides are given in Table 3, and clearly plutonium sesquicarbide exists over a range of composition as the lattice parameters are different

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[17] M. C. Krupka, *J. Less-Common Metals*, **20** (1970) 135.

in the presence of either plutonium monocarbide or carbon. Uranium sesquicarbide has a very narrow, if any, range of stoichiometry and no information is available on the variations of lattice parameter with composition for neptunium and americium sesquicarbides.

TABLE 3. LATTICE PARAMETERS OF ACTINIDE SESQUICARBIDES

Phases in equilibrium	Lattice parameter (Å)	Reference
Th_2C_3	8·5527 ± 0·0001	a
U_2C_3	8·0889 ± 0·0009	b
Np_2C_3	8·1036 ± 0·0005	c, d
$PuC+Pu_2C_3$	8·1210 ± 0·0001	e
$Pu_2C_3+PuC_2$	8·1317 ± 0·0003	f
Pu_2C_3+C	8·1330 ± 0·0010	g
Am_2C_3	8·2757	d

[a] M. C. Krupka, *J. Less-Common Metals*, **20** (1970) 135.

[b] W. G. Witteman and M. G. Bowman, see E. K. Storms, *Refractory Carbides*, p. 187.

[c] W. H. Zachariasen and H. A. Plettinger, USAEC Report ANL-4798 (1952) 38.

[d] A. W. Mitchell and D. J. Lam, *J. Nucl. Mat.* 36 (1970) 110.

[e] O. L. Kruger, *J. Nucl. Mat.* 7 (1962) 142.

[f] R. N. R. Mulford, F. H. Ellinger, G. S. Hendrix and E. D. Albrecht, *Plutonium*, p. 301, E. Grison, W. B. H. Lord, R. D. Fowler (Eds.), Cleaver-Hume Press, London (1961).

[g] T. D. Chikalla, USAEC Report HW-74024 (1962).

Dicarbides. The dicarbides occur in more than one crystal form. Thorium dicarbide possesses three different crystal forms, α-ThC_2 has monoclinic symmetry, β-ThC_2 is body-centred tetragonal, CaC_2 type structure, and γ-ThC_2 is cubic. The β- and γ-forms are only stable at high temperatures. The lattice parameters of the dicarbides are shown in Table 4. Only thorium and possibly neptunium possess a dicarbide with monoclinic symmetry. Uranium has two dicarbides, the tetragonal α-form and the high-temperature β-cubic form which is isomorphous with γ-ThC_2, and has a KCN structure with the C_2 groups either as free rotators or randomly oriented along the 111 plane. The C–C distance in α-UC_2 is equivalent to a double bond rather than a triple bond as found in CaC_2. α-UC_2 is not stable below *ca.* 1500°C, decomposing into U_2C_3 and C; PuC_2 exhibits similar behaviour and is not stable below *ca.* 1660°C decomposing to Pu_2C_3 and C, and unlike α-UC_2 cannot be easily "quenched in" by relatively rapid cooling after melting in an arc furnace, although lines of unknown phases are seen in the patterns of the X-ray powder photographs as well as some lines which have been attributed to α-PuC_2 which is isomorphous with α-UC_2. A high-temperature cubic form has also been identified[19].

[18] D. M. Chackraburtty and N. C. Jayadevan, *Acta Cryst.* **18** (1965) 811.

[19] E. A. Harper, H. J. Hedger and J. T. Dalton, *Nature*, **219** (1968) 151.

TABLE 4. LATTICE PARAMETERS OF THE ACTINIDE DICARBIDES

Compound	Symmetry	Lattice parameters (Å)	Reference
α-ThC_2	Monoclinic (space group $C2/C$)	$a = 6{\cdot}691$, $b = 4{\cdot}223$, $c = 6{\cdot}744$, $\beta = 103°12'$	a
β-ThC_2	Tetragonal (space group $I4/mmm$)	$a = 4{\cdot}235$, $c = 5{\cdot}408$ at 1460°C	b
γ-ThC_2	Fcc (space group $Fm3m$)	$a = 5{\cdot}808 \pm 0{\cdot}003$ at 1500°C $a = 5{\cdot}817 \pm 0{\cdot}002$ at 1755°C	b,c
PaC_2	Tetragonal	$a = 3{\cdot}61 \pm 0{\cdot}01$ $c = 6{\cdot}11 \pm 0{\cdot}01$	d
α-UC_2	Tetragonal $UC_{1{\cdot}89}$	$a = 3{\cdot}519 \pm 0{\cdot}001$ $c = 5{\cdot}979 \pm 0{\cdot}002$	e
	$UC_{1{\cdot}94}$	$a = 3{\cdot}5241 \pm 0{\cdot}0005$ $c = 5{\cdot}9962 \pm 0{\cdot}0008$	
β-UC_2	Fcc	$a = 5{\cdot}49$ at 1750°C	f
NpC_2	Monoclinic	$a = 3{\cdot}580 \pm 0{\cdot}005$* $c = 6{\cdot}030 \pm 0{\cdot}005$	g
α-PuC_2	Tetragonal	$a = 3{\cdot}65$ $c = 6{\cdot}094$	h
β-PuC_2	Fcc	$a = 5{\cdot}700 \pm 0{\cdot}002$ at 1700°C	

* Tetragonal pseudo cell.

[a] P. K. Gantzel and N. L. Baldwin, *Acta Cryst.* **17** (1964) 772.

[b] S. Langer, N. L. Baldwin, P. K. Gantzel, F. Kester and C. A. Hancock, *Int. Symposium on Compounds of Interest in Nuclear Reactor Technology*, p. 359, J. Weber, P. Chiotti, W. N. Miner (Eds.), Met. Soc. Am. Inst. Mining Met. Petrol Eng. (1964).

[c] N. A. Hill and O. B. Cavin, *J. Amer. Ceram. Soc.* **47** (1964) 360.

[d] R. Lorentz, H. L. Scherff and N. Toussaint, *J. Inorg. and Nuclear Chem.* **31** (1969) 2381.

[e] W. G. Witteman and M. G. Bowman, USAEC Report TID 7676 (1963); see also E. K. Storms, *Refractory Carbides*, p. 187.

[f] A. L. Bowman, G. P. Arnold, W. G. Witteman, T. C. Wallace and N. G. Nereson, *Acta Cryst.* **21** (1966) 670.

[g] W. H. Zachariasen and N. A. Plettinger, USAEC Report ANL-4798 (1952) 38.

[h] D. M. Chackraburtty and N. C. Jayadevan, *Acta Cryst.* **18** (1965) 811.

[i] E. A. Harper, H. J. Hedger and J. T. Dalton, *Nature*, **219** (1968) 151.

Heat Capacities

The review of thermodynamic data by Holley and Storms[20] considers data up to 1967, and there have not been a large number of studies since then. The uranium system is the only system for which there is an almost complete set of data.

The only measurements reported for thorium monocarbide are between 1·8 and 4·2K[21]; a low electronic specific heat was found and a Debye temperature of *ca.* 280K. There are measurements on thorium dicarbide in the temperature range 5–350K. There are no measurements on the carbides of protactinium and americium.

The several measurements of the low-temperature heat capacities of uranium monocarbide agree reasonably well. The Debye temperatures reported are 304 ± 8K[21] and

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[20] C. E. Holley Jr. and E. K. Storms, *Thermodynamics of Nuclear Materials*, p. 397, IAEA, Vienna (1968).

[21] A. de Cambarieu, P. Costa and J. C. Michel, *Compt. Rend.* **256** (1963) 5518.

$320 \pm 10K^{22}$, which compare with a value of $330K^{23}$ obtained from elastic constant measurements. Direct enthalpy increment measurements have also been made between 1273 and 2473K. For U_2C_3 the low-temperature heat capacities have been measured but there are no high-temperature data.

TABLE 5. HEAT CAPACITIES OF THE ACTINIDE CARBIDES
$C_p = a + bT + cT^2 + dT^{-2}$ (cal deg^{-1} mole^{-1})

Compound	C_p at 298K (cal deg^{-1} mole^{-1})	a	$b \times 10^3$	$c \times 10^7$	$d \times 10^{-5}$	Temperature (K)	Ref.
$ThC_{1\cdot93}$	13·55						a
		15·17	2·89		−2·21	298–1400	a
UC	12·11						b
		14·32	−3·03	10·51	−2·08	298–2823	c
U_2C_3	26·55						d
	25·66						e
α-UC_2	14·50–2						d,e
		23·40	−11·50	81·81	−5·49	298–2038	c
β-UC_2		29·44				2038–2800	f
$NpC_{0\cdot9}$	11·96						g
$PuC_{0\cdot9}$	12·03						
		13·08	1·14		−3·23	400–1300	i

[a] E. F. Westrum Jr., Y. Takahashi and N. D. Stout, *J. Phys. Chem.* 69 (1965) 1520.

[b] E. F. Westrum Jr., E. Siuts and H. K. Lonsdale, *Advances in Thermophysical Properties at Extreme Temperatures and Pressures*, p. 156, Amer. Soc. Mech. Engrs. (1965).

[c] E. K. Storms, IAEA Technical Panel on the Thermodynamics of Uranium and Plutonium Carbides, Vienna (1968).

[d] R. J. L. Andon, J. F. Counsell, J. F. Martin and H. J. Hedger, *Trans. Faraday Soc.* 60 (1964) 1030.

[e] J. D. Farr, W. G. Witteman, P. L. Stone and E. F. Westrum Jr., *Advances in Thermophysical Properties at Extreme Temperatures and Pressures*, p. 162, Amer. Soc. Mech. Engrs. (1965).

[f] C. E. Holley Jr. and E. K. Storms, *Thermodynamics of Nuclear Materials 1967*, p. 397, IAEA, Vienna (1968).

[g] T. A. Sandenaw, R. B. Gibney and C. E. Holley Jr., Private communication.

[h] J. A. Lee and P. W. Sutcliffe, Private communication.

[i] O. L. Kruger and H. Savage, *J. Chem. Phys.* **40** (1964) 3324.

Low-temperature specific heat measurements[24] (17–361K) indicated that $NpC_{0\cdot9}$ is ferromagnetic below 228K, confirming neutron diffraction measurements[25].

For the plutonium carbides, only measurements on the monocarbide have been made; the low-temperature heat capacity was found to be a smooth function from 12·5K to room temperature[26], but there is evidence from electrical resistivity and magnetic measurements[27], and from neutron diffraction[28], that plutonium monocarbide undergoes a magnetic transition at *ca.* 100K.

The heat capacity data are summarized in Table 5.

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[22] E. F. Westrum Jr., E. Suits and H. K. Lonsdale. See ref. 20.

[23] L. J. Graham and R. Chang, *Compounds of Interest in Nuclear Reactor Technology*, p. 359, J. Weber, P. Chiotti, W. N. Miner (Eds.), Met. Soc. Am. Inst. Min. Met. Pet. Engrs., New York (1964).

[24] T. A. Sandenaw, R. B. Gibney and C. E. Holley Jr. See ref. 31.

[25] S. H. Lander, L. Heaton, M. H. Mueller and K. D. Anderson, *J. Phys. Chem. Solids*, **30** (1969) 733.

[26] J. A. Lee and P. W. Sutcliffe. Private communication, AERE, Harwell.

[27] R. Costa and R. Lallement, *J. Phys. Chem. Solids*, **25** (1964) 559.

[28] J. L. Green, G. P. Arnold, J. A. Leary and N. G. Nereson, *J. Nucl. Mat.* **23** (1967) 231.

For UC_2 there is very good agreement for the low-temperature heat capacity measurements, and high-temperature enthalpy increment measurements have been made on $UC_{1.93}$ between 1484–2581K.

TABLE 6. THE HEATS OF FORMATION (ΔH°_{f298}) AND ENTROPIES (S°_{298}) OF THE ACTINIDE CARBIDES

Compound	S°_{298} (cal deg^{-1} mole^{-1})	Reference	$\Delta H_f^\circ{}_{,298}$ (kcal mole^{-1})	Reference
$ThC_{0.75}$			−16·6 ± 1·6	a
$ThC_{0.81}$			−23·5 ± 0·9	a
$ThC_{0.91}$			−28·4 ± 1·9	a
$ThC_{1.00}$			−29·6 ± 1·1	a
$ThC_{1.91}$			−29·7 ± 1·8	a
$ThC_{1.93}$	16·37	b		
$ThC_{1.97}$	16·42	c		
UC	14·15	d	−23·2 ± 0·7	d
$UC_{1.5}$	16·47	d	−21·8 ± 2·0	d
$UC_{1.94}$	16·33	d	−21·7 ± 1·3	d
$NpC_{0.91}$	16·65	e	−17·0 ± 1·4	f
$PuC_{0.87}$	17·3	g	−11·41 ± 0·7	h
$PuC_{1.5}$			−24·40	i

[a] E. J. Huber Jr., C. E. Holley Jr. and N. H. Krikorian, *J. Chem. Eng. Data*, **13** (1968) 253.

[b] E. F. Westrum Jr., Y. Takahashi and N. D. Stout, *J. Phys. Chem.* **69** (1965) 1520.

[c] Y. Takahashi and E. F. Westrum Jr., *J. Chem. Eng. Data*, **10** (1964) 128.

[d] C. E. Holley Jr. and E. K. Storms, *Thermodynamics of Nuclear Materials 1967*, p. 397, IAEA, Vienna (1968).

[e] T. A. Sandenaw, R. B. Gibney and C. E. Holley Jr., see ref. f.

[f] E. J. Huber Jr. and C. E. Holley Jr., *Proc. Int. Symposium of Thermochemistry*, Marseille (1971).

[g] J. A. Lee and P. W. Sutcliffe, Private communication.

[h] G. K. Johnson, E. H. van Devinter, O. L. Kruger and W. N. Hubbard, *J. Chem. Thermodynamics*, **2** (1970) 617.

[i] J. P. Marcon, J. Poitreau and G. Roullet, *Plutonium 1970 and Other Actinides*, W. N. Miner (Ed.), p. 799, Met. Soc. Am. Inst. Min. Met. Pet. Engrs., New York (1970).

Heats of Formation and the Entropies

The enthalpies of formation of thorium, uranium, neptunium and plutonium carbides have been measured directly in an oxygen bomb calorimeter[29–33]. The values are given in Table 6. The entropies are also included in Table 6.

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[29] E. J. Huber Jr. Reported by C. E. Holley Jr. and E. K. Storms, *Thermodynamics of Nuclear Materials 1967*, p. 397, IAEA, Vienna (1968).

[30] E. K. Storms and E. J. Huber Jr., *J. Nucl. Mat.* **23** (1967) 19.

[31] E. J. Huber Jr. and C. E. Holley Jr., *Thermochimie*, Col. Int. du C.R.N.S. No. 201, Editions du C.N.R.S., Paris (1972) p. 399.

[32] G. K. Johnson, E. H. van Devinter, O. L. Kruger and W. N. Hubberd, *J. Chem. Thermodynamics*, **2** (1970) 617.

[33] J. P. Marcon, J. Poitreau and G. Roullet, *Plutonium 1970 and Other Actinides*, p. 799, W. N. Miner (Ed.), Met. Soc. Am. Inst. Min. Met. Pet. Engrs., New York (1970).

Free Energies of Formation

Various high-temperature methods have been employed to obtain free energy data on the actinide carbides. Measurements using e.m.f. cells and vaporization methods have been reported. Some attempts have also been made to measure the free energies by measuring CO pressures over mixtures of oxides and carbides, but usually there is some difficulty in interpretation due to an unknown solubility of oxygen in the carbides. The high-temperature free energy of formation data should always be checked for consistency with the measured room temperature, heat of formation and entropy data using the high-temperature specific heat equation.

Some typical experimental techniques for the determination of the free energies of formation of the carbides will be briefly described. For the determination of the free energies of formation of thorium dicarbide[34–36] an e.m.f. cell with a fluorite electrolyte was employed, with the arrangement

$$\mathrm{Th,\ ThF_4(solid)/CaF_2(solid)/ThF_4,\ ThC_2,\ C}$$

to give information about the reaction

$$\mathrm{Th + 2C \leftrightharpoons ThC_2}$$

The other regions of the Th–C system in the two-phase region $ThC + ThC_2$ and in the single phase ThC_{1-x} were examined[37,38] with the two cells

$$\mathrm{Th,\ ThF_4(solid)/CaF_2(solid)/ThF_4,\ ThC_2,\ ThC}$$

and

$$\mathrm{Th,\ ThF_4(solid)/CaF_2(solid)/ThF_4,\ ThC_{1-x}}$$

The above cells were used in the temperature range 1000–1200K.

Measurements have also been made in cells using a LiCl–KCl eutectic liquid electrolyte[39]; a Pu–Ru alloy provided a reference electrode which was reversible to plutonium ions. To obtain data in the temperature range 950–1100K on plutonium monocarbide and plutonium sesquicarbide the following cells were employed:

$$\mathrm{Pu_2C_3 + C(solid)/Pu^{3+},\ LiCl\text{–}KCl/PuRu_2 + Ru(solid)}$$

and

$$\mathrm{PuC_{1-x} + Pu_2C_3(solid)/Pu^{3+},\ LiCl\text{–}KCl/PuRu_2 + Ru(solid)}$$

Mass spectrometric methods have been widely employed to determine the activities of the components in the actinide carbide systems. A comprehensive example of such a study is that of Storms[40], who measured the pressures of U(g) and UC_2(g); the resulting partial heats of vaporization of U(g) and UC_2(g) were measured as a function of composition from UC + U (liquid) to UC_2 + C in the temperature range 1400–2400°C. The data were used to delineate regions of the phase diagrams in the regions of uncertainty of the diagram, but

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[34] T. Satow, *J. Nucl. Mat.* **21** (1967) 249.

[35] J. J. Egan, *J. Phys. Chem.* **68** (1964) 978.

[36] S. Aronson. See ref. 23.

[37] T. Satow, *J. Nucl. Mat.* **21** (1967) 255.

[38] S. Aronson and J. Sadofsky, *J. Inorg. and Nucl. Chem.* **27** (1965) 1969.

[39] G. M. Campbell, L. J. Mullins and J. A. Leary, *Thermodynamics of Nuclear Materials 1967*, p. 75, IAEA, Vienna (1968).

[40] E. K. Storms, *Thermodynamics*, Vol. I, p. 309, IAEA, Vienna (1966).

were also consistent with the known features of the phase diagram. Some of these results for the pressures of U(g) as a function of temperature and carbon concentration are shown in Fig. 3.

Some examples of the use of indirect gas pressure measurements for the determination of the free energy of formation of carbides can be found in the literature. One of the earliest determinations[41] was a measurement of the CO pressures for the reaction

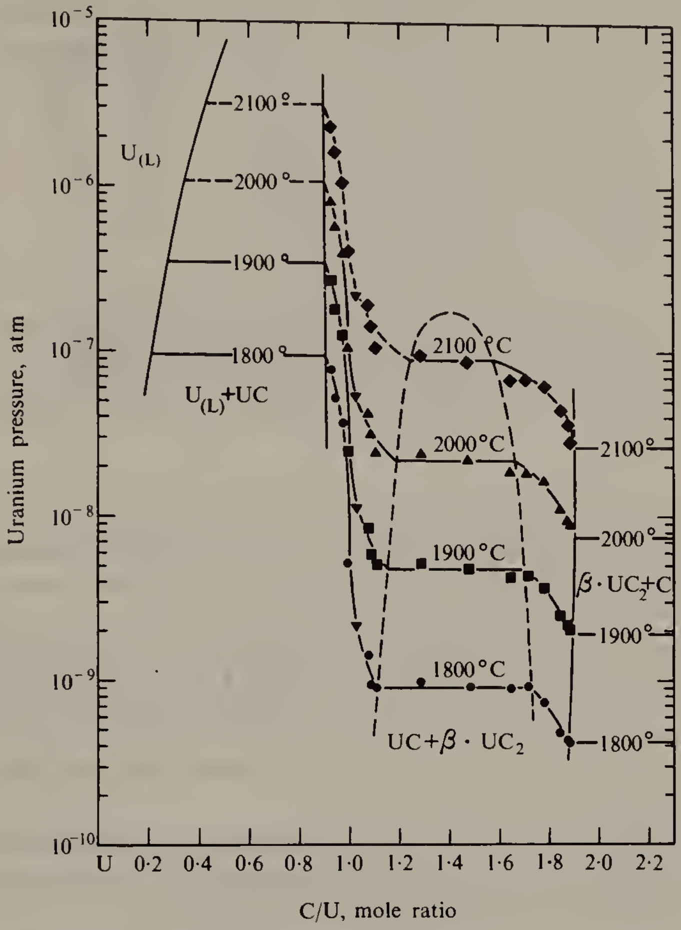

FIG. 3. Uranium gas pressures over the U–C system (after Storms[40]).

$$ThO_2(\text{solid}) + 4C(\text{solid}) \leftrightharpoons ThC_2(\text{solid}) + 2CO(\text{gas})$$

from which the value of $\Delta G^\circ_{f\langle ThC_2\rangle}$ was calculated. Other examples can be cited. For example, the attempted determination of free energies of formation of the uranium carbides by the determination of CO pressures in the univariant phase fields of the ternary U–C–O system[42].

A series of two-term equations for the free energy of formation (ΔG°_f) for the compounds as a function of temperature are given in Table 7.

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[41] C. H. Prescott Jr. and W. B. Hincke, *J. Amer. Ceram. Soc.* **49** (1927) 2744.
[42] P. E. Potter, *J. Nucl. Mat.* **42** (1972) I.

TABLE 7. STANDARD FREE ENERGIES OF FORMATION OF THE ACTINIDE CARBIDES

$\Delta G^{\circ}_{f} = A + B \times T$ (cal mole^{-1})

Material	A	B	Temperature range (K)
ThC_2[a]	−27,200	−3·67	298–2500
UC[a]	−24,260	−1·12	~800–~1200
	−25,500		~1000–~2200
$UC_{1.5}$[a]	−22,240	−1·96	~1100–~1400
	−24,250	−1·20	~1400–~2000
UC_2[a]	−21,300	−3·00	298–2200
$PuC_{0.87}$[b]	−9749	−1·49	913–1900
$PuC_{1.5}$[b]	−13,310	−2·39	1541–1987
PuC_2[b]	−4380	−6·77	2017–2472

[a] C. E. Holley Jr. and E. K. Storms, *Thermodynamics of Nuclear Materials 1967*, p. 397, I.A.E.A., Vienna (1968).

[b] M. H. Rand, IAEA Technical Panel on the Thermodynamics of Uranium and Plutonium Carbides, Vienna (1968).

Bonding

The lattice parameters give some indication of the bonding character in these compounds[43]. For example, for uranium and plutonium carbides the carbon atomic volume is larger than that in diamond and consequently a transfer of electrons from the metal to the carbon atoms is indicated. The monocarbide is, however, an exception to the above behaviour. If the removal of carbon atoms involved no other process but the removal of volume from the lattice, a Vegard's law relationship would exist between the lattice volume and the carbon sites. Uranium monocarbide deviates in a positive way, indicating a repulsive force between the carbon atoms.

The hydrolysis behaviour of the carbides described in section 2.5 also gives some indications as to the nature of the bonding of the carbon atoms; C=C bonds are present as well as strong M–C bonds in many of these compounds.

Electrical Resistivity

The data on the electrical resistivity of the actinide carbides have been collected recently by Storms[44]. The electrical resistivity of thorium monocarbide[45–48] goes through a maximum as carbon atoms are removed, when the C:Th ratio is 0·9; the resistance at this concentration is *ca.* 200 μohm-cm. Uranium monocarbide (with C:U of 1·0) has a low resistivity and when carbon is replaced by oxygen the resistivity increases[49]. The resistivity of uranium monocarbide is 30–80 μohm-cm, whilst that of U_2C_3 is *ca.* 200 μohm-cm; the latter is a much poorer conductor than UC or UC_2. A resistivity for UC of *ca.* 30 μohm-cm

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[43] E. K. Storms, *The Refractory Carbides*, p. 232.

[44] E. K. Storms, USAEC Report LA-DC-12506 (1971).

[45] A. B. Auskern and S. Aronson, *J. Appl. Phys.* **38** (1967) 3508.

[46] P. Chiotti, F. W. Korbetz and G. J. Dooley, *J. Nucl. Mat.* **23** (1967).

[47] A. B. Auskem, S. Aronson, J. Sadofsky and F. J. Salzano, *J. Phys. Chem. Solids*, **27** (1965) 613.

[48] C. P. Kempter and N. H. Krikorian, *J. Less-Common Metals*, **27** (1965) 613.

[49] J. L. Henry, R. Blickensderfer and D. Paulson, *J. Amer. Ceram. Soc.* **53** (1970) 335.

is only slightly greater than that of the metal, and the removal of carbon atoms causes the resistivity to fall. The resistivity of $PuC_{0\cdot9}$ is 250 μohm-cm[50].

Hardness

The introduction of carbon vacancies produces a marked reduction in the microhardness of the carbides, particularly for the two monocarbides of thorium and plutonium which can exist over a large stoichiometry range.

The microhardness data are shown in Table 8.

TABLE 8. MICROHARDNESS OF THE CARBIDES[a]

	Microhardness (kg mm^{-2} for a 50–100 g load)		
Compound	Th	U	Pu
MC	Max. 850	900	600–1000
M_2C_3	—	1100	1200
MC_2	600	500	—
		Pu_3C_2	70–90

[a] E. K. Storms, *The Refractory Carbides*, p. 234.

Superconductivity

Superconductivity has only been found for thorium monocarbide at 9K[51] and in thorium sesquicarbide at 4·1K[52]. Later attempts by Giorgi[53] to verify the transition in ThC have been unsuccessful above 4K.

Diffusion in Actinide Carbides

Important parameters in determining the rate of attainment of equilibrium of the actinide–carbon alloys are the diffusion coefficients of the components.

Nearly all the studies of diffusion have been confined to carbon and uranium diffusion in the U–C system; there have also been some studies on the diffusion of protactinium, plutonium and americium in U–C alloys.

Some of the recent data for uranium diffusion in U–C alloys are shown in Table 9. The diffusion coefficient (D), the entropy factor (D_0), and the activation energy (Q) are related by the equation

$$D = D_0 e^{-Q/RT}$$

The high activation energy of 174 kcal mole^{-1} for uranium diffusion is explained as being due to the strengthening of the U–U bonds in uranium carbide of the given composition ($UC_{1\cdot07}$). The change of activation energy from 174 to 106 kcal mole^{-1} at temperatures

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[50] R. Lallement, P. Costa and R. Pascard, *J. Phys. Chem. Solids*, **26** (1965) 1255.

[51] P. Costa and R. Lallement, *Carbides in Nuclear Energy*, p. 445, L. E. Russell *et al.* (Eds.), London, Macmillan (1964) and *J. Phys. Chem. Solids*, **25** (1964) 559.

[52] A. L. Giorgi, E. G. Szklarz, N. H. Krikorian and M. C. Krupka, *J. Less-Common Metals*, **22** (1970) 131.

[53] A. L. Giorgi. Private communication to E. K. Storms, USAEC Report LA-DC-12506 (1971).

TABLE 9. DIFFUSION OF URANIUM IN U–C ALLOYS

Alloy composition	Temperature (°C)	D_0 (cm² sec⁻¹)	Q (kcal mole⁻¹)	Ref.
$UC_{0\cdot975}$	800–1600	$6\cdot3\times10^{-11}$	33 ± 2	a
$UC_{0\cdot975}$	1600–2100	$6\cdot5\times10^{-6}$	70 ± 5	a
$UC_{1\cdot006}$	1000–1400	$1\cdot2\times10^{-12}$	28 ± 4	a
	1400–2000	$1\cdot9\times10^{-4}$	90 ± 6	a
$UC_{1\cdot000}$	1450–2000	7×10^{-5}	80 ± 10	b
$UC_{0\cdot96}$	1700–2300	$3\cdot6\times10^{-2}$	107 ± 3	c
$UC_{1\cdot07}$	1700–2050	4×10^{-4}	$106\pm1\cdot4$	c
$UC_{1\cdot07}$	2050–2300	9×10^{-2}	$174\pm6\cdot4$	c

Q, activation energy; D_0, entropy factor.

[a] R. Lindner, G. Riemer and H. L. Scherff, *J. Nucl. Mat.* **23** (1967) 222.

[b] P. Villaine and J. F. Marin, *C.R. Acad. Sci., Paris*, Series C, **264** (1967) 2015.

[c] H. J. Hirsch, Dr.rer.nat. thesis, University of Brunswick, Germany (1970).

below 2050°C is associated with the phase transition

$$UC_{1+x}\rightarrow UC+\beta\text{-}UC_2 \quad \text{(see section 2.4, p. 373)}$$

The diffusion data for protactinium, plutonium and americium in a U–C alloy of composition $UC_{1\cdot07}$ are very similar to those for uranium and are given in Table 10.

TABLE 10. THE DIFFUSION OF THE ACTINIDE ELEMENTS IN A U–C ALLOY OF OVERALL COMPOSITION $UC_{1\cdot07}$[a]

Temperature (IC)	Diffusion parameters	Actinide			
		Pa	U	Pu	Am
1700–2050	D_0(10⁴ cm² sec⁻¹)		$2\cdot8<3\cdot9<5\cdot4$	$1\cdot8<4\cdot8<13$	$2\cdot1<5\cdot2<13$
	Q(kcal mole⁻¹)		$105\cdot8\pm1\cdot4$	$100\cdot9\pm4\cdot3$	$105\cdot3\pm4\cdot0$
2050–2300	D_0(10⁴ cm² sec⁻¹)	$0\cdot02<0\cdot29<3\cdot4$	$0\cdot2<0\cdot9<3\cdot2$	$0\cdot7<2\cdot9<12$	$0\cdot8<2\cdot4<7\cdot4$
	Q(kcal mole⁻¹)	$176\cdot5\pm12$	$173\cdot6\pm6\cdot4$	$173\cdot1\pm6\cdot9$	$175\cdot8\pm5\cdot5$

[a] H. J. Hirsch, Dr.rer.nat. thesis, University of Brunswick, Germany (1970).

TABLE 11. CARBON DIFFUSION IN U–C ALLOYS

Composition	Temperature (°C)	D_0 (cm² sec⁻¹)	Q (kcal mole⁻¹)	Reference
$UC_{1\cdot0}$	1165–1500	$0\cdot1$	$-62\cdot5$	a
$UC_{1\cdot0}$	1185–2347	$0\cdot3$	$-63\cdot5$	b
U_2C_3	1185–1780	228	$-98\cdot3$	b
α-UC_2	1525–1780	156	$-90\cdot2$	b
β-UC_2	1830–2347	$9\cdot5$	$-77\cdot2$	b

[a] R. A. Krakowski, *J. Nucl. Mat.* **32** (1969) 120.

[b] T. C. Wallace, W. G. Witteman, C. L. Radosevich and M. G. Bowman, *High Temp. Materials*, 6th Plansee Seminar, F. Benesovsky (Ed.), p. 676, Metallwerk Plansee AG Reutre (1969).

There are also data for carbon self-diffusion in uranium monocarbide and the diffusion rates are considerably higher than those for uranium; these data are given in Table 11, together with data for the other uranium carbide phases.

Irradiation Damage

The lattice parameters of plutonium monocarbide and sesquicarbide which have been stored at ambient temperatures increase with time[54], probably owing to the formation of Frenkel defects as a result of the α-decay of the plutonium. Examination of three specimens of compositions $PuC_{0\cdot6}$, $Pu_2C_3(+PuC)$, and $Pu_2C_3(+C)$ has been reported. The increase in lattice parameter can be represented by an equation of the form

$$\frac{\Delta a}{a} = A[1 - \exp(-\beta f)]$$

where A and β are constants, and $f = \lambda t$ is the proportion of original atoms which have disintegrated. λ is the disintegration constant and t is the time since preparation of the sample. The values of A and β for the three materials are given in Table 12.

TABLE 12. THE IRRADIATION DAMAGE OF PLUTONIUM CARBIDES[a]

Material	$A \times 10^3$	$\beta \times 10^4$
'PuC'	3·59	2·70
$Pu_2C_3(+PuC)$	1·42	3·12
$Pu_2C_3(+C)$	0·86	2·11

[a] K. Mendelssohn, E. King, J. A. Lee, M. H. Rand, C. S. Griffin and R. S. Street, *Plutonium* 1965, p. 187.

The constant A, the saturation value for $\Delta a/a$, is roughly the same for the monocarbide (with the fcc NaCl structure) as for PuO_2 and AmO_2 (with the fcc CaF_2 structure), but it is much smaller for both of the two sets of results for Pu_2C_3 (body-centred cubic structure). The constant β indicates the rate at which self-damage accumulates, and it may be shown that β is in fact the number of plutonium atoms in the volume of material which is saturated with defects as a result of one α-disintegration; it has been estimated that about 1500 Frenkel defects are produced per α-disintegration, so that the saturation concentration of these defects is between one half and one defect pair per unit cell. The radiation damage can be annealed out at temperatures of *ca.* 1000°C. As self-irradiation proceeds there is no perceptible increase in the line width of the X-ray powder photographs indicating that no inhomogeneous strain is introduced by the self-damage.

2.4. Chemical properties

Thermal Stability

The mode of vaporization and the melting behaviour are important parameters in determining composition changes during the preparation by the arc-melting of the elements

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[54] K. Mendelssohn, E. King, J. A. Lee, M. H. Rand, C. S. Griffin and R. S. Street, *Plutonium* 1965, p. 187, A. E. Kay and M. B. Waldron (Eds.), London, Chapman & Hall, The Institute of Metals (1967).

and during annealing to attain equilibrium compositions at a given temperature. In order to understand the vaporization behaviour, in addition to a knowledge of the gas phase species, a knowledge of the phase relationships at a given temperature in the solid state is required. Phase diagrams have been published for the three systems Th–C, U–C, and Pu–C. The dependence of the variation of the gas phase pressures above a system with the composition of the solid can, of course, be used to determine the form of the phase diagram.

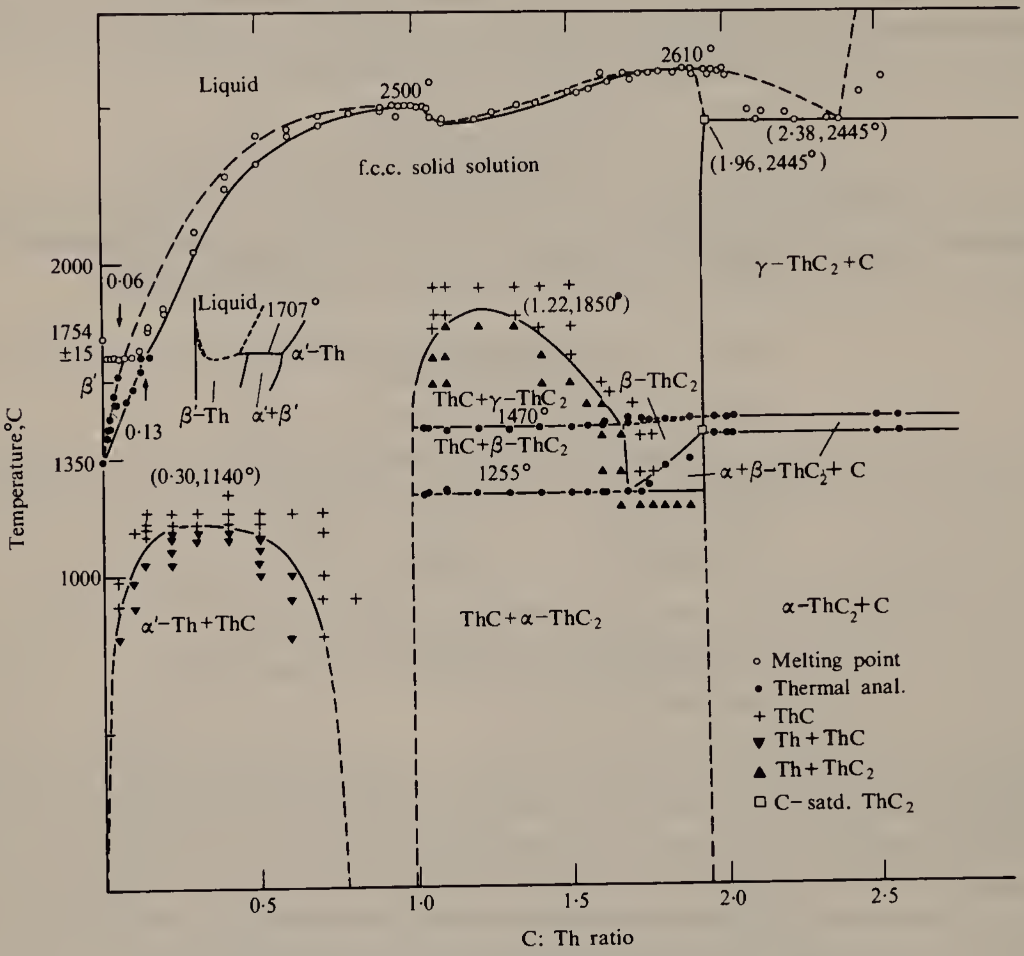

FIG. 4. The thorium-carbon phase diagram (after Benz and Stone[55]).

The Th–C phase diagram[55] is shown in Fig. 4. There is a continuous single-phase cubic region extending from pure thorium to ThC_2. The transition temperatures of the dicarbides depend on the stoichiometry of the dicarbides. There is a eutectic between carbon and γ-ThC_2 with a melting temperature of 2450 ± 25°C. The vaporization behaviour of the system has not been extensively examined, and studies have been confined to the carbon + thorium dicarbide region[56]. The thorium gas pressure over this region between 2000° and 2422°C is somewhat less than that of ThC_2, which, of course, results in a preferential evaporation of carbon from this region. Some typical pressures for thorium and ThC_2 gases

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[55] R. Benz and P. L. Stone, *High Temp. Sci.* 1 (1969) 114.
[56] E. K. Storms, *The Refractory Carbides*, p. 169.

are given by[57]

$$\mathrm{ThC_2(gas)},\ \log p(\mathrm{atm}) = -\,39{,}364\,(\pm 163)/T + 7{\cdot}20\,(\pm 0{\cdot}65)$$

$$\mathrm{Th(gas)},\ \log p(\mathrm{atm}) = -\,36{,}025\,(\pm 144)/T + 5{\cdot}74\,(\pm 0{\cdot}57)$$

although there is some evidence that they may be about one-half of an order of magnitude too low.

The phase diagram of the U–C system has been studied more than that of any other system, and has been reviewed in detail[58]. The phase diagram[59] is shown in Fig. 5. As in the Th–C system there is an extensive region of single-phase cubic solid solution between uranium monocarbide and the cubic dicarbide. The uranium dicarbide phase has a C:U ratio of less than 2·0, and the temperature of the α → β transition depends on the stoichiometry of the phase. Recent data have indicated that uranium monocarbide is the only thermodynamically stable compound. Decomposition of U_2C_3 into uranium monocarbide and carbon at *ca.* 800°C can be inferred from the recently assessed thermodynamic data[58], but this has not been observed experimentally. α-UC_2 decomposes into U_2C_3 + C at 1515°C, and the consequence of the slow decomposition rate of α-UC_2 is that it is frequently observed in alloys which have been annealed at temperatures lower than *ca.* 1500°C[60].

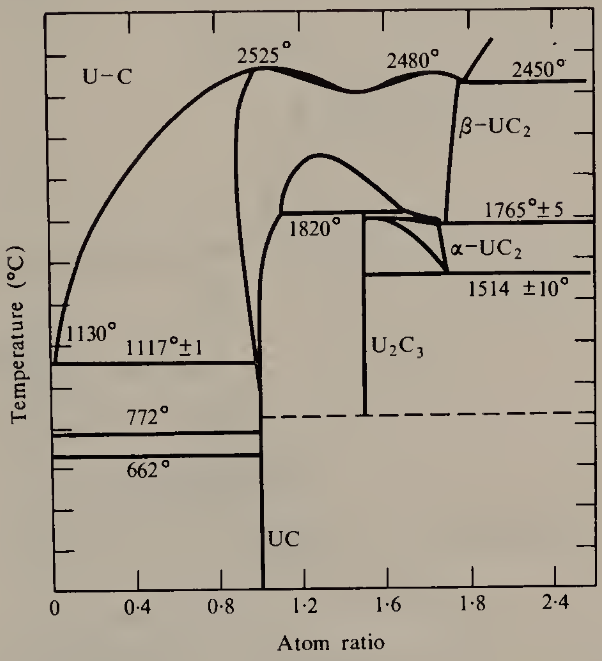

FIG. 5. The uranium–carbon phase diagram (after Benz, Hoffman and Rupert[59]).

Uranium monocarbide can possess carbon vacancies at high temperatures, and at sufficiently high temperatures it is also miscible with the UC_2 phase; C_2 groups substitute

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[57] D. D. Jackson, G. W. Barton Jr., O. H. Krikorian and R. S. Newbury, *Thermodynamics of Nuclear Materials*, p. 529, IAEA, Vienna (1962).

[58] E. K. Storms, *The Refractory Carbides*, p. 171, and paper to the IAEA Technical Panel on the Uranium and Plutonium Carbide Systems, IAEA, Vienna (1968).

[59] R. Benz, C. G. Hoffman and G. M. Rupert, *High Temp. Sci.* 1 (1969) 342.

[60] J. Laugier and P. L. Blum, *J. Nucl. Mat.* 39 (1971) 245.

for the single carbon atoms. Below the critical temperature of 2050°C at a composition with the C:U ratio *ca.* 1·3 decomposition occurs into UC (C:U ratio > 1) and β-UC_2 (C:U < 2). Neutron diffraction[61] studies have showed that on further cooling the C_2 groups in the high carbon structure assume directional ordering and a conversion to a tetragonal structure. Dissolved oxygen or nitrogen can affect the temperature of these transitions, for example both oxygen and nitrogen can dissolve in the lattice of α-UC_2 and stabilize this phase with respect to $U_2C_3 + C$. These aspects will be discussed in the sections on the U–C–O and U–C–N ternary systems.

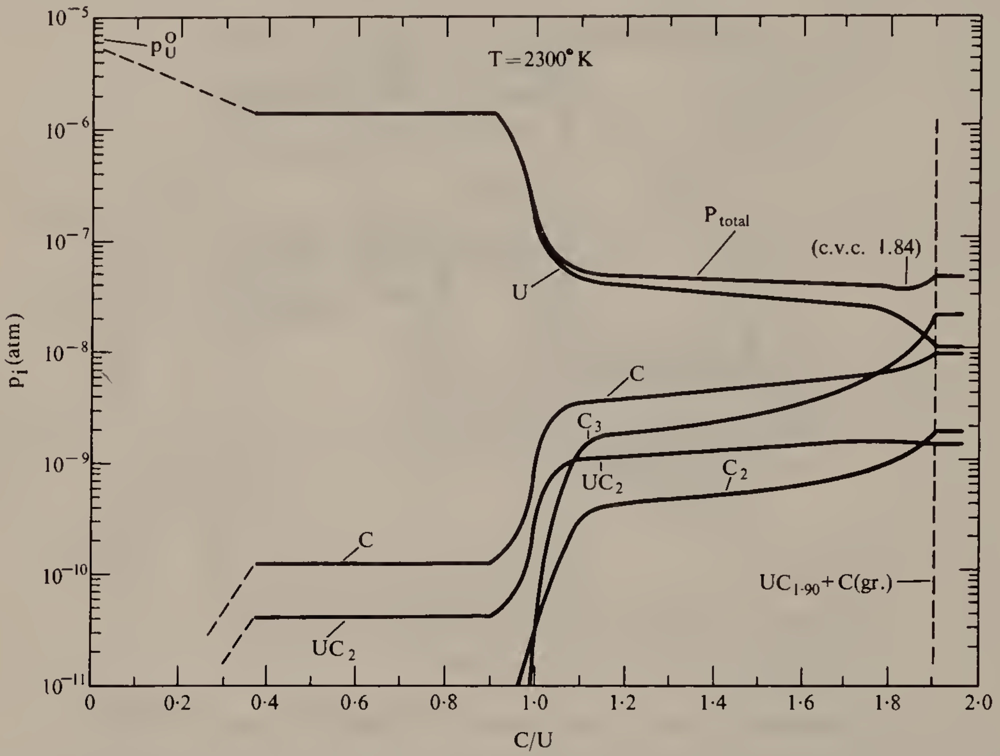

FIG. 6. Partial pressures of vapour species above the uranium–carbon system at 2300K showing the congruently vaporizing composition (after Storms[58]).

The vaporization of the system has been studied and reviewed by Storms[58]. The gas phase species above the system are U, UC_2, C, C_2 and C_3. The UC_2 gas molecule becomes important when the C:U ratio in the solid phase is greater than 1:1. A composition close to $UC_{1{\cdot}1}$ is the congruently vaporizing composition above *ca.* 2300K; this has been demonstrated experimentally and is consistent with the measured vapour pressures. Figure 6 shows an isothermal representation at 2300K of the compositional dependence of the partial pressures of various vapour species in the uranium–carbon system. This representation corresponds to a thermodynamically closed system, that is one in which no net transport of material to the surroundings occurs. The congruently vaporizing composition (cvc) corresponding to a minimum in the total pressure curve is indicated on the diagram.

The plutonium–carbon phase diagram[62] is illustrated in Fig. 7 which shows that the

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[61] A. L. Bowman, G. P. Arnold, W. G. Wittemann, T. C. Wallace and W. G. Neveson, *Acta Cryst.* **21** (1966) 670.

[62] M. H. Rand, paper presented to the IAEA Technical Panel on the Uranium and Plutonium Carbide Systems, IAEA, Vienna (1968).

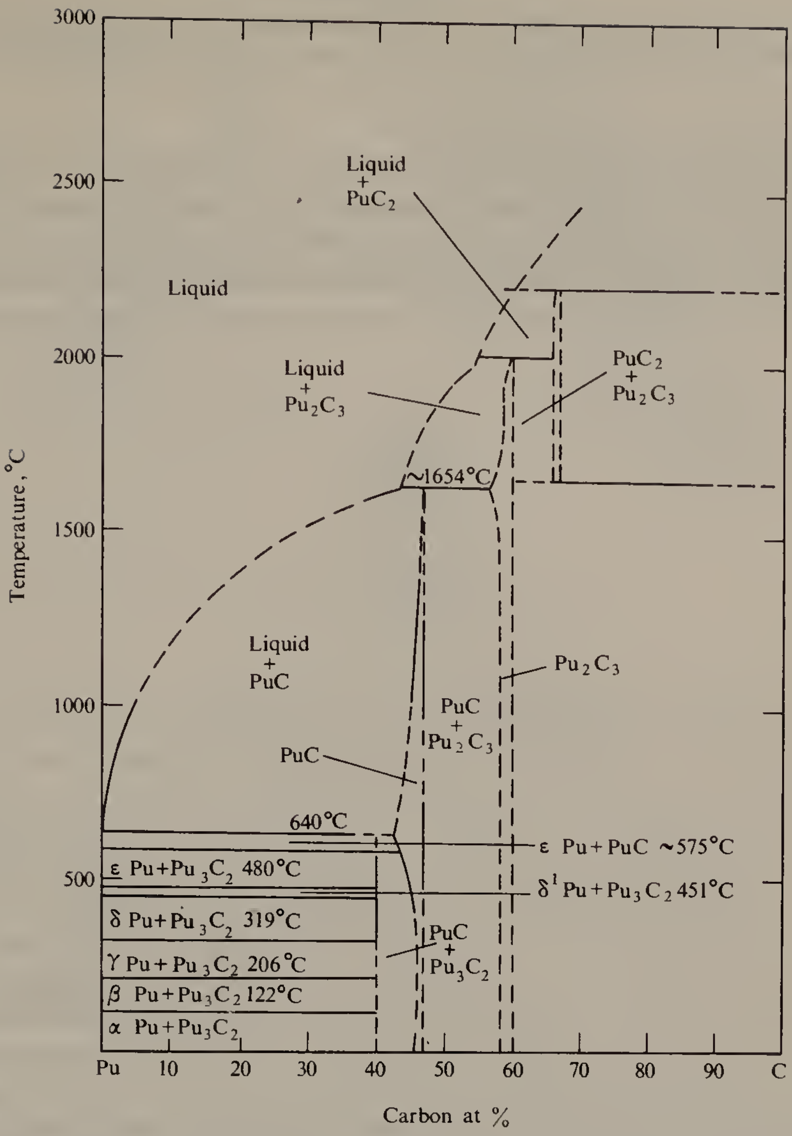

FIG. 7. The proposed plutonium–carbon phase diagram (after Rand[62]).

main features of the diagram are very different from those of the thorium and uranium systems. None of the compounds melt congruently; they all decompose. Pu_3C_2 decomposes by a peritectoid reaction

$$(1-x)\mathrm{Pu_3C_2} \rightleftharpoons (1-3x)\mathrm{Pu} + 2\mathrm{PuC}_{1-x} \text{ (at 575°C)}$$

and the other three compounds decompose by peritectic reactions

$$\mathrm{PuC_{0\cdot 87}} \rightleftharpoons \text{liquid} + \mathrm{PuC_{1\cdot 5}} \quad \text{(at 1654°C)}$$

$$\mathrm{PuC_{1\cdot 5}} \rightleftharpoons \text{liquid} + \mathrm{PuC_2} \quad \text{(at } ca. \text{ 2050°C)}$$

$$\mathrm{PuC_2} \rightleftharpoons \text{liquid} + \mathrm{C} \quad \text{(at } ca. \text{ 2300°C)}$$

Studies of the vaporization behaviour have provided most of the quantitative thermodynamic data which are available for these compounds. The gas phase species above the system is plutonium gas and at the temperatures of existence of the plutonium carbides the contribution of a gas phase species PuC_2 in the high carbon region is negligible. There are no data concerning the vaporization of the Pa–C and Np–C systems.

The Uranium–Plutonium–Carbon System

As discussed earlier, the solid solution of uranium–plutonium monocarbide is a possible fuel for a fast breeder nuclear reactor. Because of its greater theoretical density (13·6 g cm^{-3}) than the density of uranium–plutonium dioxide solid solution (11·0 g cm^{-3}) the increase in fissile atom density together with the higher thermal conductivity make it attractive as a possible high-performance fuel. The plutonium concentrations which are appropriate for a nuclear fuel are 15–30 mole % plutonium monocarbide. Because of this technological significance, the ternary system has received much attention. The phase equilibria and other thermodynamic data up to 1968 have been reviewed[63].

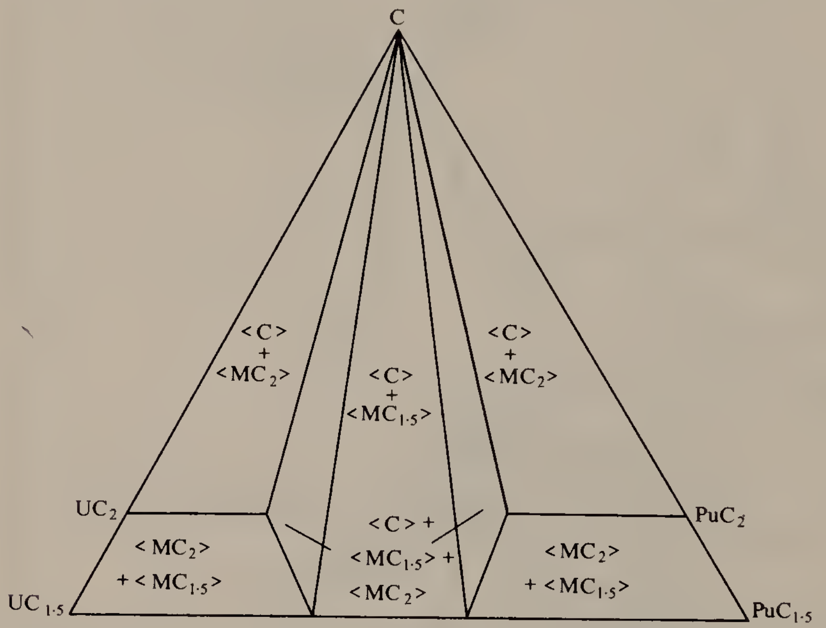

FIG. 8. The form of a section of the U–Pu–C system with > 60 at. % carbon (after Potter[63]).

Uranium and plutonium monocarbides form a complete range of solid solutions. On the U–Pu alloy rich side of the monocarbide section the (UPu) monocarbide is stoichiometric from 0 to 70 mole % PuC, at which point with increase in plutonium concentration there is an increasing carbon vacancy concentration. The measurements of the variation of lattice parameter with composition are sometimes difficult to interpret due to the presence of a second phase which, whether it be metal or sesquicarbide, will contain a higher concentration of plutonium than uranium[64].

The sesquicarbides of uranium and plutonium also form a complete range of solid solution although there may be slight negative deviations from Vegard's law. For the dicarbides, the solid solutions like the binary compounds exist in two crystal forms. Although

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[63] P. E. Potter, UKAEA Report AERE-R5922 (1968) and paper presented to the IAEA Technical Panel on the Uranium and Plutonium Carbide Systems, IAEA, Vienna (1968).

[64] P. G. Mardon and P. E. Potter, *Plutonium 1970 and Other Actinides*, W. N. Miner (Ed.), Met. Soc. Am. Inst. Min. Met. Pet. Engrs., New York (1970).

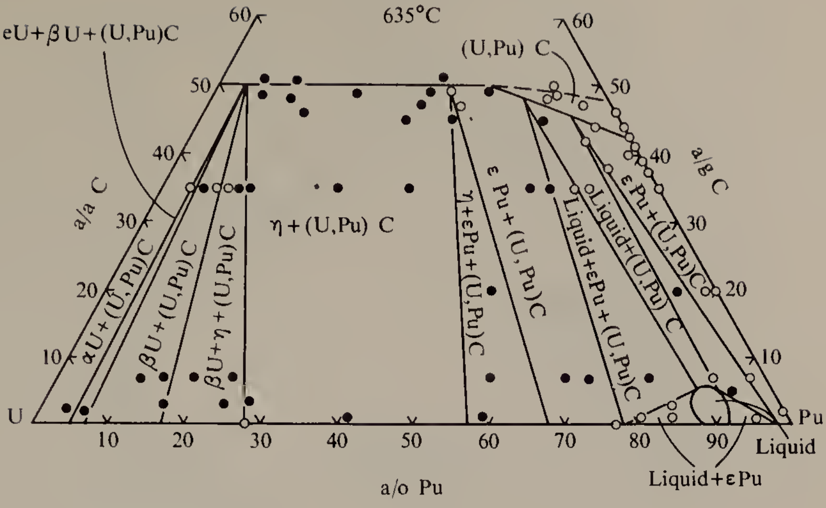

FIG. 9. An isothermal section at 635°C for the U–Pu–C system with <50 at.% carbon (after Rosen[69]).

there is some doubt as to whether a body-centred tetragonal plutonium dicarbide can be quenched on cooling arc melted alloys, the solid solutions with the body-centred tetragonal structure with a concentration from pure UC_2 to over 90 mole % PuC_2 retain the body-centred tetragonal structure in arc-melted alloys cooled to room temperature; this is a metastable phase except at low plutonium concentrations (<10 mole % PuC_2). The high-temperature cubic dicarbide phases may not be completely miscible[65]. An isothermal section for the U–Pu–C system is shown in Fig. 8 for carbon concentrations greater than 60 at %. The complex phase relationships in the region for carbon concentrations less than 50 at. % are shown in Fig. 9[13].

The thermal stability of the ternary carbides has not been examined in detail, although the phase diagram has included determinations of the melting points of the phases in the U–Pu–C system. There are no reported data on the systematic examination of the vaporization behaviour of the alloys, although an assessment of the plutonium, uranium and uranium dicarbide gas pressures over the monocarbide + sesquicarbide and dicarbide + carbon regions of the ternary system has been made[64]; the results of some of these calculations are shown in Fig. 10.

The Uranium–Thorium–Carbon System

Uranium and thorium monocarbides form a complete range of solid solutions[66]. The phase diagram at 1000°C indicates that the solid solution in equilibrium with uranium and thorium metal has a composition $Th_{0\cdot 91}U_{0\cdot 09}C_{0\cdot 71}$[67]. Lattice parameter measurements of the monocarbide solid solution indicate that any deviations from Vegard's law are small. Uranium and thorium dicarbide form a complete range of cubic solid solutions, but these solutions cannot be quenched to room temperature; there are regions of immiscibility in the system[68].

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[65] J. T. Dalton, E. A. Harper, H. J. Hedger and R. N. Stannard, *Plutonium 1970 and Other Actinides*, p. 829.

[66] F. Benesovsky and E. Rudy, *Monatsh. Chem.* **92** (1961) 1176.

[67] J. T. Venard, USAEC Report ORNL-TM-2015 (1968).

[68] N. A. Hill and O. B. Craven, USAEC Report ORNL-3670 (1964).

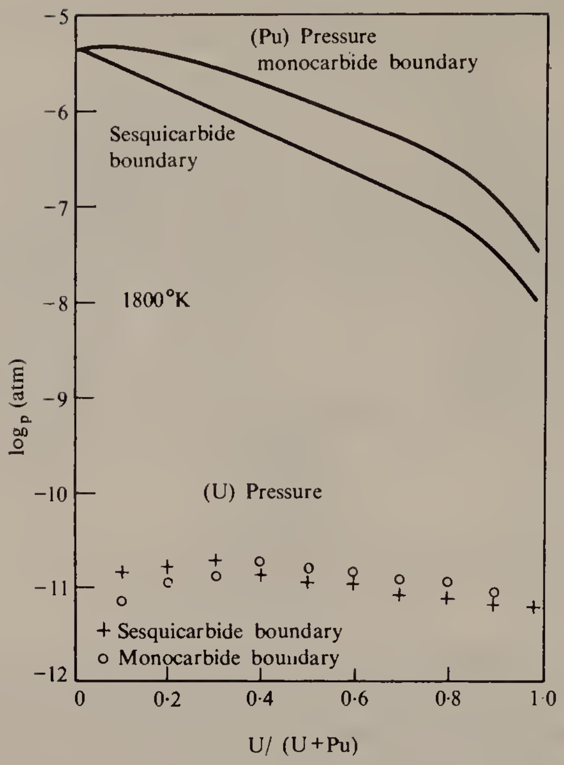

FIG. 10. The uranium and plutonium gas pressures above the two-phase monocarbide and sesquicarbide region of the U–Pu–C system (after Mardon and Potter[64]).

The Plutonium–Thorium–Carbon System

Plutonium monocarbide and thorium monocarbide are completely miscible[69] and the phase diagram for the metal–monocarbide region has been given[70]. The plutonium dicarbide–thorium dicarbide section of the ternary has been examined in some detail[71]; the cubic modifications of the dicarbides are completely miscible, but the phase relationships are considerably more complex at temperatures below the range of stability of the cubic solid solution. A section for PuC_2–ThC_2 is shown in Fig. 11.

The Neptunium–Thorium–Carbon System

Nevitt[70] found complete solubility between NpC and ThC.

2.5. Corrosion properties

Oxidation

The oxidation of finely divided uranium monocarbide is very rapid and the rates are irreproducible due to the pyrophoricity[72]. In the temperature range 140–230°C using gold powder to maintain isothermal conditions the products were $UO_{2\cdot20}$ and free carbon in oxygen pressures less than 1 atm.

The mechanism of the oxidation of uranium monocarbide at 400°C does not involve the

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[69] S. Rosen, USAEC Report ANL-6677 (1962), p. 265.

[70] M. V. Nevitt, USAEC Report ANL-6868 (1963), p. 312.

[71] J. T. Dalton, P. E. Potter and J. L. Shaw, *Plutonium 1965*, p. 725.

[72] R. G. Sowden, N. Hodge and M. J. Moreton-Smith, *Trans. Faraday Soc.* **50** (1964) 759.

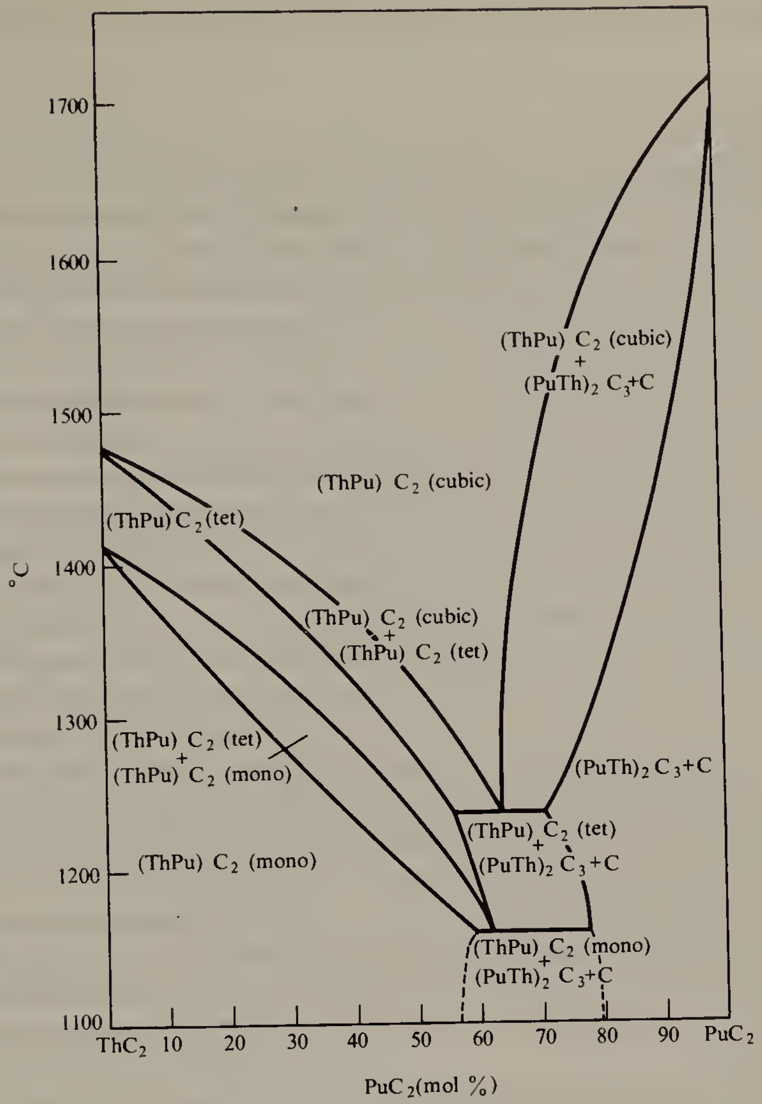

FIG. 11. A section of the Pu–Th–C system (after Dalton, Potter and Shaw[71]).

formation of an intermediate higher carbide. Although there are no higher carbides formed, the UO_2 oxidation product is oriented on the uranium monocarbide[73]. At higher temperatures the oxidation reaction is probably different. Uranium monocarbide will be unstable with respect to CO and CO_2, the primary oxidation products, and oxidation should lead to $UC_2 + UO_2$. It has been found[74] in fact that the oxidation of uranium monocarbide crystals at 900°C and 10^{-4} torr gives an epitaxially oriented sandwich structure of UC_2 and UO_2.

The oxidation of all the actinide carbides is a complex process which varies with temperature and oxygen pressure and with the rate of removal of the product gases.

Measurements[75] of the rate of uptake of oxygen by fine powders of uranium monocarbide and uranium plutonium monoxycarbides have suggested that at room temperature

[73] R. M. Dell, V. J. Wheeler and E. J. McIver, *Trans. Faraday Soc.* **52** (1966) 3591.

[74] G. Ervin and K. T. Miller, *Acta Met.* **14** (1966) 222.

[75] D. G. Cragg, R. J. Dicker, J. D. L. Harrison, J. W. Isaacs, J. R. McLaren and W. G. Roberts, *Bull. Soc. Fr. Ceram.*, p. 35, No. 77 (1967).

a coherent oxide layer, containing carbon, is formed on the surface of the particles at room temperatures.

Hydrolysis of Carbides

All the actinide carbides are very reactive towards water vapour and for this reason must be stored in very dry inert atmospheres. The studies on the hydrolysis of thorium carbides[76-80] have been recently reviewed[81]. ThC reacts with water to form ThO_2 and a mixture of gases; the gas is nearly 90 mole % CH_4 and nearly 10 mole % H_2 together with small quantities of other hydrocarbons. Hypostoichiometric thorium monocarbide ($ThC_{0\cdot81}$) reacted more slowly and gave proportionately more hydrogen. The effects of additions of NaOH, HCl, H_2SO_4 and HNO_3 as well as D_2O have been reported. The effect of additions of NaOH up to 18 M were slight, as was the substitution of D_2O. The addition of HCl increased the rate of hydrolysis in addition to the amount of H_2 compared with CH_4 for single-phase ThC, but the rate was unchanged when ThC_2 was present. H_2SO_4 decreased the reaction rate and the solid product was hydrated thorium sulphate. HNO_3 dissolved ThC with the evolution of a mixture of CO, CO_2, N_2, N_2O, and NO, when the HNO_3 concentration was less than 2 M; CH_4 was also present.

In air, ThC_2 is less reactive than the monocarbide, but more reactive than UC_2. At room temperatures the reactions are slow unless moisture is present. ThC_2 reacts with water to give ThO_2 a gas mixture by volume of $\frac{1}{3}$ H_2, $\frac{1}{3}$ C_2H_6 and the rest a mixture of hydrocarbons, mostly unsaturated. The rates of reaction for arc-melted specimens of UC_2–ThC_2 are intermediate between those for UC_2 and ThC_2[82].

The reaction heat of thorium monocarbides increases with decreasing carbon content; 160 kcal mole^{-1} for $ThC_{0\cdot98}$ and 171 kcal mole^{-1} for $ThC_{0\cdot77}$[83].

It is rather surprising that pellets of PaC are stable against air corrosion and do not react easily with hot water or dilute acids[84], such as HCl, HNO_3, and H_2SO_4. Only upon prolonged heating with concentrated H_2SO_4 and after successive additions of HNO_3 is PaC finally completely decomposed. In the presence of HF, however, it dissolves readily, even in dilute acids.

Many hydrolysis studies have been made on the uranium carbides because of the technological significance of the corrosion properties. Several studies have been made to determine the nature of the gaseous and solid reaction products as a function of temperature and the initial carbide composition.

For uranium monocarbide the reaction with water[85] at 25–100°C leads to the formation of 86 vol. % CH_4, 12 vol. % H_2, and 1·8 vol. % C_2H_6, the remainder comprising some higher hydrocarbons. UO_2 is formed in the reaction[86]. Hydrolysis studies on neutron irradiated uranium monocarbide[87] show that after irradiation the reaction rate decreases;

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[76] M. J. Bradley and L. M. Ferris, *J. Inorg. Nucl. Chem.* **27** (1965) 1021.

[77] M. B. Sears and L. M. Ferris, *ibid.* **28** (1966) 2055.

[78] M. J. Bradley, M. D. Pattengill and L. M. Ferris, *Inorg. Chem.* **4** (1965) 1080.

[79] M. B. Sears and L. M. Ferris, *J. Inorg. Nucl. Chem.* **29** (1967) 1548.

[80] J. Imai and S. Iruno, *Nature*, **206** (1965) 691.

[81] S. Peterson and C. E. Curtis, *Thorium Ceramics Data Manual.* USAEC Report ORNL-4503 (1970).

[82] G. B. Engle, W. V. Goeddel and C. S. Luby, *J. Amer. Ceram. Soc.* **45** (1962) 136.

[83] H. Imai, T. Honda and Y. Sasaki, *J. Nucl. Mat.* **39** (1971) 238.

[84] R. Lorenz, H. L. Scherff and N. Toussaint, *J. Inorg. Nucl. Chem.* **31** (1969) 2381.

[85] M. J. Bradley and L. M. Ferris, *Inorganic Chemistry*, **1** (1962) 683; **3** (1964) 189.

[86] A. Schürenkämper, *J. Inorg. Nucl. Chem.* **32** (1970) 417.

[87] M. J. Bradley, J. H. Goode, L. M. Ferris, J. R. Flanary and J. W. Ullmann, *Inorg. Chem.* **3** (1964) 454.

above a burn-up of 5000 MWD tonne^{-1} uranium monocarbide did not even react with boiling water.

The water hydrolysis of $UC_{1\cdot85}$[88] yielded a mixture of 36 hydrocarbons with an average composition of 15 vol. % CH_4, 28 vol. % C_2H_6, 7 vol. % C_3–C_8 alkanes, 8 vol. % alkenes, 0·6 vol. % alkynes, 40 vol. % H_2, a water-insoluble wax, and a hydrous U(IV) oxide. A variation of reaction temperature between 25° and 90°C causes no change in the hydrolysis products from either uranium monocarbide or dicarbide. Hydrolysis of uranium monocarbide–dicarbide mixtures results in a linear decrease in the vol. % CH_4 and a linear increase in the percentage of H_2 and C_2 to C_8 hydrocarbons in the gas as the C:U ratio increases from 1·0 to 1·85.

The reactions of these carbides with aqueous solutions of HCl and H_2SO_4 are similar to their reactions with water, although in the reaction of the dicarbide with HCl a greater amount of the carbide carbon appeared in the wax.

Reactions of the uranium carbides with 2–18 M NaOH solutions[89] have resulted in the oxidation of part of the uranium to the hexavalent state, with the accompanying evolution of H_2. The hydrocarbons produced in reactions with UC and U_2C_3 were the same as those produced with H_2O. With the dicarbide, some of the hydrogen resulting from oxidation of the uranium reacted with the carbide carbon, forming more gaseous hydrocarbons than obtained with water; the relative concentrations of the various C_2 to C_8 hydrocarbons were independent of the NaOH concentrations.

The hydrolysis of uranium–plutonium carbides has also been examined[90]; the plutonium compositions expressed as Pu/U + Pu were 0·15 and 0·30, and the carbon concentrations were slightly different. The predominant gaseous product was CH_4, and then H_2, and there was little difference at 80°C in water and N HCl. The measurements of the rate of hydrolysis were in qualitative agreement with those for uranium monocarbide and no significant rate effect exists that can be attributed to the presence of plutonium. There are changes in the products of hydrolysis, however, and the plutonium-containing carbides yield less hydrogen; this can be attributed to the final oxidation states of the cations in solution, plutonium most probably being in the trivalent state[91].

Before discussing the effects of neutron irradiation on the hydrolysis of the carbides, a few generalizations can be made regarding the hydrocarbons' behaviour. When the carbon atoms exist singly in the carbide lattice surrounded by metal atoms, as in uranium carbide, the principal hydrolysis product is methane. CH_4 is accompanied in all cases by higher hydrocarbons formed by the condensation of free radicals. For the sesquicarbides and dicarbides the hydrolysis products are more complex and depend upon the carbon–carbon bond length. In UC_2 and U_2C_3 the C–C distance approximates to that of a double bond and the hydrolysis products are principally alkanes and some alkenes.

As found for irradiated uranium carbide the (UPu) carbides are inert to water at 80°C, whilst reaction proceeds readily in 4 N hydrochloric acid at the same temperature. Materials with burn-ups of 10% were examined[90]. The reasons for the changes in reactivity to water are not clearly understood, but could arise from some oxidation of the surfaces which would protect the carbide from water but not from acid. Complete oxidation in hydrochloric acid liberates an extensive yield of hydrogen which would not be formed if much

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[88] S. Evered, M. J. Moreton-Smith and R. G. Sowden, *J. Inorg. Nucl. Chem.* **27** (1965) 1867.
[89] M. B. Sears, M. D. Pattengill and L. M. Ferris, *J. Inorg. Nucl. Chem.* **30** (1968) 2111.
[90] J. R. Findlay, M. J. Moreton-Smith and R. Moss, *J. Inorg. Nucl. Chem.* **31** (1969) 3437.
[91] J. L. Drummond, B. J. MacDonald, M. M. Ockenden and G. A. Welch, *J. Chem. Soc.* (1957) 4785.

of the specimen existed as oxide. The possible inhibition of reaction by β-radiation was also ruled out[88], as well as such marked effects being due to the presence of fission products. There are significant differences in the products of acid hydrolysis which are related to burn-up and irradiation temperature; the yield of methane from specimens irradiated at 350°C decreases with increasing burn-up whilst the yield of free hydrogen increases. The yields of other gaseous hydrocarbons are unchanged, but the lower recoveries of carbon in the gas phase suggest an increasing formation of wax residues.

A possible explanation of the effect of irradiation on the hydrolysis behaviour of these carbides is that the carbide lattice is markedly changed. Lattice atoms could be displaced or fission product atoms incorporated into the lattice and these effects are probably annealed out when the materials are irradiated at temperatures of *ca.* 1000°C or annealed after irradiation.

2.6. The systems actinide element–carbon–oxygen and actinide element–carbon–nitrogen

As discussed in section 2.2, a suitable route for the technological preparation of many of the actinide carbides is the carbothermic reduction of the oxides in either a vacuum or in a flowing inert gas, such as argon, but as previously pointed out this method is not necessarily a suitable route for the preparation of pure laboratory samples as it may be quite impossible to reduce the concentration of oxygen dissolved in the lattice of the required product.

Nitrogen contamination could be introduced also during a heat treatment in an impure atmosphere. To appreciate the behaviour of the actinide element–carbon systems in the presence of oxygen and nitrogen, a knowledge of the ternary systems actinide element–carbon–oxygen and actinide element–carbon–nitrogen systems, as well as the quaternary systems actinide element–carbon–oxygen–nitrogen, is required.

The Ternary Systems Actinide Element–Carbon–Oxygen

The thorium–carbon–oxygen system. Thorium dicarbide has been prepared by the carbothermic reduction of ThO_2[41].

$$ThO_2\ (\text{solid}) + 4C\ (\text{solid}) \rightleftharpoons ThC_2\ (\text{solid}) + CO\ (\text{gas})$$

There is no knowledge of the amount of oxygen dissolved in the dicarbide lattice. Further removal of CO gas can result in the formation of thorium monoxycarbide.

$$ThO_2\ (\text{solid}) + 3ThC_2\ (\text{solid}) \rightleftharpoons ThC\ (\text{dissolved in ThO}) + 2CO\ (\text{gas})$$

The thorium monocarbide formed is in fact dissolved in the hypothetical compound ThO, the composition of the phase being *ca.* $ThC_{0.8}O_{0.2}$[15]. To remove oxygen from the monocarbide lattice further quantities of CO must be removed from the system.

$$2ThC_2\ (\text{solid}) + ThO\ (\text{dissolved in ThC}) \rightleftharpoons 3ThC\ (\text{dissolved in ThO}) + CO$$

This must be carried out at higher temperatures and/or in a low vacuum.

The protactinium–carbon–oxygen system. The reaction of protactinium pentoxide and carbon was found to proceed in two steps[84], the first one involving the reduction of Pa_2O_5 to PaO_2 and the second step being the formation of the carbide:

$$PaO_2 + xC \rightarrow PaC_{x-2} + 2CO$$

The reactions were carried out in a vacuum and the reduction of Pa_2O_5 started at 1000°C, and up to 1100°C no appreciable carbide formation was observed.

The CO pressure for the above univariant reaction is given by

$$\log P_{(CO)}\,(\text{atm}) = 9{\cdot}19 - \frac{19{\cdot}940}{T}\quad(1560\text{–}1715\text{K})$$

The main product of the carbothermic reduction at temperatures below 2000°C was the monocarbide; only at temperatures above 2200°C were higher carbides, probably the dicarbide, found.

The systems with uranium and plutonium. The carbothermic reduction route for the production of uranium and uranium–plutonium carbides has received much attention as part of a route for the fabrication of carbides as possible fuels for fast breeder reactors. Reactions in a vacuum and in inert gases have been employed and attempts have been made to develop continuous routes in addition to batch processes. The preparation of uranium, plutonium, and uranium–plutonium will now be considered in terms of the equilibrium phase diagrams. It should be remembered that the products will always contain some oxygen.

A particularly convenient route for the preparation of uranium monocarbide is to react a mixture of U_3O_8 and graphite at 600–800°C *in vacuo*[92] or flowing argon. At these temperatures reduction to UO_2 occurs and the following reactions must be considered at temperatures between 600° and 1100°C, in the reduction steps.

$$U_3O_8\,(\text{solid}) + 0{\cdot}1C\,(\text{solid}) \rightarrow 3\,UO_{2.6}\,(\text{solid}) + 0{\cdot}1CO_2\,(\text{gas})$$

This equation represents the total reaction in the bivariant region (U_3O_{8-x} + C), and then for the two three-phase fields the two univariant equilibria are

$$UO_{2.6}\,(\text{solid}) + 0{\cdot}7C\,(\text{solid}) \rightarrow U_4O_9\,(\text{solid}) + 0{\cdot}7CO_2\,(\text{gas})$$

$$U_4O_9\,(\text{solid}) + \tfrac{1}{2}(1 - 4x)\,C\,(\text{solid}) \rightarrow UO_{2+x}\,(\text{solid}) + \tfrac{1}{2}(1 - 4x)\,CO_2\,(\text{gas})$$

From the partial molal free energies of oxygen ($\Delta\bar{G}_{O_2}$) for the U–O system[93], it is apparent that the gaseous products of the reaction between carbon and the above oxides will be almost entirely CO_2 and not until the reduction has reached the bivariant phase field UO_{2+x} + C does the contribution of CO become appreciable. At temperatures below 1500°C, UO_2 is the composition of the oxide in equilibrium with uranium metal, but at higher temperatures hypostoichiometric oxide (UO_{2-x}) can be formed. Further reduction of UO_2 and UO_{2-x} at temperatures above 1000°C produces carbide phases and the gas phase is now predominately CO.

The various reactions for the formation of the carbides are best discussed in terms of the ternary U–C–O system. The phase equilibria in this system together with those in the Pu–C–O and U–Pu–C–O have been reviewed recently[42]; an isothermal section of the U–C–O system[94] is shown in Fig. 12.

Pure uranium monoxide does not exist in the bulk form but has been observed as surface layers on uranium metal, and these layers may have been stabilized by impurities such as carbon[95]. The compound can, however, be regarded as stabilized by solution in uranium monocarbide. Up to 35 mole % "UO" is soluble in UC in the presence of uranium

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[92] N. R. Williams, *Proc. Brit. Ceram. Soc.* 7 (1967) 1.

[93] M. H. Rand and O. Kubaschewski, *The Thermochemical Properties of Uranium Compounds*, p. 26, Oliver & Boyd, Edinburgh and London (1963).

[94] J. L. Henry, D. L. Paulson, R. Blickensderfer and H. J. Kelly, U.S. Dept. of the Interior Report BM RI 6963 (1967).

[95] L. E. J. Roberts, *Quart. Rev.* 15 (1961) 442.

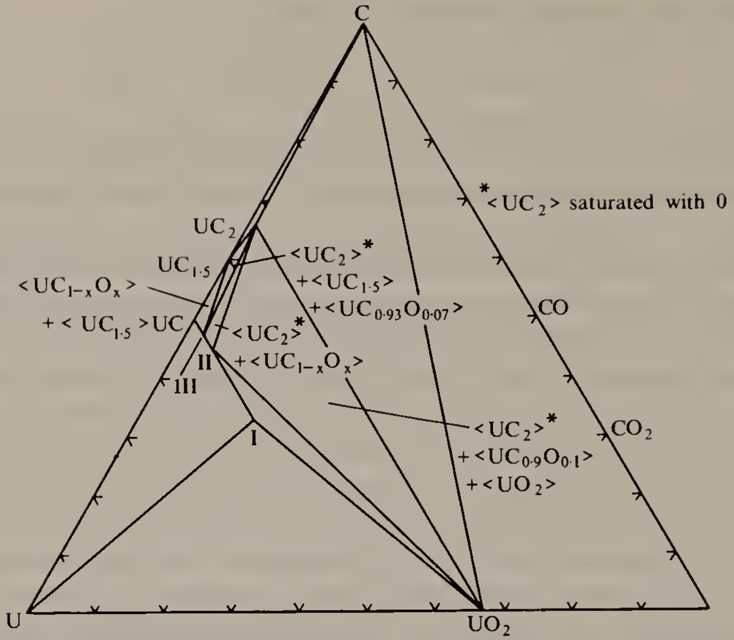

FIG. 12. The phase diagram for the U–C–O system at 1700°C (after Potter[42]).

metal, and up to *ca.* 11 mole % in the presence of "UC_2". The lattice parameter of the monocarbide phase decreases with solubility of oxygen in the lattice and although there is a large scatter on the plot of lattice parameter versus composition[42], there is some indication that the lattice parameters may have a maximum value at compositions between 5 and 10 mole % "UO" which may be due to a small concentration of carbon vacancies being filled by the oxygen atoms before the onset of substitution of carbon atoms by oxygen atoms. Variations of lattice parameter of uranium dicarbide have also been attributed to the dissolution of oxygen in the lattice of this compound[96]. An analysis of the phase equilibria data as well as experimental measurements[97] indicates that the UC–UO solid solution has a negative deviation from ideality; a regular solution with a heat of mixing of *ca.* —20 kcal can be used to describe this solution.

The reduction path of a mixture of C + UO_2 will follow the extension of a line joining the point on the ternary phase diagram representing CO to the point representing the initial mixture. For the formation of uranium monocarbide the various equilibrium reactions which have to be considered as the reaction path is followed are given below.

In the phase field C, UC_2 and UO_2*

$$UO_2\ (\text{solid}) + 4C\ (\text{solid}) \rightleftharpoons UC_2\ (\text{dissolved in } UO_2) + 2CO\ (\text{gas})$$

In the phase field UC_2, $UC_{0\cdot9}O_{0\cdot1}$, UO_2*

$$3UC_2\ (\text{dissolved in } UO_2) + UO_2\ (\text{solid}) \rightleftharpoons 4UC\ (\text{dissolved in UO}) + 2(CO)$$

In the bivariant two-phase field UC_2 (dissolved in UO_2) and $UC_{1-x}O_x$

$$UO\ (\text{dissolved in UC}) + 2\ UC_2\ (\text{dissolved in } UO_2) \rightleftharpoons 3UC\ (\text{dissolved in UO}) + CO$$

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* UC_2 probably contains some dissolved oxygen.

[96] J. Henney, UKAEA Report AERE-R4661 (1966).

[97] B. C. H. Steele, N. A. Javed and C. B. Alcock, *J. Nucl. Mat.* 35 (1970) 1.

and then *the univariant three-phase field*

$$2{\cdot}5UC_2 \text{ (dissolved in } UO_2\text{)} + 0{\cdot}5UO \text{ (dissolved in UC)} \rightleftharpoons 3UC_{1{\cdot}5} \text{ (solid)} + 0{\cdot}5CO \text{ (gas)}$$

and then finally *the bivariant two-phase field*

$$UO \text{ (dissolved in UC)} + 4UC_{1{\cdot}5} \text{ (solid)} \rightleftharpoons 5UC \text{ (dissolved in UO)} + CO \text{ (gas)}$$

By increasing the initial carbon:UO_2 ratio, uranium carbide compositions with varying carbon contents can be prepared, and by decreasing the amount of carbon, alloys with compositions in the two-phase region uranium metal and uranium monoxycarbide can be prepared.

The equilibrium reactions that are appropriate for these regions are:
For *the two-phase bivariant region* UO_2, $UC_{1-x}O_x$

$$2UO_2 \text{ (solid)} + UC \text{ (dissolved in UO)} \rightleftharpoons 3UO \text{ (dissolved in UC)} + CO$$

and for *the two-phase bivariant region U metal*, $UC_{1-x}O_x$

$$UC \text{ (dissolved in UO)} + UO \text{ (dissolved in UC)} \rightleftharpoons 2U \text{ (solid or liquid)} + CO \text{ (gas)}$$

The CO pressures for the phase fields bounding the uranium monoxycarbide phase at 1700°C are shown in Fig. 13[42]. Uranium monocarbide can be prepared in a vacuum of 10^{-4} atm by heating at only 1400°C and according to the thermodynamic calculations should contain only 50 ppm of oxygen impurity.

The carbothermic reduction route cannot be used for the preparation of plutonium monocarbide because of the very high vapour pressure of plutonium over the appropriate

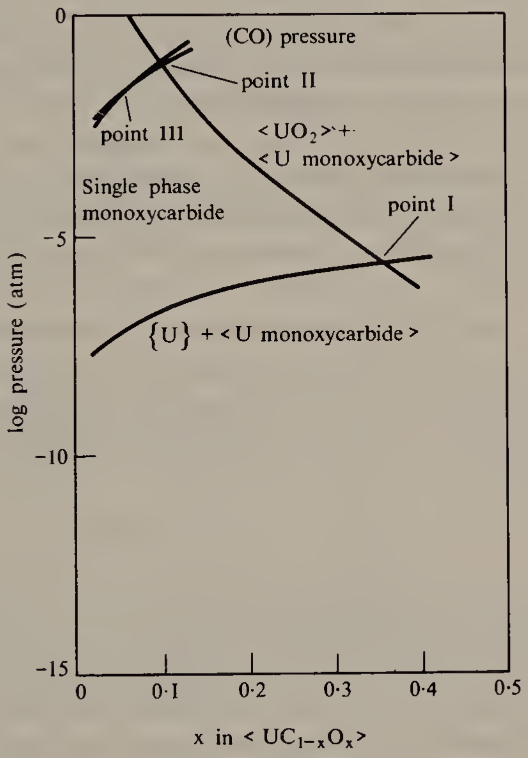

FIG. 13. The CO pressures over the U–C–O system at 1700°C (P. E. Potter, UKAEA Report R6890 (1971)).

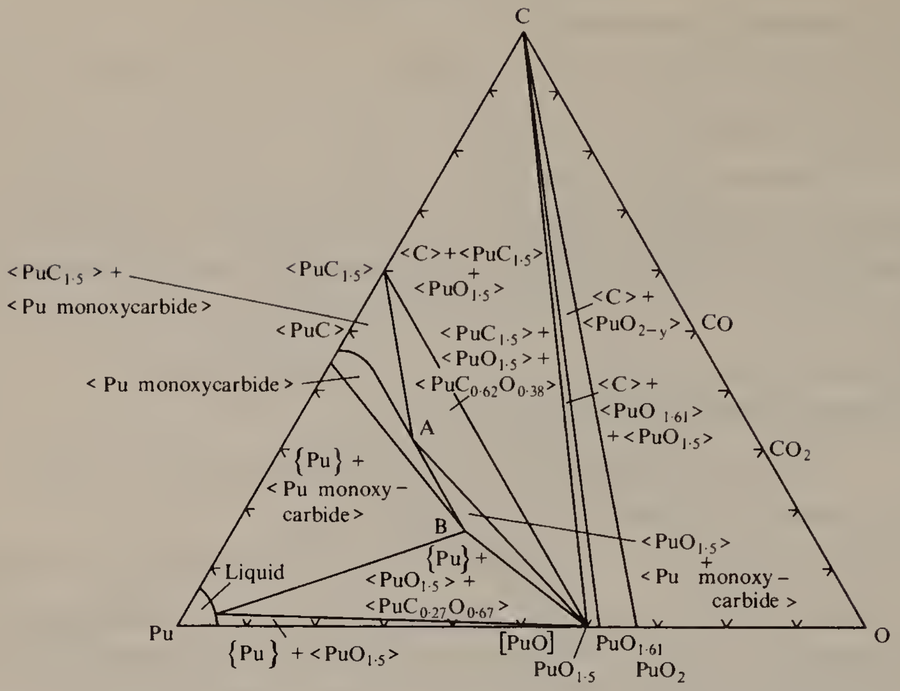

FIG. 14. The phase diagram for the Pu–C–O system at *ca.* 1300°C (after Potter[42]).

regions of the ternary Pu–C–O system. The phase diagram is shown in Fig. 14. The maximum substitution of oxygen in plutonium monocarbide is 66 mole % "PuO" (point B, Fig. 14). Plutonium monoxide does not exist as a phase of the Pu–O system. In the presence of Pu_2O_3 and Pu_2C_3 the limit of PuO solubility in PuC is *ca.* 36 mole %. The variation of lattice parameter with oxygen content of the plutonium monoxycarbide phase increases up to 10 mole % PuO, due to the filling of the vacancies in the carbon-deficient plutonium monocarbide lattice. The substitution of oxygen for carbon in the plutonium monocarbide results in a decrease in the lattice parameter which is linear with oxygen concentration. An assessment of the phase equilibria data suggests that the PuC–PuO solid solution possesses only a small deviation from ideality; a regular solution interaction parameter of *ca.* —2·0 kcal is suggested.

The main gas phase species above the system in the region of the plutonium monoxycarbide phase are Pu, PuO, and CO, and the high plutonium pressures do not allow the preparation of plutonium monocarbide. One consequence of the high plutonium pressures is that an alloy of composition $PuC_{0\cdot5}O_{0\cdot5}$ is practically congruently vaporizing at temperatures in the region 1300–1500°C.

$$PuC_{0\cdot5}O_{0\cdot5}\ \text{(solid)} \rightleftharpoons Pu\ \text{(gas)} + 0\cdot5CO\ \text{(gas)}$$

These high plutonium pressures prevent the reduction in this ternary system reaching the plutonium metal + plutonium monoxycarbide region.

For the reduction of uranium–plutonium oxides of compositions of technological significance the volatility of plutonium has not caused difficulties. For the reduction of 85 % UO_2–15 % PuO_2[11] it was found that the reaction occurred smoothly in flowing argon at 1500–1650°C to give products of predictable compositions. Carbon contents of the product could be controlled to ±0·05 wt. %, and oxygen impurity levels as low as 200 ppm could be attained. Loss of plutonium due to volatilization was low, *ca.* 1 wt. % of the total. The reaction product could be sintered to a high density in argon at 1550°C. For the reduction process *in vacuo* the plutonium losses were higher; 2–4 wt. % of the plutonium at 1450°C in 4 hr[98].

There are very few experimental data available on the phase equilibria of the quaternary system U–Pu–C–O.

There are no data for the Np–C–O system.

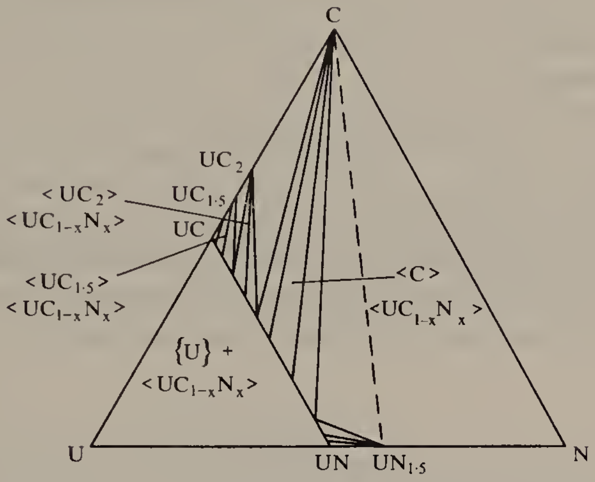

FIG. 15. A section for the U–C–N system in the temperature range *ca.* 1500–1750°C.

The Ternary Systems Actinide Element–Carbon–Nitrogen

The thorium–carbon–nitrogen system. The monocarbide and mononitride form a complete range of solid solutions; the lattice parameters do not show any marked deviations from Vegard's law[99].

The uranium–carbon–nitrogen system. A section of the U–C–N system is shown in Fig. 15. This section is applicable to the temperature region in which U_2C_3 and UC_2 coexist, namely 1500–1780°C. The lattice parameter of the solid solution between UN and UC shows a slight positive deviation from Vegard's law[100] (UN $a_0 = 4{\cdot}8892$ Å $\pm\ 0{\cdot}0002$). Nitrogen pressure measurements[101] for the equilibrium reaction

$$\text{UC (dissolved in UN)} + \tfrac{1}{2}\text{N}_2\text{ (gas)} \rightleftharpoons \text{UN (dissolved in UC)} + \text{C (solid)}$$

have shown that the solution can be considered ideal.

The UC–UN solid solution is in equilibrium with carbon between a UN concentration of 20 mole % and pure UN. UC_2 can also be stabilized with respect to U_2C_3 and carbon by dissolution of nitrogen in the tetragonal lattice[102].

There have been several measurements of the nitrogen pressures over the phase field carbon + UC–UN solid solution and these are of significance not only in understanding the nature of the UC–UN solid solution but also in determining the conditions under which traces of nitrogen impurity can be removed from the uranium carbides which have been

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[98] J. M. Horspool, J. A. S. Mowat and S. Pickles, *Carbides in Nuclear Energy.*

[99] R. S. Street and T. N. Waters, *J. Less-Common Metals,* 5 (1963) 295.

[100] J. M. Leitnaker, R. A. Potter, K. E. Spear and W. R. Laing, *High Temp. Sci.* 1 (1969) 389.

[101] J. M. Leitnaker, *Thermodynamics of Nuclear Materials 1967,* p. 317, IAEA, Vienna (1968).

[102] R. Lorenzelli, CEA Report R-3536 (1968).

contaminated with nitrogen. Any contamination of the monocarbide by nitrogen probably results in the overall composition lying within the bivariant regions mononitride solid solution + U_2C_3 or mononitride solid solution + UC_2, and the reactions which must be considered for nitrogen removal are:

$$\text{UN (dissolved in UC)} + 2\text{UC}_{1\cdot5} \text{ (solid)} \rightleftharpoons 3\text{UC (dissolved in UN)} + \tfrac{1}{2}\text{N}_2 \text{ (gas)}$$

and

$$\text{UN (dissolved in UC)} + 2\text{UC}_2 \text{ (solid)} \rightleftharpoons 2\text{UC (dissolved in UN)} + \tfrac{1}{2}\text{N}_2$$

The nitrogen levels attainable at a given pressure and temperature can easily be calculated from the above equilibria.

The plutonium–carbon–nitrogen system. Calculations[103] have shown that by assuming an ideal solution of PuC and PuN reasonably good agreement can be obtained for the composition of the solid solution which is in equilibrium with carbon. The solid solution of compositions between PuN and $PuN_{0\cdot75}C_{0\cdot25}$ are in equilibrium with carbon between 1400° and 1600°C, and the calculated values are at 1000K between PuN and $PuN_{0\cdot89}C_{0\cdot11}$ and at 1900K between PuN and $PuN_{0\cdot75}C_{0\cdot25}$[104]. No nitrogen pressure measurements have been reported for this system, but calculations have been made.

3. SILICIDES

3.1. Introduction

All the silicides with the exception of the compounds with very low silicon contents, for example U_3Si, are characterized by Si–Si bonds. The silicon atoms are in pairs, chains, layers or three-dimensional networks.

The silicide phases which have been characterized are listed with their ideal formulae in Table 13.

TABLE 13. IDEAL FORMULAE OF THE ACTINIDE SILICIDE PHASES

	U_3Si		
			Pu_5Si_3
Th_3Si_2	U_3Si_2		Pu_3Si_2
ThSi	USi		PuSi
Th_3Si_5	U_3Si_5		Pu_3Si_5
$ThSi_2$	USi_2	$NpSi_2$	$PuSi_2$
	USi_3		

3.2. Preparation

The most widely employed method for the preparation of the actinide silicides is the direct reaction between the actinide element and silicon, usually in an arc-melting furnace under an inert atmosphere, such as argon or helium. This method has been used for the preparation of thorium, uranium and plutonium silicides. In addition to arc-melting the

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[103] R. Lorenzelli, P. Delaroche, M. Housseau and P. Petit, *Plutonium 1970 and Other Actinides*, W. N. Miner (Ed.), p. 818.

[104] P. E. Potter, *J. Nucl. Mat.* 34 (1970) 193.

elements together, the elements can be heated together in powder form, for example USi_3 has been prepared in this way in beryllia crucibles, and the thorium silicides have been prepared by heating the elements together in graphite, tungsten, and alumina crucibles in a vacuum at temperatures between 1400° and 1700°C. The low-temperature forms of the higher thorium silicides which have been reported[105] were prepared by heating thorium and silicon powders together in the required proportions in liquid bismuth in evacuated sealed silica capsules at 700–750°C. Uranium silicides have recently been prepared[106] by heating the elements in an induction furnace; the alloys were then annealed in tungsten crucibles and contained less than 50 ppm of carbon and less than 200 ppm of oxygen impurities.

Other preparative routes which can be used are from the fluorides

$$NpF_3 + 11Si \xrightarrow{1500°C} 4NpSi_2 + 3SiF_4$$

and from the oxides.

The details of the phase relationships, the nature of the decomposition, and the regions of stability must be known before the correct annealing conditions can be employed to obtain pure compounds. The phase diagrams and chemical stability are discussed later.

3.3. Crystal structures

The structures will be considered in groups.

U_3Si. This compound exists in two crystalline forms, the low-temperature δ-form, which has tetragonal symmetry, with space group *I4/mcm*, and the lattice parameters $a_0 = 6{\cdot}030$ Å and $c_0 = 8{\cdot}696$ Å[107], and a high-temperature δ′-form, which is stable above 765 ± 3°C, the transformation temperature for $\delta \rightleftharpoons \delta'$. The cubic high-temperature form has the Cu_3Au structure, and the silicon atoms occupy the (0,0,0) positions and the uranium atoms the positions $(0,\frac{1}{2},\frac{1}{2};\ \frac{1}{2},0,\frac{1}{2};\ \frac{1}{2},\frac{1}{2},0)$. The lattice parameter of the phase is $a = 4{\cdot}346$ Å at 780°C[108]; the phase is stable up to 930°C, the temperature of the peritectic decomposition.

Pu_5Si_3 (zeta phase). This compound has a body-centred tetragonal unit cell containing four formula units of Pu_5Si_3[109]. The structure type is that of W_5Si_3, with space group

TABLE 14. LATTICE PARAMETERS OF Pu_5Si_3 (zeta phase)[a]

Composition	Method of preparation	Lattice parameters (Å)	
		a	*c*
33 at.% Si	Arc melted, slowly cooled	11·385 ±0·005	5·443 ±0·003
37 at.% Si (single phase)	Arc melted	11·407 ±0·005	5·444 ±0·003
		(calculated density, 12·00±0·02 g cm^{-3})	

[a] C. C. Land, K. A. Johnson and F. H. Ellinger, *J. Nucl. Mat.* 15 (1965) 23.

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[105] A. Brown and J. J. Norreys, *J. Inst. Metals*, 89 (1960) 238.
[106] H. Vaugoyeau, L. Lombard and J. P. Morlevat, *J. Nucl. Mat.* 39 (1971) 323.
[107] W. H. Zachariasen, *Acta Cryst.* 2 (1949) 94.
[108] P. L. Blum, G. Silvestre and H. Vaugoyeau, *Compt. Rend.* 260 (1965) 5538.
[109] D. T. Cromer, A. C. Larson and R. B. Roof Jr., *Acta Cryst.* 17 (1964) 947.

I4/mcm. The lattice parameters (Table 14) of the zeta phase vary somewhat depending on the amount of silicon present.

M_3Si_2 compounds. These compounds of the general formula M_3Si_2 have a primitive tetragonal cell, space group *P4/mbm*. The lattice parameters and densities of these phases are given in Table 15. Th_3Si_2 does not possess any noticeable variation in stoichiometry[105], as is the case for Pu_3Si_2.

TABLE 15. LATTICE PARAMETERS OF THE M_3Si_2 COMPOUNDS

Compound	Lattice parameter (Å) *a*	Lattice parameter (Å) *c*	Calculated density (g cm^{-3})	Reference
Th_3Si_2	7·835	4·154	9·75	a
U_3Si_2	7·3297	3·9005	12·20	b
Pu_3Si_2	7·483	4·048	11·33	c
(eta phase)	±0·002	±0·002		

[a] E. L. Jacobson, R. D. Freeman, A. G. Thorp and A. W. Searoy, *J. Amer. Chem. Soc.* **78** (1956) 4850.
[b] W. H. Zachariason, *Acta Cryst.* **2** (1949) 94.
[c] C. C. Land, K. A. Johnson and F. H. Ellinger, *J. Nucl. Mat.* **15** (1965) 23.

The monosilicides (*MSi*). The monosilicides of thorium, uranium, and plutonium are reported to possess orthorhombic symmetry, space group *Pbnm*[110] with a structure of the FeB type. The lattice parameters and calculated densities are given in Table 16. Some recent results, however, suggest that the uranium monosilicide cell is not that previously determined[107], and that the compound is tetragonal[111], with 68 molecules per unit cell, and that the orthorhombic form can only be formed in the presence of a small quantity of oxygen.

TABLE 16. LATTICE PARAMETERS OF THE MONOSILICIDES

Compound	Lattice parameters (Å) *a*	Lattice parameters (Å) *b*	Lattice parameters (Å) *c*	Calculated density (g cm^{-3})	Reference
ThSi	5·89	7·88	4·15	8·92	a
USi	5·66	7·65	3·91	10·40	b
PuSi	5·727	7·933	3·847	10·15	c
	±0·005	±0·003	±0·001		

[a] E. L. Jacobson, R. D. Freeman, A. G. Thorp and A. W. Searcy, *J. Amer. Chem. Soc.* **78** (1956) 4850.
[b] W. H. Zachariasen, *Acta Cryst.* **2** (1949) 94.
[c] C. C. Land, K. A. Johnson and F. H. Ellinger, *J. Nucl. Mat.* **15** (1965) 23.

M_3Si_5 compounds. These compounds possess the AlB_2-hexagonal type structure (space group *C6/mmm*). The lattice parameters of the reported compounds are shown in Table 17.

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[110] E. L. Jacobson, R. D. Freeman, A. G. Tharp and A. W. Searcy, *J. Amer. Chem. Soc.* **78** (1956) 4850.

[111] J. Laugier, P. L. Blum and R. de Tournemine, *J. Nucl. Mat.* **41** (1971) 106.

Table 17. Lattice Parameters of the M_3Si_5 Compounds

Compound	Lattice parameter (Å) *a*	Lattice parameter (Å) *c*	Calculated density (g cm^{-3})	Reference
Th_3Si_5	3·986	4·228	7·91	a
U_3Si_5	3·843	4·069		b
Pu_3Si_5	3·875	4·102	9·03	c
	±0·004	±0·007		

[a] A. Brown and J. J. Norreys, *J. Inst. Metals*, **89** (1960) 238.
[b] A. Brown and J. J. Norreys, *Nature*, **191** (1961) 61.
[c] C. C. Land, K. A. Johnson and F. H. Ellinger, *J. Nucl. Mat.* **15** (1965) 23.

MSi_2 compounds. These compounds possess a tetragonal cell (space group *I4/amd*) but in the case of $PuSi_2$ removal of silicon from the compound results in distortion to an orthorhombic cell[112]. In addition to the $ThSi_2$ compound, another with stoichiometry Th_5Si_{11} with the same tetragonal symmetry has been reported[105]. For the Th–Si system there are low-temperature hexagonal forms of Th_5Si_{11} and $ThSi_2$ which are isomorphous with Th_3Si_5. Recent work on the U–Si system has suggested that the low-temperature hexagonal form of USi_2 is in fact a ternary compound $U_6Si_{11}O$[106,113]. The stoichiometry of the uranium disilicide is given as $USi_{1\cdot88}$.

The lattice parameters of these phases are shown in Table 18.

Table 18. Lattice Parameters of the Disilicides

Compound	Lattice parameter (Å) *a*	Lattice parameter (Å) *b*	Lattice parameter (Å) *c*	Calculated density (g cm^{-3})	Reference
Th_5Si_{11}	4·01		13·89	7·89	a
$ThSi_2$	4·126		14·346	7·79	b
$USi_{1\cdot88}$	3·98		13·74	8·98	c
$NpSi_2$	3·96		13·67	9·03	c
$PuSi_{1\cdot82}$	3·988	3·957	13·54		d
$PuSi_{1\cdot86}$	3·978	3·964	13·60		d
$PuSi_{1\cdot94}$	3·973	3·966	13·64		d
$PuSi_2$	3·968		13·71	9·08	d
The low-temperature forms of Th_5Si_{11} and $ThSi_2$—hexagonal lattice[a]					
Th_5Si_{11}	4·013		4·258	7·88	
$ThSi_2$	4·136		4·126	7·78	

[a] A. Brown and J. J. Norreys, *J. Inst. Metals*, **89** (1960) 238.
[b] G. Brauer and A. Mitius, *Z. anorg. Chem.* **249** (1942) 325.
[c] W. H. Zachariasen, *Acta Cryst.* **2** (1949) 94.
[d] C. C. Land, K. A. Johnson and F. H. Ellinger, *J. Nucl. Mat.* **15** (1965) 23.

The only trisilicide reported is that of uranium[114], USi_3 which has the Cu_3Au face-centred cubic structure, with $a = 4\cdot0853$ Å and a theoretical density of 8·298 g cm^{-3}.

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[112] C. C. Land, K. A. Johnson and F. H. Ellinger, *J. Nucl. Mat.* **15** (1965) 23.
[113] P. L. Blum, J. Laugier, J. P. Morlevat and H. Vaugoyeau, *Compt. Rend.* **265** (1967) 1328.

3.4. Thermodynamic data for the actinide silicides

The only thermodynamic data available on these compounds have been obtained from Knudsen vaporization studies on the Th–Si[115] and U–Si[116] systems.

The free energies of formation (ΔG°_f) of the thorium silicides are given in Table 19.

TABLE 19. FREE ENERGIES OF FORMATION (ΔG°_f) OF THE THORIUM SILICIDES[a]

Compound	ΔG°_f (kcal mole^{-1})	Temperature (K)
Th_3Si_2	$-64700 + 3{\cdot}90T$	1800–1960
ThSi	$-29200 + 1{\cdot}21T$	1800–1960
Th_3Si_5	$-110700 + 2{\cdot}88T$	1700–1800
$ThSi_2$	$-39500 + 0{\cdot}58T$	1700–1800

[a] C. B. Alcock, J. B. Cornish and P. Grieveson, *Thermodynamics*, Vol. I, p. 211, IAEA, Vienna (1966).

For the uranium silicides the heats of formation (ΔH°_{f298}) have been determined[117], and are given in Table 20; their free energies of formation are given in Table 21.

TABLE 20. HEATS OF FORMATION (ΔH°_{f298}) OF URANIUM SILICIDES[a]

Compound	ΔH°_{f298} (kcal-g atom^{-1})
U_3Si_2	8·16
USi	9·55
USi_2	10·40
USi_3	7·90

[a] P. Gross, C. Hayman and H. Clayton, *Thermodynamics of Nuclear Materials*, p. 653, IAEA, Vienna (1962).

TABLE 21. FREE ENERGIES OF FORMATION (ΔG°_f) OF URANIUM SILICIDES[a]

Compound	ΔG°_f (kcal mole^{-1})	Temperature (K)
U_3Si_2	$-43050 + 1{\cdot}05T$	1700–1835
USi	$-19980 + 0{\cdot}44T$	1700–1835
U_3Si_5	$-81360 + 2{\cdot}08T$	1700–1835
USi_2	$-29670 + 0{\cdot}87T$	1680–1790
USi_3	$-32360 + 1{\cdot}00T$	1680–1790

[a] C. B. Alcock and P. Grieveson, *J. Inst. Met.* 90 (1962) 302.

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[114] B. R. T. Frost and J. T. Maskrey, *J. Inst. Metals*, **82** (1953) 171.

[115] C. B. Alcock, J. B. Cornish and P. Grieveson, *Thermodynamics*, Vol. I, p. 211, IAEA, Vienna (1966).

[116] C. B. Alcock and P. Grieveson, *J. Inst. Met.* **90** (1962) 302.

[117] P. Gross, C. Hayman and H. Clayton, *Thermodynamics of Nuclear Materials*, p. 653, IAEA, Vienna (1962).

3.5. Physical properties

The microhardnesses of some uranium[118] and plutonium silicides[112] have been determined and are given in Table 22.

TABLE 22. THE MICROHARDNESSES OF SOME ACTINIDE SILICIDES

Compound	Microhardness	Reference
U_3Si	190 ± 5 KHN	a
U_3Si_2	630 ± 30 KHN	a
Pu_5Si_3	350–490 DPH	b
Pu_3Si_2	ca. 660 DPH	b
PuSi	600–1000 DPH	b

[a] D. G. Walker, *J. Nucl. Mat.* **37** (1970) 48.
[b] C. C. Land, K. A. Johnson and F. H. Ellinger, *J. Nucl. Mat.* **15** (1965) 23.

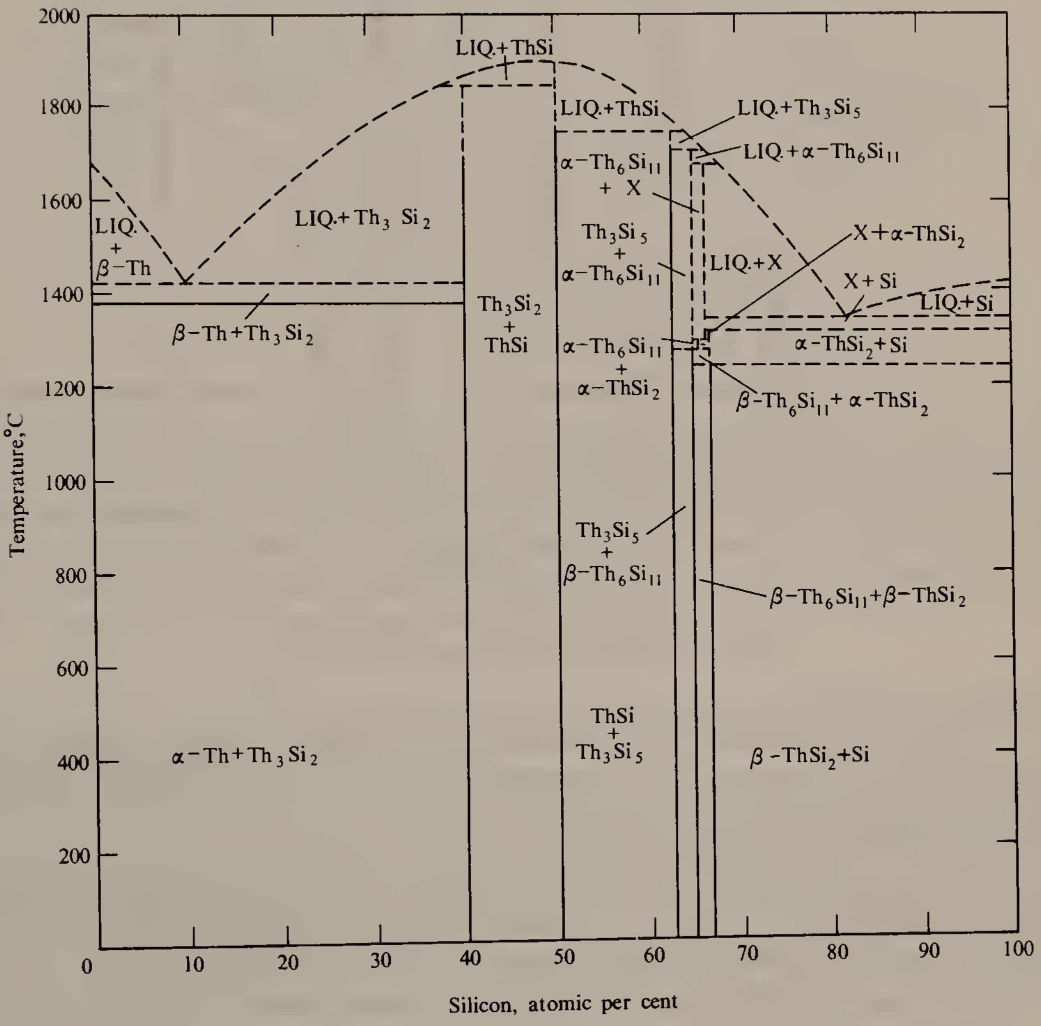

FIG. 16. The thorium–silicon phase diagram (after Brown and Norreys[105]).

3.6. Chemical properties

The thorium silicides are more stable than those of uranium at 1700K by *ca.* 4 kcal at equi-atomic proportions. The greater stability of the thorium compounds is related to the larger heat of sublimation of elemental thorium compared with that of uranium. The plutonium silicides must be less stable than those of uranium. The greater stability of the thorium compounds is reflected in their higher melting points; the melting behaviour of all the thorium, uranium and plutonium silicides can be seen in the phase diagrams shown in Figs. 16, 17, and 18. The only congruent melting compound in the Th–Si system is ThSi, whilst in each of the U–Si and Pu–Si systems there are two congruent melting compositions: U_3Si_2 and U_3Si_5, PuSi and Pu_3Si_5, respectively.

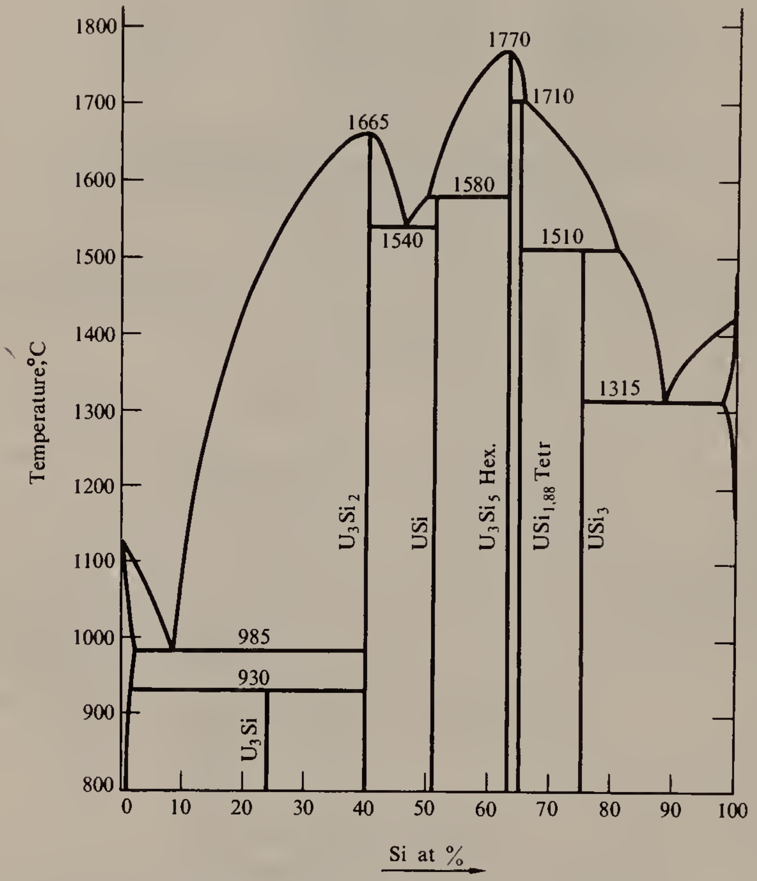

FIG. 17. The uranium–silicon phase diagram (after Vaugoyeau, Lombard and Morlevat[106]).

There are few data available on the corrosion properties of the silicides; by comparison with the carbides they are relatively stable to moist air but thorium silicides[110] are unstable to prolonged standing in moist air, and react in the cold with concentrated HI, HCl, HF or aqua regia, and all the thorium silicides except Th_3Si_2 react with 5 % HCl.

$NpSi_2$ has been reported to react with 6 M HCl, probably with the evolution of silanes.

[118] D. G. Walker, *J. Nucl. Mat.* 37 (1970) 48.

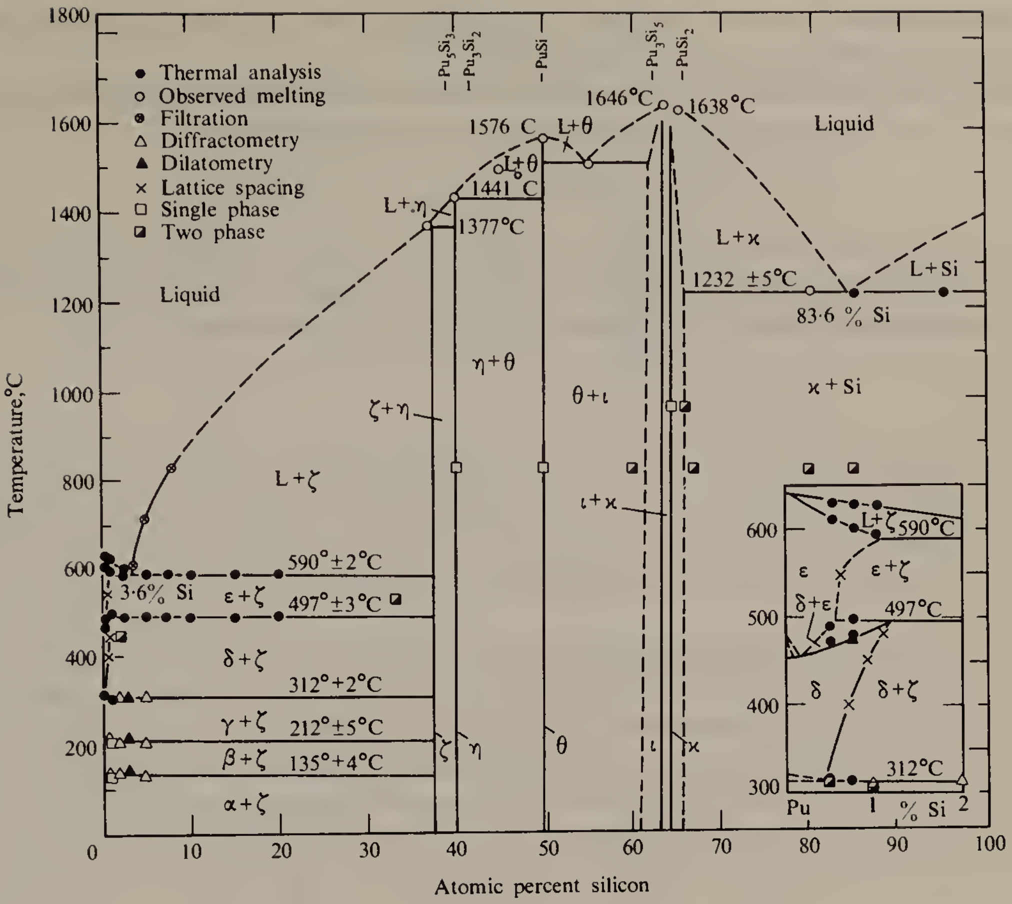

FIG. 18. The plutonium–silicon phase diagram (after Land, Johnson and Ellinger[112]).

3.7. Industrial applications of silicides

The use of U_3Si as an alternative to UO_2 in water-cooled reactors has been considered[119]; the features which allow this are the higher uranium density than UO_2, good aqueous corrosion resistance, and low parasitic neutron absorption. Successful application requires small changes in the length and diameter of a U_3Si fuel element during irradiation up to at least 10,000 MWd/tonne, and consequently much attention has been paid to the swelling of this compound.

3.8. The influence of oxygen and carbon on the phase relationships of the uranium–silicon and plutonium–silicon systems

Some attention has been given to the influence of both oxygen and carbon on the phase relationships of the U–Si and Pu–Si systems, indeed there is enough information available for phase diagrams to be drawn for the U–Si–C and Pu–Si–C systems.

Recent data[106] have shown that orthorhombic "USi" is in fact the ternary compound U_8Si_8O; USi in the absence of oxygen has tetragonal symmetry ($a = 10\cdot61 \pm 0\cdot01$ Å and $c = 24\cdot42 \pm 0\cdot02$ Å, $\rho = 10\cdot093 \pm 0\cdot004$ g cm^{-3})[111].

[119] I. J. Hastings and R. L. Stoute, *J. Nucl. Mat.* 37 (1970) 295.

The compound previously reported[120] to be USi_2 with hexagonal symmetry has been found to be the ternary compound $U_6Si_{11}O$[113].

Studies have been made on the behaviour of the U_3Si phase in the ternary U–Si–C system[121]. A four-phase equilibrium reaction was found at 815 ± 5°C

$$2U_3Si + xUC \rightleftharpoons U_3Si_2C_x + (3 + x)\,U$$

The U_3Si_2 phase dissolves carbon into interstitial positions up to 4 at. %; there can also be a variation in silicon content of 0·9 at. %. The lattice parameters of U_3Si_2 change with the addition of carbon: a decreases by ~0·2 % and c increases by 0·6 %.

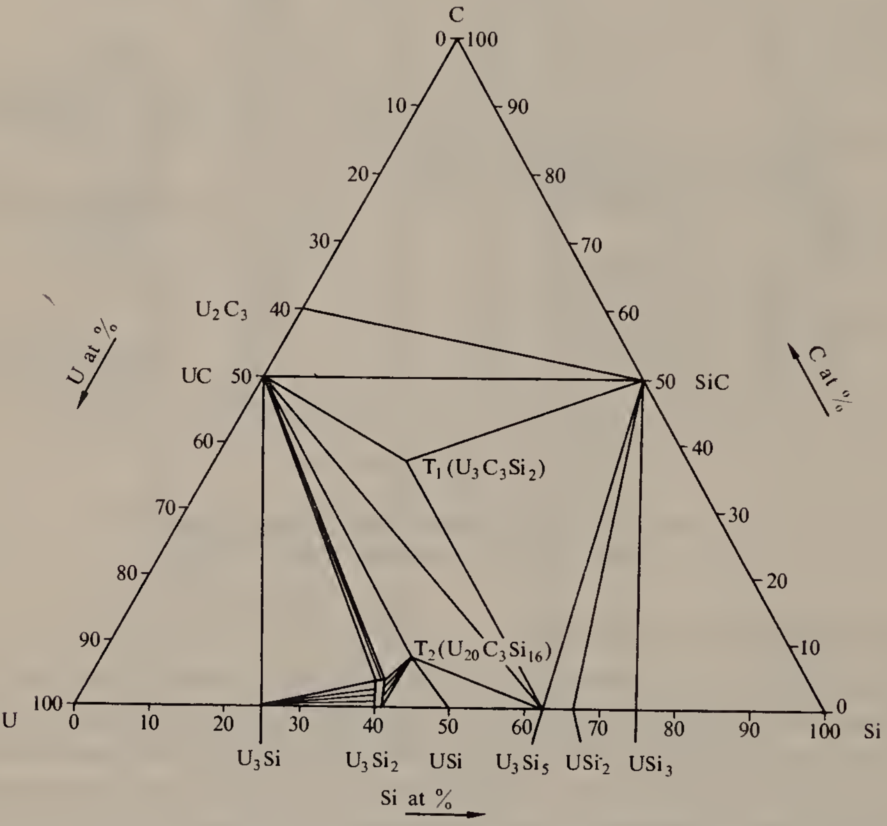

FIG. 19. A section of the U–Si–C system (after Guinet, Vaugoyeau and Blum[122]).

Two ternary compounds in the U–Si–C system have been reported[122,123]. $U_{20}C_3Si_{16}$, with hexagonal symmetry, which decomposes peritectically at *ca.* 1600°C, and $U_3Si_2C_3$, with orthorhombic (*I*/*mmm*) symmetry ($a = 3{\cdot}598$ Å, $b = 3{\cdot}535$ Å, $c = 18{\cdot}96$ Å, $Z = 2$, and density (ρ) = 10·82 g cm^{-3}). A section for the ternary phase diagram U–Si–C is shown in Fig. 19. There are no Pu–Si–C ternary compounds[71].

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[120] A. Brown and J. J. Norreys, *Nature*, **191** (1961) 61.

[121] P. Guinet, H. Vaugoyeau, J. Laugier and P. L. Blum, *J. Nucl. Mat.* **21** (1967) 21.

[122] R. Guinet, H. Vaugoyeau and P. L. Blum, *Compt. Rend.* (C) **262** (1966) 1856.

[123] P. L. Blum, P. Guinet and G. Silvestre, *Compt. Rend.* **260** (1965) 1911.

4. THE BORIDES

The ideal formulae of the known actinide borides are shown in Table 23.

TABLE 23. THE IDEAL FORMULAE OF THE ACTINIDE BORIDES

ThB			PuB	
	UB_2	NpB_2	PuB_2	
ThB_4	UB_4	NpB_4	PuB_4	AmB_4
ThB_6		NpB_6	PuB_6	AmB_6
	UB_{12}	NpB_{12}	PuB_{12}	
ThB_{66}			'PuB_{100}'	

The boron-rich phases are formed most commonly with the actinides and the lanthanides. The borides with greater than 80 at. % are unique and no analogous compounds are found in the carbides, silicides, nitrides, oxides, etc. Those actinide borides that have low vapour pressures and high melting temperatures are in general chemically inert and would be expected to exhibit great hardness.

The strongly bonded two- and three-dimensional frameworks of boron atoms in the boride structures must be the reason for the high stability of these compounds.

The compounds are prepared by melting the elements together, or by sintering powders of the elements together. The metal could also be present as the hydride. The only phase relationships of these systems available are those for the U–B system so that the conditions required for annealing of the alloys prepared by the melting of the elements together cannot be determined.

4.1. Crystal structures

There are parallels between boride phases of the lanthanides and those of the actinides. The existence or non-existence of lanthanide borides is closely correlated with the radii of the metal atoms involved. Dysprosium and holmium, which have radii close to that calculated for plutonium from the unit cell dimensions of PuB_4 and PuB_2, form MB_2, MB_4, MB_6 and MB_{12} type compounds as does plutonium. Uranium and erbium have similar effective radii and both form MB_2, MB_4 and MB_{12} phases. MB_6 phases, however, cannot be prepared with a cation radius comparable to that of erbium.

The effective radius of thorium is large and comparable to that of lanthanum or cerium, and thorium only forms ThB_4 and ThB_6.

Monoborides. The only monoborides reported are those of thorium and plutonium. ThB has only been reported as having a complex structure[124] and its existence seems unlikely as no other monoborides have been reported and further studies[125] have failed to confirm the existence of PuB[126]. It seems likely that the compound reported with the NaCl structure was in fact PuN, which has the same structure and a lattice parameter which is very close (PuN, $a_0 = 4{\cdot}906$ Å, reported "PuB", $a_0 = 4{\cdot}92$ Å). A face-centred cubic phase believed to be a solid solution of thorium boride and ThO_2 has also been reported[127].

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[124] L. H. Anderson and R. Kiessling, *Acta Chem. Scand.* 4 (1950) 163.
[125] H. A. Eick, *Inorg. Chem.* 4 (1966) 1237.
[126] B. J. MacDonald and W. L. Stuart, *Acta Cryst.* 13 (1960) 447.
[127] L. Brewer, D. L. Sawyer, D. H. Templeton and C. H. Dauben, *J. Amer. Ceram. Soc.* 34 (1951) 173.

Diborides. The diborides have been reported for uranium, neptunium and plutonium, and these compounds have the hexagonal AlB_2 ($C32$) type of structure (space group $P6/mmm$). Their lattice parameters are given in Table 24. The variation of lattice parameter with the ratio B:U suggests that UB_2 exists over a range of composition.

TABLE 24. THE LATTICE PARAMETERS OF THE ACTINIDE DIBORIDES

Compound	Lattice parameters (Å)		Reference
	a	c	
UB_2(B rich)	3·1293 ± 3	3·9893 ± 5	a
UB_2(B rich)	3·1314 ± 3	3·9857 ± 5	a
NpB_2	3·165	3·975	b
PuB_2	3·18	3·90	c

[a] B. W. Howlett, *J. Inst. Metals*, **88** (1959–60) 91.

[b] H. A. Eick and R. N. R. Mulford, *J. Inorg. Nuclear Chem.* **31** (1969) 371.

[c] J. McDonald and W. U. Stuart, *Acta Cryst.* **13** (1960) 447.

Borides of the type MB_4. The borides with formula MB_4 which have been identified for thorium, uranium, neptunium, plutonium and americium have a tetragonal (D/c) structure (space group $P4/mbm$) and are isomorphous with CeB_4. The lattice parameters of these phases are given in Table 25.

TABLE 25. LATTICE PARAMETERS OF THE ACTINIDE BORIDES (MB_4)

Compound	Lattice parameters (Å)		Reference
	a	c	
ThB_4	7·256 ± 4	4·113 ± 2	a
UB_4	7·075 ± 4	3·979 ± 2	a
NpB_4	7·0901	3·9938	b
PuB_4	7·1018	4·0028	c
AmB_4	7·105	4·006	b

[a] A. Zalken and D. H. Templeton, *J. Chem. Phys.* **18** (1950) 391; *Acta Cryst.* **6** (1953) 269.

[b] H. A. Eick and R. N. R. Mulford, *J. Inorg. Nuclear Chem.* **31** (1969) 371.

[c] H. A. Eick, *Inorg. Chem.* **4** (1966) 1237.

Borides of the type MB_6. The borides of general formula MB_6 have been found for thorium, neptunium, plutonium and americium; there is apparently no uranium compound in this series. These compounds have a cubic CaB_6 type ($D21$) structure (space group $Pm3m$). The lattice parameters are shown in Table 26.

TABLE 26. LATTICE PARAMETERS OF THE ACTINIDE BORIDES (MB_6)

Compound	Lattice parameter (Å)	Reference
ThB_6	4·1132	a
NpB_6	4·1129	b
PuB_6	4·1134	c
AmB_6	4·1154	b

[a] P. Blum and F. Bertaut, *Acta Cryst.* 7 (1954) 81.

[b] H. A. Eick and R. N. R. Mulford, *J. Inorg. Nucl. Chem.* **31** (1969) 371.

[c] H. A. Eick, *Inorg. Chem.* **4** (1966) 1237.

Borides of the type MB_{12}. The MB_{12} compounds have been reported for uranium, neptunium and plutonium and have a cubic *D*21 type structure (space group *Fm*3*m* or a sub-group), that is the metal atoms and the B_{12} octahedra are arranged in an NaCl type of packing. Each metal atom is adjacent to one cubic face of six B_{12} groups; the face is occupied by four boron atoms and thus each metal atom is surrounded by twenty-four boron atoms[128]. The lattice parameters are shown in Table 27.

TABLE 27. THE LATTICE PARAMETERS OF THE BORIDES —MB_{12}

Compound	Lattice parameter (Å)	Reference
UB_{12}	7·468	a
NpB_{12}	7·478	b
PuB_{12}	7·4843	c

[a] P. Blum and F. Bertaut, *Acta Cryst.* 7 (1954) 81.

[b] H. A. Eick and R. N. R. Mulford, *J. Inorg. Nucl. Chem.* **31** (1969) 371.

[c] H. A. Eick, *Inorg. Chem.* **4** (1966) 1237.

Higher borides. PuB_{100} has a face-centred cubic structure with a lattice parameter, $a = 23 \cdot 43$ Å. Thus it is analogous to the lanthanide B_{66} compounds[129], and should have a formula PuB_{66}; ThB_{66} has also recently been described[130]. The unit cell contains approximately 1584 boron atoms and 24 actinide or lanthanide atoms. The face-centred cubic phase has the space group *Fm*3*c*. Icosahedra made up of thirteen B_{12} icosahedra are the basic units of the structure[131]. The lattice parameter of ThB_{66} is 23·53 Å.

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[128] P. L. Blum and F. Bertaut, *Acta Cryst.* 7 (1954) 81.

[129] K. E. Spear and G. I. Solovyev, *Solid State Chemistry 1972*, p. 597, National Bureau of Standards Special Publication 364.

[130] R. Naslain, J. Etourneau and J. S. Kasper, *J. Solid State Chem.* 3 (1971) 101.

[131] D. W. Oliver and G. G. Brower, GE Report 71-C-162 (1971).

4.2. Thermodynamic properties

Specific Heat

The low-temperature specific heat of ThB_6 has been measured[132] between 2 and 12K using an adiabatic calorimeter. The specific heat is given by

$$C_p = \gamma T + \beta T^3$$

with $\gamma = 4{\cdot}8$ mjoule mole^{-1} K^{-2}, and $\beta = 0{\cdot}3$ mjoule mole^{-1} K^{-4}. The Debye temperature is given as 188K.

The low-temperature specific heat has also been determined by the same technique for UB_2[133] in the temperature range 0·84 to 350K. The C_p below 4·2K is given by

$$C_p = (9{\cdot}40 \pm 0{\cdot}01)T + (3{\cdot}18 \pm 0{\cdot}14) \times 10^{-2}T^3 \text{ mjoule mole}^{-1}\text{K}^{-1}$$

The Debye temperature is 394 ± 17K.

The values for C_p and the entropy ($S°$) at 298·15 are 13·23 ± 0·03 cal K^{-1} mole^{-1} and 13·17 ± 0·03 cal K^{-1} mole^{-1}.

From measurements of the enthalpy by drop calorimetry in the temperature range 600–2300K, together with the C_p data for the low temperature, the relation between C_p and temperature obtained is given by[134]

$$C_p = 13{\cdot}0711 + 16{\cdot}7305 \times 10^{-3}T - 2{\cdot}63522 \times 10^{-4}T^{3/2} - 3{\cdot}08426 \times 10^{5}T^{-2} \text{ cal mole}^{-1}\text{K}^{-1} \text{ (298–2300K)}$$

The Standard Free Energies of Formation of the Borides ($\Delta G°_f$)

The free energies of formation of ThB_4 and ThB_6 have been obtained from measurements using solid e.m.f. cells[135]. The e.m.f. cells used were of the fluoride electrolyte types

$$\text{Th, ThF}_4/\text{CaF}_2/\text{ThF}_4\text{, ThB}_6\text{, B}$$
$$\text{Th, ThF}_4/\text{CaF}_2/\text{ThF}_4\text{, ThB}_6\text{, ThB}_4$$
$$\text{Th, ThF}_4/\text{CaF}_2/\text{ThF}_4\text{, ThB}_4\text{, Th}_\alpha$$

Th_α represents thorium metal containing dissolved boron in equilibrium with ThB_4. In each case, the reaction at the left-hand electrode is

$$\text{Th} = 4\text{e} + \text{Th}^{4+}$$

and at the right-hand electrode the reactions are

$$\text{ThF}_4 + 6\text{B} + 4\text{e} = \text{ThB}_6 + 4\text{F}^-$$
$$\text{ThF}_4 + 2\text{ThB}_6 + 4\text{e} = 3\text{ThB}_4 + 4\text{F}^-$$
$$\text{ThF}_4 + y\text{ThB}_4 + 4\text{e} = (1 + y)\text{Th}_\alpha + 4\text{F}^-.$$

The value of y depends on the solubility of boron in thorium and has not been determined.

In these cells fluoride ions are transported from the right-hand electrode to the left-hand electrode through the solid CaF_2 electrolyte. The free energy for each reaction, $\Delta G°$, is

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[132] J-P. Mercurio, J. Etourneau, R. Naslain and J. Bonnerat, *Compt. Rend.* (B) **268** (1969) 1766.

[133] H. E. Flotow, D. W. Osborne, P. A. G. O'Hare, J. Settle, F. C. Mrazek and W. N. Hubbard, *J. Chem. Phys.* **51** (1969) 583.

[134] D. R. Fredrickson, R. D. Barnes, M. G. Chasanov, R. L. Nutall, R. Kleb and W. N. Hubbard, *High Temp. Sci.* **1** (1969) 373; **2** (1970) 299.

[135] S. Aronson and A. Auskern, *Thermodynamics*, Vol. I, p. 165, IAEA, Vienna (1966).

obtained from the cell e.m.f., *E*, using the standard relationship

$$\Delta G = -nFE$$

where *F* is Faraday's number and *n* the number of equivalents of fluoride ion transferred and has the value of 4.

The thorium borides were prepared by heating mixtures of thorium and boron powders, pressed into the shape of cylinders *in vacuo* at either 1400–1450°C for 2–3 hr or at 1000°C for 300–500 hr.

The values for the standard free energy of formation were for the average temperature of 850°C; there was some irreproducibility and curvature in the e.m.f. temperature relationship which did not enable the calculation of the enthalpy and entropy.

The standard free energies of formation of the uranium borides have been determined[136] using the Knudsen technique to determine vapour pressures, by weight loss and collection techniques and additionally uranium activities were measured by equilibrating gold–uranium alloys with mixtures of two coexisting phases, and from the measured gold pressures the uranium activities were calculated using the previously established activity relationships in the gold–uranium system. The values of the standard free energies of formation of the thorium and uranium borides are shown in Table 28.

TABLE 28. THE FREE ENERGIES OF FORMATION (ΔG°_f) OF THE ACTINIDE BORIDES

$\Delta G^\circ_f = \Delta H^\circ_f - TS^\circ_f$ (cal mole^{-1})

Compound	ΔG°_f	Temperature (K)	Reference
ThB_4	-52000	1123	a
ThB_6	-54040	1123	a
UB_2	$-3660 - 1{\cdot}0T$	1723–1823	b
UB_4	$-60000 + 0{\cdot}6T$	1723–1823	b
UB_{12}	$-10400 - 4{\cdot}6T$	1723–1823	b

[a] S. Aronson and A. Auskern, *Thermodynamics*, p. 165, IAEA, Vienna (1966).

[b] C. B. Alcock and P. Grieveson, *Thermodynamics of Nuclear Materials*, p. 563, IAEA, Vienna (1962).

Heats of Formation and Entropies

The heats of formation and the entropies of uranium borides have been estimated from the measurements of the vapour pressures of uranium and boron over the various phase fields of the binary systems. Recently there has also been a determination of the heat of formation at 298K by fluorine bomb calorimetry. When vapour pressure data are used together with the high-temperature enthalpy increment measurements to calculate the enthalpy of formation the agreement with the direct measurement is very good. The data are shown in Table 29, together with the earlier estimated values for UB_2 and the other uranium borides[137].

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[136] C. B. Alcock and P. Grieveson, *Thermodynamics of Nuclear Materials*, p. 563, IAEA, Vienna (1962).

[137] M. H. Rand and O. Kubaschewski, *The Thermochemical Properties of Uranium Compounds*, p. 49, Oliver & Boyd, London (1965).

TABLE 29. THE HEATS OF FORMATION AND ENTROPY OF THE ACTINIDE BORIDES

Compound	ΔH°_{f298} (kcal mole^{-1})	S°_{298} (cal mole^{-1}K^{-1})	Reference
UB_2	−35·3	15·8	a
	−39·3	13·17	b
UB_4	−58·7	17·0	a
UB_{12}	−103·5	33·4	a

[a] M. H. Rand and O. Kubaschewski, *The Thermochemical Properties of Uranium Compounds*, p. 49, Oliver & Boyd Ltd, London (1965).

[b] H. E. Flotow, D. W. Osborne, P. A. G. O'Hare, J. Settle, F. C. Mrazek and W. N. Hubbard, *J. Chem. Phys.* **51** (1969) 583.

4.3. Thermal behaviour of the borides

The thermal behaviour of americium borides differs markedly from those of plutonium and neptunium[125,138]. AmB_4 during free evaporation in an effusion cell loses americium to form AmB_6. PuB_4 and NpB_4, however, evaporate congruently giving plutonium or neptunium gas and boron gas.

The study[139] of the gaseous equilibria

$$ThB(g) \rightleftharpoons Th(g) + B(g)$$

above Th–B alloys using mass spectrometric effusion techniques at 2804K enabled the determination of the dissociation energy of 70 ± 8 kcal mole^{-1} and a heat of formation (ΔH°_{f298}) of 200 ± 13 kcal mole^{-1}.

The dissociation energy or heat of atomization of UB gas of 76 ± 8 kcal mole^{-1}, and of UB_2 gas of 227 ± 10 kcal mole^{-1} were obtained from the equilibria[140]

$$UB_2(g) + 2(C)g \leftrightharpoons UC_2(g) + 2B(g)$$
$$UB(g) + C(g) \leftrightharpoons UC(g) + B(g)$$

in a similar way as for ThB(g).

The only phase diagram study is that of the U–B system[141] which is shown in Fig. 20. All the uranium borides are shown as melting congruently. The melting points are all in excess of 2300°C whilst those of PuB_4, PuB_6 and PuB_{12} are greater than 2150°C. PuB_4 melts congruently whilst the other plutonium borides melt peritectically. ThB_6 melts at 2195°C[142].

4.4. Ternary systems

The Thorium–Uranium–Boron System

ThB_4 and UB_4 form a continuous solid solution[143]. The lattice parameters of the solid solution deviate only slightly from Vegard's law.

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[138] H. A. Eick and R. N. R. Mulford, *J. Inorg. Nucl. Chem.* **81** (1969) 371.

[139] K. A. Gingerich, *High Temp. Sci.* **1** (1969) 258.

[140] K. A. Gingerich, *J. Chem. Phys.* **53** (1970) 746.

[141] B. W. Howlett, *J. Inst. Met.* **88** (1959) 91, 467.

[142] J. M. Lafferty, *J. Appl. Phys.* **22** (1951) 299.

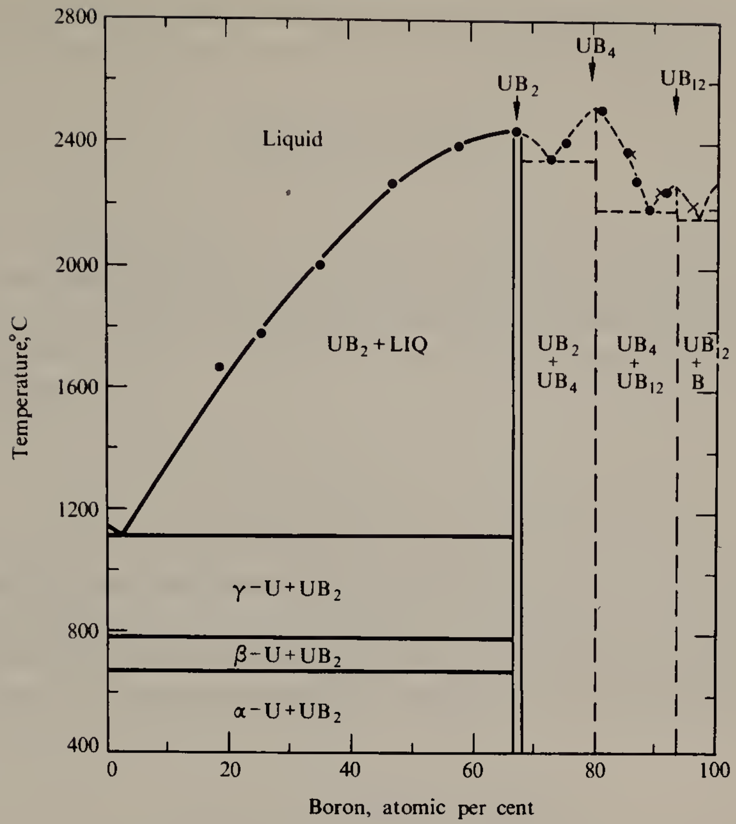

FIG. 20. The uranium–boron phase diagram (after Howlett[141]).

The Thorium–Boron–Carbon System

At least four ternary phases have been found in this system[144], ThB_2C, ThBC, $ThBC_2$ and Th_2BC_2. ThB_2C has hexagonal symmetry with a structure resembling the *C*32 type, and probably exists over a range of composition as the lattice parameters vary with carbon content of the phase; at the carbon-rich boundary $a = 3{\cdot}868$ Å, $c = 3{\cdot}810$ Å; at the low carbon boundary the lattice parameters are smaller, $a = 3{\cdot}860$ Å, $c = 3{\cdot}793$ Å.

[143] L. E. Toth, H. Nowotny, F. Benesovsky and E. Rudy, *Monatsh. Chem.* **92** (1961) 945.
[144] L. E. Toth, F. Benesovsky, H. Nowotny and E. Rudy, *Monatsh. Chem.* **92** (1961) 956.

ORGANOMETALLIC COMPOUNDS, ALKOXIDES, DIALKYLAMIDES, CHELATES AND RELATED COMPLEXES

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Although the actinide alkoxides and alkylamides are not organometallic compounds in that they do not involve metal–carbon bonds, they are discussed, for convenience, following the organometallic complexes. In treating the chelate compounds, carboxylates and salts of mineral acids which behave as bidentate ligands have been omitted and these are described in other sections.

1. ORGANOMETALLIC COMPOUNDS

Actinide organometallic compounds have been known only since 1956. All of the published research to date has been concerned with π-bonded complexes, notably the π-allyl, π-cyclopentadienyl and π-cyclooctatetraenyl compounds, and species in which the carbon is σ-bonded to the actinide metal have not yet been reported. Detailed reviews of both lanthanide and actinide organometallic chemistry covering the literature to 1970 are available[1].

2. ALLYL COMPLEXES

The dark yellow thorium[2] and dark red uranium[3] tetraallyl complexes, $M(C_3H_5)_4$, decompose at room temperature; the thorium compound is stable only below 0°C and the uranium one only below −20°C. The latter yields a mixture of propane (18·5 %) and propylene (81·5 %) above −20°C and is spontaneously inflammable in air. Both compounds are prepared by reaction of the metal tetrahalide with an allyl Grignard in ether at low temperature:

$$MX_4 + 4C_3H_5MgY \rightarrow M(C_3H_5)_4 + 4MgXY$$

The proton nmr spectra of the two compounds[2,4] indicate that both are classical π-allyl complexes.

3. *TRIS*CYCLOPENTADIENYL COMPLEXES

The known *tris*cyclopentadienyl actinide complexes are listed in Table 1. Neither thorium nor protactinium *tris* complexes are known, and it is unlikely that they could be prepared, whereas the absence of any report of the existence of *tris*cyclopentadienyl neptunium most probably indicates the lack of any attempt to prepare the compound.

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[1] (a) H. Gysling and M. Tsutsui, *Adv. Organometallic Chemistry*, **9** (1970) 361. (b) B. Kanellakopulos and K. W. Bagnall, *Int. Rev. Sci.* 7 (1971) 299, Medical and Technical Publ. Co. Ltd., Aylesbury and Butterworths, Ltd., London. (c) R. G. Hayes and J. L. Thomas, *Organometallic Chem. Rev.* **7** (1971) 1.

[2] G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Körner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter and H. Zimmermann, *Angew. Chem.* **78** (1966) 157.

[3] G. Lugli, W. Marconi, A. Mazzei, N. Paladino and U. Pedretti, *Inorg. Chim. Acta*, **3** (1969) 253.

[4] N. Paladino, G. Lugli, U. Pedretti and M. Brunelli, *Chem. Phys. Letters*, **5** (1970) 15.

TABLE 1. *Tris*CYCLOPENTADIENYL COMPLEXES

Compound	Colour	Preparative method	Sublimation* temperature, °C	Reference
$U(C_5H_5)_3$	Bronze	a, b	120–150° (d)†	5
$Pu(C_5H_5)_3$	Moss green	c	140–165	6
$Am(C_5H_5)_3$	Rose‡	c	160–200	7
$Cm(C_5H_5)_3$	Colourless	c (^{248}Cm), d (^{244}Cm)	180	8, 9
$Bk(C_5H_5)_3$	Amber	c	135–165	10
$Cf(C_5H_5)_3$	Ruby red	c	135–220	10

* Sublimation temperatures refer to high vacuum; this usually means about 10^{-5} Torr.
† Only traces sublime and there is a considerable amount of decomposition.
‡ Also described as orange-yellow[11].

Preparative Methods

Four principal methods are used for the preparation of the known compounds. These are:

(a) Reduction of the *tetrakis*cyclopentadienyl complex, used for the preparation of the uranium compound:

$$U + 3U(C_5H_5)_4 \rightarrow 4U(C_5H_5)_3$$

This reaction is conveniently carried out by treating the *tetrakis*uranium complex with potassium in benzene, the elementary uranium so produced being highly reactive and so in a suitable form for the above reduction. More convenient preparative routes are by reaction of the actinide trichloride with:

(b) Potassium cyclopentadienide in benzene[5]:

$$UCl_3 + 3KC_5H_5 \rightarrow U(C_5H_5)_3 + 3KCl$$

This reaction in tetrahydrofuran (THF) yields an adduct, $U(C_5H_5)_3 \cdot THF$.

(c) Molten beryllium dicyclopentadienide[6,7,9,10]:

$$2MCl_3 + 3Be(C_5H_5)_2 \rightarrow 2M(C_5H_5)_3 + 3BeCl_2$$

or

(d) The analogous reaction with magnesium dicyclopentadienide[8].

In methods (c) and (d) the products are isolated and purified by vacuum sublimation; these two methods are particularly useful for the preparation of the *tris* complexes of the more intensely radioactive transuranium elements for which the solution method (b) would be inappropriate because of the radiolysis of the solvent by the α-particles emitted by these

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[5] B. Kanellakopulos, E. O. Fischer, E. Dornberger and F. Baumgärtner, *J. Organomet. Chem.* **24** (1970) 507.

[6] F. Baumgärtner, E. O. Fischer, B. Kanellakopulos and P. Laubereau, *Angew. Chem.* **77** (1965) 866; *Int. Edn.* **4** (1965) 878.

[7] F. Baumgärtner, E. O. Fischer, B. Kanellakopulos and P. Laubereau, *Angew. Chem.* **78** (1966) 112; *Int. Edn.* (1966) 134.

[8] F. Baumgärtner, E. O. Fischer, H. Billich, E. Dornberger, B. Kanellakopulos, W. Roth and L. Steiglitz, *J. Organomet. Chem.* **22** (1970) C17.

[9] P. G. Laubereau and J. H. Burns, *Inorg. Nuclear Chem. Letters*, **6** (1970) 59.

[10] P. G. Laubereau and J. H. Burns, *Inorg. Chem.* **9** (1970) 1091.

[11] R. Pappalardo, W. T. Carnall and P. R. Fields, *J. Chem. Phys.* **51** (1969) 842.

nuclides. In addition, preparative reactions which do not involve inflammable organic solvents are always preferable for glove-box work since the possible explosion hazard is thereby eliminated.

Some *bis*cyclopentadienyl berkelium chloride, $[(C_5H_5)_2BkCl]_2$, is formed along with the *tris* complex in reaction (c); it is less volatile than the latter, subliming at 220–300°C in a vacuum, and can therefore be separated from the *tris* complex by fractional sublimation[12].

Structures

The dimeric *bis*cyclopentadienyl berkelium chloride complex is isostructural[12] with the analogous samarium compound, in which the chlorine atoms of the two formula units act as bridges between the metal atoms. It is also known that $Bk(C_5H_5)_3$ and $Cf(C_5H_5)_3$ are isostructural[9,10] with a number of the *tris*cyclopentadienyl lanthanides, including the samarium compound, the crystal symmetry being orthorhombic (*Pbcm*). The uranium, plutonium, americium and curium compounds should also be isostructural with the samarium compound. The structure of this last consists of two independent, infinite zig-zag chains of $Sm(C_5H_5)_3$ molecules; in each chain the samarium atom is surrounded by the three bonded cyclopentadienyl rings, and a fourth ring from an adjacent molecule is sufficiently close to complete a distorted tetrahedral array of rings about the metal atom. In one of the chains the three bonded rings are almost equidistant from the samarium atom (Sm–ring distance 2·49–2·55 Å), whereas in the other chain there is an appreciable amount of disorder and one of the three rings is displaced by 0·6 Å along the plane of the ring from the position observed for the rings in the first chain[13]. It seems that the Sm–C bond in this compound has about 37 % ionic character; this is in accord with the chemical behaviour of the lanthanide complexes, which react with ferrous chloride to form ferrocene[14]. It is not clear whether the actinide *tris* complexes behave in this manner or not.

Physical and Chemical Properties

Apart from the uranium compound (Table 1), all the *tris*cyclopentadienyl actinide complexes are stable to heat and are appreciably volatile; they are usually soluble in solvents such as benzene or tetrahydrofuran and are all sensitive to air or atmospheric oxygen, but only the uranium and plutonium compounds are pyrophoric in air. The analogous lanthanide compounds appear to be much more stable in this respect.

The *tris*cyclopentadienyl uranium complex, like the lanthanide compounds, exhibits Lewis acid character, readily forming 1:1 complexes[5] with basic ligands such as cyclohexyl*iso*nitrile (red–brown, slightly soluble in benzene), 1-nicotine (black–brown; both nitrogen atoms appear to be bonded to the uranium atom) and tetrahydrofuran (brown). A cyclohexyl*iso*nitrile adduct of *tris*cyclopentadienyl plutonium is also known[15] and the other actinide *tris* complexes should behave in the same manner.

The cyclohexyl*iso*nitrile complexes are particularly interesting, for the C–N band in the infrared spectrum, which appears at 2130 cm^{-1} in the free ligand, is shifted to 2160 cm^{-1} in the uranium complex[5] and to 2190 cm^{-1} in the plutonium one, the latter being much closer to the frequencies reported for the analogous lanthanide complexes[1]. It has been suggested[5] that the M–C bond in the uranium complex has a much more marked σ-donor

[12] P. G. Laubereau, *Inorg. Nuclear Chem. Letters*, 6 (1970) 611.

[13] C.-H. Wong, T.-Y. Lee and Y.-T. Lee, *Acta Cryst.* **25B** (1969) 2580.

[14] L. T. Reynolds and G. Wilkinson, *J. Inorg. Nuclear Chem.* 2 (1956) 246.

[15] R. D. Fischer, P. Laubereau and B. Kanellakopulos, Westdeutsche Chemiedozententagung, Hamburg (1963).

character than that in the corresponding lanthanide complexes, and that there is some back donation from the metal orbitals to the ligand. The extent of this back donation should decrease as the atomic number increases in the actinide series, because of the spatial contraction of the *f*-orbitals with the increasing effective nuclear charge to which they are exposed.

The uv/visible, infrared, ^{1}H–nmr and mass spectra of the *tris* complexes, and of the adducts formed by them, are usually available in the original papers describing the preparation of these complexes. Summaries of these data, and of the magnetic behaviour of these compounds, are given in recent reviews[1b,c]. Fluorescence studies of many of the *tris*cyclopentadienyl lanthanides and of the curium (^{248}Cm) compound have been reported. The latter exhibits a bright red fluorescence when excited with ultraviolet radiation[9] (wavelength 3600 Å); the solid compound using the relatively short-lived isotope, ^{244}Cm, also exhibits this red fluorescence in the dark, the excitation being provided by the α-radiation[8].

4. *TETRAKIS*CYCLOPENTADIENYL COMPLEXES

Actinide complexes of this type are known only for thorium, protactinium, uranium and neptunium (Table 2).

TABLE 2. *Tetrakis*CYCLOPENTADIENYL COMPLEXES

Compound	Colour	Preparative method	Sublimation* or decomposition (d) temperature, °C	Reference
$Th(C_5H_5)_4$	Colourless	a, c	170–290	16, 20
$Pa(C_5H_5)_4$	Orange	b	(d) 220	17
$U(C_5H_5)_4$	Red	a, c	(d) 200–220	18, 20
$Np(C_5H_5)_4$	Brown–red	a	(d) 200–220	19

* High vacuum.

Preparative Methods

The thorium compound, $Th(C_5H_5)_4$, seems to be formed in very poor yield by the reaction of thorium tetrachloride with an excess of sodium cyclopentadienide in tetrahydrofuran[14], a reaction which gives moderate yields[21] in the case of the uranium analogue. More success has been achieved by using methods described for the *tris* complexes, namely:

(a) The reaction of the metal tetrachloride with an excess of potassium cyclopentadienide in benzene under reflux.

(b) Reaction of the metal *pentahalide* (Pa) with beryllium dicyclopentadienide at 65°C, which should be equally applicable to the tetrachlorides, and

(c) Reaction of the metal tetrafluoride with magnesium dicyclopentadienide in a sealed tube at 180–280°C[20], which appears to be the most convenient preparative route of all.

[16] E. O. Fischer and A. Treiber, *Z. Naturforsch.* **17b** (1962) 276.

[17] F. Baumgärtner, E. O. Fischer, B. Kanellakopulos and P. Laubereau, *Angew. Chem.* **81** (1969) 182.

[18] E. O. Fischer and Y. Hristidu, *Z. Naturforsch.* **17b** (1962) 275.

[19] F. Baumgärtner, E. O. Fischer, B. Kanellakopulos and P. Laubereau, *Angew. Chem.* **80** (1968) 661.

[20] A. F. Reid and P. C. Wailes, *Inorg. Chem.* **5** (1966) 1213.

[21] M. L. Anderson and L. R. Crisler, *J. Organomet. Chem.* **17** (1969) 345.

The thorium compound can be purified by vacuum sublimation, but the other compounds decompose when heated and are usually isolated from the reaction products by extraction into n-pentane ($U(C_5H_5)_4$) or benzene (all) after evaporation to dryness (method a) or removal of excess reagent by vacuum sublimation (methods b, c).

Structures

The dipole moment of the uranium compound is zero[18], which supports the view that the four C_5H_5 rings are arranged tetrahedrally about the metal atom. In addition, only one proton signal is observed in the ^{1}H–nmr spectra of these compounds, so that all the ring protons in the complexes must be equivalent. The infrared spectra of the four compounds are almost identical, so that it is reasonable to conclude that the compounds have similar structures[22].

Physical and Chemical Properties

The *tetrakis* complexes are not appreciably volatile and are moderately air-sensitive; they are decomposed by water or acids and are moderately soluble in solvents such as benzene, bromoform, chloroform, dichloromethane, n-pentane and tetrahydrofuran. The uranium compound reacts with halogens (Cl_2, Br_2, I_2) to form the *tris*cyclopentadienyl halide[23] and the other *tetrakis* complexes will presumably react in the same manner. They are reduced to the metals when treated with a suspension of potassium in benzene[23].

Magnetic susceptibility data, ^{1}H–nmr and mass spectra have been reported for most of these compounds; the results have been discussed in the reviews[1b,c].

TABLE 3. *Tris*CYCLOPENTADIENYL ACTINIDE HALIDES

Compound	Colour	Sublimation temperature*, °C	Reference
$Th(C_5H_5)_3F$	Pale yellow	200	24
$Th(C_5H_5)_3Cl$	Colourless	200	25
$Th(C_5H_5)_3Br$	Pale yellow	180	24
$Th(C_5H_5)_3I$	Pale yellow	190	24
$U(C_5H_5)_3F$	Green	170	24
$U(C_5H_5)_3Cl$	Pale brown	120–130	14
$U(C_5H_5)_3Br$	Dark brown	160	26
$U(C_5H_5)_3I$	Brown	170	26
$Np(C_5H_5)_3F$	Green	170	27, 28
$Np(C_5H_5)_3Cl$	Dark brown	100–105	27

* Under high vacuum.

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[22] B. Kanellakopulos, IIIrd Internat. Protactinium Conf., Schloss Elmau, Germany (1969).

[23] B. Kanellakopulos, F. Baumgärtner and E. Dornberger, Unpublished results (according to ref. 1b).

[24] P. Laubereau, Unpublished results (according to ref. 1b).

[25] G. L. ter Haar and M. Dubeck, *Inorg. Chem.* 3 (1964) 1648.

[26] R. D. Fischer, R. von Ammon and B. Kanellakopulos, *J. Organomet. Chem.* **25** (1970) 123.

[27] E. O. Fischer, P. Laubereau, F. Baumgärtner and B. Kanellakopulos, *J. Organomet. Chem.* **5** (1966) 583.

[28] W. T. Carnall, P. R. Fields and R. G. Pappalardo, *Progress in Coord. Chem.* M. Cais (Ed.), p. 411, Elsevier (1968).

5. *TRIS*CYCLOPENTADIENYL HALIDES

The known compounds are listed in Table 3.

Preparative Methods

Apart from $Th(C_5H_5)_3Cl$ and $U(C_5H_5)_3F$, all are prepared from the tetrahalide in the same manner as the *tris* and *tetrakis* complexes, but with the quantity of ionic cyclopentadienide slightly less than that required for the reactions:

$$MX_4 + 3M^IC_5H_5 \rightarrow M(C_5H_5)_3X + 3M^IX$$

and

$$2MX_4 + 3M^{II}(C_5H_5)_2 \rightarrow 2M(C_5H_5)_3X + 3M^{II}X_2$$

*Tris*cyclopentadienyl thorium chloride is obtained[25] by reaction of thorium tetrachloride with a large excess of potassium cyclopentadienide at room temperature in diethyl ether, in which the complex is insoluble. It is purified by vacuum sublimation, like the other *tris*cyclopentadienyl halides. The corresponding uranium fluoride complex, $U(C_5H_5)_3F$, could probably be prepared from uranium tetrafluoride, like the neptunium compound, but so far it has only been obtained by heating the corresponding bromide with sodium fluoride. An alternative method of preparing the two *tris*cyclopentadienyl neptunium halides is by reaction of the corresponding *trihalides* with molten beryllium dicyclopentadienide[27]; the oxidation mechanism is uncertain.

The greenish brown *bis*cyclopentadienyl uranium dichloride, $U(C_5H_5)_2Cl_2$, is also known, prepared by the reaction of uranium tetrachloride with the stoichiometric quantity of $Tl(C_5H_5)$ in dimethoxyethane. The compound is thermally unstable and cannot be sublimed[29].

Structures

*Tris*cyclopentadienyl uranium chloride possesses monoclinic symmetry ($P2_1/n$); the three C_5H_5 rings and the single chlorine atom lie at the apices of a distorted tetrahedron with the uranium atom at the centre[30]. The metal–halogen bond is ionic; the infrared and uv/visible spectra of the chlorides, bromides and iodides are very similar and these presumably have the same structure as the chloride. In contrast, the corresponding fluoride is a fluorine bridged dimer, the bridging fluorine vibration appearing at 466 cm^{-1} in the infrared spectrum[26].

Physical and Chemical Properties

The *tris*cyclopentadienyl halides are appreciably more stable to heat than are the *tetrakis* complexes, but like the latter they are moderately air-sensitive, particularly in solution. They are soluble in a range of organic solvents similar to that given for the *tetrakis* compounds. The halide ion is easily replaceable by other anions and a range of compounds can be prepared by reactions with alkali metal salts in non-aqueous solvents. In this way alkoxides (Th, U) and the *tris*cyclopentadienyl uranium thiocyanate, cyanate and borohydride are readily obtained. Even the hydroxide, $U(C_5H_5)_3OH$, can be prepared by treating the bromide with alkali hydroxide, while the tetrafluoroborate is most conveniently made by reaction of the uranium fluoride with boron trifluoride in benzene. Most of these compounds have well-defined melting points and sublime in a vacuum[1b].

[29] P. Zanella, S. Faleschini, L. Doretti and G. Faraglia, *J. Organomet. Chem.* **26** (1971) 353.
[30] C.-H. Wong, T.-U. Yen and T.-Y. Lee, *Acta Cryst.* **18** (1965) 340.

The uranium fluoride, $U(C_5H_5)_3F$, forms well-defined adducts with some of the *tris*-cyclopentadienyl lanthanides and actinides; the uranium–fluorine stretching vibration appears at lower frequency in these compounds[31], at 432 cm^{-1} in $(C_5H_5)_3UF \cdot Yb(C_5H_5)_3$ and at 423 cm^{-1} in $(C_5H_5)_3UF \cdot U(C_5H_5)_3$.

Fragmentation patterns in the mass spectra of the *tris*cyclopentadienyl halide and *tetrakis* complexes have been investigated[32]; the results indicate that the principal fragments formed from the halides depend on the relative strength of the metal–halogen bond. For example, a C_5H_5 ring is lost from $Th(C_5H_5)_3F$ to give $(C_5H_5)_2FTh^+$ whereas the iodide yields mainly $(C_5H_5)_3Th^+$.

6. CYCLOOCTATETRAENYL COMPLEXES

The four known actinide *bis*cyclooctatetraenyl complexes (Table 4) form an isostructural series. The molecular structure of the uranium compound[33], the crystals of which possess monoclinic symmetry ($P2_1/n$), is a sandwich with the two C_8H_8 rings eclipsed, the symmetry of the molecule being D_{8h}.

Table 4. Actinide Cyclooctatetraenyl Complexes

Compound	Colour	Sublimation temperature, °C	Reference
$Th(C_8H_8)_2$	Bright yellow	160/0·01 Torr	34
$U(C_8H_8)_2$	Green	180/0·03 Torr	35
$Np(C_8H_8)_2$	Yellow–red	—	36
$Pu(C_8H_8)_2$	Cherry red	—	36

Preparation

The complexes are prepared by the reaction of potassium cyclooctatetraenide, $K_2(C_8H_8)$, with the metal tetrachloride (Th[34], U[35], Np[36]) or with a hexachloro-complex[36], $A^I_2MCl_6$ ($M=U$, $A^I=C_5H_5NH^+$; $M=Pu$, $A^I=(C_2H_5)_4N^+$), in dry, oxygen-free tetrahydrofuran below 0°C. The thorium complex is isolated by evaporation of the solvent, whereas the three other complexes are precipitated from tetrahydrofuran solution on the addition of water and subsequently extracted into benzene or toluene. It is probable that the higher actinides will form sandwich complexes of the type $KM(C_8H_8)_2$, analogous to those obtained for the lanthanides[37].

Physical and Chemical Properties

All four of the known complexes are air-sensitive, but only the uranium one inflames on exposure to air. The thorium and uranium compounds sublime when heated in a vacuum, but no data are available for the behaviour of their neptunium and plutonium analogues.

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[31] B. Kanellakopulos, E. Dornberger, R. von Ammon and R. D. Fischer, *Angew. Chem.* **82** (1970) 956.
[32] J. Müller, *Chem. Ber.* **102** (1969) 152.
[33] A. Zalkin and K. N. Raymond, *J. Amer. Chem. Soc.* **91** (1969) 5667.
[34] A. Streitwieser, Jr. and N. Yoshida, *J. Amer. Chem. Soc.* **91** (1969) 7528.
[35] A. Streitwieser, Jr. and U. Müller-Westerhof, *J. Amer. Chem. Soc.* **90** (1968) 7364.
[36] D. G. Karracker, J. A. Stone, E. R. Jones, Jr. and N. Edelstein, *J. Amer. Chem. Soc.* **92** (1970) 4841.
[37] F. Mares, K. Hodgson and A. Streitwieser, Jr., *J. Organomet. Chem.* **24** (1970) C68.

The thorium complex decomposes above 190° and explodes at red heat[34]. The complexes are sparingly soluble in organic solvents and, apart from the thorium compound, are stable to water and to dilute aqueous solutions of alkali. The ^{1}H–nmr spectrum of the thorium compound in solution in dimethyl sulphoxide indicates that an adduct with the solvent is probably formed.

Mass spectrometric, nmr and magnetic susceptibility data have been reported for these compounds[35,36]. The large and positive isomer shift ($+2{\cdot}5$ cm sec^{-1}) observed[36] in the Mössbauer spectrum of $Np(C_8H_8)_2$ at 4·2K suggests that there is a large contribution from the ligand to the metal orbitals. There is probably an unusually high degree of mixing between the 5*f* and 6*d* orbitals in these complexes, for the intensities of the absorption bands in the visible spectra of the uranium, neptunium and plutonium complexes are approximately tenfold greater than those of the bands which result from normal *f–f* transitions in actinide complexes[36].

7. ALKOXIDES, PHENOXIDES AND MERCAPTIDES

Alkoxides have been reported for quadrivalent thorium, uranium, neptunium and plutonium, and for uranium(V) and uranium(VI); the last gives rise to both hexaalkoxides and uranyl dialkoxides (Table 5). Penta- and hexatrialkylsilyloxides, analogous to the corresponding uranium alkoxides, are also known and are included in Table 5. The corresponding aryl species are less well known, and the only examples appear to be a few uranium(IV), uranium(V) and uranyl(VI) compounds, while in the case of the mercaptides only two examples, both uranium(IV) compounds, seem to have been prepared. In addition to these, a variety of alkoxohalides, *tris*cyclopentadienylalkoxides and mixed alkoxide-β-diketone or β-ketoester complexes have been reported in the literature.

Alkoxides and phenoxides

Preparative Methods

In principle, any tetraalkoxide can be prepared by the reaction of the tetrachloride with an alkali metal alkoxide in solution in the parent alcohol[38,41,43,44]:

$$M^{IV}Cl_4 + 4M^IOR \xrightarrow{ROH} M^{IV}(OR_4) + 4M^ICl$$

Alternatives equivalent to this are the reaction of the tetrachloride with the alcohol and potassamide in liquid ammonia[41]:

$$UCl_4 + 4KNH_2 \xrightarrow{NH_3(l)} [U(NH_2)_4] + 4KCl \xrightarrow{4ROH} U(OR)_4 + 4NH_3$$

and treatment of a suspension of the hexachlorometallate(IV) in benzene with the alcohol and an excess of ammonia[44]:

$$(C_5H_5NH)_2PuCl_6 + 4ROH + 4NH_3 \longrightarrow Pu(OR)_4 + 4NH_4Cl + 2C_5H_5NHCl$$

In some cases the yields obtained by the first procedure are rather poor and an alternative route to the more difficultly preparable tetraalkoxides is by alcohol exchange with the tetra *iso*propoxide (Th[38–40], Pu[44]), which can be prepared in good yield, respectively by the first and last of the methods given above. To achieve this exchange, a large excess of the appropriate alcohol is added to the *iso*propoxide and the mixture is heated under reflux. Uranium(IV) methoxide and ethoxide are also obtained by the reaction of the uranium(IV) diethylamide, $U[N(C_2H_5)_2]_4$, in ether with the appropriate alcohol[41].

TABLE 5. ACTINIDE ALKOXIDES, PHENOXIDES[a] AND MERCAPTIDES

Compound type	Colour	Alkyl[b] or aryl group R
$Th(OR)_4$	White solids	R = Me, Et, iPr[38], nBu[39], iBu, secBu[40], nPe, neoPe[39]
$U(OR)_4$	Light green solids	R = Me, Et, tBu[41], C_6H_5, *o*-, *m*-, *p*-C_6H_4Cl, *o*-, *p*-$C_6H_4CH_3$, α, β$C_{10}H_7$[42]
$Np(OR)_4$	Brown solids	R = Me, Et[43]
$Pu(OR)_4$	Green solids	R = iPr, tBu, 3EtPe[44]
$U(OR)_5$	Dark brown liquids[d]	R = Me[45,46], Et[46–48], CF_3CH_2[45], nPr[45,46], iPr[45,48], nBu[45,46], secBu, iBu[45], tBu[45,49b], nPe[46], Pe(7 isomers), tHex(3 isomers), tHept (2 isomers)[49b]
	Brown to orange solids	R = $SiMe_3$, $SiEtMe_2$, $SiEt_2Me$, $SiEt_3$[49a]
$U(OR)_6$	Red liquids or solids	R = Me, Et, nPr[50], iPr[50,51], nBu[50], secBu, tBu[51]
	Orange or red solids	R = $SiMe_3$, $SiEtMe_2$, $SiEt_2Me$, $SiEt_3$[49a]
$UO_2(OR)_2$	Brown or red solids	R = Me[51], Et[51,53], nPr, iBu[51], tBu[53], iPe[51,52], C_6H_5, *p*-C_6H_4Cl, *o*-, *p*-$C_6H_4CH_3$[54c]
$U(SR)_4$	Light green solids	R = Et, nBu[41]

[a] $U(OR)_4$ phenoxides are adducts with 1–2 molecules of ammonia.
[b] Me = CH_3; Et = C_2H_5; Pr = C_3H_7; Bu = C_4H_9; Pe = C_5H_{11}; Hex = C_6H_{13}; Hept = C_7H_{15}.
[c] $UO_2(OR)_2$ phenoxides are adducts with 1-3 molecules of pyridine.
[d] $U(OMe)_5$ and $U(OiPr)_5$ are red and brown solids respectively.

The corresponding tetraphenoxides, $U(OR)_4$, have been prepared[42] by treating uranium tetrachloride in solution in tetrahydrofuran, or suspended in benzene, with the phenol and ammonia:

$$UCl_4 + 4ROH + (n + 4)NH_3 \longrightarrow U(OR)_4 \cdot nNH_3 + 4NH_4Cl$$

The best known uranium pentaalkoxide is the ethoxide; although this can be prepared by treating an ethanolic solution of uranium pentachloride with sodium ethoxide or ammonia, it is best prepared by bromine oxidation of the tetraethoxide in ethanol in the

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[54] H. Funk and K. Andrä, *Z. anorg. allgem. Chem.* **362** (1968) 93.

presence of sodium ethoxide, a reaction which proceeds by way of the bromide alkoxide[47], $U(OC_2H_5)_4Br$. Other uranium pentaalkoxides can be prepared in the same way, but it is generally more efficient to prepare them from the pentaethoxide by alcohol exchange[45,46]; this method is also used to prepare the uranium(V) silyloxides[49]. An alternative preparative method is to treat the compound described as $(C_5H_5NH)_2UOCl_5$, which may be an equimolar mixture of the uranium(IV) and uranyl(VI) chlorometallates, $(C_5H_5NH)_2UCl_6$ and $(C_5H_5NH)_2UO_2Cl_4$, with the alcohol and ammonia in benzene. The primary product was thought to be $UO(OR)_3$, which decomposed to yield $U(OR)_5$ at 140–160°C/0·05 Torr[48], but the reaction may well involve oxidation of $U(OR)_4$ by $UO_2(OR)_2$.

Although protactinium and neptunium pentaalkoxides are unknown, alkoxide halides have been reported for both elements. The phosphine oxide complexes $Pa(OC_2H_5)_2X_3$ (tppo)(X=Cl, white; Br, pale yellow) have been prepared[55] by treating the corresponding pentahalide complex, $PaX_5(tppo)_2$, with hot, anhydrous ethanol and by adding the ligand to an ethanol solution of the pentahalide. Somewhat similar thorium(IV) alkoxohalide complexes with 1,10-phenanthroline (phen) and triphenylphosphine oxide (tppo), $ThCl_3(OC_2H_5)(phen)_2$ and $ThBr_3(OC_2H_5)(tppo)_x$ ($x = 2$ or 3), result from ethanolysis of the tetrahalide in the presence of the ligand[55a]. The white complex salts, $(C_2H_5)_4N[Pa(OC_2H_5)_2X_4]$, where X is again Cl or Br, precipitate when the pentahalides are treated with the corresponding tetraalkylammonium halide in anhydrous ethanol at room temperature. In the case of neptunium, bromine oxidation of $Np(OC_2H_5)_4$ in carbon tetrachloride, in the presence of sodium ethoxide, yields the green compound $Np(OC_2H_5)_4Br$; a dibromocomplex, $Np(OC_2H_5)_3Br_2$, a tan solid, has also been reported[43]. Analogous uranium alkoxide halides, $U(OR)_{5-n}Cl_n$ ($n = 1$, 2 and 3; R = Et, nPr), all of which are green liquids, are obtained by reaction of the pentaalkoxide with hydrogen chloride[56].

Compounds of this type are also formed by treating the pentaalkoxide (R = Et, iPr) with acetyl chloride in dry benzene[57] and the analogous alkoxide bromides are obtained when acetyl bromide is used[58]. They react with alcohols in the presence of ammonia, or with the sodium alkoxide, to yield the pentaalkoxide[56]. Mixed halide species have also been reported[59], $UCl_2Br(OR)_2$ (R = Me, nBu, C_6H_5), prepared, for example, by treating $UCl_2(OBu)_2$ with bromine in tetrahydrofuran. These are said to react with sodium cyclopentadienide in tetrahydrofuran, yielding $U(C_5H_5)_3(OR)_2$, described as volatile green solids.

Uranium hexaethoxide is best prepared[50] by oxidation of the sodium salt derived from the pentaalkoxide, $NaU(OC_2H_5)_6$, with benzoyl peroxide in ethanol; oxidation with lead tetraacetate or bromine is less effective. Other uranium hexaalkoxides can be made in the same way, but alcohol exchange with the ethoxide is more effective[50] and this has been applied also to the preparation of the hexasilyloxides[51].

The analogous uranyl(VI) alkoxides, $UO_2(OR)_2$, are obtained by reaction of uranyl chloride with the lithium[51,52] or sodium[53] alkoxide in the corresponding alcohol and by alcohol exchange with uranyl(VI) methoxide[53]. In some cases (R = iPr, secBu, tBu) this reaction yields $UO(OR)_4 \cdot ROH$ as a result of disproportionation and this yields the hexaalkoxide when heated[51]. The corresponding uranyl(VI) phenoxides are obtained as the

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pyridine adducts by melting the phenol with anhydrous uranyl(VI) chloride and extracting the mixture with pyridine. Analogous dimethylamine adducts are also known[54].

Mixed alkoxides, such as $U(OEt)_2(OtBu)_3$, exist[49b] and it appears that the compound originally reported[45] to be $U(OtBu)_5$ may have been a mixed alkoxide compound of this type[49b]. Solvates, such as $Pu(OiPr)_4 \cdot iPrOH$ (emerald green[44]) and[49b] $U(OtBu)_5 \cdot tBuOH$, as well as pyridine adducts of the type[44] $Pu(OiPr)_4 \cdot C_5H_5N$ and[49b] $U(OR)_5 \cdot C_5H_5N$ have also been recorded.

Physical and Chemical Properties

The uranium tetraalkoxides and tetraphenoxides are very sensitive to atmospheric oxygen, the former yielding some pentaalkoxide. All of the known alkoxides are moisture-sensitive and are very readily hydrolysed. The thorium and uranium tetramethoxides and tetraethoxides do not sublime when heated in a vacuum but decompose above about 300°C. These four compounds are at best very slightly soluble in the parent alcohol or in benzene. In contrast, all the other known tetra-, penta- and hexaalkoxides sublime or distil at quite moderate temperatures under high vacuum, and are readily soluble in the parent alcohols, carbon tetrachloride, benzene and other hydrocarbons. In general, the boiling points, at the same pressure, appear to increase with chain length in the tetraalkoxides.

Most of the hexaalkoxides are rather unstable to heat; for example, although the ethoxide can be distilled at 74–76°C/0·003 Torr, it decomposes[50] at 86°C. The most thermally stable uranium(VI) compounds are the *iso*propoxide[50] and the hexasilyloxides[49a].

The uranium hexaalkoxides are quite powerful oxidants and react with the corresponding tetraalkoxide to form the pentaalkoxide[50], the reverse of the behaviour of the uranium pentahalides, which disproportionate.

The thorium alkoxides are known to be highly associated in benzene solution, the molecular complexity being highest for a normal alkoxide (n-butyl, 6·44; n-pentyl[39], 6·20) and appreciably lower for the branched chain alkoxides (*iso*propyl[38], 3·8; *sec*butyl[40], 4·2; *iso*butyl[40], 4·1; *neo*pentyl[39], 4·01). The molecular complexity of the uranium pentaalkoxides in benzene is much lower, all except the pentamethoxide being dimers; this last may exist as an equilibrium mixture of the dimer and tetramer[46] in benzene. The corresponding silyloxides are also associated, but to a lesser degree. All of the known uranium hexaalkoxides are monomeric in benzene, although the hexa*iso*propoxide shows a very slight tendency to dimerize[51]. The complexity of the phenoxides is uncertain, but it is known that the tetraphenoxides, which are soluble in tetrahydrofuran (THF) and dioxane, but only slightly soluble in benzene and insoluble in other hydrocarbons[42], form adducts with pyridine which are monomeric in THF. Triethylamine adducts are also known and phenoxides derived from $UOCl_2$, $UO(OR)_2 \cdot 4ROH \cdot NH_3$, have also been reported. The uranyl(VI) phenoxides are insoluble in hydrocarbons, carbon tetrachloride and diethyl ether, but are soluble in pyridine[54]. In contrast to the solubility behaviour of the phenoxides, most of the alkoxides are quite soluble in benzene and many of them are also soluble in other hydrocarbons, ether, dioxan and carbon tetrachloride.

Uranium pentaethoxide reacts with sodium, calcium and aluminium ethoxides in ethanol to form the hexaethoxide compounds, respectively $Na[U(OC_2H_5)_6]$, a green crystalline solid, $Ca[U(OC_2H_5)_6]_2$, a sublimable light green solid, and $Al[U(OC_2H_5)_6]_3$, a volatile green liquid[56]. The sodium salt reacts with hydrogen chloride in ethanol to yield very pure uranium pentaethoxide. This last also forms 1:2 adducts with trimethylamine or di-n-propylamine, and a 1:3 adduct with dimethylamine. All three are green liquids which are more volatile than the parent alkoxide[56].

Substitution of ethoxide groups by β-ketoesters and β-diketones has also been reported; uranium pentaethoxide forms the compound $U(OC_2H_5)_3(CF_3COCHCOOC_2H_5)_2$ when treated with ethyl trifluoroacetate, but with an excess of the ligand some of the uranium *tetrakis* β-ketoester complex is formed. In this work[56], ethyl acetoacetate was reported to cause reduction of the pentaethoxide, yielding only the uranium(IV) β-ketoester complex, whereas other work[60], in which the ethoxide was treated with methyl or ethyl acetoacetate (L) in benzene under reflux, indicates that mixed complexes of the type $U(OC_2H_5)_xL_{5-x}$, where $x = 2$, 3 or 4, are formed. These are dark brown liquids or pasty solids which can be distilled under reduced pressure. Somewhat similar compounds are obtained by treating the pentaethoxide with acetylacetone, benzoylacetone[61], and other β-diketones or β-ketoesters[62].

Mercaptides

The only mercaptides known are the uranium(IV) compounds, $U(SR)_4$ (R = Et, nBu), prepared by treating the *tetrakis*diethylamide with the appropriate mercaptan in ether. They are light green solids which decompose when heated; they are moisture-sensitive and are spontaneously inflammable in air[41].

8. ACTINIDE DIALKYLAMIDES

Diethylamides of the type $M(NEt_2)_4$ are known only for thorium and uranium. They are prepared by treating the metal tetrachloride with lithium diethylamide in solvents such as ether, n-hexane, tetrahydrofuran or diethylamine. The thorium compound, a yellow solid which is reported to sublime at 130–140°/0·1 Torr, was obtained in very poor yield by vacuum sublimation of the product of the above reaction[63], but later work indicates that the preparative reaction gives a high yield, subsequent losses being due to thermal decomposition[64]. The Th–N stretching mode appears at 540 cm^{-1} in the infrared spectrum[63].

The corresponding uranium compound[41] melts at 35·5–36·5°C and is obtained in better yield (25–30 %) than the thorium one by vacuum sublimation; it is also formed in the reaction of uranium pentachloride with lithium diethylamide[41]. Analogous uranium compounds are probably formed when uranium tetrachloride is treated with other lithium dialkylamides, $LiNR_2$ (R = Me, iPr, nBu, allyl or piperidine), but no products could be isolated on vacuum sublimation of the residues from these reactions, probably because of thermal decomposition[41].

The diethylamides are soluble in non-polar solvents such as benzene, diethyl ether or petroleum ether, and are very sensitive to oxygen. They are very readily hydrolysed and they react with alcohols or mercaptans, as mentioned earlier, to form alkoxides or mercaptides[41]. They also react, as would be expected, with carbon dioxide, carbon disulphide and carbon diselenide to form the corresponding carbamates by insertion of the reactant molecule into the metal–nitrogen bond[64].

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9. CHELATE COMPLEXES

The β-diketonates and the related β-ketoester compounds are the most extensively investigated group of actinide complexes of this type, primarily because of the possibility of their being sufficiently volatile to be of use in the separation chemistry of these elements. The analogous tropolonates and oxinates have also attracted attention, the latter especially for their use in the analytical chemistry of the actinides, in which cupferron, the ammonium salt of N-nitroso-N-phenyl hydroxylamine, and its derivatives also have possible applications. The remaining chelating ligands that are discussed in this section comprise the dialkyldithiocarbamate, maleonitriledithiolate, xanthate and phthalocyanine complexes; these are examples of sulphur and nitrogen chelates that are rather uncommon in this area of the Periodic Table. The few known Schiff's base complexes are also described. Chelating ligands, such as octamethylpyrophosphoramide, which form neutral complexes with actinide halides and thiocyanates, are not discussed in this section but are included with the parent compounds in the appropriate sections.

10. β-DIKETONE AND β-KETOESTER COMPLEXES

A very large number of uranium(IV) complexes, UL_4, have been prepared[65-66] and the ligands used are listed in Table 6. More complicated variations of this kind of ligand are known, several thorium(IV)[68] and uranyl(VI)[67] complexes of which have been reported, but only a few of these ligands have been applied to the other actinide elements, and the discussion is therefore restricted, for reasons of space, to those ligands for which complexes with more than one actinide element, or more than one oxidation state of a given element, are known. These ligands, and the complexes reported for them, are given in Tables 7 and 8.

Preparative Methods

The general preparative method for all the known actinide compounds of this type consists in treating an aqueous solution of the tri-, tetra- or hexavalent actinide with the ligand and then adjusting the pH of the solution by adding alkali (ammonia, sodium

TABLE 6. URANIUM(IV) COMPLEXES OF β-DIKETONES AND RELATED LIGANDS[65-66], UL_4
LIGANDS, $RCOCH_2COR'$

$R = CH_3$	$R' = H, CH_3, C_2H_5, nC_3H_7, iC_3H_7, nC_4H_9, tC_4H_9, nC_5H_{11}, nC_6H_{13}, C_6H_5, CH_2OC_2H_5, OnC_4H_9$, 2-furyl
$R = CF_3$	$R' = CH_3, CF_3, C_2H_5, nC_3H_7, iC_3H_7, nC_4H_9, iC_4H_9, tC_4H_9, nC_5H_{11}, C_6H_5, OCH_3, OC_2H_5, OnC_4H_9$
$R = C_2H_5$	$R' = C_2H_5$
$R = nC_3H_7$	$R' = nC_3H_7$
$R = C_6H_5$	$R' = H, C_6H_5$, *o*-, *m*-, *p*-$CH_3OC_6H_4$, *o*-, *m*-, *p*-$C_6H_4NO_2$, *m*-, *p*-$C_6H_4NH_2$

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TABLE 7. ACTINIDE(III) and (IV) β-DIKETONE COMPLEXES

(a) Ligands, $RCOCH_2COR'$, nomenclature and abbreviations

$R = CH_3, R' = CH_3$	Acetylacetone; pentane-2,4-dione	(H)*AA
$R = CF_3, R' = CF_3$	Hexafluoroacetylacetone; 1,1,1,5,5,5-hexafluoropentane-2,4-dione	(H)HFAA
$R = C_6H_5, R' = CH_3$	Benzoylacetone; 1-phenyl-butane-1,3-dione	(H)BA
$R = C_6H_5, R' = C_3H_7$	1-phenyl-hexane-1,3-dione	(H)PHD
$R = C_6H_5, R' = CF_3$	Benzoyltrifluoroacetone; 1-phenyl-4,4,4-trifluorobutane-1,3-dione	(H)BTA
$R = C_6H_5, R' = C_6H_5$	Dibenzoylmethane; 1,3-diphenyl-propane-1,3-dione	(H)DBM
$R = CF_3, R' =$ 	Thenoyltrifluoroacetone; 1,1,1-trifluoro-4α-thienyl-butane-2,4-dione	(H)TTA
$R = C(CH_3)_3, R' = C(CH_3)_3$	Dipivaloylmethane; 2,2,6,6-tetramethylheptane-3,5-dione	(H)THD
$R = C(CH_3)_3, R' = C_3F_7$	1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione	(H)FOD

* Acidic proton in parentheses.

(b) Complexes reported for these ligands

$Am(AA)_3 \cdot H_2O$		$Th(AA)_4$	$U(AA)_4$	$Np(AA)_4$	$Pu(AA)_4$
$CsAm(HFAA)_4$	$CsCm(HFAA)_4$		$U(HFAA)_4$		
		$Th(BA)_4$	$U(BA)_4$		$Pu(BA)_4$
		$Th(PHD)_4$	$U(PHD)_4$		
$Am(BTA)_3 \cdot 3H_2O$			$U(BTA)_4$		
$Am(TTA)_3 \cdot 3H_2O$		$Th(TTA)_4$	$U(TTA)_4$	$Np(TTA)_4$†	$Pu(TTA)_4$
$Am(THD)_3$		$Th(THD)_4$	$U(THD)_4$		
		$Th(FOD)_4$	$U(FOD)_4$	$Np(FOD)_4$	

† Identification uncertain.

hydroxide, etc.) until the complex separates from the aqueous phase. The pale rose americium(III) *tris* chelates are prepared in this way using the ligand (HAA[71], HTHD[72]) or its ammonium salt (HBTA, HTTA[71]), the product finally being recrystallized from ethanol. Use of the caesium salt ((H)HFAA) yields yellow, hydrated $CsAm(HFAA)_4 \cdot H_2O$, which

TABLE 8. URANYL(VI) β-DIKETONE COMPLEXES, UO_2L_2

$L = RCOCH_2COR'$

$R = CH_3$, $R' = H$, CH_3[65], CF_3[65a], C_2H_5, iC_3H_7, tC_4H_9, C_6H_5, C_4H_3O (2-furyl)[65]
$R = C_6H_5$, $R' = H$[65], C_6H_5[69]
$R = C(CH_3)_3$, $R' = H$, CF_3[65]
$R = CF_3$, $R' = C_4H_3S$* (thenoyl)[70]

* Dihydrate.

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dehydrates to the pale rose anhydrous compound when recrystallized from 1-butanol; in this case an excess (8:1) of the caesium salt must be used and the mixture is evaporated to half its original volume to promote crystallization[73]; the hydrated curium complex, $CsCm(HFAA)_4 \cdot H_2O$, is obtained in the same way[74].

The white to cream-yellow quadrivalent thorium (HAA[75], HBA[68], HPHD[76], HDBM[68], HTHD, HFOD[78]), green to dark brown uranium (HAA, H(HFAA), HBA[66], HPHD[76], HBTA, HDBM[66], HTHD, HFOD[78]), green neptunium (HFOD[78]) and brown plutonium (HAA[80, 81], HBA[81], HFOD[78]) complexes are made by the general method, but the HTTA complexes (Th, U[77], Np[79], Pu[77]) precipitate from aqueous solutions of the actinide(IV) on addition of the ligand in the absence of alkali. The neptunium *tetrakis*acetylacetonate has been prepared by a variant of the general method in which the complex is formed in an aqueous medium at pH 4·5–5·0 and is then extracted into benzene, from which it is recovered by evaporation of the solvent[82].

The yellow, or orange to red, uranyl(VI) complexes, UO_2L_2 (Table 8), are prepared by adding the ligand to aqueous alcoholic (MeOH, EtOH) solutions of uranyl nitrate[65,70] or acetate[69,83]; in some cases[65] it is necessary to add sodium hydroxide in order to increase the pH of the solution so that the complex precipitates, but addition of ammonia, primary or secondary amines yields β-ketoamine adducts[84], such as $[UO_2(AA)_2 \cdot (O = CMeCH = CMeNH_2)]$.

The only examples of β-diketonates derived from pentavalent actinides are the bright yellow protactinium compound[85], $Pa(AA)_2Cl_3$, formed when an excess of HAA is added to a suspension of protactinium pentachloride in dichloromethane, and the alkoxycompounds discussed earlier (p. 416).

Structures

$Am(THD)_3$ is of monoclinic symmetry (space group $P2_1/c$) and is isomorphous with the corresponding praseodymium and neodymium *tris* chelates; the structure consists of dimeric units in which the metal atom is surrounded by seven oxygen atoms[72]. In $CsAm(HFAA)_4$, which possesses orthorhombic symmetry (*Pbcn*), the americium atom is dodecahedrally coordinated to eight oxygen atoms[73], the symmetry being approximately D_2. The monohydrate is of monoclinic symmetry[72] ($P2_1/c$), as is the analogous curium compound[74], but the coordination geometry is uncertain.

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The thorium[86] and uranium[87,88] *tetrakis*acetylacetonates, $M(AA)_4$, are dimorphic, both forms being of monoclinic symmetry but different space groups ($P2_1/c$ (α) and $C2/c$ (β)). The $\beta \rightarrow \alpha$ transformation in the thorium compound occurs spontaneously at room temperature[86]; the neptunium[82] and plutonium[89] complexes are isostructural with β-$Th(AA)_4$. The molecular geometry in both forms appears to be a slightly distorted square antiprism in the solid, but the nmr spectra[90] for solutions of $U(AA)_4$, and some other uranium(IV) β-diketone complexes, in deuterochloroform indicate that the molecular structure in solution is less symmetrical than the square antiprism (D_2) or triangular-faced dodecahedron (D_{2d}). The latter structure has been assigned to the solid thorium and uranium *tetrakis*dibenzoylmethane complexes, the crystals of which are of orthorhombic symmetry[91] (space group *Pccn*). However, in deuterochloroform solution the nmr spectra indicate that the molecular geometry is an undistorted square antiprism[76]. The nmr spectrum of $U(PHD)_4$ has also been recorded and the results suggest that there is some interaction between the metal *f*-orbitals and the ligand orbitals[76]. Preliminary structural results for $UO_2(AA)_2 \cdot H_2O$ are also available[92].

Physical and Chemical Properties

Very little is known about the americium(III) chelates; three of them (HAA, HBTA, HTTA) decompose to the metal dioxide between 200° and 400°C, and two (HBTA, HTTA) are known to be soluble in ethanol and in chloroform[71]. $Am(THD)_3$ is moderately volatile[72], subliming at 124–135°C/10^{-5} Torr, and it melts at 216–218°C (sealed tube). It is interesting to note that $CsAm(HFAA)_4$ sublimes at 130–140°C/10^{-6} Torr[72] and that the monohydrate also appears to sublime, although it is possible that the reported sublimation behaviour is simply the result of dehydration.

The information available for the uranium(IV) complexes (Table 6) shows that for a series of ligands CH_3COCH_2COR, the melting points of the complexes decrease with the chain length of the group R so that only a few of them ($R = CH_3$, C_2H_5, C_4H_3O, C_6H_5, $CH_2OC_2H_5$) are solids at room temperature, the remainder being liquids. In the analogous complexes derived from the fluorinated ligands, CF_3COCH_2COR, only the complexes in which R is an appreciably longer chain (nC_4H_9, nC_5H_{11}, OnC_4H_9) are liquids at room temperature[66]. These generalizations should be equally applicable to the other actinide(IV) β-diketone or β-ketoester complexes. Nearly all the recorded actinide(IV) compounds can be sublimed in a vacuum, and this procedure is frequently used to purify these compounds. They are all soluble in solvents such as benzene, chloroform, toluene and xylene, and are insoluble, or at most slightly soluble, in water and diethyl ether. $Th(AA)_4$ is reported to form 1:1 adducts with ammonia and aniline[75], but no data for the other actinide *tetrakis*-chelates are available.

The uranyl(VI) β-diketonates (Table 8) have been less extensively investigated than the analogous uranium(IV) compounds, and much of the information about them is concerned with their use in the solvent extraction of uranium.

Uranyl(VI) acetylacetonate, $UO_2(AA)_2$, is dimeric in benzene[93]; anionic species of the

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[86] D. Grdenic and B. Matović, *Acta Cryst.* **12** (1959) 817.
[87] D. Grdenic and B. Matović, *Nature, London*, **182** (1958) 465.
[88] H. Titze, *Acta Chem. Scand.* **24** (1970) 405.
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[90] T. H. Siddall, Tert., and W. E. Stewart, *Chem. Commun.* (1969) 922.
[91] V. L. Wolf and H. Bärnighausen, *Acta Cryst.* **10** (1957) 605; **13** (1960) 778.
[92] K. Dornberger-Schiff and H. Titze, *Acta Chem. Scand.* **23** (1969) 1685.

type $R^+[UO_2(AA)_3]^-$, where R is NH_4, CH_3NH_3 or $C_6H_5NH_3$, have been reported[93], but these are probably β-ketoamine adducts[84] (p. 419). However, $UO_2(DBM)_2$, and the analogous uranyl(VI) *bis*(β-methoxybenzoylmethane) complex, form normal 1:1 adducts with primary aliphatic amines[84] and 1:1 adducts of $UO_2(AA)_2$ with trimethylamine[84], water, acetylacetone and some alcohols[94] are known. Heat of solution measurements on these compounds indicate that the nitrogen donor solvates are more stable thermally than the oxygen donor ones[94]. More recently, 1:1 adducts of $UO_2(AA)_2$, $UO_2(TTA)_2$ and $UO_2(DBM)_2$ with sulphoxides (diphenyl, dibenzyl) have been isolated[95] and $UO_2(TTA)_2$ also forms 1:1 adducts with tri-n-butyl phosphate and tri-n-octyl phosphine oxide[96]. The $UO_2(TTA)_2$ complexes with these sulphoxides are soluble in benzene.

The uranyl(VI) compounds of the more complex β-diketones also form 1:1 adducts with ammonia, diethyl ether and pyridine[69] and the uranyl(VI) acetoacetarylamide complexes crystallize with an additional molecule of ligand. The uranium atom in these 1:1 adducts is presumably 7-coordinate, provided that both the β-diketone groups remain bidentate.

11. TROPOLONE COMPLEXES

Tropolone(HT) is the enolic form of a cyclic α-diketone and behaves in much the same way as the β-diketones as far as complex formation is concerned; the known actinide complexes are listed in Table 9.

Preparation

The *tetrakis* complexes, MT_4(Th, pale yellow[98]; Pa, blue–green[99]; U, orange–brown[98]; Np, reddish-brown[99]; Pu, red–brown[100]), are prepared by treating the actinide(IV) halides in chloroform (Th[97]) or ethanol (Th, U, Np[99]), the acetate in methyl cyanide (U[98]), and the hydrated nitrate in ethanol (Th[98]) or methanol (Pu[100]), with the free ligand. Alternatively, the complexes can be prepared by treating the tetrahalide with the stoichiometric amount of lithium tropolonate in dichloromethane (Pa[99]) and they are also precipitated from aqueous solutions of the actinide(IV) in oxygen-free M perchloric acid on the addition of lithium tropolonate (Th, Pa, U, Np[99]). In the presence of oxygen the reaction with Pa(IV) yields[99] PaT_4ClO_4. The uranium compound can be purified by vacuum sublimation[98] at 340°C, and the plutonium one by recrystallization from N,N-dimethylformamide[100].

TABLE 9. TROPOLONE (2-HYDROXY-2,4,6-CYCLOHEPTATRIEN-1-ONE, HT) COMPLEXES OF THE ACTINIDES

ThT_4[97,98]	PaT_4[99]	UT_4[98]	NpT_4[99]	PuT_4[99,100]
M^IThT_5[98]*	$LiPaT_5$[99]	$LiUT_5$[98]		
	PaT_4X[99]†			PuO_2T_2[100]
	$UO_2T_2 \cdot HT$[102]			$PuO_2T_2 \cdot HT$[100]

* M^I = Li, Na, K. † X = Cl, Br.

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[93] K. Hager, *Z. anorg. Chem.* **162** (1927) 82.

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The anionic compounds of the type $M^IM^{IV}T_5$ are prepared from the *tetrakis*tropolonates either by slurrying them with the alkali metal tropolonate in a mixture of methyl cyanide, water and ethanol (Th[98]) or methanol (U[98]), or by treating them with lithium tropolonate in oxygen-free N,N-dimethylformamide (Th, Pa, U[99]). Protactinium(IV) and uranium(IV) compounds are known for the lithium cation, the smallest alkali metal, whereas lithium, sodium and potassium salts of the larger Th^{4+} can be isolated. Analogous thorium[98, 101] (ThL_4, $NaThL_5$) and uranium[101] $(UL)_4$ complexes of the isomeric isopropyltropolones (HL) are also known.

Tropolonates of the pentavalent actinides have been reported only for protactinium; the neutral *pentakis*tropolonate is not known, but reaction of protactinium pentachloride, pentabromide or oxotribromide with an excess of the ligand in dichloromethane yields the insoluble yellow complexes[99] PaT_4X (X = Cl, Br).

Reddish-orange[102] UO_2T_2 and brown[100] PuO_2T_2 are precipitated on reaction of the stoichiometric quantities of tropolone with uranyl salts in methanol or of aqueous tropolone and methanolic plutonyl(VI) nitrate. With an excess of the ligand the 1:1 adducts MO_2T_2, HT are formed.

Physical and Chemical Properties

ThT_4 is dimorphic and neither form is isostructural with any of the other actinide(IV) tropolonates, but no structural data are available for any of these compounds. Infrared spectral data are available in the references quoted for the preparation of these complexes and nmr, melting point and sublimation data are also available for some of them, notably the isopropyltropolonates[101].

Thorium, protactinium and uranium(IV) tropolonates, but not the neptunium and plutonium compounds, form 1:1 adducts with N,N-dimethylformamide[99], $MT_4 \cdot DMF$, behaviour which parallels the formation of the *pentakis* anionic species, $M^IM^{IV}T_5$. The structure of the thorium complex, $ThT_4 \cdot DMF$, has been determined[101a]. The 9-coordinate, singly capped square antiprismatic arrangement of oxygen atoms about the thorium atom is somewhat unusual in that one of the tropolonate groups spans a slant edge of the cap on the antiprism, with the DMF molecule at a vertex of the square antiprism (overall symmetry C_s), whereas one would have expected the DMF molecule to be sited at the apex of the cap. The yellow thorium and brown uranium complexes with dimethyl sulphoxide, $M^{IV}T_4 \cdot DMSO$, are also known[98,99], but analogous complexes with the other actinide(IV) tropolonates have not been reported. PaT_4Cl also forms a complex of this type, the dark red compound[99], $PaT_4Cl \cdot DMSO$; reaction of the unsolvated chloride with lithium tropolonate in ethanol at 60°C yields only the yellow ethoxide, $PaT_4(OC_2H_5)$, which is moderately soluble in dichloromethane, in contrast to the chloride and bromide, which appear to be insoluble in all types of organic solvent, but are hydrolysed completely by a mixture of aqueous ammonia and acetone[99]. The ethoxide reacts with 4 M perchloric acid in acetone to form the perchlorate, PaT_4ClO_4, and is converted back to the chloride by hydrochloric acid (6 M) in acetone[99]. The chloride and bromide, PaT_4X, are stable to water and in the atmosphere, but not to heat, for PaT_4Cl decomposes above 300°C.

The uranyl[102] and plutonyl[100] tropolonates, MO_2T_2 and $MO_2T_2 \cdot HT$, are soluble in dimethyl sulphoxide and in N,N-dimethylformamide; the uranyl compound is reported to

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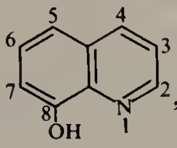
[101] E. L. Muetterties and C. W. Alegranti, *J. Amer. Chem. Soc.* **91** (1969) 4420.
[101a] V. W. Day and J. L. Hoard, *J. Amer. Chem. Soc.* **92** (1970) 3626.

be monomeric in DMSO, whereas $UO_2T_2 \cdot HT$ appears to dissociate in that solvent[102]. Both UO_2T_2 and $UO_2T_2 \cdot HT$ are hygroscopic, but no definite hydrates have been reported. $UO_2T_2 \cdot HT$ loses HT above 155°C and decomposes[102] to UO_2 above 400°C.

12. COMPLEXES WITH 8-HYDROXYQUINOLINE

8-Hydroxyquinoline, 

, and the products obtained by substituting one or more of the ring protons by halide or alkyl groups, are used extensively for the gravimetric determination of thorium(IV) and uranium(VI). Although such usage would be equally applicable to the other actinide elements, it is generally more convenient to determine them radiometrically or spectrophotometrically. *Tris* complexes are known only for plutonium(III) and americium(III); this is because of the ease of oxidation of uranium(III) and neptunium(III) to the quadrivalent state. The best known complexes are the *tetrakis* derivatives of the tetravalent metals and the *bis* complexes of the actinyl(VI) ions. Examples of the ligands and the complexes formed from them are given in Table 10. In addition to the complexes of the ligands listed in this table, complexes of a number of other derivatives have been isolated, namely those of 5-iodo-, 5-iodo-7-chloro- (Th(IV), UO_2^{++}(VI)[108]), 5,7-dibromo- (Th(IV)[108], U(IV)[105], UO_2^{++}(VI)[108]), 3-methyl-, 7-methyl-, 5-nitro-, 5-acetyl-, 5-phenyl-, 7-phenyl-, 7-t-butyl (Th(IV)[109], UO_2^{++}(VI)[110]), and 2,7-dimethyl- (UO_2^{++}(VI)[110]) 8-hydroxyquinoline.

TABLE 10. SOME ACTINIDE COMPLEXES OF 8-HYDROXYQUINOLINE AND ITS DERIVATIVES

Ligand	Complexes			
	ML_3	ML_4*	MO_2L	MO_2L_2
Hox[a]	Pu[103], Am[103]	Th[104], U[105], Np[106], Pu[106]	Np[e], Pu[f]	U[108]
Hmox[b]		Th[108], Np[106]	Np, Pu[g]	U[108]
Hcox[c]	Am[103]	Np[106], Pu[106]	Pu[h]	
Hdcox[d]	Am[103]	Th[108], U[105], Np[106], Pu[106]	Pu[i]	U[108]

* $ThL_4 \cdot HL$ also known; $UL_4 \cdot HL$ well established; UL_4 uncertain.

[a] 8-hydroxyquinoline.

[b] 2-methyl-Hox.

[c] 5-chloro-Hox.

[d] 5,7-dichloro-Hox.

[e] $NpO_2ox \cdot 2H_2O$[107].

[f] $PuO_2ox \cdot (Hox)_2 \cdot xH_2O$[107].

[g] $MO_2mox \cdot Hmox \cdot H_2O$[107].

[h] $PuO_2cox \cdot (Hcox)_2 \cdot H_2O$[107].

[i] $PuO_2dcox \cdot (Hdcox)_2 \cdot 2H_2O$[107].

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[102] D. L. Plymale and W. H. Smith, *J. Inorg. Nuclear Chem.* **30** (1968) 2267.

[103] C. Keller, S. H. Eberle and K. Mosdzelewski, *Radiochim. Acta*, **5** (1966) 185.

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[107] C. Keller and S. H. Eberle, *Radiochim. Acta*, **8** (1967) 65.

[108] G. R. Horton and W. W. Wendlandt, *J. Inorg. Nuclear Chem.* **25** (1963) 241, 247.

[109] J. Abraham and A. Corsini, *Analyt. Chem.* **42** (1970) 1528.

[110] A. Corsini, J. Abraham and M. Thompson, *Chem. Commun.* (1967) 1101.

Preparative Methods

The yellow–green plutonium(III) and americium(III) *tris* complexes, $M(ox)_3$, are precipitated when the ligand is added to an aqueous solution of plutonium(III) under reducing conditions in the absence of oxygen or when an americium(III) solution is added to a solution of the ligand. Dark green $Am(cox)_3$ and green $Am(dcox)_3$ are prepared in the same way as $Am(ox)_3$ but with aqueous dioxane, at about pH 6, as the solvent[103]. The plutonium(III) compound is rapidly oxidized in air. Thorium(IV)[104, 108] and uranium(IV)[105] yield adducts of the type $ML_4 \cdot HL$ when Hox, or its derivatives, are added to an aqueous solution of the tetravalent metal at acidities between pH 5 and pH 8, depending on the ligand. The yellow to orange–red thorium compounds decompose to the unsolvated *tetrakis* complexes when heated in a vacuum[108]; a thermogravimetric study of the analogous uranium(IV) complexes, $UL_4 \cdot HL$, showed that some free ligand sublimed from the heated adduct, and it is probable, but not completely certain, that this procedure yielded some of the unsolvated complex[105] UL_4. The yellow neptunium(IV) and red–brown plutonium(IV) complexes are precipitated free of adducted ligand from aqueous solutions of the tetravalent metal at pH 4·5–4·9(Hox), a difference in behaviour resembling that observed for the tropolonates. The same method is used to prepare the neptunium(IV) and plutonium(IV) complexes derived from substituted 8-hydroxyquinoline, modified by the use of aqueous dioxane instead of water where the ligand is only slightly soluble in the latter (Hcox, Hdcox) or by using a very concentrated solution of the ligand in water (Hmox) in order to avoid hydrolysis[106]. The 5,7-dibromo- and 5-chloro-7-iodo-8-hydroxyquinoline complexes (Np(IV), Pu(IV)) are made in the same way as the Hcox compounds; they are appreciably darker in colour than the latter[106].

Actinide(V) complexes are known only for neptunium and plutonium; yellow $NpO_2(ox) \cdot 2H_2O$, $NpO_2(mox) \cdot H_2O$, green–brown $PuO_2(ox) \cdot (Hox)_2 \cdot xH_2O$ and green $PuO_2(mox) \cdot (Hmox) \cdot H_2O$ are precipitated from aqueous perchlorate (0·1 M) solutions of the actinide(V) at pH 6·5 (Hox) or pH 9 (Hmox) in the presence of the ligand. The green plutonium(V) Hcox and Hdcox chelates are precipitated in a similar manner at pH 5–6 from aqueous dioxane[107]. When an excess of Hox is used, neptunium(V) forms the anionic complex $[NpO_2(ox)_2]^-$ and the yellow–green salt $(C_6H_5)_4AsNpO_2(ox)_2 \cdot H_2O$ is precipitated at pH 10·3–10·4.

The orange to red uranyl(VI) complexes, of the form $UO_2L_2 \cdot HL$, are precipitated when the ligand is added to an aqueous solution of a uranyl salt (acetate, nitrate) at acidities between pH 5 and pH 9, depending on the ligand used. It has been found that whereas 5-substituted 8-hydroxyquinolines yield adducts of this type, the 7-substituted ligands yield the complexes $UO_2L_2 \cdot Y$, where Y is a molecule of the solvent (H_2O, NH_3, $(CH_3)_2CO$) used for the preparation of the complex. The difference in behaviour is due to steric repulsions which make it easy for a relatively small solvent molecule to replace the extra molecule of ligand[110]. The third molecule of ligand is lost when the compounds $UO_2L_2 \cdot HL$ are heated in a vacuum, leaving the *bis* chelates[108], UO_2L_2. Neptunium(VI) and plutonium(VI) analogues of the uranyl(VI) complexes are unknown; the ligands reduce both hexavalent elements to lower oxidation states[107].

Structures

In $[UO_2(ox)_2 \cdot Hox]$, which possesses monoclinic symmetry ($P2_1/n$), two ox groups are bidentate and the third group, from the additional molecule of ligand, is bonded to the uranium by way of the phenolic oxygen atom only. The three ligand groups lie very approximately in a plane normal to the linear O=U=O group, so that the overall coordination geometry is roughly a pentagonal bipyramid. A molecule of solvent (chloroform), from which the complex was crystallized, is also present in the lattice[111]. The corresponding thorium complex, $Th(ox)_4 \cdot Hox$, also appears to have the additional molecule of ligand coordinated to the thorium atom in the same way, the acidic proton being located on the nitrogen atom of the monodentate ligand[109,112].

Physical and Chemical Properties

The majority of the chelates and their adducts are soluble in polar organic solvents, such as chloroform, and uv/visible spectral data are given in most of the references quoted in the preparative section. The thermal decomposition of the adducts $ThL_4 \cdot HL$ and $UO_2L_2 \cdot HL$ to the simple compounds ThL_4 and UO_2L_2, respectively, has been investigated in some detail; heats of dissociation and DTA studies of these systems have been reported[108] and it has been shown by tracer techniques that the dissociation involves intermolecular ligand exchange in the solid phase[113].

The extra molecule of ligand in the adducts is displaced by donor ligands[109]. For example, $Th(ox)_4 \cdot Hox$ yields the orange complex $Th(ox)_4 \cdot 2DMSO$ ($\Delta\nu_{s=o}$, 25 cm^{-1}) in dimethyl sulphoxide[112], while in ethanol $Th(ox)_4 \cdot C_2H_5OH$ is formed and with ethylene diamine(en) in dichloroethane the complex $(Th(ox)_4 \cdot Hox)_2en$ results[108]. This last is probably[109] $(enH_2)^{++}(Th(ox)_5)_2^{-}$. Dark red $UO_2(ox)_2 \cdot DMSO$ is likewise obtained from the adduct $UO_2(ox)_2 \cdot Hox$ in dimethyl sulphoxide and an analogous urea complex is known[116]. The unsolvated uranyl(VI) complex reacts with ethanol in chloroform to yield the ethoxide, $UO_2(ox)(OC_2H_5)$ and $UO_2(ox)_2 \cdot Hox$[114]. A *bis* adduct, $UO_2(ox)_2 \cdot 2Hox$, may also be formed in chloroform solution[114].

Anionic complexes of the type $M^IUO_2(ox)_3$(M^I = Na, $(C_2H_5)_4N$, $(C_6H_5)_4As$) have also been reported[115]. These are orange or red solids. The sodium salt precipitates when Hox in aqueous sodium carbonate solution is added to aqueous uranyl nitrate, and the other two compounds are precipitated when tetraethylammonium bromide or tetraphenylarsonium chloride is added to a solution of uranyl nitrate in alkaline (NaOH) 8-hydroxyquinoline[115]. The tetraethylammonium salt can be recrystallized from methyl*iso*butyl ketone. The red solution obtained when $Th(ox)_4 \cdot Hox$ is dissolved in a concentrated solution of Hox in dichloroethane may contain the ion pair $H_2ox^+[Th(ox)_5]^-$ in which the ligands in the anion may all be bidentate[109] (cf. Tropolone complexes). No structural data are available for the anionic or oxygen donor complexes.

13. N-NITROSO-N-PHENYLHYDROXYLAMINE (CUPFERRON) COMPLEXES

Most of the reported work on actinide cupferron complexes relates either to the solvent extraction of the complexes as a separation procedure or to the gravimetric estimation of the actinide metal concerned. In the latter case the complex serves only as the means of isolating

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[111] D. Hall, A. D. Rae and T. N. Waters, *Acta Cryst.* **22** (1967) 258.
[112] A. Corsini and J. Abraham, *Chem. Commun.* (1968) 856.
[113] A. Corsini and J. Abraham, *Canad. J. Chem.* **47** (1967) 1435.
[114] S. Oki, *Analyt. Chim. Acta*, **44** (1969) 315.
[115] E. P. Bullwinkel and P. Nobel, Jr., *J. Amer. Chem. Soc.* **80** (1958) 2955.

the metal, for it is subsequently ignited to the metal oxide for weighing. Very few of these complexes have been isolated and fully identified; in most cases the only analytical result given is the metal content. *Tetrakis* complexes, ML_4, are known for thorium, uranium (brown) and plutonium (orange yellow), while uranium(VI) forms complexes of the type UO_2L_2 or $M^IUO_2L_3$.

Preparation

The thorium(IV)[117], uranium(IV)[118,119] and plutonium(IV)[120] complexes, ML_4, are precipitated from dilute acid solutions of the actinide(IV) on addition of an excess of the ligand. The uranyl complex does not precipitate from strongly acid solutions, but by mixing a methanol or ethanol solution of uranyl nitrate hexahydrate with cupferron in 50 % aqueous methanol, the orange–yellow ammonium salt, $NH_4UO_2L_3$, results. The corresponding sodium and potassium salts are prepared in the same way, but using the alkali metal cupferrate, and the rubidium or caesium salts are obtained by metathesis of the sodium salt, which is the most soluble in water or aqueous ethanol of this group of salts[121]. N-acetyl- and N-nitrobenzoyl-N-phenylhydroxylamine, and some other ligands of this type, yield orange–yellow to orange precipitates of the uranyl(VI) complexes, UO_2L_2, at moderate pH (e.g. 4·5–5·0)[122]. Plutonium(VI) is reduced by cupferron[120] so that it is not possible to prepare the plutonium analogues of these compounds.

Physical and Chemical Properties

The thorium(IV) and uranyl(VI) complexes can be extracted into chloroform or methyl*iso*butyl ketone[123], and the uranium(IV) complex can be recrystallized from chloroform[118], and is also soluble in diethyl ether. The uranyl (VI) complex, $NH_4UO_2L_3$, possesses cubic symmetry (T^4–$P2_13$) but the full structure has not been determined[121].

14. SCHIFF'S BASE COMPLEXES

Thorium(IV) and uranium(IV) complexes of the type ML_2 have been reported for the Schiff's bases, L, derived from salicylaldehyde and 1-amino-8-naphthol-3,6-disulphonic acid (Th[125]) or ethylenediamine (U[124]); the former is used for the colorimetric determination of thorium. The uranium(IV) complex is obtained by treating uranium tetrachloride in ethanol with the ligand (salen, 2 moles) in the presence of sodium acetate[124] (4 moles). The complexes presumably involve the 8-coordinate metals.

15. N,N-DIALKYLDITHIOCARBAMATE COMPLEXES

Diethyldithiocarbamate (dtc) complexes are the most widely known of this group and the compounds recorded to date are given in Table 11. There is also evidence for the

[116] A. Corsini and J. Abraham, *Canad. J. Chem.* **48** (1970) 2360.
[117] G. E. F. Lundell and H. B. Knowles, *Ind. Eng. Chem.* **12** (1920) 344.
[118] V. Auger, *Compt. Rend.* **170** (1920) 995.
[119] J. A. Holladay and T. R. Cunningham, *Trans. Amer. Electrochem. Soc.* **43** (1923) 329.
[120] I. V. Moiseev, N. N. Borodina and V. T. Tsvetkova, *Zhur. Neorg. Khim.* **6** (1961) 543; *Russ. J. Inorg. Chem.* **6** (1961) 277.
[121] W. S. Horton, *J. Amer. Chem. Soc.* **78** (1956) 897.
[122] N. N. Ghosh, and G. Siddhanta, *J. Ind. Chem. Soc.* **45** (1968) 1049; **46** (1969) 488.
[123] D. Dyrssen and V. Dahlberg, *Acta Chem. Scand.* **7** (1953) 1186.
[124] S. N. Poddar and D. K. Biswas, *Sci. Culture* (*Calcutta*) **34** (1968) 117.
[125] S. N. Poddar and K. Dey, *Indian J. Chem.* **3** (1965) 407.

formation of a purple–brown plutonyl(VI) complex, but its composition is unknown[131]. Uranyl(VI) N,N-dipropyl, N,N-dibutyl, N-ethyl and N-*iso*butyl dithiocarbamates are also known[130].

TABLE 11. ACTINIDE DIETHYLDITHIOCARBAMATE (dtc) COMPLEXES

$M(dtc)_3$	$(Et_4N)M(dtc)_4$	$M(dtc)_4$	$MO_2(dtc)_2$
Pu[126]	Np, Pu[126]	Th, U, Np, Pu[127,128]	U[130]

Preparative Methods

Bright green $Pu(dtc)_3$ is prepared by the reaction of $PuBr_3$ with the stoichiometric quantity of Na(dtc) in anhydrous ethanol, oxygen and water being excluded during the preparation and subsequent working up. Although a dark brown solution of $Np(dtc)_3$ is formed in the analogous reaction with neptunium tribromide, oxidation to $Np(dtc)_4$ occurs even in the absence of oxygen. The corresponding neptunium(III) anionic complex, $(Et_4N)Np(dtc)_4$, a dark green solid, can be isolated from the reaction mixture when tetraethylammonium bromide is present; the bright green plutonium(III) *tetrakis* complex salt is made in the same way. All three compounds can be recrystallized from dichloromethane[126].

The white thorium(IV), golden-yellow uranium(IV), orange–red neptunium(IV) and black plutonium(IV) compounds, $M(dtc)_4$, are prepared by reaction of the tetrachlorides (Th,U,[127,128]Np[127]), the hexachlorometallate(IV), $M^I_2M^{IV}Cl_6$ (M^I = Cs, M^{IV} = Pu[127]; $M^I = Et_4N$, M^{IV} = Th, U, Np, Pu[128]) or $PuCl_4 \cdot 3DMSO$ with the stoichiometric quantity of sodium[127] or lithium[128] diethyldithiocarbamate in ethanol. After vacuum evaporation of the solvent, the residue is extracted with benzene and the product is precipitated with diethyl ether[127] or petroleum ether[128].

The protactinium(V) complexes, $Pa(dtc)_4X$ (X = Cl, Br), are prepared by treating a suspension of the pentahalide in dichloromethane with an excess of sodium diethyldithiocarbamate. The residue left by vacuum evaporation of the filtrate is then recrystallized from a mixture of benzene and ether or of dichloromethane and isopentane[129].

The uranyl(VI) *bis* complexes, UO_2L_2, where L is the N,N-diethyl-, N,N-dipropyl-, N,N-dibutyl-, N-ethyl- or N-*iso*butyldithiocarbamate anion, are red solids, prepared by treating aqueous uranyl nitrate with the sodium dithiocarbamate[130]. They are recrystallized from water. Anionic complexes of composition $M^I\,UO_2(dtc)_3$ (M^I = K, Me_4N[132]) are also red solids, prepared in a similar manner to the *bis* complexes. The tetramethylammonium compound can also be prepared using anhydrous methanol as the solvent[133].

The corresponding uranium(IV) *tetrakis*diethyldiselenocarbamate, an orange solid which melts at 112°C and decomposes in air like the thio compound, is prepared by reaction

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[126] D. Brown, D. G. Holah and C. E. F. Rickard, *J. Chem. Soc.* (A) (1970) 786.
[127] K. W. Bagnall, D. Brown and D. G. Holah, *J. Chem. Soc.* (A) (1968) 1149.
[128] J. P. Bibler and D. G. Karracker, *Inorg. Chem.* **7** (1968) 982.
[129] P. R. Heckley, D. G. Holah and D. Brown, *Canad. J. Chem.* **49** (1971) 1151.
[130] L. Malatesta, *Gazzetta*, **69** (1939) 752.
[131] B. G. Harvey, H. G. Heal, A. G. Maddock and E. L. Rowley, *J. Chem. Soc.* (1947) 1010.
[132] R. A. Zingaro, *J. Amer. Chem. Soc.* **78** (1956) 3568.
[133] K. Bowman and Z. Dori, *Chem. Commun.* (1968) 636.

of uranium tetrachloride with diethylammonium diselenocarbamate in methanol[133a] and by the insertion of carbon diselenide into the uranium–nitrogen bond of uranium tetradiethylamide[64].

Structures

The neptunium and plutonium(III) complexes, $Et_4N\,M(dtc)_4$, are isostructural with the analogous lanthanide compounds; the crystals possess monoclinic symmetry ($P2_1/c$) and the coordination geometry of the eight sulphur atoms surrounding the metal is a distorted dodecahedral array of approximately C_s symmetry. Five sulphur atoms lie at the apices of a planar pentagon with one sulphur atom above and two below this plane. The neptunium atom lies slightly above the plane[134]. The plutonium *tris* complex, $Pu(dtc)_3$ is not, however, isostructural with any of the lanthanide *tris* chelates[134].

The *tetrakis* complexes, $M(dtc)_4$, form an isostructural series; they possess monoclinic symmetry ($C2/c$–$C^6{}_{2h}$) and the structure was originally[135] thought to be a distorted dodecahedral array of eight sulphur atoms about the metal atom, but is now considered to be close to an ideal dodecahedral array[136].

Spectrophotometric data for the anionic uranyl complexes, $M^IUO_2(dtc)_3$, were initially taken to indicate[132] that the compounds might be of the form $UO_2(dtc)_2 \cdot M^I{}_2UO_2(dtc)_4$, but an X-ray structure determination of the tetramethylammonium salt, crystals of which are of orthorhombic symmetry ($Pna2_1$), has shown that the $[UO_2(dtc)_3]^-$ anion is approximately hexagonal bipyramidal. The six sulphur atoms are not, however, coplanar in the hexagon, but are staggered with respect to the plane, and the linear O=U=O group is normal to the hexagon plane[133]. The structures of the triphenylphosphine oxide and triphenylarsine oxide complexes, $UO_2(dtc)_2 \cdot (C_6H_5)_3MO$, both of which possess monoclinic symmetry ($P2_1/c$), are essentially pentagonal bipyramidal, four sulphur atoms and the ligand oxygen atom lying in the plane of the pentagon, to which the O=U=O group is again normal[137].

Physical and Chemical Properties

The actinide(III) complexes ($Pu(dtc)_3$, $Et_4NM(dtc)_4$) are soluble in dichloromethane and in methyl cyanide, but are insoluble in carbon tetrachloride, diethyl ether and in isopentane. $Pu(dtc)_3$ is also insoluble in benzene and in other hydrocarbons, but is soluble in acetone[126]. The corresponding actinide(IV) complexes, $M(dtc)_4$, are soluble in a similar range of solvents and in benzene[127,128]. All of the above compounds are very sensitive to oxygen, particularly in ethanol solution, used as the preparative medium, and are also sensitive to water vapour. The protactinium(V) compounds, $Pa(dtc)_4X$ ($X = Cl, Br$), are also sensitive to water vapour; they are soluble in benzene and in dichloromethane, but are insoluble in diethyl ether or isopentane[129], whereas the uranyl complexes, $[UO_2(dtc)_3]^-$, are soluble in chloroform, alcohols, ethers and ketones, but are not very stable in solution[132].

Proton nmr spectra of the actinide(IV) complexes in $CDCl_3$ or C_6D_6 solution indicate that all the ethyl groups in the thorium and uranium compounds are equivalent[128]. Infrared

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[133a] B. Lorenz, R. Kirmse and E. Hoyer, *Z. anorg. allgem. Chem.* **378** (1970) 144.
[134] D. Brown, D. G. Holah and C. E. F. Rickard, *J. Chem. Soc.* (A) (1970) 786.
[135] D. Brown, D. G. Holah and C. E. F. Rickard, *J. Chem. Soc.* (A) (1970) 423.
[136] D. Brown, D. G. Holah, C. E. F. Rickard and P. T. Moseley, Report AERE-R-6907 (1971).
[137] G. Bombieri, A. Cassol, R. Graziani and E. Forsellini, *Acta Cryst.* **A25** (1969) S168.

and uv/visible spectra of the known complexes are reported in the papers referred to in the preparative section.

16. MALEONITRILEDITHIOLATE (MNT) COMPLEXES

The only actinide compounds known are the anionic uranyl(VI) chelates, $(R_4N)_2UO_2(mnt)_2$, where R is Et or nPr. These are black, crystalline solids, prepared from uranyl nitrate, Na_2mnt and the tetraalkylammonium bromide in aqueous solution. The corresponding *iso*mnt complexes are also known. All four complexes are soluble in acetone, methyl cyanide, nitromethane and pyridine; they are very soluble in ethanol, but insoluble in ether, hydrocarbons or water, and are decomposed by acids or bases. Their infrared and uv/visible spectra have been reported[138].

17. ALKYL XANTHATE COMPLEXES

The attempted preparation of actinide(IV) ethyl xanthate ($[EtOCS_2]^-$) complexes by reaction of the tetrachloride with potassium ethyl xanthate in ethanol, methyl cyanide, acetone or chloroform did not yield any identifiable products[127], but the red–orange uranyl complexes, $UO_2(ROCS_2)_2$ (R = methyl, ethyl, n- and *iso*propyl, n- and *iso*butyl, *iso*amyl and cyclohexyl), have been isolated in poor yield from concentrated aqueous solutions of uranyl nitrate and the potassium alkyl xanthate. They are very readily hydrolysed and are much less stable with respect to decomposition than are the corresponding N,N-dialkyldithiocarbamates[139]. Very little is known about these compounds.

18. PHTHALOCYANINE (Pc) COMPLEXES

Thorium[140], protactinium[141] and uranium[140] complexes of composition MPc_2 are obtained by reaction of the actinide tetraiodide with phthalodinitrile at 240°C. After extracting the excess nitrile with benzene, the product is sublimed at 550°C/10^{-5} Torr from the residue to yield the dark violet complex. The analogous reaction of the dinitrile with the actinide tetrachloride yields a complex of the chlorinated phthalocyanine[140]. Trace scale evidence for the formation of the neptunium complex, $^{239}NpPc_2$, has also been obtained; the complex is formed by the β-decay of ^{239}U in the neutron-irradiated UPc_2 complex and by synthesis from neutron irradiated uranium metal, which is converted to the tetraiodide and then reacted with phthalodinitrile in 1-chloronaphthalene[142], a reaction which suggests that trace amounts of the unknown $^{239}NpI_4$ may be formed in a UI_4 matrix.

The thorium and uranium compounds are stable to air and to heat; they are appreciably soluble in pyridine, quinoline, hexamethylphosphoramide, 1,2,4-trichlorobenzene and 1-chloronaphthalene, but are difficultly soluble in benzene and in tetrahydrofuran. Infrared spectroscopic data for the thorium, protactinium and uranium compounds are available[140–141].

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[138] L. Zimmer and K. H. Lieser, *Inorg. Nuclear Chem. Letters*, **7** (1971) 563.

[139] L. Malatesta, *Gazzetta*, **69** (1939) 408.

[140] F. Lux, D. Dempf and D. Graw, *Angew. Chem., Int. Ed. Eng.* **7** (1968) 819.

[141] F. Lux, D. Brown, D. Dempf, R. D. Fischer and W. Hagenberg, *Angew. Chem., Int. Ed. Eng.* **8** (1969) 894.

[142] F. Lux, F. Ammentorp-Schmidt, D. Dempf, D. Graw and W. Hagenberg, *Radiochim. Acta*, **14** (1970) 57.

Structure

The uranium complex, UPc_2, is of monoclinic symmetry ($C2/c$) and the metal atom is coordinated to the eight nitrogen atoms of the two Pc groups. These are rotated by about 37° from a prismatic configuration about the uranium atom, so that the geometry with respect to the nitrogen atoms deviates by about 8° from that of a square antiprism. The Pc groups are not planar but are saucer shaped with the four nitrogen atoms at the base of the saucer[143].

Note added in proof

Subsequent work[144] has shown that weighable amounts of $^{237}NpPc_2$ and $^{241}AmPc_2$ can be prepared by reaction of the actinide *triiodides* with phthalodinitrile in 1-chloronaphthalene at 200°C.

[143] A. Gieren and W. Hoppe, *Chem. Commun.* (1971) 413.

[144] W. Hangenberg, R. Gradl and F. Lux, GDCh-Hauptversammlung, GDCh-Fachgruppe, *Kern-, Radio- und Strahlenchemie*, Karlsruhe (1971).

SALTS OF CARBOXYLIC ACIDS AND HEXACYANOFERRATES

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This section is concerned essentially with the preparation of solid compounds and the properties of the compounds. Some appropriate data on complex formation equilibria in solution are also provided.

Actinide chemistry is characterized by the similarity in behaviour of ions of the same valence state. This holds especially for the properties of compounds in the solid state, the differences developing slowly with the change in atomic number. The compounds, therefore, are treated separately for each valence state.

There is an immense unequality in the amount of information available for the individual actinides, decreasing in the order $U \gg Th > Pu > Np > Am > Cm >$ others. Solid carboxylates are known for Th(IV), U(IV), U(VI), Np(IV), Np(V), Np(VI), Pu (all valence states), Am(III), Am(VI) and Cm(III). Although numerous compounds have now been characterized, the structures of very few of them have been determined and this is one area to which some attention should be given in the future. The same holds for thermodynamic data (ΔH, ΔS etc.).

1. TRIVALENT ACTINIDE IONS

Trivalent actinides have only a small tendency to hydrolyse and, therefore, neutral salts of strong and weak acids can be prepared from aqueous solution without difficulty. The carboxylates of the trivalent actinides are, in general, similar to those of the trivalent lanthanides. Analogous compounds are formed within the homologous series of actinide(III) cations and there is an almost continuous variation of their properties. One exception is the behaviour towards oxygen: compounds of Np(III) and Pu(III) are relatively easily oxidized, especially in solution, whilst Am(III) does not react with oxygen at all. As might be expected for the large actinide(III) ions the structures of the carboxylates and the other organic compounds involve coordination numbers of at least eight for the central atom.

Only a few carboxylic acid salts of trivalent actinides have been isolated in the solid form. This contrasts with the many investigations reported on the solution chemistry[1].

Formic acid

Pink $Am(HCOO)_3$ is obtained by dissolution of $Am(OH)_3$ in formic acid followed by evaporation of the solution. It has a hexagonal unit cell (Table 1) and a powder pattern very similar to that of $Gd(HCOO)_3$. The volumes of the unit cells of the compounds ($Am(HCOO)_3$: 392·3 Å^3) differ by less than 1 %. The thermal decomposition proceeds in three steps with the formation of a basic formate and a basic carbonate as intermediates[2]:

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[1] S. H. Eberle, KFK-1136 (1970).
[2] F. Weigel and N. ter Meer, *Z. Naturf.* **26B** (1971) 504.

$$\begin{tikzcd}
Am(HCOO)_3 \arrow[d, "300\text{–}350°C"] \\
AmO(HCOO) \arrow[d, "400\text{–}500°C"] \\
Am_2O_2CO_3 \arrow[d, ">520°C"] \\
Am_2O_3
\end{tikzcd}$$

Acetic acid

No solid compounds of the trivalent actinide ions have been prepared. In solution, complexes with up to five acetate anions per metal atom are known.

Thermodynamic data (Table 2) show the acetates to be inner sphere complexes. Both the enthalpy and entropy values are larger for the actinides than for the lanthanides, reflecting a greater degree of dehydration of the former upon acetate formation.

Oxalic acid

Ac(III), Pu(III), Am(III) and Cm(III) form salts of the composition $M_2(C_2O_4)_3 \cdot xH_2O$, the degree of hydration depending on the conditions of preparation. With Pu, Am and Cm at room temperature decahydrates form and at higher temperatures, or by drying *in vacuo*, lower hydrates are obtained. The water content of the actinium compound has not yet been determined[3]. The compounds precipitate on addition of a solution of oxalic acid, or of an alkali metal oxalate, to a slightly acidic solution of the cation. They dissolve in solutions of alkali metal or ammonium oxalate to a final concentration of about 0·01 M, forming complex anions of general formula $M(C_2O_4)_x^{(2x-3)-}$. For M = Pu(III) and Am(III) species with $x = 1$, 2 and 3, and for M = Ac and M = Cm species with $x = 1$ and 2, respectively, have been identified in these solutions (Table 3).

The solubility of the transuranium oxalates in dilute mineral acid ($\simeq$0·1 M) is at a minimum at approximately 0·1 M oxalic acid and rises with increasing pH (increasing oxalate ion concentration). Data on the solubility and the complexation of actinium and the trivalent actinides in oxalate solutions are provided in Table 3. Precipitation of the oxalate is the method commonly employed to isolate americium and curium in gram amounts from solutions.

All the known actinide oxalates decompose under the action of their own α-radiation. Pu(III) oxalate decomposes at a rate of *ca.* 0·4 % per 100 days, and Am(III) oxalate at several percent per day; the residue is Am carbonate $Am_2(CO_3)_3 \cdot 5H_2O$. The light green ^{244}Cm compound is converted to a carbonate species a few hours after removal from the precipitation solution.

The thermal degradation of the decahydrates proceeds stepwise. At about 50°C, $Pu_2(C_2O_4)_3 \cdot 9H_2O$, $Am_2(C_2O_4)_3 \cdot 6H_2O$ and possibly $Cm_2(C_2O_4)_3 \cdot 3H_2O$ are obtained[2,5,6].

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[3] D. Butterfield and R. Wollat, *J. Inorg. Nucl. Chem.* 30 (1968) 801.

[4] G. S. Rao, M. S. Subramanian and G. A. Welch, *J. Inorg. Nucl. Chem.* 25 (1963) 1293.

[5] V. Scherer and M. Fochler, *J. Inorg. Nucl. Chem.* 30 (1970) 1433.

[6] O. Y. Zvyagintsev and B. N. Sudarikov, *Russ. J. Inorg. Chem.* 3 (1958) 217.

TABLE 1. CRYSTALLOGRAPHIC DATA FOR CARBOXYLIC ACID COMPLEXES OF TRIVALENT AND TETRAVALENT ACTINIDE IONS

Compound	Symmetry	Space group	Lattice parameters				Z	Density (g/cm³)	Ref.
			a(Å)	b(Å)	c(Å)	Angles			
$Am(HCOO)_3$	Hexagonal		10·55		4·07				a
$Pu_2(C_2O_4)_3 \cdot 10H_2O$	Monoclinic	$P2_1/m$	11·595	9·599	10·171	$\beta = 118{\cdot}94°$			b
$Am_2(C_2O_4)_3 \cdot 10H_2O$	Monoclinic		11·19	9·63	10·24	$\beta = 114{\cdot}4°$	2	3·06 (calc)	a
$Th(HCOO)_4 \cdot 3H_2O$	Monoclinic	$P2_1/m$	6·77	8·81	9·61	$\beta = 109{\cdot}25°$	2	2·86 (obs)	c
$Th(HCOO)_4$	Orthorhombic	$Pmn2_1$?	6·78	7·32	16·92		4	3·1 (obs)	c
$Th(CH_3COO)_4$	Monoclinic	$C2/c$	17·829	8·285	8·388	$\beta = 105{\cdot}42°$	4	2·52 (obs)	d
$U(CH_3COO)_4$	Monoclinic	$C2/c$	17·645	8·192	8·267	$\beta = 105{\cdot}35°$	4	2·62 (obs)	d
$Th(C_2O_4)_2 \cdot 6H_2O$	Tetragonal		6·51		7·90		1	2·51 (obs)	e
$U(C_2O_4)_2 \cdot 6H_2O$	Triclinic		6·388	6·388	7·881	$\alpha, \beta = 91{\cdot}64°$ $\gamma = 89{\cdot}45°$		2·58 (obs)	f
$Pu(C_2O_4)_2 \cdot 6H_2O$	Triclinic		6·377	6·377	7·931	$\alpha, \beta = 91{\cdot}74$ $\gamma = 89{\cdot}26$			f
$Th(C_2O_4)_2 \cdot 2H_2O$	Orthorhombic		10·504	9·735	8·506		4	3·31 (obs)	f, e
$U(C_2O_4)_2 \cdot 2H_2O$	Orthorhombic		10·479	9·443	8·572		4	3·10 (obs)	f, e
$Pu(C_2O_4)_2 \cdot 2H_2O$	Orthorhombic		10·527	10·527	8·861				f
$Th(C_2O_4)_2 \cdot H_2O$	Orthorhombic		9·90	9·52	8·71				e
$U(C_2O_4)_2 \cdot H_2O$	Orthorhombic		8·71	10·80	8·46				e
$Th(C_2O_4)_2$	Orthorhombic		9·65	10·55	8·43		4	3·14 (obs)	e
$K_4[Th(C_2O_4)_4] \cdot 4H_2O$	Triclinic	$P\bar{1}$	9·562	13·087	10·387	$\alpha = 115{\cdot}75°$ $\beta = 80{\cdot}90°$ $\gamma = 112{\cdot}66°$	2	2·48 (obs)	g

[a] F. Weigel and N. ter Meer, *Inorg. Nucl. Chem. Lett.* **3** (1967) 403.

[b] I. L. Jenkins, F. H. Moore and E. M. Waterman, *J. Inorg. Nucl. Chem.* **27** (1965) 77.

[c] M. Chevreton, B. Claudel and B. Mentzen, *J. Chim. Phys.* **65** (1968) 890.

[d] R. Bressat, B. Claudel, G. Giorgio and B. Mentzen, *J. Chim. Phys.* **65** (1968) 1615.

[e] R. Bressat, B. Claudel and Y. Trambouze, *J. Chim. Phys.* **60** (1963) 1265.

[f] I. L. Jenkins, F. H. Moore and M. J. Waterman, *J. Inorg. Nucl. Chem.* **27** (1965) 81.

[g] M. N. Akhtar and A. J. Smith, *Chem. Comm.* D (1969) 705.

A number of lower hydrates are formed at increasing temperatures, the anhydrous oxalates being obtained at about 300°C. These decompose in air between 350°C and 500°C to form the dioxides and in an inert gas to form the actinide(III) oxide. The formation of carbonates, $M_2(CO_3)_3$ or $M_2O_2CO_3$, as intermediates during the final stages of such decompositions is reported for all solid actinide(III) oxalates. Actinium oxalate is difficult to calcinate; even at 1340°C only a basic carbonate $(AcO_2)CO_3$ is obtained[3,4].

The oxalate decahydrates of Pu(III) and Am(III) possess monoclinic symmetry (Table 1), being isomorphous with those of Nd(III) and Sm(III).

TABLE 2. THERMODYNAMIC DATA FOR ACTINIDE(III)-COMPLEXES

	log K	ΔG_0 (kcal/mole)	ΔH_0 (kcal/mole)	ΔS_0 (eu)	Ionic strength	Temp. (°C)	Ref.
Acetic acid							
$Am(CH_3COO)^{2+}\cdot aq$	1·95	−2·68	4·3	23·4	2	25	a
$Cm(CH_3COO)^{2+}\cdot aq$	2·03	−2·79	4·3	23·8	2	25	a
$Bk(CH_3COO)^{2+}\cdot aq$	2·03	−2·79	4·4	24·1	2	25	a
$Cf(CH_3COO)^{2+}\cdot aq$	2·12	−2·88	3·8	22·4	2	25	a
Oxalic acid							
$Pu(C_2O_4)^+$		−12·66	1·3	46·8			b
$Pu(C_2O_4)_2^-$		−12·77	1·2	46·9			
$Pu(C_2O_4)_3^{3-}$		−13·49	1·3	49·6			
Aminoacetic acid							
$Am(CH_2NH_2COOH)^{3+}\cdot aq$	0·69	−0·93	2·9	13	2	25	c
$Cm(CH_2NH_2COOH)^{3+}\cdot aq$	0·81	−1·12	3·3	15	2	25	
Iminodiacetic acid							
$Am(C_4H_5NO_4)^+\cdot aq$	6·93		6·9	13·1	0·1		d
Ethylenediaminetetraacetic acid							
$Pu(C_{10}H_{12}O_8N_2)^-\cdot aq$	18·07	−24·65	−4·23	68·6	0·1	25	e
$Am(C_{10}H_{12}O_8N_2)^-\cdot aq$	18·16	−24·78	−4·67	67·5	0·1	25	

[a] G. R. Choppin and J. K. Schneider, *J. Inorg. Nucl. Chem.* **32** (1970) 3283.
[b] A. D. Gelman, N. N. Matorina and A. I. Moskvin, *Dokl. Akad. Nauk SSSR*, **117** (1957) 88.
[c] S. P. Tamm and G. R. Choppin, *Inorg. Chem.* **7** (1968) 2046.
[d] J. T. Bell, R. D. Baybarz and D. M. Helton, *J. Inorg. Nucl. Chem.* **33** (1971) 3077.
[e] J. Fuger and B. B. Cunningham, *J. Inorg. Nucl. Chem.* **27** (1965) 1079.

Salicylic acid

Addition of a salicylic acid solution to a solution of Pu(III) containing sulfur dioxide or rongalite at pH 0–1 yields a light blue deposit, which, after drying in a desiccator, has the composition $Pu(C_6H_4OHCOO)_3\cdot 1\cdot 5H_2O$[7]. The compound is sparingly soluble in aqueous solutions of the acid ($\simeq 8 \times 10^{-6}$ mole/l in 1 M salicylic acid at pH 3·5) and also in many organic solvents (e.g. ethanol, 2×10^{-6} mole/l, acetone $1\cdot 5 \times 10^{-5}$ mole/l). When immersed in water in the presence of air, oxidation occurs to yield a Pu(IV) compound ($PuO(C_6H_4OHCOO)_2$?).

Aminocarboxylic acids

The faint violet Am(III) ethylenediaminetetraacetate, $H[AmC_{10}H_6O_8]\cdot xH_2O$, forms when $Am(OH)_3$ is treated with an aqueous solution containing the stoichiometric amount

[7] R. L. Patton, CK-1371 (1944) 16.

of the acid. It is considerably more soluble in water than the lanthanum compound and insoluble in methanol and acetone.

No other solid actinide(III) aminocarboxylates have been prepared, but there have been many investigations of the solution chemistry of these species[1]. These show that the actinide(III) aminopolycarboxylates are strong complexes. Their composition is controlled by the tendency of the cations to fill the inner coordination sphere with eight or nine donor atoms. Hence, iminodiacetic acid forms 1:3 complexes, nitrilotriacetic acid forms 1:2 complexes, and diethylenetriaminepentaacetic acid forms only 1:1 complexes. Some thermodynamic data have been determined (Table 2), showing a strong entropy stabilization. Aminoacetic acid forms rather unstable complexes; at pH 3·6 only the hydrogen complex $M(CH_2NH_2COOH)^{3+}\cdot aq$ is present.

Precipitation of Pu(III) with carboxylic acids

According to an early report[7], Pu(III) in "dilute solution", buffered with sodium acetate to pH 4, forms precipitates with benzoic acids (white, amorphous) and picrolonic acid (green, crystalline), but not with *m*-nitrobenzoic acid, phthalic acid, sebacic acid and fumaric acid.

Hexacyanoferric acids

Potassium ferrocyanide and potassium ferricyanide form insoluble compounds with Pu(III) and Am(III) when added to solutions of the cations in dilute acid. The formulae and the solubilities are:

$HPu[Fe(CN)_6]\cdot 7H_2O$	sky-blue	0·9 mg Pu/l
$Pu[Fe(CN)_6]\cdot 7H_2O$	black	12 mg Pu/l
$HAm[Fe(CN)_6]\cdot aq$	light violet	< 10 mg Am/l

In each case the exact degree of hydration is not known with certainty[69].

2. TETRAVALENT ACTINIDE IONS

The general tendency of the tetravalent actinide ions in aqueous solution is to form neutral salts with strong acids and basic salts with weak acids. In non-aqueous solvents neutral salts of weak acids can also be obtained. Most actinide(IV) carboxylates form more highly coordinated compounds with the corresponding alkali metal carboxylates. The salts of aliphatic acids and pyridine carboxylic acids are not very soluble in organic solvents whereas those of aromatic acids are soluble in polar organic solvents, a property which enables them to be extracted from an aqueous solution. Polybasic hydroxy acids such as tartaric and citric acids form water-soluble salts which prevent precipitation of the hydroxides at high pH values. The aminopolycarbonates are even more stable towards hydrolysis. The coordination number of the tetravalent actinide ions in the carboxylates ranges from 8 to 10, the former type often having square antiprismatic configuration.

The thorium compounds are the most well characterized, but there is enough information to make it clear that at least U(IV) behaves in general like thorium. The main differences arise from its much stronger tendency to hydrolyse (even in 0·1 M perchloric acid the monohydroxide $U(OH)^{3+}$ is present) as well as from the ease of oxidation by oxygen. Therefore, the compounds must be prepared and handled in an inert atmosphere and in

TABLE 3. SOLUBILITY AND COMPLEXATION OF TRIVALENT AND TETRAVALENT ACTINIDE IONS IN OXALIC ACID SOLUTION

	Ac(III)	Pu(III)	Am(III)	Cm(III)	Th(IV)	U(IV)	Np(IV)	Pu(IV)
Solubility product		$1{\cdot}62 \times 10^{-25}$	$2{\cdot}2 \times 10^{-31}$		$4{\cdot}2 \times 10^{-22}$	$4{\cdot}3 \times 10^{-22}$	$8{\cdot}6 \times 10^{-23}$	3×10^{-22}
Temperature (°C)		20	25		25	(20?)	19	20
Medium		H_2O	$\simeq 0{\cdot}2$ M $HClO_4$		1 M NH_4ClO_4	0·5 M HCl	0·5–1 M HCl	1 M $HClO_4$
Reference		b	d		f	g	h	i
Solubility (mole/l)		$2{\cdot}1 \times 10^{-5}$	$2{\cdot}9 \times 10^{-6}$	$1{\cdot}4 \times 10^{-6}$	$3{\cdot}9 \times 10^{-5}$	$9{\cdot}4 \times 10^{-5}$	$2{\cdot}9 \times 10^{-5}$	$1{\cdot}03 \times 10^{-4}$
Temperature (°C)		room temp.	room temp.	room temp.	20	(20?)	20	20
Medium		0·1 M $H_2C_2O_4$ 0·5 M HNO_3	0·1 M $H_2C_2O_4$ 0·1 M HNO_3	0·1 M $H_2C_2O_4$ 0·1 M HNO_3	H_2O	H_2O	H_2O	H_2O
Reference		c	c	c	f	g	h	i
Stability constant								
log β_1	3·56		4·63	4·80	8·23	8·61	8·68	8·74
log β_2	6·16	9·15	8·36	8·61	16·8	16·9	17·5	16·9
log β_3		10·04	11·15		22·8	22·77	24·0	23·4
log β_4					27·2	27·7	27·4	27·5
Temperature (°C)	25	20	25	25	25	(20?)	25	20
Medium	1 M $NaClO_4$	1 M NH_4Cl	1 M $NaClO_4$	0·5 M $NaClO_4$	1 M NH_4ClO_4	0·5 M HCl	1 M HCl	1 M HNO_3
Reference	a	b	a	e	f	g	h	i

[a] T. Sekine and M. Sakairi, *Bull. Chem. Soc. Japan* **42** (1969) 2712.

[b] A. D. Gelman, N. N. Matorina and A. I. Moskvin, *Kernenergie*, **1** (1958) 588, 850.

[c] G. A. Burney and J. A. Porter, *Inorg. Nucl. Chem. Lett.* 3 (1967) 79.

[d] I. A. Lebedev, S. V. Pirozhkov, V. M. Razbitnoi and G. N. Yakovlev, *Radiokhimiya*, **2** (1960) 351.

[e] A. Aziz, S. J. Lyle and S. J. Naqvi, *J. Inorg. Nucl. Chem.* **30** (1968) 1013.

[f] A. I. Moskvin and L. N. Essen, *Russ. J. Inorg. Chem.* **12** (1967) 359.

[g] F. A. Zakharova and A. I. Moskvin, *Russ. J. Inorg. Chem.* **5** (1960) 592.

[h] P. I. Kondratev and A. D. Gelman, *Radiochemistry*, **2** (1960) 52.

[i] A. I. Moskvin and A. D. Gelman, *Zhur. Neorg. Khim.* 3 (1958) 956, 962.

many cases with exclusion of water. Np(IV) and Pu(IV) behave in a similar fashion to U(IV) with less (Np) or no (Pu) tendency to oxidize.

Formic acid

Thorium Formates

Dissolution of $Th(OH)_4$ in 40 % formic acid followed by evaporation of the solution yields $Th(HCOO)_4 \cdot 3H_2O$ whilst addition of $Th(NO_3)_4 \cdot 4H_2O$ to pure formic acid yields $Th(HCOO)_4 \cdot 1{\cdot}5H_2O$. At 100–200°C the hydrates lose water with the formation of $Th(HCOO)_4$. The basic formate $Th(OH)(HCOO)_3$ forms when an inert gas, saturated with water vapour, is passed over $Th(HCOO)_4$[8]. A whole series of formato-complexes, of general

TABLE 4. PHYSICOCHEMICAL DATA FOR THE FORMATES, ACETATES AND OXALATES OF TETRAVALENT ACTINIDE IONS

Compound	cond: conductivity ohm^{-1} cm^2 (dilution d l/mole) at 25°C IR: frequency cm^{-1} (assignment) mm: magnetic moment μ_B (Curie-temp.)	Reference
$Th(HCOO)_4 \cdot 3H_2O$	cond: 163 (d = 1000)	a
$K[Th(HCOO)_5]$	cond: 218 (d = 1000)	a
$Cs_x[Th(HCOO)_{4+x}]$	cond: 193 (x = 1), 308 (x = 2), 403 (x = 3), 550 (x = 4) (d = 1000)	a
$U(HCOO)_4$	mm: 2·98 (Δ = 74°)	b
$K[U(OH)(HCOO)_4] \cdot 3H_2O$	cond: 290 (d = 1074)	c
$K[U(OH)(HCOO)_3SCN] \cdot 2H_2O$	cond: 329 (d = 1138)	c
$Th(CH_3COO)_4$	cond: 70·9 (d = 1000), 345 (d = ∞) IR: 1568, 1545 (CO_2, as); 1410, 1350 (CO_2, sym)	d
$[CN_3H_6]_2[Th(CH_3COO)_6]$	cond: 248 (d = 1000) FP: 175°C symmetry: cubic Pa_3 a = 13·5 IR: 1560, 1470 (CO_2, as); 1420, 1360 (CO_2, sym)	d
$U(CH_3COO)_4$	IR: 1560, 1510 (CO_2, as); 1402 (CO_2, sym); 570 (U–O); mm: 2·69	e, f
$U(OH)(CH_3COO)_3$	IR: 3500 (H_2O); 1550, 1515 (CO_2, as); 1410, 1345 (CO_2, sym); 570, 395 (U–O)	e
$UO(CH_3COO)_2$	IR: 1550 (CO_2, as); 1410, 1340 (CO_2, sym); 570, 400 (U–O)	e
$Mg[U(CH_3COO)_6]$	IR: 1600, 1530 (CO_2, as); 1380 (CO_2, sym); mm: 2·66	f
$Fe[U(CH_3COO)_6]$	IR: 1580, 1520 (CO_2, as); 1400 (CO_2, sym); mm: 7·42	f
$Th(C_2O_4)_2 \cdot 6H_2O$	IR: 1649 (CO_2, as); 1359, 1320 (CO_2, sym)	g
$U(C_2O_4)_2 \cdot 6H_2O$	mm: 3·70 (Δ = 188°)	h
$K_4[U(C_2O_4)_4] \cdot 5H_2O$	mm: 3·62 (Δ = 60°)	h
$Ba_2[U(C_2O_4)_4] \cdot 6H_2O$	mm: 3·60 (Δ = 132°)	h
$Pu(C_2O_4)_2 \cdot 6H_2O$	mm: 2·99 (Δ = 610°)	i
$Pu(C_2O_4)_2 \cdot 3H_2O$	mm: 2·42 (Δ = 350°)	j

[a] V. A. Golovnya and O. M. Ivanova, *Russ. J. Inorg. Chim.* **8** (1963) 1290.
[b] C. Keller, *The Chemistry of the Transuranium Elements*, Verlag Chemie, Weinheim (1971).
[c] I. I. Chernyaev, *Complex Compound of Uranium*, p. 486, Jerusalem (1966).
[d] A. K. Molodkin, O. M. Ivanova and G. A. Skotkinova, *Russ. J. Inorg. Chim.* **12** (1967) 57.
[e] J. Selbin, M. Schober and J. D. Ortego, *J. Inorg. Nucl. Chem.* **28** (1966) 1385.
[f] D. Grdenic and B. Koprar-Colig, *J. Inorg. Nucl. Chem.* **30** (1968) 1751.
[g] Y. Y. Kharitonov, A. K. Molodkin and T. A. Balakaeva, *Russ. J. Inorg. Chem.* **14** (1969) 174.
[h] C. Keller, *The Chemistry of the Transuranium Elements*, Verlag Chemie, Weinheim (1971).
[i] W. B. Lewis and N. Elliot, *J. Phys. Chem.* **27** (1957) 904.
[j] T. G. Aminov, V. B. Evdovonko, V. V. Zelentsov and F. A. Zakharova, *Dokl. Akad. Nauk SSSR*, **175** (1967) 1309.

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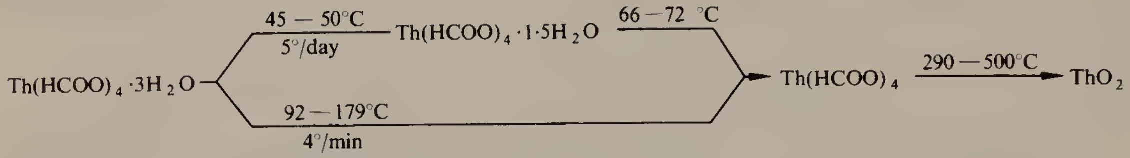
[8] B. Claudel and B. Mentzen, *Bull. Soc. Chim. France* (1966) 1547.

formula $M_x[Th(HCOO)_{4+x}]\cdot nH_2O$, may be prepared by mixing solutions of thorium tetraformate with solutions of formates of monovalent and divalent cations (Table 4). Several types of mixed thorium formato-complexes are also known, e.g. the compounds $[Th_3(OH)_5(HCOO)_6SCN]\cdot 7H_2O$[9] and $Th(HCOO)_4\cdot H_2O\cdot DMSO$[10].

All the formates are soluble in water and only slightly soluble in organic solvents ($Th(HCOO)_4$: 137 mg/l in methanol, 23·6 mg/l in ethanol, 10·7 mg/l in ether). The electrical conductivities of aqueous solutions of the formates (Table 4) indicate weak hydrolysis in the case of $Th(HCOO)_4\cdot 3H_2O$ and $Cs[Th(HCOO)_5]$, but not in the case of the higher cesium formato-thorates(IV).

The thermal decomposition of $Th(HCOO)_4\cdot 3H_2O$ proceeds in either two or three steps (as shown below) depending on the heating rate; about 500°C is required for complete decomposition[8].



$Th(HCOO)_4\cdot 3H_2O$ and $Th(HCOO)_4$ have been investigated by X-ray techniques (Table 1). In the tris-hydrate each metal atom is surrounded by eight oxygen atoms, from eight formato-groups, located at the vertices of a distorted archimedian antiprism, and by two oxygen atoms from water molecules, located above the square bases of the antiprism[10,11]. Thorium thus has a coordination number of 10 (Th–O: 2·41 Å, Th–OH_2: 3·0 and 3·2 Å). According to this structure the compound must be formulated as $[Th(HCOO)_4\cdot(H_2O)_2]\cdot H_2O$.

Uranium(IV) Formates

The deep green compound $U(HCOO)_4$ is obtained by treating UCl_4 with formic acid under reflux or by heating uranium metal with formic acid, in the presence of HCl. A basic formate, $[U(OH)_2(HCOO)_2]\cdot 2H_2O$, forms when ammonium-U(IV) carbonate is boiled with formic acid, and the related compound, $UO(HCOO)_2$, has been prepared by electrolysis of an aqueous solution of uranyl formate, followed by addition of methanol[12]. Several mixed formato-complexes containing hydroxyl or thiocyanato ions (Table 4) have been crystallized from aqueous solution.

Thermal decomposition of $U(HCOO)_4$ in air leads initially to $UO_2(HCOO)_2$ at 120–220°C. The further decomposition then follows the pattern found for uranyl formate[14].

The tetraformate exists in three crystallographic modifications[13]. The α-modification and the γ-modification are enantiotropic with each other. The reversible transmutation exhibits a large hysteresis.

$$\alpha\text{-}U(HCOO)_4 \underset{90^\circ C,\ \text{exotherm}}{\overset{140^\circ C,\text{endotherm}}{\rightleftharpoons}} \gamma\text{-}U(HCOO)_4$$

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[9] V. A. Golovnya and O. M. Ivanova, *Russ. J. Inorg. Chem.* **8** (1963) 1290.

[10] B. K. Molodkin, O. M. Ivanova, Z. V. Belyakova and L. E. Kolosnikova, *Russ. J. Inorg. Chem.* **15** (1970) 1692.

[11] E. G. Arutyunyan, A. S. Ansyshkin and E. Y. Balta, *Zhur. Strukt. Khim.* 7 (1966) 471.

[12] R. Bressat, B. Claudel and A. Navarro, *Bull. Soc. Chim. France* (1968) 4807.

[13] R. Bressat, B. Claudel and A. Navarro, *Compt. Rend.* Ser. C, **266** (1968) 1260.

[14] G. D. Buttres and M. A. Hughes, *J. Chem. Soc.* (A) (1968) 1272.

The third modification, β-$U(HCOO)_4$, is metastable at all temperatures and transmutes irreversibly into the γ-modification at 210°C.

Magnetic measurements on $U(HCOO)_4$ have shown the compound to obey the Curie–Weiss law; the magnetic moment (Table 4) confirms a $5f^2$ configuration for U(IV).

Acetic acid

Three classes of Th(IV) and U(IV) acetates are known. These are the normal acetates $M(CH_3COO)_4$, basic acetates $MO_x(CH_3COO)_{4-x}\cdot xH_2O$ and acetato-metallates(IV) with the anion $[M(CH_3COO)_{4+x}]^{x-}$.

The normal acetates are obtained as precipitates when the tetrachlorides are boiled with glacial acetic acid. $Th(CH_3COO)_4$, but not the U(IV) compound, can also be prepared by dissolution of the hydroxide in 50% acetic acid; it precipitates immediately as white, elongated prisms. The pure U(IV) compound can be obtained by reduction of $UO_2(CH_3COO)_2$, dissolved in glacial acetic acid, either photochemically in the presence of ethanol or by refluxing with Zn amalgam[15,16]. The crystals obtained are light green fibres. Only one type of acetato-metallate(IV) is known, $M''_2[M(IV)(CH_3COO)_6]$ (M″ = guanidine with M(IV) = Th and M″ = Zn, Mg, Fe and M(IV) = U). This is in striking contrast to the range of formato-complexes, which contain up to eight formato anions. Basic acetates, $M(OH)(CH_3COO)_3$, with M = Th(IV) and U(IV), are obtained by boiling the tetraacetate with acetic acid in the presence of water ($CH_3COOH{:}H_2O = 2{:}1$). These compounds decompose to those of the type $MO(CH_3COO)_2$ at 190°C[18]. Thorium(IV) also forms a series of basic acetates, $Th(OH)_x(CH_3COO)_{4-x}\cdot nH_2O$ ($x/n = 1/1{\cdot}5$; $1{\cdot}5/2$; $2/2{\cdot}5$ and $2{\cdot}5/1$).

All the acetato-compounds appear to be insoluble in normal organic solvents, but slightly soluble in water ($Th(CH_3COO)_4 \simeq 1{\cdot}5$ g/100 ml). Data on the physicochemical properties are given in Table 4.

The electrical conductivities indicate appreciable dissociation of $Th(CH_3COO)_4$ in aqueous solution, whereas the hexaacetatothorate(IV) anion remains undissociated. The limiting molar conductance of $Th(CH_3COO)_4$ corresponds to an equivalent mobility of thorium of 45·4 $ohm^{-1}\ cm^2$ at 25°C.

The infrared spectrum of $U(OH)(CH_3COO)_3$ indicates the presence of the hydroxyl ion by the strong, narrow bands at 3500 and 3200 cm^{-1}. Both disappear when the compound is dried, and a new band appears at 395 cm^{-1}. This is assigned to a metal–oxygen bond. There is no infrared evidence for a $U{=}O^{++}$ entity in the structure as is the case for actinide(IV) oxydichlorides: a polymeric structure with O–U–O–U linkages is tentatively suggested[18].

$Th(CH_3COO)_4$ and $U(CH_3COO)_4$ are isostructural, possessing monoclinic symmetry (Table 1), and show a contraction in unit cell volume of 3·6% going from thorium to uranium[15]. The crystal structure of $U(CH_3COO)_4$ is shown in Fig. 1. The polymeric structure is formed by infinite columns (parallel to the *c*-axis) in which each acetate group belongs to two uranium ions. The uranium atom is surrounded by eight oxygen atoms which form a distorted archimedian antiprism (mean U–O distance 2·52 Å). Each following

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[15] R. Bressat, B. Claudel, G. Giorgio and B. Mentzen, *J. Chim. Phys.* **65** (1968) 1615.

[16] R. C. Paul, J. S. Ghotra and M. S. Bains, *J. Inorg. Nucl. Chem.* **27** (1965) 265.

[17] A. K. Molodkin, G. M. Ivanova and G. A. Skotkinova, *Russ. J. Inorg. Chem.* **12** (1967) 57.

[18] J. Selbin, M. Schober and J. D. Ortega, *J. Inorg. Nucl. Chem.* **28** (1966) 1385.

antiprism is displaced by about half of its square face edge and, therefore, two oxygen atoms of two neighbouring polyhedra are considerably nearer to the uranium ion than are the others, 2·8 Å instead of the mean U–O distance of 3·58 Å. If these oxygen atoms are regarded as coordinated, one has a coordination number of 10 for the uranium. In guanidinium hexaacetatothorate[17], which is cubic ($a \simeq 13{\cdot}6$ Å), twelve oxygen atoms are bonded to the thorium atom in the form of an icosahedron.

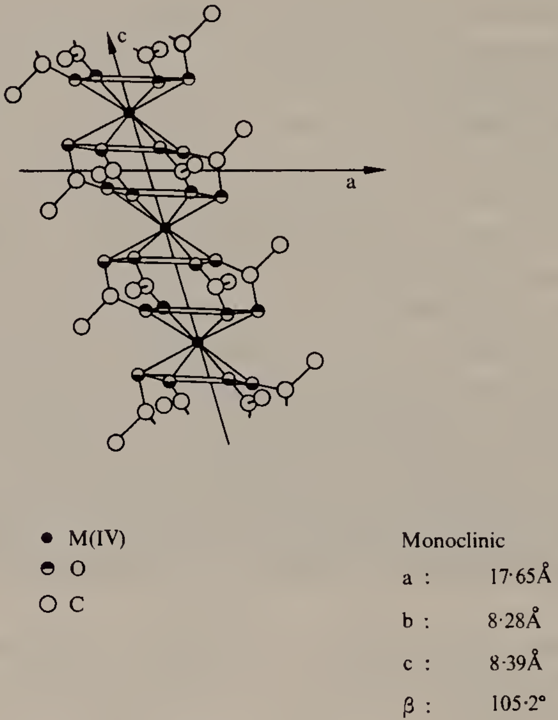

FIG. 1. Structure of $U(CH_3COO)_4$[19].

Other monodentate acids

As shown in Table 5, many other monodentate acids form compounds analogous to those formed with acetic acid. No attempts to prepare hexacoordinated species have been reported.

The thermal decomposition of the carboxylates proceeds in at least two steps, dehydration at about 100°C and decomposition of the organic groups at ≃200°C. Heating the U(IV) compounds often results in oxidation before the final decomposition occurs. For the U(IV) tetradichloracetate, for example, the following reactions were found[21]:

$$U(CHCl_2COO)_4 \xrightarrow[O_2]{90^\circ C} UO_2(CHCl_2COO)_2 \xrightarrow[O_2]{240^\circ C} UO_2Cl_2 \xrightarrow[O_2]{>300^\circ C} UO_2$$

The sparingly soluble benzoate and phenyl acetate of thorium have been proposed for analytical purposes, as they precipitate quantitatively with known composition from aqueous solution and can be dried to constant weight at 100°C or ignited to the oxide at 500–510°C.

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[19] I. Jelenic, D. Gredenic and A. Bezjak, *Acta Cryst.* 17 (1964) 758.

[20] I. L. Jenkins, F. H. Moore and M. J. Waterman, *J. Inorg. Nucl. Chem.* 27 (1965) 81.

[21] I. I. Chernyaev, *Complex Compounds of Uranium*, Oldbourne Press, London (1966).

TABLE 5. SALTS OF TETRAVALENT ACTINIDE IONS WITH MONODENTATE CARBOXYLIC ACIDS

Acid	Salt	Characterized by	Reference
Propionic acid	$U(C_2H_5COO)_4$	anal., IR, VIS	a
	$U(OH)_2(C_2H_5COO)_2$	anal., IR, VIS	a
	$UO_{1,5}(C_2H_5COO)$	anal., IR, VIS	a
Isobutyric acid	$Th(C_3H_7COO)_4\cdot 2H_2O$	anal., IR, VIS	b
	$U(C_3H_7COO)_4$	anal.	c
Isovaleric acid	$U(C_4H_9COO)_4$	anal.	c
Caproic acid	$U(C_5H_{11}COO)_4$	anal.	c
Heptanoic acid	$U(C_6H_{13}COO)_4$	anal., IR, VIS	a
Benzoic acid	$Th(C_6H_5COO)_4$	anal., TG	f
	$U(C_6H_5COO)_4$	anal., IR	b
	$Pu(C_6H_5COO)_4$	?	h
Trifluoracetic acid	$U(CF_3COO)_4$	anal., IR, VIS	a
Trichloracetic acid	$Pu(CCl_3COO)_4$ (?)		d
	$Th(CCl_3COO)_4\cdot 2H_2O$	anal., IR, cryoscopy, nmr	i
	$Th(OH)(CCl_3COO)_3\cdot 3H_2O$	anal., IR, cryoscopy, nmr	i
	$Th(OH)_2(CCl_3COO)_2\cdot 2H_2O$	anal., IR, cryoscopy, nmr	i
Dichloracetic acid	$U(CHCl_2COO)_4$	anal., IR, TG	e
Phenylacetic acid	$Th(C_6H_5CH_2COO)_4$	anal., TG	f,g

[a] J. Selbin, M. Schober, and J. D. Ortego, *J. Inorg. Nucl. Chem.* **28** (1966) 1385.
[b] I. Galaceann, *Stud. Cerc. Chim.* **11** (1963) 343.
[c] R. C. Paul, J. S. Ghotra and M. S. Bains, *J. Inorg. Nucl. Chem.* **27** (1965) 265.
[d] W. C. Beard, Natl. Nucl. Energy Series Div. IV, Vol. 14B, p. 637.
[e] T. S. Lobanova, A. V. Ivanov and K. M. Dunaeva, *Russ. J. Inorg. Chem.* **16** (1971) 1087.
[f] W. W. Wendlandt, *Anal. Chem.* **29** (1957) 800.
[g] K. N. Kavalenko and M. N. Tarasova, *Russ. J. Inorg. Chem.* **5** (1960) 184.
[h] R. L. Patton, Natl. Nucl. Energy Series Div. IV, Vol. 14B, p. 851.
[i] I. Geletseanu, A. V. Lapitsky, M. Veiner, M. A. Salimov and E. P. Artamonova, *Sov. Radiochem.* **6** (1964) 83.

Oxalic acid

The oxalate hexahydrates, $M(IV)(C_2O_4)_2\cdot 6H_2O$, normally form on addition of an oxalic acid solution to an acidified solution of a tetravalent actinide ion. These compounds are frequently used for the isolation of Th(IV), U(IV), Np(IV) and Pu(IV) from aqueous solution and as the starting materials for the preparation of the dioxides. In the case of uranium an especially pure product can be prepared by electrolytic reduction of a saturated solution of uranyl oxalate in oxalic acid[20]. Dihydrates are obtained by drying $Th(C_2O_4)_2\cdot 6H_2O$ and $U(C_2O_4)_2\cdot 6H_2O$ at 110°C. The analogous Pu(IV) compound cannot be prepared in this way, but is obtained by heating to 50–70°C during precipitation. When freshly precipitated $Pu(C_2O_4)_2\cdot 6H_2O$ is repeatedly shaken with acetone, a bright pink compound forms, which loses acetone on standing and leaves $Pu(C_2O_4)_2\cdot 2H_2O$ as the final product. It is presumed that the initial pink compound is a solvate, $Pu(C_2O_4)_2\cdot 2H_2O\cdot$ACETONE[20]. A similar compound is described for uranium(IV); this appears to be even less stable.

All the normal actinide(IV) oxalates are only slightly soluble in water and in mineral acids of moderate concentration (Table 3). With concentrated strong acids the compounds dissolve and precipitate again on dilution. $U(C_2O_4)_2\cdot 6H_2O$ and $Pu(C_2O_4)_2\cdot 6H_2O$ dissociate in aqueous solution to an extend of about 10% according to the equation

$$M(C_2O_4)_2\cdot aq \leftrightharpoons M(C_2O_4)_2\,(OH)\cdot aq + H^+$$

but thorium oxalate shows practically no acidity[30].

The actinide di-oxalates dissolve in solutions of alkali metal or ammonium oxalates (e.g. $Th(C_2O_4)_2 \cdot 6H_2O$: 0·54 moles/l in 1·42 M $(NH_4)_2C_2O_4$). The solutions contain complex species $[M(C_2O_4)_x]^{(4-2x)-}$ with $x = 1$–4 (Table 3); evaporation or addition of alcohol yields solid compounds, $M'_4[M(IV)(C_2O_4)_4] \cdot nH_2O$ ($M' = Na^+, K^+, NH_4^+$; $M(IV) = Th^{4+}$, U^{4+}, Np^{4+}, Pu^{4+}). Uranium(IV) tetraoxalato-complexes of many other univalent, divalent and trivalent cations have been prepared by cocrystallization[21]. Lesser coordinated species are also known with Th(IV) and U(IV), for example $(NH_4)_2[Th(C_2O_4)_3] \cdot 3H_2O$.

Two modifications exist for $K_4[Pu(C_2O_4)_4] \cdot 4H_2O$ and the analogous sodium salt: a red one, which precipitates on the addition of ethanol to the aqueous solution, and a yellow–green one, into which the former is rapidly converted on standing[22,30].

The hexahydrates, $M(C_2O_4)_2 \cdot 6H_2O$, dissolve in aqueous solutions of alkali metal carbonates, from which mixed complexes have been isolated $M'[M(IV)(CO_3)_x(C_2O_4)_y] \cdot nH_2O$ with $M' = Na, K$; $M(IV) = Th, U, Pu$ and $x = 2, y = 2$ or $x = 3, y = 1$[22,23,30]. Mixed acido-complexes of U(IV) containing F^-, SO_4^{--}, or SCN^- in addition to oxalate are also known[21].

The thermal decomposition of thorium and uranium oxalate hexahydrates proceeds in several steps[24]. As seen below, with a heating rate of 5°C per minute, two intermediate hydrates are observed.

$$\begin{array}{cl}
M(C_2O_4)_2 \cdot 6H_2O & \\
\big\downarrow & 40\text{–}130°C \\
(MC_2O_4)_2 \cdot 2H_2O & \\
\big\downarrow & 150\text{–}220°C \\
M(C_2O_4)_2 \cdot H_2O & \\
\big\downarrow & >260°C \\
(M(C_2O_4)_2)? & \\
| & \\
(M(CO_3)_2)? & \\
\big\downarrow & \\
MO_2 &
\end{array}$$

The formation of the anhydrous oxalate is not unambiguously established; above 260°C the water is totally lost, but a simultaneous slight decomposition of the oxalate groups occurs. However, the anhydrous compounds can be prepared by prolonged heating of the hexahydrates at 160°C *in vacuo*. Samples heated to 400°C consist of mixtures of carbonate, $M(CO_3)_2$, and oxide, MO_2[24,25].

The alkali metal actinide tetra-oxalate hydrates lose water between 60° and 230°C, the anhydrous compounds decomposing between 400° and 530°C to the actinide dioxide and alkali carbonate[26].

The thermal decomposition of $Pu(C_2O_4)_2 \cdot 6H_2O$ is less well established. $Pu(C_2O_4)_2$ and $Pu_2(C_2O_4)_3$ have been suggested as intermediates of the decomposition in an inert atmosphere[27]. In air the loss of water starts at 45°C, but no stable intermediate is found. A residue

[22] A. D. Gelman and L. P. Sokhina, *Zhur. Neorg. Khim.* 3 (1958) 1100.

[23] A. D. Gelman and L. M. Zaitseva, *Russ. J. Inorg. Chem.* 3 (1958) 49.

[24] R. Bressat, B. Claudel and Y. Trambonze, *J. Chim. Phys.* **60** (1963) 1265; *Bull. Soc. Chim. France* (1963) 464.

[25] Y. Y. Kharitonov, A. K. Molodkin, and T. A. Balakaeve, *Russ. J. Inorg. Chem.* **14** (1969) 174.

[26] A. K. Molodkin, T. A. Balakaeva and A. N. Kuchumova, *Russ. J. Inorg. Chem.* **16** (1971) 1004.

[27] M. N. Myers, HW-45128 (1956).

obtained by heating $Pu(C_2O_4)_2 \cdot 2H_2O$ to constant weight at 230°C has been shown to be a mixture of PuO_2 and $Pu(CO_3)_2$[28].

The isostructural hexahydrates of the tetravalent actinide oxalates crystallize with triclinic symmetry. Their lattice constants are given in Table 1. Infrared investigations[25] have led to the conclusion that in $Th(C_2O_4)_2 \cdot 6H_2O$ and $U(C_2O_4)_2 \cdot 6H_2O$ two water molecules are bound more firmly than the other four, and that thorium oxalate monohydrate contains a hydroxy group, $Th(OH)(C_2O_4)(HC_2O_4)$.

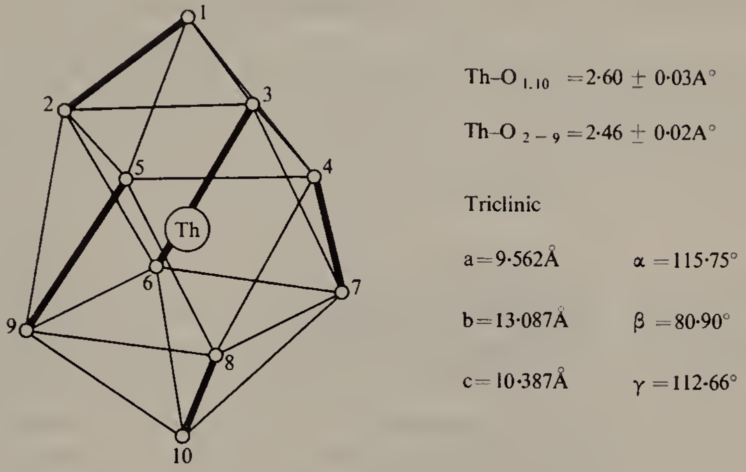

FIG. 2. Structure of triclinic $K_4[Th(C_2O_4)_4] \cdot 4H_2O$ (only the ligand oxygen atoms in the coordination sphere are shown; the polyhedron edges spanned by oxalate groups are indicated by heavy lines).

The structure of triclinic $K_4[Th(C_2O_4)_4] \cdot 4H_2O$ (Table 1) has been determined[29]. As is shown in Fig. 2, ten oxygen atoms form a bicapped square antiprism around the thorium. Two oxalate groups, 1–2 and 8–10, are quadridentate and form chains parallel to [110] by bridging adjacent polyhedra.

Some magnetic data for actinide(IV) oxalates are incorporated in Table 4. These indicate a $5f^2$ configuration for U(IV) and a $5f^4$ configuration for Pu(IV).

Hydroxycarboxylic acids and polycarboxylic acids

Some actinide(IV) salts of these acids are tabulated in Table 6. For weak monobasic acids (pK > 4) the common type of compound obtained from aqueous solution is the dibasic salt, for example the salicylate $ThO(C_6H_4OHCOO)_2 \cdot aq$, or the malonate $UO(OOCCH_2COO)_2 \cdot 6H_2O$. It is not clear whether they contain metal–oxygen groups $>M{=}O$ or metal–dihydroxy groups $>M(OH)_2$. The only acid for which salts of Th(IV), U(IV) and Pu(IV) have been prepared is salicylic acid. All three salicylates $M(IV)(O)(C_6H_4OHCOO)_2$ are insoluble in water (e.g. $PuO(C_6H_4OH)_2$: 2·9 mg/l at pH 3) and soluble in polar organic solvents, by which they can be extracted from an aqueous

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[28] I. L. Jenkins and M. J. Waterman. *J. Inorg. Nucl. Chem.* **26** (1964) 131.

[29] M. N. Akhtar and A. J. Smith, *J. Chem. Soc.* (D) (1969) 705.

[30] A. D. Gelman, A. I. Moskvin, L. M. Zaitsev and M. P. Mefodeva, *The Complex Compounds of Transuranium Elements*, English transition FTD-TT-61-246 of *Komplexnyye Soyedineniya Transuranovykh Elementov*, Moscow (1961).

solution. The actinide(IV) salicylates also dissolve in sodium salicylate solutions to form complexes. $ThO(C_6H_4OHCOO)_2 \cdot 3H_2O$ has a dipole moment of 3·43 Debye, is stable up to 120°C and begins to decompose at 226°C[32].

The easily dissociating monobasic acids form neutral salts ML_4 that can be prepared by reaction of inorganic actinide(IV) salts with an excess of the free acid in aqueous solution. They contain one or two molecules of water when crystallized from aqueous solution (Table 6). The salts of aliphatic hydroxycarboxylic acids, for example $Th(CH_2OHCOO)_4 \cdot 2H_2O$, dissolve rather easily in water, whilst those of acids containing aromatic rings, as for instance mandelic acid, are only slightly soluble in water.

TABLE 6. ACTINIDE(IV) SALTS OF HYDROXYCARBOXYLIC ACIDS AND DICARBOXYLIC ACIDS

Acid	Composition	Characterized by	Ref.
Glycollic acid	$Th(CH_2OHCOO)_4 \cdot 2H_2O$	anal., TA, conductivity	a
	$ThO(CH_2OHCOO)_2 \cdot 2H_2O$	anal.	a
Alphahydroxyisobutyric acid	$Th(C_3H_6OHCOO)_4 \cdot 2H_2O$	anal., IR	b
Mandelic acid	$Th(C_6H_5CHOHCOO)_4 \cdot H_2O$	anal., IR	b
m-Hydroxybenzoic acid	$Th(OH)_2(C_6H_4OHCOO)_2$	anal., thermograv.	c
Salicylic acid	$ThO(C_6H_4OHCOO)_2 \cdot 3H_2O$	anal., conductivity, thermograv.	d
	$UO(C_6H_4OHCOO)_2$	anal.	e
	$U(C_6H_4OCOO)_2 \cdot 4H_2O$	anal.	f
	$PuO(C_6H_4OHCOO)_2$	anal.	g
Malonic acid	$UO(OOCCH_2COO)_2 \cdot 6H_2O$	anal.	h
Succinic acid	$UO(OOCC_2H_4COO)_2 \cdot 2H_2O$	anal.	h
Malic acid	$Th(OH)_2(OOCCH_2CHOHCOO)_3 \cdot 4H_2O$	anal., conductivity, stab. const.	i
	$Na[ThOH(OOCCH_2CHOHCOO)_2] \cdot 6H_2O$	anal.	
	$Na_2[ThO(OOCCH_2CHOHCOO)_2] \cdot 5H_2O$	anal.	i
Tartaric acid	$Th(OH)_2C_4H_4O_6 \cdot 3H_2O$	anal., conductivity, stab. const.	k
	$K[Th(OH)C_4H_2O_6] \cdot 10H_2O$	anal.	k
	$K_2[Th(OH)_2C_4H_2O_6] \cdot 4H_2O$	anal.	k
	$K[Th(OH)(C_4H_4O_6)_2] \cdot 7H_2O$	anal.	k
	$K_2[Th(OH)_2(C_4H_4O_6)_2] \cdot 8H_2O$	anal.	k
	$Th(C_4H_2O_6) \cdot 9H_2O$	anal.	k
	$U(C_4H_4O_6)_2 \cdot 2H_2O$	anal.	l
	$UOC_4H_4O_6 \cdot 6H_2O$	anal.	l
Citric acid	$Th_3(C_6H_5O_7)_4 \cdot 7{,}5H_2O$	anal., thermograv., stab. const.	m
	$U_3(C_6H_5O_7)_4 \cdot xH_2O$	anal.	e

[a] D. V. Kazachenko and K. N. Kovatenko, *Russ. J. Inorg. Chem.* **11** (1966) 871.
[b] I. Galateanu, *Stud. Cerc.* **11** (1963) 343.
[c] W. W. Wendtland, *Anal. Chem.* **29** (1957) 800.
[d] K. N. Kovalenko, D. V. Kazachenko and E. M. Ivanova, *Russ. J. Inorg. Chem.* **7** (1962) 1213.
[e] M. Lobanov, *Rocz. Chem.* **5** (1926) 1389.
[f] S. Rosenblum and S. Weil, *Chem. Zentr.* (1929) 2222.
[g] O. Y. Zvyagintsev and B. N. Sudarikov, *Russ. J. Inorg. Chem.* **3** (1958) 217.
[h] A. Mazzuchelli and O. G. D'Alceo, *Atti Linc.* **21** (1912) 625.
[i] O. E. Zvyagintsev and L. G. Khromenkov, *Russ. J. Inorg. Chem.* **6** (1961) 301.
[k] O. E. Zvyagintsev and L. G. Khromenkov, *Russ. J. Inorg. Chem.* **6** (1961) 445.
[l] M. Lobanov, *Rocz. Chem.* **5** (1925) 437.
[m] N. A. Skoric, V. N. Kumole and V. V. Serebrennikov, *Sov. Radiochem.* **9** (1967) 499.

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[32] K. N. Kovalenka, D. V. Kazachenko and E. M. Ivanova, *Russ. J. Inorg. Chem.* **7** (1962) 1213.

Due to the greater complexing ability of these acids, their thorium salts do not hydrolyse in water, but basic compounds are obtained on addition of ammonia. At pH values higher than 7 the metal hydroxide precipitates.

Neutral and basic Th(IV) and U(IV) salts are formed from aqueous solutions of tartaric and citric acid (Table 6). With both acids, salts are known with a main valence bond from the hydroxy group of the ligand to the metal atom, for example $Th(OOC–CHO–CHO–COO)\cdot 2H_2O$ and $Th[C_3H_4O(COO)_3]$. The latter compound precipitates at $pH = 1\cdot 8$, when the Th(IV) aquo-cation does not hydrolyse and it cannot be regarded as a basic salt; it is formed by proton dissociation of a complex acid:

$$Th[C_3H_4OH(COO)_3]^+ \rightleftharpoons Th[C_3H_4O(COO)_3]^\circ + H^+$$

The dissociation constant is $pK = 4\cdot 6$[31]. Actinide(IV) tartrates and citrates dissolve in a solution of the sodium salt of the acid, forming complexes with up to three anions per metal ion. These solutions are stable towards hydroxide precipitation up to pH 10.

Aminopolycarboxylic acids

With Th(IV), U(IV), Np(IV) and Pu(IV) aminopolycarboxylic acids form compounds containing from 0·5 to 3 molecules of the anion per metal ion[33]. With most aminopolycarboxylic acids the different species have been identified in solution; only the main types are known in the solid form and these only for thorium and uranium (Table 7).

Ethylenediaminetetraacetic acid (H_4EDTA) forms 1:1 salts with Th(IV) and U(IV) which are only slightly soluble in water (e.g. $ThC_{10}H_{12}N_2O_8\cdot 2H_2O$: 0·00645 mol/l at 25°C) and which crystallize when a hot solution containing the metal tetrachloride and the acid in stoichiometric amounts is cooled[34]. They dissolve in dilute sodium hydroxide solution and also in a solution of the disodium salt of the acid. The reactions occurring are:

$$MEDTA\cdot 2H_2O + OH^- \rightleftharpoons M(OH)EDTA^-\cdot aq \rightleftharpoons [M(OH)EDTA]_2{}^{2-}\cdot aq \tag{1}$$

TABLE 7. SALTS OF TETRAVALENT ACTINIDE IONS WITH AMINOPOLYCARBOXYLIC ACIDS

Acid	Compound	Characterized by	Ref.
Ethylenediaminetetraacetic acid	$ThC_{10}H_{12}N_2O_8\cdot 2H_2O$	anal., IR: $\nu_{as(CO_2)} = 1575, 1610\ cm^{-1}$	a, b
	$Na[Th(OH)C_{10}H_{12}N_2O_8]\cdot 4H_2O$	anal., IR: $\nu_{as(CO_2)} = 1600–1640\ cm^{-1}$	b
	$UC_{10}H_{12}N_2O_8\cdot 2H_2O$	anal.	a
	$K_2H_2[U_2(C_{10}H_{12}N_2O_8)_3]\cdot xH_2O$	anal.	c
	$Ba_2[U_2(C_{10}H_{12}N_2O_8)_3]\cdot 18H_2O$	anal.	c
Diethylenetriaminepentaacetic acid	$H[ThC_{14}H_{18}N_3O_{10}]\cdot H_2O$	anal., IR: $\nu_{as(CO_2)} = 1600\ cm^{-1}$	d

[a] H. Brintzinger, H. Thiele and U. Müller, *Z. allg. anorg. Chem.* **251** (1943) 285.
[b] H. G. Langer, *J. Amer. Chem. Soc.* **85** (1963) 2390.
[c] N. P. Ermolaev and N. N. Krot, *Russ. J. Inorg. Chem.* **8** (1963) 1282.
[d] R. E. Sievers and J. C. Bailar, *Inorg. Chem.* **1** (1962) 174.

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[31] M. Bobtelsky and B. Grans, *J. Amer. Chem. Soc.* **76** (1954) 1536.

[33] S. H. Eberle and M. Paul, *J. Inorg. Nucl. Chem.* **33** (1971) 3067.

[34] H. Brintzinger, H. Thiele and U. Müller, *Z. allg. anorg. Chem.* **251** (1943) 285.

$$2MEDTA \cdot 2H_2O + H_2EDTA^{2-} \rightleftharpoons H_2[M_2(EDTA)_3]^{2-} \cdot aq \rightleftharpoons [M_2(EDTA)_3]^{4-} \cdot aq + 2H^+ \qquad (2)$$

Hydrolysis and dimerization (eq. 1) have been proved by preparation of basic salts, determination of the equilibrium constants, analysis and nmr measurements in D_2O solution[35].

Many other actinide(IV) aminocarboxylates show the same reactions as those described for U(EDTA)·aq. As is seen from the equilibrium constants (Table 8), the aminocarboxylates of U(IV) are more stable and have a greater tendency to hydrolyse than those of Th(IV) but have less tendency to dimerize. The tendency to hydrolyse increases with decreasing number of available coordination sites of the acid.

The existence of the 2:1 species $U_2(EDTA)^{4-} \cdot aq$ is indicated by the fact that the hydroxide does not precipitate from a solution of U(IV) and ethylenediaminetetraacetic acid with U(IV):H_4EDTA = 2:1 up to pH 3; in the absence of the ligand, hydroxide formation occurs[36].

Only formation constants are available for Np(IV) and Pu(IV) species, no solid salts having been isolated and no quantitative data on hydrolysis being available. However, it is likely that these systems will resemble those of U(IV).

In $Th(EDTA) \cdot 2H_2O$, $Na[Th(OH)EDTA] \cdot 4H_2O$ and $H[ThDTPA] \cdot H_2O$ all the carboxylic acid groups are coordinated to the thorium, as is shown by the infrared bands, $\nu_{as,CO_2} = 1610$, 1620 and 1600 cm^{-1}, respectively. The same holds for the U(IV)–EDTA complex in D_2O solution, $\nu_{as,CO_2} = 1605$ cm^{-1} [37]. It is likely that the metal atoms in the actinide(IV)–EDTA salts have a coordination number of eight.

TABLE 8. EQUILIBRIUM CONSTANTS FOR THE FORMATION AND HYDROLYSIS OF ACTINIDE(IV) AMINOPOLYCARBOXYLATES
(25°C, ionic strength 0·1)

Reaction	Th[a] log *K*	U(IV)[b] log *K*
Diethylenetriaminepentaacetic acid (H_5DTPE)		
$MDTPE^- \cdot aq \leftrightharpoons M(OH)DTPE^{2-} \cdot aq + H^+$	~ −8·9	−7·69
Ethylenediaminetetraacetic acid (H_4EDTA)		
$M^{4+} \cdot aq + EDTA^{4-} \leftrightharpoons MEDTA \cdot aq$	23·2 ±0·1	25·8 ±0·2
$MEDTA \cdot aq \leftrightharpoons M(OH)EDTA^- \cdot aq + H^+$	−7·04±0·05	−4·72±0·1
$2M(OH)EDTA^- \cdot aq \leftrightharpoons [M(OH)EDTA]_2^{2-} \cdot aq$	4·3 ±0·1	2·9 ±0·05
Cyclohexanediaminetetraacetic acid (H_4CDTA)		
$M^{4+} \cdot aq + CDTA^{4-} \leftrightharpoons MCDTA \cdot aq$	24·9 ±0·2	26·9 ±0·2
$MCDTA \cdot aq \leftrightharpoons M(OH)CDTA^- \cdot aq + H^+$	−7·58±0·05	−4·85±0·01
$2M(OH)CDTA^- \cdot aq \leftrightharpoons [M(OH)CDTA]_2^{2-}$	4·3±0·1	3·50±0·05
Hydroxyethylethylenediaminetriacetic acid (H_3HEDTA)		
$M^{4+} \cdot aq + HEDTA^{3-} \leftrightharpoons MHEDTA^+ \cdot aq$	18·5[c]	
$MHEDTA^{2-} \cdot aq \rightleftharpoons M(OH)HEDTA \cdot aq + H^+$	−5·4[c]	
$2M(OH)HEDTA \cdot aq \rightleftharpoons [M(OH)HEDTA]_2 \cdot aq$	5·2[c]	
N-hydroxyethyliminodiacetic acid (H_2HIMDA)		
$M(HIMDA)_2 \cdot aq \rightleftharpoons M(OH)HIMDA)_2^- \cdot aq + H^+$		−3·67±0·2

[a] R. F. Bogucki and A. E. Martell, *J. Amer. Chem. Soc.* **80** (1958) 4170.
[b] C. H. Carey and A. E. Martell, *J. Amer. Chem. Soc.* **90** (1968) 32.
[c] R. F. Bogucki and A. E. Martell, *J. Amer. Chem. Soc.* **90** (1968) 6022.

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[35] D. L. Ehmann and D. T. Sawyer, *Inorg. Chem.* **9** (1970) 204.

[36] N. P. Ermolaev and N. N. Krot, *Russ. J. Inorg. Chem.* **8** (1963) 1282.

[37] D. T. Sawyer and J. E. Tackett, *J. Amer. Chem. Soc.* **85** (1963) 2390.

Pyridine carboxylic acid and quinaldinic acid

The actinide(IV) compounds with picolinic acid (C_5H_4NCOOH) and N-oxypicolinic acid ($C_5H_4NOCOOH$) are appreciably soluble in water, but can be precipitated by addition of acetone. The composition of the product depends on the conditions of precipitation. Thus for reactions involving the tetrachloride, the product may contain three to six molecules of picolinic acid per metal atom and one to two chloride ions[1]. In solution stable complexes with up to four acid anions per metal atom are formed by Th(IV), U(IV) and Np(IV)[38].

Since the picolinates and N-oxypicolinates of the hexavalent actinide ions are insoluble in water, the separation of U(VI) and Pu(IV) by selective precipitation of the former has been proposed.

Addition of quinaldinic acid (C_9H_7NCOOH) to an aqueous solution of $ThCl_4$ or UCl_4 yields white precipitates of composition $MCl_4 \cdot 8C_9H_7NCOOH$[1] or $MCl_2(C_9H_7NCOO)_2 \cdot 2C_9H_7NCOOH$[39] depending on the pH. This reaction has been suggested for the gravimetric determination of thorium in presence of rare earths[40].

Hexacyanoferric acids

Insoluble compounds have been obtained by addition of potassium ferrocyanide or potassium ferricyanide to acidic solutions of Th(IV), Np(IV) and Pu(IV). The compounds isolated are:

$Th[Fe(CN)_6]$	pale green $\nu_{CN} = 2060\ cm^{-1}$[70]
$Np[Fe(CN)_6] \cdot aq$	green[71]
$Pu[Fe(CN)_6] \cdot 3{,}5H_2O$	black[69] solubility $\simeq$ 10 mg Pu/l
$Pu_3[Fe(CN)_6]_4 \cdot 15H_2O$	black[69] solubility $\simeq$ 7·5 mg Pu/l

The degree of hydration, given above for the Pu compounds, has not been established with certainty.

3. PENTAVALENT ACTINIDE IONS

The pentavalent actinide ions differ considerably in the composition and properties of their carboxylates. Protactinium(V) resembles Nb(V) and Ta(V) and its carboxylates contain the cation PaO^{3+}, whereas the pentavalent transuranium ions form dioxycations MO_2^+ which are present in aqueous solutions and in all salts prepared from aqueous solution. PaO^{3+} forms strong complexes and is easily hydrolysed, whereas NpO_2^+, PuO_2^+ and AmO_2^+ have a low tendency towards complex formation and hydrolysis.

A common type of salt is $MO_2L \cdot 2H_2O$ with L being the monovalent anion of a carboxylic acid. In most cases these salts are appreciably soluble in water and form complex species of the type $NpO_2L_2^{x-}$ with excess acid.

The few known U(V) carboxylates are derived formally from the U^{5+} cation. Solid carboxylates with the dioxo cation have not yet been reported.

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[38] M. Paul, KFK-1210 (1970).

[39] J. T. Barr and C. A. Horten, *J. Amer. Chem. Soc.* 74 (1952) 4430.

[40] L. Shu-chuan and H. Shui-chieh, *Acta chim. Sin.* 28 (1962) 100.

TABLE 9. INFRARED BANDS AND MAGNETIC DATA FOR CARBOXYLIC ACID SALTS OF PENTAVALENT AND HEXAVALENT ACTINIDE IONS

Compound	Band position (cm^{-1})	Assignment	χ_M(cgs units)	Ref.
$NpO_2CH_3COO \cdot H_2O$	1642, 708	coordinated H_2O		a
	1546, 1546	CO_2 asym/sym		
$NpO_2(\alpha\text{-}C_5H_4NCOO) \cdot 2H_2O$	1650, 674	coordinated H_2O		a, b
	1586, 1568, 1414	CO_2 asym/sym		
	1018	ring breathing		
$NpO_2(\alpha\text{-}C_5H_4NCOO) \cdot 2D_2O$	2400	OD valence		a, b
	1212	coordinated D_2O		
$NpO_2(\alpha\text{-}C_5H_4NOCOO) \cdot 2H_2O$	1654, 1648/1442	CO_2 asym/sym		a, b
	1204, 1215	$N \rightarrow O$		
$UO_2(OH)(HCOO) \cdot H_2O$	3440	OH		c
	1605, 1566	CO_2 asym		
	1360, 1308	CO_2 sym		
	947, 915/847	UO_2 asym/sym		
$UO_2(CH_3COO)_2 \cdot 2H_2O$	945/870	UO_2 asym/sym	109·6	d
$Na[UO_2(CH_3COO)_3]$	1537/1472	CO_2 asym/sym		e
	931/856	UO_2 asym/sym		
$Na[NpO_2(CH_3COO)_3]$	1536/1472	CO_2 asym/sym		e
	934/844	NpO_2 asym/sym		
$Na[PuO_2(CH_3COO)_3]$	1540/1470	CO_2 asym/sym		e
	930/818	PuO_2 asym/sym		
$Na[AmO_2(CH_3COO)_3]$	1541/1467	CO_2 asym/sym		e
	914/749	AmO_2 asym/sym		
$UO_2C_2O_4 \cdot 3H_2O$	960/870	UO_2 asym/sym	77·8	c
$M_2[UO_2(C_2O_4)_2] \cdot 3H_2O$ M = Na ··· Cs	922–934	UO_2 asym		f
$M_3[UO_2(C_2O_4)_2OH] \cdot aq$ M = Na, K, Cs	863–900	UO_2 asym		g
$M_5[(UO_2)_2(C_2O_4)OH] \cdot aq$ M = Na ··· Cs	898–905	UO_2 asym		g
$UO_2(CH_3CHOHCOO)_2 \cdot 5H_2O$	943/860	UO_2 asym/sym	132·0	c
$UO_2(C_4H_4O_6) \cdot 4H_2O$	935/848	UO_2 asym/sym	122·0	c
$UO_2(C_6H_6O_7) \cdot 4H_2O$	940/855	UO_2 asym/sym		c
$UO_2(C_6H_4OHCOO)_2 \cdot 5H_2O$	935/855	UO_2 asym/sym	170·4	c
$UO_2(C_4H_4COO)_2 \cdot 3H_2O$	940/865	UO_2 asym/sym	140·9	c
$NH_4[UO_2(\alpha\text{-}C_4H_3OCOO)_3]$	942, 935	UO_2 asym		b
$NH_4[UO_2(\alpha\text{-}C_4H_3SCOO)_3]$	938	UO_2 asym		b
$H[UO_2(\alpha\text{-}C_5H_4NCOO)_3]$	2600, 2057, 1544	N . . . H		h
	1017, 1005	ring breathing		
	905	UO_2 asym		
$UO_2(\alpha\text{-}C_5H_4NCOO)_2$	1017	ring breathing		h
	929	UO_2 asym		
$UO_2(\beta\text{-}C_5H_4NCOO)_2 \cdot 2H_2O$ (D_2O)	1655, 678 (1208, 506)	coordinated H_2O (D_2O)		h
	920	UO_2 asym		
$MO_2(\alpha\text{-}C_5H_4NOCOO)_2 \cdot 2H_2O$ M = U/Np	1207, 1217/1206, 1217	$N \rightarrow O$		h
	916/916	MO_2 asym		
$MO_2(\alpha\text{-}C_5H_4NOCOO)_2 \cdot 2H_2O$ M = Pu, Am	1208, 1217/1207, 1216	$N \rightarrow O$		h
	915/898	MO_2 asym		

[a] S. H. Eberle, KFK-1136 (1970) 95.

[b] E. Brandau, KFK-1068 (1970) 19.

[c] M. Bideau, R. Bressat, B. Mentzen and A. Navarro, *Compt. Rend.* **C271** (1970) 225.

[d] M. P. Sahakari and A. J. Mukhedkar, *J. Inorg. Nucl. Chem.* **33** (1971) 888.

[e] L. H. Jones, *J. Chem. Phys.* **23** (1955) 2105.

[f] R. N. Shchelokov and V. I. Belomstnykh, *Russ. J. Inorg. Chem.* **14** (1969) 1491.

[g] R. N. Shchelokov and V. I. Belomstnykh, *Russ. J. Inorg. Chem.* **15** (1970) 70, 74.

[h] W. Robel, KFK-1070 (1970).

Acetic acid

The compound $NpO_2(CH_3COO)\cdot 2H_2O$ can be prepared by treating wet, freshly precipitated NpO_2OH with glacial acetic acid[1]. Efforts to prepare a Pu(V) acetate in this way failed due to disproportionation into a mixture of Pu(IV) and Pu(VI) acetates[41]. $NpO_2(CH_3COO)\cdot 2H_2O$ is readily soluble in water but insoluble in alcohols. On heating, the water is lost in two steps at about 90°C and at about 160°C, respectively. The final decomposition occurs at 280–310°C and leads to the dioxide NpO_2. In the infrared spectrum (Table 9) no band is observed that can be assigned to the neptunyl(V) group itself. This is in contrast to the corresponding actinide(VI) compounds, for which the asymmetric stretching frequency is always seen as strong band.

Oxalic acid

Oxalates of NpO_2^+ and PuO_2^+ containing one and two oxalate anions are known. The pale-green $NpO_2HC_2O_4\cdot 2H_2O$ precipitates when a solution of Np(V) in 1 M HCl and a solution of oxalic acid in anhydrous t-butanol are mixed. The compound has a magnetic moment of 3·17 μ_B. It is acidic, being appreciably dissociated in aqueous solution. Salts of the composition $M[NpO_2C_2O_4\cdot H_2O]\cdot nH_2O$ with $M = Na^+, K^+, NH_4{}^+$ have been prepared from aqueous media[42]. An analogous Pu compound is also known: $NH_4[PuO_2C_2O_4]\cdot 6H_2O$[30].

Np(V) and Pu(V) are very soluble in water in the presence of oxalic acid or alkali metal oxalates. Depending on the oxalate ion concentration the solutions contain the complexes $MO_2(C_2O_4)^-$ or $MO_2(C_2O_4)_2{}^{3-}$, the stability constants of which have been determined[30]. Green–yellow $[Co(NH_3)_6][NpO_2(C_2O_4)_2]\cdot 2H_2O$ precipitates at about pH 5 on addition of a solution of $[Co(NH_3)_6]Cl_3$. It is insoluble in water and organic solvents and stable up to 110°C[42].

The behaviour of Pa(V) towards oxalic acid is different from that of Np(V) and Pu(V). The compounds form at high hydrogen ion concentration and do not contain a dioxocation. Freshly precipitated $Pa_2O_5\cdot aq$ dissolves in 0·1 M oxalic acid solution and white, sparingly soluble $PaO(OH)(C_2O_4)\cdot 2H_2O$ precipitates on acidification of this solution with hydrochloric acid ($\geq$1 M)[43]. Addition of aqueous ammonia to increase the pH results in the formation of soluble, higher oxalato-complexes such as $PaO(C_2O_4)_2{}^-$. At pH > 5 protactinium hydroxide precipitates. $Pa(OH)(C_2O_4)_2\cdot 6H_2O$ has been isolated from 0·5 M oxalic acid solution. The mono-oxalate compound loses water at 120–130°C and at 335°C the decomposition to the pentoxide starts. Light absorption and infrared measurements (ν: 778, 500, 245 cm^{-1}) indicate the presence of a polymeric grouping, –O–Pa–O–Pa, in this compound.

Oxycarboxylic acids and thiocarboxylic acids

Compounds of the composition $NpO_2L\cdot 2H_2O$ with HL = glycollic acid, thiophencarboxylic acid and furancarboxylic acid have been prepared by treating $NpO_2CH_3COO\cdot 2H_2O$ with the appropriate acid in a small amount of water and evaporating the acetic acid and the water under reduced pressure at 50°C[1, 44]. The water hydration is lost in one step

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[41] M. Aley, Q. C. Johnson, H. D. Cowan and J. F. Lemon, *J. Inorg. Nucl. Chem.* **29** (1967) 2327.
[42] A. D. Gelman, V. I. Blokhin, T. N. Bukhtiyarova and N. N. Krot, *Russ. J. Inorg. Chem.* **15** (1970) 975.
[43] R. Muxart, R. Guillanmont and G. Boussières, *Actinide Rev.* **1** (1969) 223.
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at about 100°C and the anhydrous compounds decompose to NpO_2 at about 300°C. All the salts are quite soluble in water.

Different types of thiocarboxylates are known for U(V). Thus, reaction of uranium pentaethoxide with thiosalicylic acid yields compounds[45] such as

$U(C_2H_5O)_3(C_6H_4SCOO)$	brown
$U_2(C_6H_4SCOO)_5$	light brown

Similar compounds are formed with thiolactic acid, $CH_3CHSHCOOH$, and thiobenzoic acid, C_6H_5COSH.

Aminopolycarboxylic acids

Only two solid salts of a pentavalent actinide ion are known at present. Grey $(NpO_2)_2H_2EDTA \cdot 5H_2O$, obtained by addition of ethylene-diaminetetraacetic acid (H_4EDTA) to a neutral solution of Np(V), and reddish-yellow $[Co(HN_3)_6]NpO_2(EDTA) \cdot 3H_2O$, which precipitates from a solution of the former at pH 7 on addition of a 0·05 M $[Co(NH_3)_6]Cl_3$ solution[42].

Investigations of complex formation with many other aminopolycarboxylic acids in solution have been reported[46]. These show that Np(V) and Pu(V) form 1:1 complexes and 1:2 complexes with bidentate acids, for example glycine, and 1:1 complexes with acids containing three and more coordination sites. The stability constants of the latter are about 10^7, irrespective of the type of acid. From this it is concluded that the actinide(V)-yl ions coordinate only with one iminodiacetic acid group of an aminopolyacetic acid. At high pH all the aminopolycarboxylates form soluble hydroxy complexes such as $NpO_2(EDTA)(OH)^{4-}$ for example[1], and no hydroxide precipitation occurs up to pH 12.

Pyridine carboxylic acids

Salts of the composition $NpO_2L \cdot 2H_2O$ with HL = picolinic acid (green) and HL = N-oxy-pyridine-2-carboxylic acid (brown) have been prepared by precipitation from aqueous solution[44]. They are sparingly soluble in water, alcohol and acetone, but dissolve readily in aqueous solution containing excess ligand at pH ≃ 4 to form complex anions of the type $NpO_2L_2 \cdot aq^-$. The water molecules of the picolinate dihydrate can be replaced by other monodentate non-acidic ligands, for example dimethylsulfoxide (DMSO), to yield the solvate $NpO_2(C_5H_4NCOO) \cdot 2DMSO$.

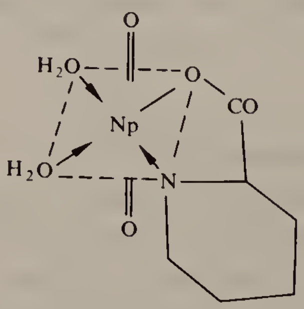

FIG. 3. Structure of neptunyl(V)-pyridine-2-carboxylate.

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[45] S. Dubey, A. M. Bhandari, S. N. Mistra and R. N. Kapoor, *Ind. J. Chem.* **8** (1970) 97.
[46] S. H. Eberle and U. Wede, *J. Inorg. Nucl. Chem.* **32** (1970) 109.

The thermogravimetric decomposition of $NpO_2(C_5H_4NCOO)\cdot 2H_2O$ results in dehydration at 125°C followed by decomposition at 370°C.

Details of the infrared spectra of the salts are given in Table 9. These indicate the structure shown in Fig. 3 for $NpO_2(C_5H_4NCOO)\cdot 2H_2O$, with a tetracoordinated NpO_2^+ ion.

4. HEXAVALENT ACTINIDE IONS

This valence state is known for the elements U, Np, Pu and Am. In aqueous solution and in most crystalline compounds the metal dioxo group MO_2^{++} (often called "yl" group) is present as a structural unit, the metal–oxygen bond strength decreasing in the sequence U > Np > Pu > Am. As has been revealed primarily with the acetate compounds, the yl group has a linear structure. In the actinyl(VI) compounds further coordination generally occurs on or near the equatorial plane, the coordination polyhedron being either a pentagonal or a hexagonal bipyramid. Strong steric hindrance is caused by the yl oxygens with ligands that tend to envelop the central cation.

With strong and weak acids, salts containing up to three anion molecules per metal atom may be obtained from aqueous solution. Hydrolysis of the hexavalent actinide ions occurs at low pH ($\simeq 3$) and basic carboxylates are formed easily; these have a strong tendency to polymerize.

Formic acid

Uranium forms salts containing either one or two ligand anions per metal atom. No information is available on reactions involving the hexavalent transuranium ions, but it is likely that they are quickly reduced to a lower oxidation state.

Yellow $UO_2(HCOO)_2\cdot H_2O$ is obtained by evaporation of a solution of ammonium diuranate in dilute formic acid; the anhydrous compound $UO_2(HCOO)_2$ is formed at 170°C[14]. The basic salt $UO_2(OH)(HCOO)\cdot H_2O$ can be prepared by ligand displacement:

$$UO_2(HCOO)_2\cdot H_2O_{(s)} + H_2O_{(g)} \rightarrow UO_2(OH)(HCOO)\cdot H_2O_{(s)} + HCOOH_{(g)}$$

Thermal decomposition involves four steps giving U_3O_8 at about 690°C (Table 12). According to the positions of the carboxyl frequencies the formic acid anion is thought to be bidentate (Table 9), forming a bridge between two uranium atoms[47].

Acetic acid

A great variety of compounds is formed between acetic acid and the hexavalent actinide ions, the most characteristic type being the triacetate $NaMO_2(CH_3COO)_3$.

A diacetate, $UO_2(CH_3COO)_2\cdot 2H_2O$, is obtained as prismatic yellow crystals by concentrating on acetic acid solution of U(VI). Depending on the proportions of acid and uranium, the solvate $UO_2(CH_3COO)_2\cdot 2CH_3COOH\cdot 2H_2O$ or basic acetates such as $UO_2CH_3COO(OH)\cdot 1\cdot 5H_2O$ can also be obtained[48]. These types of salts have not been prepared for other actinide(VI) ions.

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[48] A. Colani, *Bull. Soc. Chim. France*, **41** (1927) 1291.

TABLE 10. CRYSTALLOGRAPHIC DATA FOR CARBOXYLIC ACID SALTS OF HEXAVALENT ACTINIDE IONS

Compound	Symmetry	Space group	Lattice parameters				Z	Density (g/cm)	Ref.
			a(Å)	b(Å)	c(Å)	Angles			
$UO_2C_2O_4 \cdot 3H_2O$	Monoclinic	$P2_1/C$	5·623	17·065	9·451	$\beta = 98 \cdot 74°$		3·076 (obs)	a
$UO_2C_2O_4 \cdot H_2O$	Monoclinic		5·52	16·98	10·15	$\beta = 100 \cdot 05°$			b
$UO_2C_2O_4$	Monoclinic		5·50	16·67	10·57	$\beta = 96 \cdot 63°$			b
$PuO_2C_2O_4 \cdot 3H_2O$	Monoclinic		5·619	16·865	9·42	$\beta = 98 \cdot 43°$			a
$UO_2(CH_3COO)_2 \cdot 2(C_6H_5)_3AsO$	Monoclinic	$P2_1/C$	9·868	19·166	10·880	$\beta = 116 \cdot 53°$	2	1·85 (obs)	c
$[UO_2(CH_3COO)_2(C_6H_5)_3AsO]_2$	Triclinic	$P\bar{1}$	8·31	11·05	13·66	$\alpha = 101 \cdot 83°$ $\beta = 91 \cdot 17°$ $\gamma = 109 \cdot 20°$	1	2·03 (obs)	c
$[UO_2(CH_3COO)_2(C_6H_5)_3PO]_2$	Triclinic	$P\bar{1}$	8·346	11·022	13·680	$\alpha = 101 \cdot 83°$ $\beta = 91 \cdot 17°$ $\gamma = 109 \cdot 20°$	1	1·91 (obs)	d
$UO_2(CH_3COO)_2 \cdot 2H_2O$	Orthorhombic	$Pbn2_1$	14·95	9·61	6·93		4		e
$UO_2(C_6H_4OHCOO)_2 \cdot 2H_2O$	Triclinic	$P1$	6·49	7·87	9·00	$\alpha = 114 \cdot 57°$ $\beta = 97 \cdot 33°$ $\gamma = 95 \cdot 15°$	1		f
$Na[UO_2(CH_3COO)_3]$	Cubic	$P2_13$	10·688				4		g
α-$K[UO_2(CH_3COO)_3]$	Tetragonal	$I4_12$	14·41		25·85		16		h
β-$K[UO_2(CH_3COO)_3]$	Tetragonal	$I4_12$	14·02		27·76		16		h
$NH_4[UO_2(CH_3COO)_3]$	Tetragonal	$I4_12$	13·82		27·76		16		i
$Rb[UO_2(CH_3COO)_3]$	Tetragonal	$I4_12$	13·84		25·57		16		i
$Ca(UO_2)_2(CH_3COO)_6 \cdot 6H_2O$	Orthorhombic		17·02	17·02	28·45		12		j
$Sr(UO_2)_2(CH_3COO)_6 \cdot 6H_2O$	Tetragonal	$I4_1md$ or $I\bar{4}2d$	17·26		28·62		12		j
$Ba(UO_2)_2(CH_3COO)_6 \cdot 6H_2O$	Orthorhombic	$Pna2r$ or $Pnma$	13·89	13·89	29·98		8		j
$K[UO_2(C_2H_5COO)_3]$	Cubic	$P2_13$	11·52				4		k
$NH_4[UO_2(C_2H_5COO)_3]$	Cubic	$P2_13$	11·64				4		k
$K[UO_2(CH_3CH_2CH_2COO)_3]$	Cubic	$I23$ or $I2_13$	20·84				20		k
$UO_2(OH)(HCOO) \cdot H_2O$	Orthorhombic	$C_2{}^8v$ or $D_2{}^9h$	10·55	13·52	16·02		14	3·45 (obs)	l
$Na[NpO_2(CH_3COO)_3]$	Cubic	$P2_13$	10·679				4	2·556 (calc)	m
$Na[PuO_2(CH_3COO)_3]$	Cubic	$P2_13$	10·670				4	2·578 (calc)	m
$Na[AmO_2(CH_3COO)_3]$	Cubic		10·653						m

Triacetates $NaMO_2(CH_3COO)_3$, with M=U (yellow), Np, Pu (pink), and Am (lemon-yellow), precipitate from solutions of the appropriate actinide(VI) ion on addition of an excess of $NaCH_3COO$ and $NaNO_3$[49]. Typical precipitation conditions are: 0·2 M CH_3COOH–0·6 M $NaCH_3COO$–4 M $NaNO_3$. Coprecipitation with $NaUO_2(CH_3COO)_3$ is an excellent way to separate Np, Pu and Am in tracer amounts from other elements, especially the products of nuclear fission. Isolation as the triacetate is also valuable for the purification of gram amounts of these three transuranium elements.

The sodium actinide(VI) triacetates are one group of a whole series of double and triple acetates. Formation of slightly soluble, well-crystalline compounds of the types $MO_2(CH_3COO)_2 \cdot M'(CH_3COO)_x \cdot aq$ and $MO_2(CH_3COO)_2 \cdot M'(CH_3COO)_y \cdot M''(CH_3COO)_y \cdot aq$ is a characteristic property of the hexavalent actinide ions, although most compounds are known only for uranium (Table 10). The nonactinide metals M′ and M″ may be alkali metals, alkaline earth metals or *d*-transition element metals[21,50,52].

All actinide(VI) acetates are moderately soluble in water. The solubility decreases from the 1:2 acetates ($UO_2(CH_3COO)_2 \cdot 2H_2O$: 77 g/l at 15°C) to the double acetates and the triple acetates, being roughly parallel to the increasing molecular weight. Some data on the solubility and the complexation of hexavalent actinide ions by acetic acid are collected in Table 11. The aqueous solutions contain complex ions of the types $MO_2(CH_3COO)^+ \cdot aq$, $MO_2(CH_3COO)_2{}^0 \cdot aq$ and $MO_2(CH_3COO)_3{}^- \cdot aq$, depending on the acetate ion concentration. The negatively charged species adsorb on anion exchangers and are efficiently extracted by tertiary amines or long-chain quaternary ammonium salts, dissolved in an organic diluent[53]. In these solutions the tetraacetato anions $UO_2(CH_3COO)_4{}^{2-}$, $NpO_2(CH_3COO)_4{}^{2-}$ and $PuO_2(CH_3COO)_4{}^{2-}$ have been identified. The association constant of a fourth acetate anion onto $UO_2(CH_3COO)_3^-$ is about 2 in acetonitrile. At high pH and low acetate concentration a hydroxo acetate $UO_2(CH_3COO)_2(OH)_2{}^{2-}$ has been identified, the formation constant of which is 4×10^{18} at 20°C and $\mu = 0{\cdot}5$[51,52].

The thermal decomposition of the actinide(VI) acetates proceeds generally in two steps, first dehydration at $\simeq$100°C and then the decomposition of the organic matter with the formation of MO_2 at >300°C[54]. Detailed thermogravimetric results are shown in Table 12.

Some infrared and magnetic data for actinide(VI) acetates are given in Table 9. The

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Notes to Table 10.

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[m] L. H. Jones, *J. Chem. Phys.* **23** (1955) 2105.

bond force constants, and thus the stability, of the yl group in the sodium actinide triacetates decreases in the order $UO_2^{2+} > NpO_2^{2+} > PuO_2^{2+} > AmO_2^{2+} = 0{\cdot}705 > 0{\cdot}698 > 0{\cdot}675 > 0{\cdot}612$ megadyne/cm[49]. This decrease is associated with the decreasing ability of the *f*-orbitals to overlap with the oxygen orbitals to form σ- and π-bonds.

The isomorphous salts $NaMO_2(CH_3COO)_3$ possess cubic symmetry (Table 10). In $NaUO_2(CH_3COO)_3$ (Fig. 4) there is a nearly coplanar arrangement of the three acetate anions in the equatorial plane of the linear O–U–O group; each carboxylic group is bidentate. Crystal data for several other uranium(VI) acetates are given in Table 10.

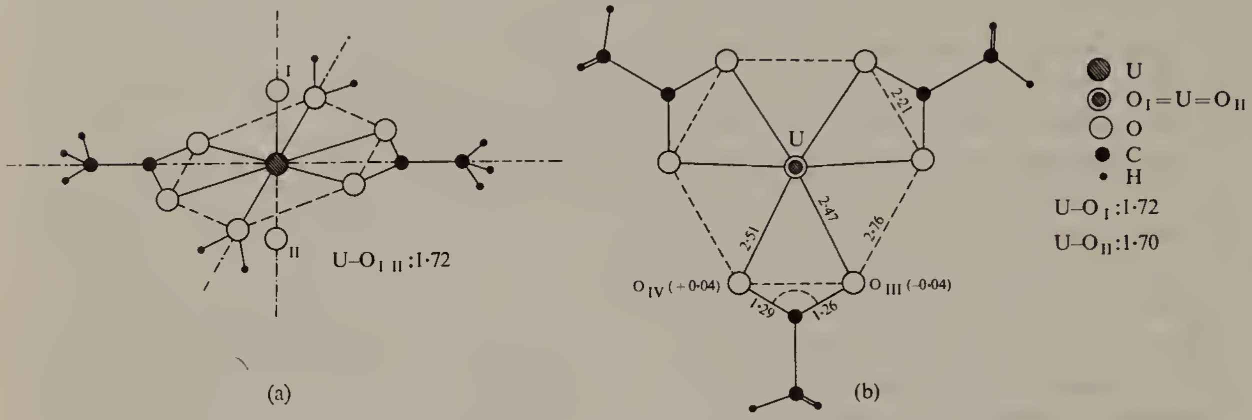

FIG. 4. Structure of $UO_2(CH_3COO)_2{\cdot}2H_2O$ (a) and $NaUO_2(CH_3COO)_3$ (b).

Other monodentate carboxylic acids

Aliphatic and aromatic carboxylic acids containing the carboxyl as the only coordinating group generally form the same types of compounds with hexavalent actinide ions as do acetic acid. In aqueous solutions the complex species $MO_2(CH_2ClOO)_x^{(2-x)+}$ and $MO_2(CH_2Cl\text{–}CH_2COO)_x^{(2-x)+}$ with M=U, Np, Pu are known, the stabilities of which have been determined[55]. Solid salts of the type $UO_2L_2{\cdot}nH_2O$ have been prepared, for example, with propionic acid ($n = 2$), isobutyric acid ($n = 2$), valeric acid ($n = 3$), monochloracetic acid ($n = 0$), trichloracetic acid ($n = 0$), benzoic acid ($n = 0$), phenylacetic acid ($n = 0$), naphthoic acid ($n = 3$) and oleic acid ($n = 2$)[56]. Double acetates and triple acetates of U(VI) with most of these acids are also known and details of their conductivities, luminescence spectra[50,57], thermal decomposition (Table 12), infrared spectra (Table 9) and lattice parameters (Table 10) are available.

Oxalic acid

On addition of oxalic acid to a mineral acid solution of an actinide(VI) ion the appropriate monooxalate trihydrate precipitates: $UO_2C_2O_4{\cdot}3H_2O$ (yellow), $NpO_2C_2O_4{\cdot}3H_2O$ (greyish-green), $PuO_2C_2O_4{\cdot}3H_2O$ (rose). The compounds are slightly soluble in water, the solubility increasing on addition of mineral acid. Data on the solubility and the solubility products are collected in Table 11. $UO_2C_2O_4{\cdot}3H_2O$ solubility isotherms of many water–acid

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TABLE 11. SOLUBILITY AND COMPLEXATION OF HEXAVALENT ACTINIDE IONS IN SOLUTIONS OF ACETIC ACID AND OXALIC ACID

Compound	Solubility		Temp. (°C)	Reference
	Data	Medium		
$UO_2(CH_3COO)_2$	solubility product $6\cdot9\times10^{-7}$	$HClO_4$ var.	?	a
$Na[UO_2(CH_3COO)_3]$	solubility $0\cdot13$ mole/l	H_2O	20	a
$Na[NpO_2(CH_3COO)_3]$	solubility $\simeq 0\cdot1$ mole/l	$0\cdot5$ M H_2SO_4	?	b
$PuO_2(CH_3COO)_2$	solubility product $2\cdot8\times10^{-8}$	HCl var.	?	c
$Na[PuO_2(CH_3COO)_3]$	solubility $0\cdot04$ mole/l	H_2O	25	c
$Na[AmO_2(CH_3COO)_3]$	solubility $0\cdot0014$ mole/l	3 M $NaCH_3COO$	22	d
$UO_2C_2O_4\cdot3H_2O$	solubility $0\cdot014$ mole/l	H_2O	20	l
	solubility product $2\cdot2\times10^{-9}$	$HClO_4$		j
$NpO_2C_2O_4\cdot3H_2O$	solubility $0\cdot0017$ mole/l	1 M HNO_3	14	h
	solubility product $2\cdot3\times10^{-9}$	1 M HNO_3	14	h
$PuO_2C_2O_4\cdot3H_2O$	solubility $0\cdot0024$ mole/l	H_2O	20	i
	solubility product	1–3 M HNO_3	20	k

System	Stability constant	Medium	Temp. (°C)	Reference
UO_2^{++}/CH_3COOH	$\log\beta_1 = 2\cdot40$	1 M $NaClO_4$	25	f
	$\log\beta_2 = 4\cdot43$	1 M $NaClO_4$	25	
	$\log\beta_3 = 6\cdot37$	1 M $NaClO_4$	25	
NpO_2^{++}/CH_3COOH	$\log\beta_1 = 2\cdot31$	1 M $NaClO_4$	25	e
	$\log\beta_2 = 4\cdot23$	1 M $NaClO_4$	25	
	$\log\beta_3 = 6\cdot00$	1 M $NaClO_4$	25	
Pu_2^{++}/CH_3COOH	$\log\beta_1 = 2\cdot13$	1 M $NaClO_4$	25	g
	$\log\beta_2 = 3\cdot49$	1 M $NaClO_4$	25	
	$\log\beta_3 = 5\cdot01$	1 M $NaClO_4$	25	
$UO_2^{++}/C_2O_4H_2$	$\log\beta_1 = 4\cdot63$	1 M $NaClO_4$	20	m
	$\log\beta_2 = 8\cdot69$	1 M $NaClO_4$	20	
	$\log\beta_3 = 11\cdot98$	1 M $NaClO_4$	20	
$NpO_2^{++}/C_2O_4H_2$	$\log\beta_1 = 6\cdot00$	1 M $NaClO_4$	20	h
$PuO_2^{++}/C_2O_4H_2$	$\log\beta_1 = 6\cdot66$	1 M $NaClO_4$	20	n
	$\log\beta_2 = 11\cdot47$	1 M $NaClO_4$		

[a] I. I. Chernyaev, *Complex Compounds of Uranium*, Jerusalem (1966).

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TABLE 12. THERMAL DECOMPOSITION OF CARBOXYLIC ACID SALTS OF HEXAVALENT ACTINIDE IONS

Compound	Temperature (°C)	Reaction	Ref.
$UO_2(HCOO)_2 \cdot H_2O$	145–195	release of H_2O	a
	370–690	decomposition of org. matter	
$UO_2(CH_3COO)_2 \cdot 2H_2O$	96–140	release of H_2O	b
	300–345	decomposition of org. matter	
$NaUO_2(CH_3COO)_3$	365	decomposition of org. matter	c
$NH_4UO_2(CH_3COO)_3$	235–250	$-NH_4CH_3COO$?	d
$NaZn(UO_2)_3(CH_3COO)_9 \cdot 6H_2O$	140	release of H_2O	
	360	decomposition of org. matter	c
$NaMg(UO_2)_3(CH_3COO)_9 \cdot 9H_2O$	$\simeq 100$	release of H_2O	
	360	decomposition of org. matter	c
$LaUO_2(CH_3COO)_5 \cdot 3H_2O$	130–195	release of H_2O	e
	410–460	decomposition of org. matter	
$LaUO_2(C_2H_5COO)_5 \cdot 3H_2O$	100–155	release of H_2O	e
	265–470	decomposition of org. matter	
$UO_2C_2O_4 \cdot 3H_2O$	80–160	release of 2 H_2O	f
	175–230	release of 1 H_2O	
$UO_2(C_4H_3SCOO)_2 \cdot H_2O$	$\simeq 110$	release of 1 H_2O	g
$UO_2(C_4H_3OCOO)_2 \cdot H_2O$	$\simeq 100$	release of 1 H_2O	g
$NH_4[MO_2(C_4H_3SCOO)_3]$	260/210/220	$NH_4C_4H_3SCOO$ sublimes off	g
M = U/Np/Pu	345/370/390	decomposition of org. matter	
$NH_4[MO_2(C_4O_3OCOO)_3]$	240/200/180	$NH_4C_4H_3OCOO$ sublimes off	g
M = U/Np/Pu	310/290/230	decomposition of org. matter	
$H[MO_2(C_5H_4NCOO)_3]$	210/190/160	C_5H_4NCOOH sublimes off	h
M = U/Np/Pu	390/>200/ >230	decomposition of org. matter	
$MO_2(C_5H_4NOCOO)_2 \cdot 2H_2O$	130/110/105/70	formation of $MO_2(C_5H_4NOCOO)_2$	h
M = U/Np/Pu/Am	300/>120/ >120/>100	decomposition of org. matter	
$UO_2(C_2H_4N_2(CH_2COO)_4H_2) \cdot 2H_2O$	40–125	release of H_2O	i
	175≃500	decomposition of org. matter	

[a] G. D. Buttrers and M. A. Hughes, *J. Chem. Soc.* A (1968) 1272.
[b] P. S. Clough, D. Dollimore and P. Grundy, *J. Inorg. Nucl. Chem.* **31** (1969) 361.
[c] I. I. Chernyaer, *Complex Compounds of Uranium*, Jerusalem (1966).
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[e] Z. M. Alikhanova and G. V. Ellert, *Russ. J. Inorg. Chem.* **16** (1971) 816.
[f] R. Bressat, B. Claudel and Y. Trambonze, *J. Chim. Phys.* **61** (1964) 816.
[g] E. Brandau, KFK-1068 (1970).
[h] W. Robel, KFK-1070 (1970).
[i] M. Krishnamurthy and K. B. Morris, *Inorg. Chem.* **8** (1969) 2620.

systems have been investigated[21]. The molar conductivity is $22 \cdot 4$ cm^2 ohm^{-1} for the uranium compound at 25°C[21].

$UO_2C_2O_4 \cdot 3H_2O$ acts as an acid, as is shown by the pH ($=3 \cdot 9$) of the saturated aqueous solution. The acidity constant corresponding to the dissociation

$$UO_2C_2O_4 \cdot aq \rightleftharpoons UO_2(C_2O_4)(OH)^- \cdot aq + H^+$$

is 5×10^{-7} [21]. The compound has an acid strength equal to that of carbonic acid. The ammonium salt $NH_4[UO_2(C_2O_4)(OH)] \cdot 3H_2O$ has also been prepared[21]. No measurements of the acidity of Np(VI) or Pu(VI) oxalate exist.

The mono-oxalates dissolve easily in solutions of alkali metal oxalates or ammonium oxalate, forming complexes with up to three oxalate anions per metal atom (Table 11).

Solid complexes of the types $M_2[(UO_2)_2(C_2O_4)_5]\cdot aq$, $M_2[UO_2(C_2O_4)_2]\cdot aq$, $M_4[UO_2(C_2O_4)_3]\cdot aq$, $M_3[UO_2(C_2O_4)_2OH]\cdot aq$ and $M_5[(UO_2)_2(C_2O_4)_4OH]\cdot aq$ have been prepared, M being an alkali metal, a quaternary ammonium salt or an alkaline earth metal[21,34,58,59,60]. The compounds have been characterized by refractive index, molar conductivity and infrared studies (Table 9).

The thermal decomposition of $UO_2C_2O_4\cdot 3H_2O$ proceeds in three steps, the stable intermediates $UO_2C_2O_4\cdot H_2O$ and $UO_2C_2O_4$ (Table 12) being obtained by prolonged heating at the appropriate temperatures. The final product seems to be UO_2, which is obtained at about 370°C. Plutonyl(VI) oxalate decomposes explosively to PuO_2 at 180°C. When stored at room temperature it undergoes radiolytic reduction.

X-ray data for the actinide(VI) oxalates are given in Table 10.

Hydroxycarboxylic acids and thiocarboxylic acids

With monocarboxylic acids three types of compounds have been characterized: the 1:2 salts, $MO_2L_2\cdot nH_2O$ (and the corresponding anhydrous compounds), the double salts, $M'[MO_2L_3]$, with $M' = Na, K, NH_4$ (analogous to the triacetates), and basic salts of the type $(MO_2)_2L_3(OH)\cdot nH_2O$.

Many uranyl(VI)-1:2 salts with monocarboxylic acids have been described by Müller[56], e.g. with glycollic acid, lactic acid, mandelic acid and salicylic acid. Preparation is achieved by dissolving uranyl nitrate and the sodium salt of the acid in water and concentrating until crystallization occurs. The products contain one or two molecules of water of hydration, can be dried to give the anhydrous salt and are generally readily soluble (except the salicylate) in water and alcohol but insoluble in ether. Some other properties are summarized in Tables 9 and 12. The only known transuranyl(VI) salt is that of plutonium with α-hydroxy caproic acid $PuO_2(C_4H_9CHOHCOO)_2$, which is only slightly soluble in water[1]. Complex species $MO_2L_x^{(x-2)-}$ with glycollic acid and lactic acid with $x = 1, 2, 3$ and $M = U, Pu$ are known in solution[1].

All three types of salts described above are known for U(VI), Np(VI) and Pu(VI) with furan-2-carboxylic acid:

(I)	$MO_2(C_4H_3OCOO)_2\cdot H_2O$	M: U
(II)	$NH_4[MO_2(C_4H_3OCOO)_3]$	M: U, Np, Pu
(III)	$(MO_2)_2(C_4H_3OCOO)_3(OH)$	M: U, Np, Pu

The compounds crystallize from aqueous or methanolic solutions of the hexavalent cation and the acid, the nature of the product depending on the pH value and the ratio acid:cation. Excess of acid favors type II, low pH favors type I and at pH > 4 type III is formed[56,61]. The same situation is true with thiophene-2-carboxylic acid.

The compounds are moderately soluble in water and ethanol, the basic and triacido salts being less soluble than the 1:2 salts. They are extracted from aqueous solution by ether, ketones and chloroform, with distribution coefficients less than 100[61].

Data on the thermal stability of the different compounds are incorporated in Table 12.

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[59] R. N. Shchelokov and V. I. Belomestnykh, *Russ. J. Inorg. Chem.* **14** (1969) 1491.

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The decomposition of the 1:3 salts proceeds in two steps with the 1:2 salt as an isolable intermediate ($L = C_4H_3OCOO$, C_4H_3SCOO):

$$NH_4[MO_2L_3] \xrightarrow[-\,NH_4L]{\simeq 200^\circ C} MO_2L_2 \xrightarrow{\simeq 300^\circ C} MO_2$$

The thermal stability decreases in the order U > Np > Pu. Water is lost from the hydrated U(VI) compounds at ≃100°C, the final decomposition starting at about 300°C. Infrared frequencies for the asymmetric uranyl vibrations are given in Table 9.

With salicylic acid the normal 1:2 salt $UO_2(C_6H_4OHCOO)_2 \cdot 4H_2O$ (triclinic, Table 10), the triacido salts $M[UO_2(C_6H_4OHCOO)_3] \cdot 9H_2O$ (orange) with $M = K, NH_4$, and the red species $M_2UO_2(C_6H_4OCOO)_2 \cdot 9H_2O$ ($M = K, NH_4$) are known[62]. Tartaric acid and citric acid form water-soluble 1:1 salts $UO_2(C_4H_4O_6) \cdot 4H_2O$ and $(UO_2)_3(C_3H_4OH(COO)_3) \cdot 6H_2O$, respectively. Infrared and magnetic data are given in Table 9. When $UO_2(OH)_2$ is boiled with a solution of $KHC_2H_4O_6$ and alcohol then added, the complex $K_2[UO_2(C_4H_4O_6)_2] \cdot 2H_2O$ is precipitated. In solution both acids form 1:2 complexes[1].

Aminopolycarboxylic acids

Solid hydrated compounds of hexavalent uranium with the stoichiometric ratio UO_2^{++} : ligand = 1:1 are formed with all types of aminopolycarboxylic acids. Lesser coordinated compounds are known only with some acids having four carboxylic groups (Table 13). Higher coordinated compounds are generally not formed, neither in the solid nor or in solution, an exception being the nitrilotriacetate $(UO_2)_3(NTA)_2 \cdot 10H_2O$. Most of the salts are only slightly soluble in water and are insoluble in the common organic solvents. The solubility product of uranyl ethylenediaminetetraacetate, $H_2[UO_2(EDTA)] \cdot 2H_2O$, has been determined to be $2{\cdot}25 \times 10^{-6}$ mole²/l² at 25°C[63]. Compounds of the acids containing a hydroxyethylene group are more soluble (>0·01 mole/l).

In aqueous solution the complex species $(UO_2)_2L$, UO_2HL and UO_2L are known. Some thermodynamic data for individual complexes are included in Table 13, showing these to be highly entropy-stabilized and to have an endothermic formation reaction. At high pH (>4) hydrolysis and dimerization occurs[64,65], for example:

$$UO_2ADTE^{2-} \cdot aq \leftrightharpoons UO_2ADTE(OH)^{3-} \cdot aq + H^+ \qquad \log \beta_{OH} = -6{\cdot}30$$

$$2UO_2ADTE(OH)^{3-} \cdot aq \leftrightharpoons UO_2ADTE(OH)^{6-} \cdot aq \qquad \log \beta_D = 3{\cdot}27$$

The hydroxo-complexes are soluble in water, therefore all 1:1 salts dissolve easily in solutions of alkali metal hydroxides.

The salts generally retain at least one molecule of water up to 110°C, and complete dehydration is frequently not possible without decomposition. Complete decomposition is observed at 200–300°C. Salts not containing free carboxylic groups have a higher thermal stability than others.

Salts containing more than two carboxylic groups exhibit infrared bands of the dissociated as well as of the undissociated carboxyl entity and the stability constants vary only slightly with the type of ligand. The same is true for the formation entropy (Table 13). This

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TABLE 13. DATA ON AMINOPOLYCARBOXYLIC ACID COMPOUNDS OF URANIUM(VI)

Acid	Properties of the solid compounds				Equilibrium data of $UO_2L \cdot aq$				Ref.
	Composition	$\nu_{as}(UO_2)$ (cm^{-1})	$\nu_{as}(CO_2)$ (cm^{-1})	$\nu_s(CO_2)$ (cm^{-1})	log β	ΔG_0 (kcal/mole)	ΔH_0 (kcal/mole)	ΔS_0 (eu)	
Iminodiacetic acid (H_2IMDA)	$UO_2IMDA \cdot H_2O$	915			8·93				a, b
	$UO_2(HIMDA)_2 \cdot H_2O$	916	1590	1412					c
N-methyliminodiacetic acid (H_2MIMDA)	$UO_2MIMDA \cdot H_2O$				9·71	−13·2	1·0	48	a, d
N-hydroxyethyliminodiacetic acid (H_2HIMDA)	$UO_2HIMDA \cdot aq$				8·34	−11·4	2·2	46	a, d
Nitrilotriacetic acid (H_3NTA)	$H[UO_2NTA] \cdot 2H_2O$	950		1412	9·56				c, e
	$(UO_2)_3(NTA)_2 \cdot 10H_2O$	938	1564/1628	1412					c
N-hydroxyethylethylenediamine-tetraacetic acid (H_3HEDTA)	$H[UO_2HEDTA] \cdot H_2O$				6·36				a, g
Ethylenediaminetetraacetic acid (H_4EDTA)	$H_2[UO_2ADTE] \cdot 2H_2O$	917	1630/1658		7·40*	−10·1	3·2	45	c, d
	$(UO_2)_2EDTA] \cdot 4H_2O$	920	1620						f
Cyclohexanediaminetetraacetic acid (H_4CDTA)	$H_2[UO_2CDTA] \cdot 3H_2O$	939	1625/1660	1402					c
	$(UO_2)_2(CDTA) \cdot 6H_2O$	920	1625	1405					c
Ethyleneglycol bis (2-aminoethyl)-ether tetraacetic acid (H_4EGTA)	$[(UO_2)_2EGTA] \cdot 2H_2O$				9·49*	−13·0	2·4	51	h, d
	$NaH[UO_2EGTA] \cdot H_2O$								h
Ethylenediamine-N,N′-diacetic acid (H_4EDDA)	—				11·41	−15·6	1·5	57	d

* Stability constant of hydrogen complex UO_2HL.

[a] S. H. Eberle, KFK-1136 (1970).

[b] N. S. Rajan and A. E. Martell, *J. Inorg. Nucl. Chem.* **26** (1964) 1927.

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[d] J. J. R. F. Da Silva and M. L. Simoes, *Rev. Port. Quim.* **11** (1969) 54.

[e] J. Stary and J. Prasilova, *J. Inorg. Nucl. Chem.* **17** (1961) 361.

[f] T. R. Bhat and M. Krishnamurthy, *J. Inorg. Nucl. Chem.* **26** (1964) 587.

[g] T. R. Bhat and T. V. Rao, *Z. anorg. allg. Chem.* **354** (1967) 201.

[h] J. J. R. F. Da Silva and M. L. S. Simoes, *Rev. Port. Quim.* **7** (1965) 137.

has been interpreted as indicating threefold coordination of the uranium with one iminodiacetic acid group, all other available coordination sites not being bonded.

Hexavalent transuranium ions are reduced quickly by the aminopolycarboxylic acids to give ions of lower valence state[63]. Solid compounds are unknown. The only reliable data on complex formation in solution were determined for plutonyl(VI) by following spectrophotometrically the reduction kinetics (1): N-hydroxyiminodiacetic acid $\log \beta_1 = 8{\cdot}48$ and nitrilotriacetic acid $\log \beta_1 = 10{\cdot}3$ ($\mu = 1$, 25°C).

Pyridine carboxylic acids

Pyridine derivatives are the only type of nitrogen-containing organic acids that do not reduce hexavalent transuranium ions. Two types of compound are known with acids capable of forming a five-membered chelate ring: "normal" chelates, MO_2L_2, and "solvated" chelates, $H[MO_2L_3]$. A complete series is known with pyridine-2-carboxylic acid[66].

$MO_2(C_5H_4NCOO)_2$ $\quad$ M = U, Np, Pu, Am
$H[MO_2(C_5H_4NCOO)_3]$

All are insoluble in water ($H[UO_2(C_5H_4NCOO)_3]$ 5×10^{-6} mole/l at 25°C), ethanol and ether, but dissolve in highly polar solvents such as dimethylsulfoxide. The solvated chelates precipitate from aqueous solution at pH 2–5 on addition of a tenfold excess of the acid. With less acid the 1:2 compound is obtained. Like other solvated chelates of the hexavalent actinide ions the pyridine-2-carboxylates behave as acids and form water-soluble salts with alkali metal ions. The dissociation constant of $H[UO_2(C_5H_4NCOO)_3]$ has been determined to be $1{\cdot}2 \times 10^{-4}$ at 25°C and $\mu = 0{\cdot}1$; the compound is a stronger acid than pyridine-2-carboxylic acid itself.

Solvated chelates yield the normal chelate when heated to about 200°C, the latter decomposing at higher temperature (Table 12).

Pyridine carboxylic acids not capable of forming five-membered chelate rings form only hydrated 1:2 compounds, solvated chelates could not be prepared[66]. Examples are the salts of N-oxypyridine-2-carboxylic acid, $MO_2(C_5H_4NOCOO)_2{\cdot}2H_2O$ (M = U, Np, Pu, Am), and of pyridine-3-carboxylic acid, $MO_2(C_5H_4NCOO)_2{\cdot}2H_2O$ (M = U, Pu). These are insoluble in water and can be dehydrated (Table 12).

Infrared (Table 9) and nmr measurements[66] indicate that the solvated pyridine-2-carboxylates contain two ligand anions bonded via one oxygen of the carboxylic group and the nitrogen of the pyridine ring to the metal, and one further ligand (the solvate molecule) bonded via only the carboxylic group; the dissociable hydrogen is attached to the nitrogen of this molecule. The pyridine-3-carboxylates do not contain a coordinated nitrogen but bidentate carboxylic groups; the two water molecules also being coordinated. Thus the coordination around the actinide atom is similar to that shown in Fig. 4 for uranyl(VI) acetate.

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[68] V. Balzani and V. Cacassiti, *Photochemistry of Coordination Compounds*, Academic Press, London and New York (1970).

Hexacyanoferric acids

The following insoluble compounds have been described:

$(UO_2)_2[Fe(CN)_6]\cdot 6H_2O$	dark brown[70] $\nu_{CN} = 2600\ cm^{-1}$
$M_xUO_y[Fe(CN)_6$	M = alkali metal[70]
$(UO_2)_3[Fe(CN)_6]_2$	brown[70]
$(PuO_2)_3[Fe(CN)_6]_2\cdot nH_2O$	red-brown[69] solubility 0·4 mg Pu/l H_2O

Alkali metal uranyl ferrocyanides with different ratios of U:M^I have been proposed for analytical use[72].

Hexavalent neptunium (rose) in aqueous solution is reduced instantly to pentavalent neptunium (green) by potassium ferrocyanide. On prolonged standing a green Np(IV) ferrocyanide forms. With Pu(VI) a black deposit forms rapidly, presumably due to reduction to Pu(IV).

Uranium(VI) ferrocyanide possesses the ability to adsorb various cations. The sorption affinity of alkali metal ions increases with increasing atomic number, reaching a distribution coefficient of 2×10^5 for Cs in 0·12 M HNO_3[72]. Thus U(VI) ferrocyanide seems to be a promising selective sorbent for Cs and Rb, and may serve for the isolation and concentration of these elements from acid solution.

Mixed acido complexes of U(VI)

Uranyl(VI) compounds can contain two or three different anions. Such compounds, first identified by Chernyaev[21], are named "mixed acido compounds". Examples of this type containing anions of carboxylic acids are listed in Table 14. No analogous compounds are yet known for the hexavalent transuranium ions. The general method of preparation involves mixing an uranyl monoacido salt solution with a solution of an alkali metal salt of the desired second acid and slowly evaporating until crystals appear. The compounds do not dissociate in aqueous solutions, as is shown by the electrical conductivity, and therefore they must be regarded as complexes.

It is not possible to prepare all conceivable mixed acido compounds and Chernyaev[21] has identified three governing factors:

1. The ligands are preferentially accommodated on or near the mid-plane of the uranyl(VI) ion.
2. For each type of ligand there is a specific, narrow limit for the bond length (U–F, U–O, U–N etc.).
3. A displacement series exists, that regulates the preferred or sometimes exclusive direction of intraspheric substitution.

The first two factors limit the nature of the stable compounds. Within the series of acetatofluorides $UO_2(CH_3COO)_xF_y(H_2O)_z$, for example, only species with $x = 1$, $y = 3$ and $x = 2$, $y = 1$ can be prepared. The other species are obviously unstable because the U–F or U–O distance would become too large.

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[69] H. H. Anderson, Natl. Nucl. Energy Series Div. IV, Vol. 14B, p. 801.
[70] J. B. Ayers and W. H. Waggoner, *J. Inorg. Nucl. Chem.* **31** (1969) 2045.
[71] S. H. Eberle, private communication.
[72] J. Kritil, *Radiochim. Acta*, 7 (1967) 30.

The third factor, the displacement series, is of importance for the synthesis of mixed acido-complexes. The order is:

$$CO_3^{--} > O_2^{--} > OH^- > F^- > CH_3COO^- > C_2O_4^{--} > SO_4^{--} > Cl^- > NO_3^- > Br^- > I^-$$

Each ligand can replace all ligands to the right in uranyl compounds but not (or only under extreme conditions) those to the left. Accordingly no mixed uranyl carbonate compounds can be prepared starting with the $UO_2(CO_3)_3^{4-}$ anion.

TABLE 14. MIXED CARBOXYLATO-COMPOUNDS OF HEXAVALENT URANIUM

Composition	Characterized by mc: molar conductivity $cm^2\ ohm^{-1}$ at 500 l/mole, 25°C tds: thermal disintegration steps °C	Ref.
$NH_4[UO_2F(CH_3COO)_2]$	anal., mc: 125 tds: 260–275, 300–350	a
$[CN_3H_6]_2[UO_2F_3(CH_3COO)H_2O]$	anal., mc: 167	a
$[NH_4]_2[(UO_2)_2O_2(CH_3COO)_4]$	anal.	a
$Ba[UO_2O_2(CH_3COO)_2]\cdot 6H_2O$	anal.	a
$Cs[UO_2(SCN)(CH_3COO)_2]\cdot 3H_2O$	anal., IR, mc: 208 tds: 130	b
$M[(UO_2)_3(CH_3COO)_7(SCN)_2]\cdot aq$ M = Cs, Rb, NH_4	anal., IR, mc: 554/647/646	b
$M_2[(UO_2)(CH_3COO)_2C_2O_4]$ M = NH_4^+, $CN_3H_6^+$	anal., mc: 231/290 tds: 220, 300/210, 300	c
$M_2[(UO_2)_2(CH_3COO)_4C_2O_4(H_2O)_2]\cdot nH_2O$	anal., mc: 267/211	c
M = K(n = 0), NH_4^+ (n = 2), $CN_3H_6^+$ (n = O)	tds: 200, 290/95–110, 230–245, 310–330/ >255	
$M_3[UO_2F(C_2O_4)_2H_2O]\cdot nH_2O$ M = Na ··· Cs, NH_4^+	anal., mc tds solubility refr. index	d
$M_3[UO_2F_3(C_2O_4)H_2O]\cdot nH_2O$ M = Na ··· Cs	anal., mc tds solubility refr. index	d
$[HN(C_8H_{17})_3]_3[UO_2NO_3(C_2O_4)_2]$	anal., IR, vis. spectrum	e
$M[UO_2(C_2O_4)SCN(H_2O)_2[$ M = K, Cs, NH_4	anal., mc: 172/134/151 tds	a
$M_4[(UO_2)_2(C_2O_4)_3(SCN)_2(H_2O)_2]$ M = K, NH_4	anal., mc: 500/– tds	
$Ba_2[UO_2(C_2O_4)_2(SCN)_2]\cdot 6H_2O$	anal., tds: 110–135, 310–320, 365–385	a
$M_2[UO_2SO_4(C_2O_4)(H_2O)_2]\cdot H_2O$ M = K, Rb, Cs	anal., mc: 306/308/$\simeq$330 tds	a
$M_2[UO_2CO_3(C_2O_4)(H_2O)]\cdot nH_2O$ M = Na, K, NH_4	anal., mc: 230/236/239	a
$K_3[UO_2(C_2O_4)SO_4(SCN)]$	anal., mc: 330	a
$M_4[(UO_2)_2C_2O_4(SO_4)_2(SCN)_2]$ M = K, Rb, Cs	anal., mc: 550/550/– tds: 320–330	a

[a] I. I. Chernyaev, *Complex Compounds of Uranium*, Jerusalem (1966).
[b] R. N. Shchelokov and I. M. Orlova, *Russ. J. Inorg. Chem.* **14** (1969) 753.
[c] I. I. Chernyaev, G. V. Ellert, L. K. Subochkhin and R. N. Shchelokov, *Zhur. Neorg. Khim.* **8** (1963) 1584.
[d] R. N. Shchelokov and V. I. Belomestnykh, *Russ. J. Inorg. Chem.* **14** (1969) 123.
[e] M. G. Kuzina and A. A. Liporskii, *Russ. J. Inorg. Chem.* **14** (1969) 1292.

Adducts of actinide(VI) carboxylates

Neutral ligands containing oxygen or nitrogen can enter the coordination sphere of the actinide(VI) carboxylates with the formation of adduct complexes. The usual types are $MO_2L_2\cdot 2A$, $MO_2L_2\cdot A$ and $MO_2L_2\cdot B$ with L being the carboxylate ligand, A a neutral monodentate ligand and B a neutral bidentate ligand. Typical adduct-forming neutral ligands are: amines, pyridines, pyridine-N-oxides, α,α-bipyridyl, phenanthrolin, urea, ketones, dialkylsulfoxides, phosphoric acid, triesters, phosphine oxides, arsine oxides and nitriles. The adducts are generally prepared by treating the carboxylates with an alcoholic solution of the reagent.

Most of the adducts are known only for U(VI)[21]. Examples of series of analogous compounds are[1]: MO_2(pyridine-2-carboxylic acid)$_2\cdot$DMSO, and MO_2(nicotinic acid)$\cdot$2DMSO (M = U, Np, Pu).

The adducts are generally more soluble in organic solvents than are the carboxylates themselves and their formation can be employed in the extraction of the cations from aqueous solution. Ketones often act as extractants by adduct formation.

Some crystal data for the acetate adducts are included in Table 10. The structure of $UO_2(CH_3COO)_2\cdot(C_6H_5)_3PO$ is shown in Fig. 5. It is a dimer with two bridging acetate groups, each uranium atom being 7-coordinate within a pentagonal bipyramid arrangement. The compound is also dimeric in solution[67]. The corresponding $UO_2L_2\cdot 2A$ compound is monomeric, the uranium atom being 8-coordinate.

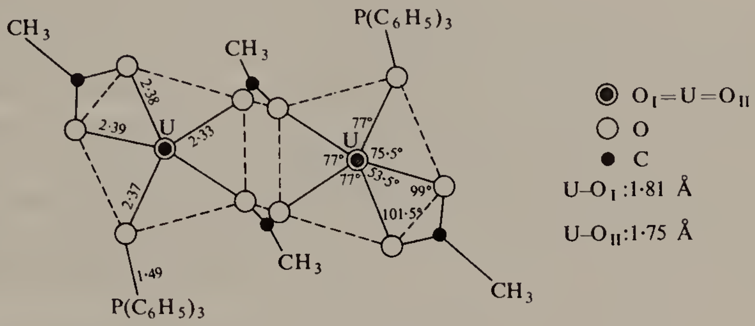

Fig. 5. Structure of $UO_2(CH_3COO)_2\cdot(C_5H_5)_3PO$.

Photochemical reactions

In the presence of U(VI) many organic acids are easily oxidized by the action of light. Generally there are two mechanisms, as shown here for acetic acid:

1. Sensitized decomposition:

$$CH_3COOH \xrightarrow[(UO_2^{++})]{h\nu} CH_4 + CO_2$$

2. Photochemically induced oxidation:

$$2CH_3COOH + 2H^+ + UO_2^{++} \xrightarrow{h\nu} C_2H_6 + 2CO_2 + 2H_2O + U^{4+}$$

Reaction (1) occurs when the light is absorbed by free uranyl(VI) ions, which then react by encounters with CH_3COOH molecules. Reaction (2) involves excited uranyl acetate complex molecules. Many systems with different organic compounds have been investigated[68], for example reduction of uranyl(VI) in aqueous acetate media yields the tetravalent acetate[15].

The hexavalent transuranium ions behave in a similar manner. Rapid reduction by light is observed, for example, in the presence of glycollic acid and oxalic acid. With the latter a slow chemical reduction occurs also.

SOLUTION CHEMISTRY

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1. GENERAL PROPERTIES OF ACTINIDE IONS

1.1. Electronic structure and oxidation states

The actinide solution chemistry reflects the peculiar electron configuration of the actinide elements. The 5*f* and 6*d* shells are of similar energy and the 5*f* electrons are, moreover, not so well shielded as the 4*f* electrons of the formally analogous lanthanide series. These features are especially marked at the beginning of the series. As a consequence, the redox chemistry of these elements is extremely complicated and some of them exhibit an extensive array of different oxidation states. The standard potentials of the various couples are often so close that appreciable concentrations of several oxidation states can coexist in the same solution. A survey of the known oxidation states of the actinides, and for comparison those of the lanthanides, is given in Table 1 where the most stable state is marked for each element.

TABLE 1. OXIDATION STATES OF THE ACTINIDES AND THE LANTHANIDES
(The most stable oxidation states are in bold figures, those not known in solutions are within parentheses.)

89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
						(2)		(2)				2	**2**	
3	(3)	(3)	3	3	3	**3**	**3**	**3**	**3**	**3**	**3**	**3**	3	**3**
	4	4	4	4	**4**	4	4	4						
		5	5	**5**	5	5								
			6	6	6	6								
				7	7									

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
			(2)		2	2						(2)	2	
3	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**
	4	(4)						(4)						

At the very beginning of the actinide series, the 6*d* shell is still preferred before the 5*f* shell. Actinium and thorium therefore behave chemically as true homologs of lanthanum and hafnium, respectively. Trivalent thorium may possibly exist in the solid state, in the very easily oxidized triiodide, but certainly not at all in aqueous solutions[1]. For gaseous atoms in their ground state, the 5*f* state is preferred from protactinium on, and this shell is therefore progressively filled. In the metallic state, on the other hand, the 6*d* shell is certainly preferred as far as uranium, or possibly neptunium, at least for the crystal modifications stable at ordinary temperature. This is evident from the variation of the metallic radius deduced from these structures (Table 2). Such a rapid contraction, as initially observed, is generally found when an outer electron shell is successively filled, owing to the increased attraction exerted

[1] D. E. Scaife and A. W. Wylie, *J. Chem. Soc.* **1964**, 5450.

Table 2. Metallic and Ionic Radii[a] of the Actinides, and the Interatomic Distances in the Actinyl(V) and Actinyl(VI) Ions (Å)

Element	M^0	M^{3+}	M^{4+}	M^{5+}	M^{6+}	M(V)–O	M(VI)–O
Ac	1·88[b]	1·076[c]					
Th	1·80		0·984[d]				
Pa	1·63		0·944	0·90[e]			
U	1·56	1·005	0·929	0·88	0·83[e]		1·71[g]
Np	1·55	0·986	0·913	0·87	0·82	1·98[f]	
Pu	1·60	0·974	0·896	0·87	0·81	1·94	
Am	1·74	0·962	0·888	0·86	0·80	1·92	
Cm	1·75	0·946	0·886				
Bk		0·935	0·870				

[a] According to the usual conventions, the metallic radii refer to the coordination number 12, the ionic radii to the coordination number 6 (see text and refs. 18 and 27).

[b] Ref. 2.

[c] J. R. Peterson and B. B. Cunningham, *J. Inorg. Nucl. Chem.* 30 (1968) 1775.

[d] J. R. Peterson and B. B. Cunningham, *Inorg. Nucl. Chem. Letters*, 3 (1967) 327.

[e] Ref. 27.

[f] Ref. 24.

[g] See text.

on the electrons in outer shells by the increasing nuclear charge. Beyond neptunium, however, a sudden increase of the radius takes place; this is certainly due to a switch of electrons from the 6*d* to the 5*f* shell. Such a change of configuration would tend to increase the metallic radius for two reasons. First, it would bring about a shielding of the outer shells from the nuclear charge and hence prevent their contraction, and second it would decrease the number of electrons in these shells and hence the strength of the metallic bonds. The increase of radius results in a decrease of density from plutonium on, in spite of the increasing atomic weight. The decrease of bonding strength accompanying the change of configuration is also reflected in a lowering of the melting point along the series, with a minimum at neptunium and plutonium[2]. It must then be remembered that the melting points depend upon the bond strength of the high-temperature modifications. These may not have the same electron configuration as the modifications which are stable at room temperature and which have been used for the determination of the metallic radii of Table 2. Therefore, the variations found for the radii and for the melting points need not necessarily indicate a switch from 6*d* to 5*f* configuration at the same element in the series.

From protactinium to neptunium, the energy differences between the 6*d* and the 5*f* shells are in fact not larger than ordinary bonding energies and the actual electron configuration will therefore depend upon the nature of the atoms bound to the actinide. Beyond neptunium, however, the electrons entering always seem to prefer the 5*f* shell. The half-filled shell, of configuration f^7, is therefore reached with element 96, curium, and the completely filled shell, f^{14}, with element 103, lawrencium.

As pointed out, especially the first electrons entering the 5*f* shell are not as well shielded as the 4*f* electrons of the lanthanides. Moreover, as their energy is fairly high, they are prone to participate in bonding. Even in such cases where the 5*f* shell is preferred, the actinides are therefore able to exhibit high oxidation states, as is particularly evident for neptunium, plutonium and americium (Table 1).

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[2] L. B. Asprey and R. A. Penneman, *Chem. Engin. News*, **45** (1967) No. 32, 75.

As the 5*f* shell is filled, the increasing nuclear charge will bring about a successive contraction, analogous to the lanthanide contraction. The shell will then be better shielded from the fields of neighboring atoms and simultaneously the energy differences between the 5*f* and the outer orbitals will grow. As a consequence, the participation of the 5*f* electrons in bonding becomes more difficult, resulting in a very marked stabilization of the trivalent oxidation state for the heavier actinides. Other oxidation states are prominent only when they represent either a half-filled or filled shell, i.e. the electron configurations f^7 or f^{14}. These are evidently preferred to such a degree, that an oxidation or reduction involving even the *f* shell readily takes place in order that they be reached.

The behavior in solution of each particular actinide will be a consequence of the conditions just described. The stabilities of the various oxidation states of the actinides in solution may be outlined as follows. Actinium and thorium exist only as Ac(III) and Th(IV), respectively. For protactinium, Pa(V) is the most stable state, though Pa(IV) can also be prepared and handled in aqueous solution[3,4]. The most stable oxidation state of uranium is U(VI). Its reduction in aqueous media generally leads to U(IV), the intermediate U(V) being prone to disproportionation[5]. The lowest state known, U(III), is a strong reducing agent which is slowly oxidized by water with evolution of hydrogen[6].

For elements up to uranium the highest oxidation state is the most stable and as far as actinium and thorium are concerned, even the only one existing in solution. With neptunium, this is no longer the case. The highest oxidation state is Np(VII) which, like U(VI), Pa(V), Th(IV) and Ac(III), has the electron configuration f^0. Contrary to these last states, however, Np(VII) is a strong oxidizing agent, especially in acid media[8,9]. Np(VI) is also fairly strongly oxidizing while Np(V) may be looked upon as the most stable state. Np(IV) is already a mild reductant and Np(III) a more powerful one, though less so than U(III). Thus Np(III) does not decompose water[6].

With plutonium and americium, the stabilization of the lower oxidation states becomes increasingly marked[6,7]. To date, the f^0 state, Pu(VIII), has never been prepared; the highest state so far observed[8], Pu(VII), is a considerably stronger oxidant than Np(VII), and Pu(VI) is also easily reduced. In solution, reduction also occurs as a consequence of products formed by the radiolysis due to radioactive decay of the isotope of plutonium ordinarily used for chemical work, i.e. ^{239}Pu, with a half-life of $t_{1/2} = 24{,}300$ years. Solutions of these high oxidation states are therefore unstable when plutonium is present in the form of its most readily available isotope. The use of the longer-lived ^{242}Pu, $t_{1/2} = 3{\cdot}8 \times 10^5$ years, recently[10] isolated in kilogram quantities from heavily neutron-irradiated ^{239}Pu, will certainly improve this situation in the future. Like U(V), but unlike Np(V), Pu(V) is prone to disproportionation and therefore difficult to prepare free from the adjacent oxidation states. In aqueous solution, Pu(IV) is also inclined to disproportionate when no stabilizing agents are present. Pu(III) may be classified as mildly reducing. The standard potentials of

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[3] *Physico-chimie du protactinium*, Centre National de la Recherche Scientifique, Paris 1966 (Colloque International No. 154, Orsay, 1965).

[4] R. Guillaumont, G. Bouissières and R. Muxart, *Actinides Rev.* **1** (1968) 135.

[5] J. Selbin and J. D. Ortego, *Chem. Rev.* **69** (1969) 657.

[6] A. D. Jones and G. R. Choppin, *Actinides Rev.* **1** (1969) 311.

[7] L. J. Nugent, R. D. Baybarz, J. L. Burnett and J. L. Ryan, *J. Inorg. Nucl. Chem.* **33** (1971) 2503.

[8] V. I. Spitsyn, A. D. Gelman, N. N. Krot, M. P. Mefodiyeva, F. A. Zacharova, Yu. A. Komkov, V. P. Shilov and I. V. Smirnova, *J. Inorg. Nucl. Chem.* **31** (1969) 2733.

[9] J. C. Sullivan and A. J. Zielen, *Inorg. Nucl. Chem. Letters*, **5** (1969) 927.

[10] G. T. Seaborg, J. L. Crandall, P. R. Fields, A. Ghiorso, O. L. Keller, Jr. and R. A. Penneman, *Proc. 4th U.N. Intern. Conf. Peaceful Uses Atomic Energy*, P./841, Geneva (1971).

the couples involved are so close to each other, however, that all the four oxidation states Pu(III), Pu(IV), Pu(V) and Pu(VI) may coexist in appreciable amounts in the same solution, a condition which is certainly unique within the periodic system.

For americium, Am(VI) is the highest state known. It is a strong oxidizing agent; when the most readily available americium isotope, ^{241}Am, is used, Am(VI) is very rapidly reduced by the products formed as a result of the α-decay. The speed of reduction is of course due in part to the short half-life of this isotope (458 years) which results in high concentrations of reducing agents in the solution. Both Am(V) and Am(IV) are also easily reduced and, moreover, liable to disproportionation. In particular Am(IV) cannot exist in solution, except in the presence of high concentrations of strongly complexing agents, such as fluoride[11]. The really stable oxidation state is Am(III). At americium, the actinide series thus clearly shows those features due to a well-shielded f shell which are so characteristic of the lanthanide series.

With curium, these traits are fully developed, helped by the stable f^7 configuration of Cm(III). This oxidation state is the only one existing for this element, apart from the metallic Cm(0) and the extremely strongly oxidizing Cm(IV), so far observed only in concentrated fluoride solutions[12]. Also for berkelium, the trivalent state is by far the most stable one, though Bk(IV) is not such a strong oxidant as Cm(IV)[7]. The relative stability of Bk(IV), and that of its lanthanide counterpart Tb(IV), is evidently due to the stabilizing influence of their f^7 configurations. In this connexion it is worth noting, however, that the f^7 state, Am(II), corresponding to Eu(II) in the lanthanide series, does not seem to exist in solution (though it may exist in solids at low temperature)[2]. Evidently the preference for higher oxidation states shown by the lighter actinides is still strong enough to outweigh the stabilization brought about by a half-filled f shell.

The following three elements, californium, einsteinium and fermium, are, as far as known, all strictly trivalent[2,7,13]. With mendelevium the tendency to approach a filled shell becomes perceptible, Md(III) with the configuration f^{12} being fairly easily reduced[14,15] to Md(II) with f^{13} and for nobelium the filled shell f^{14} makes No(II) to the most stable oxidation state of this element, which therefore mostly behaves like an alkaline earth rather than like a typical actinide[16]. With the last actinide, lawrencium, the trivalent state again becomes preponderant, as this state here represents the filled shell.

The intricate redox conditions characterizing several of the actinides are more fully treated in section 3 where the formal standard potentials of the various couples are tabulated for different media (Table 19). From these potentials, redox diagrams have been constructed which allow a rapid and reliable estimate of the oxidation states prevailing in the solutions under different conditions. In this connexion, important redox reactions are also treated, both the interesting disproportionation reactions involving only one actinide and those reactions where other oxidizing and reducing agents are reacting.

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[11] L. B. Asprey and R. A. Penneman, *Inorg. Chem.* **1** (1962) 134.

[12] T. K. Keenan, *J. Amer. Chem. Soc.* **83** (1961) 3719.

[13] S. Fried and D. Cohen, *Inorg. Nucl. Chem. Letters*, **4** (1968) 611.

[14] J. Malý and B. B. Cunningham, *Inorg. Nucl. Chem. Letters*, **3** (1967) 445.

[15] E. K. Hulet, R. W. Lougheed, J. D. Brady, R. E. Stone and M. S. Coops, *Science*, **158** (1967) 486.

[16] R. J. Silva, T. Sikkeland, M. Nurmia, A. Ghiorso and E. K. Hulet, *J. Inorg. Nucl. Chem.* **31** (1969) 3405.

1.2. Ionic species in solution

The ions normally formed by the oxidation states II to VI are M^{2+}, M^{3+}, M^{4+}, MO_2^+ and MO_2^{2+}, respectively. These ions are all electron acceptors which in solvents of donor properties coordinate the solvent molecules. The affinity is generally stronger, the more highly charged the acceptor. It must also be remembered, however, that the effective charge on the acceptor atom M is considerably higher than the total charge of the entities MO_2^+ and MO_2^{2+}. These are linear groups where the oxygens carry a net negative charge; consequently the charge on M where the solvent molecules are to be coordinated becomes higher than the ionic charge, and the coordinating field is proportionately stronger.

The coordination numbers and the coordination figures of the actinide ions in solutions are in general not well known. Little reliable evidence therefore exists about the structures of the solvates formed in various solvents. This is particularly true for the ions of the types M^{2+} and M^{3+}.

The two divalent ions so far characterized in solution, Md^{2+} and No^{2+}, are available only in extremely minute amounts. For the more abundant of the elements concerned, mendelevium, the experiments have been conducted with the isotope ^{256}Md, $t_{1/2} = 77$ min. Only recently[17], as much as $\simeq 10^5$ atoms have become available for one experiment; many experiments have been performed with as little as $\simeq 100$ atoms. The last-mentioned very modest scale has only recently been reached for nobelium[16], with the preparation of the isotope ^{255}No. The same scale means much larger experimental difficulties for nobelium than for mendelevium, however, on account of the short half-life of ^{255}No, $t_{1/2} = 3$ min. Not unexpectedly, little detailed knowledge is as yet available about the coordination chemistry of the divalent ions formed by these elements. One may confidently predict, however, that their solvates will resemble those of the heavy rare earth ions Ra^{2+} and Ba^{2+}.

Many of the trivalent ions are also in scarce supply, viz. Ac^{3+} and, to a varying degree, those formed by the heavy actinides. Quite a few, however, are available in amounts suitable for conventional chemical investigations, viz. U^{3+}, Np^{3+}, Pu^{3+}, Am^{3+} and Cm^{3+}. Some of the more scarce ones, viz. Ac^{3+}, Bk^{3+} and Cf^{3+}, have nevertheless been prepared on milligram scale[10]. Especially for U^{3+}, and to some extent also for Np^{3+}, investigations in solution are made difficult by the strongly reducing properties of these ions.

Much information is available concerning the composition of complexes of trivalent actinides in various organic solvents. Though completely unequivocal conclusions about the coordination number cannot generally be drawn from such formulae, it is nevertheless obvious that the number of coordinated donor atoms is high and, moreover, varies between different complexes. Coordination numbers 6, 7 and 8 seem all to be well established, and there are indications of even higher ones (see section 4).

With some reservations, supporting evidence about the stereochemistry of actinide ions in solution may be gathered from the structure of solid actinide compounds, as well as from the chemistry of the homologous lanthanide(III) ions which have been more thoroughly investigated. The coordination numbers of actinide ions are high in solid phases[18]. Very frequently 9 is found, and 8 and 6 are common. The solid lanthanide(III) compounds also show high coordination numbers; in addition to those mentioned, 10 seems to be definitely established[19a]. Very often corresponding actinide and lanthanide compounds are isostruc-

[17] E. P. Horwitz and C. A. A. Bloomquist, *Inorg. Nucl. Chem. Letters*, **5** (1969) 753.

[18] A. F. Wells, *Structural Inorganic Chemistry*, 3rd ed. Clarendon Press, Oxford (1961).

[19a] M. D. Lind, B. Lee and J. L. Hoard, *J. Amer. Chem. Soc.* **87** (1965) 1611.

tural (this applies, for example, to many halides, oxides and hydroxides) which certainly supports the notion that, with due caution, conclusions about the coordination chemistry of the actinide(III) ions may be drawn from that of the lanthanide(III) ions. It is therefore of interest that lanthanide compounds are known[18] where the central ion coordinates nine water molecules (for example in $[Nd(H_2O)_9](BrO_3)$) or nine hydroxide ions (in the lanthanide trihydroxides, e.g. $La(OH)_3$). This shows that such a coordination is *per se* possible for both lanthanide(III) and actinide(III) ions. Quite probably the hydrates of these ions are therefore 9-coordinated.

The stereochemistry of these hydrates is most probably a trigonal prism, with the donor atoms in the apices and above the centers of the rectangular faces. The structures of the 8-coordinated species present in solution are unknown, but for the 6-coordinated ones, the ligands are certainly arranged octahedrally.

Protons may be split off from the water molecules of the hydrates thus formed in aqueous solutions, which will thus act as Brönsted acids. On account of the large radii of the central ions (see Table 2) the repelling force between the protons and the ionic charge will be relatively weak, however, and the acid properties will consequently also be fairly weak, and generally much weaker than for other hydrated ions of the same charges. Quantitative measurements seem to exist only for Pu^{3+} (see 2.2.1).

More data are available for actinide ions of the type M^{4+} than for those of lower oxidation states since several of these ions (viz. Th^{4+}, U^{4+}, Np^{4+} and Pu^{4+}) are at least reasonably easy to investigate. In solutions, several investigations point to a preferred coordination number of 8. In particular the composition of many chelate complexes, the formation of which permits the extraction of actinides from aqueous solutions into organic solvents, strongly support this. These complexes will be more closely discussed in section 4. Nine-coordination has also been postulated, from measurements of the proton magnetic resonance of species in solution. Separate resonances are exhibited by the hydrate water and the non-bonded water, provided that the exchange of water molecules between the inner coordination sphere and the bulk of the solution does not take place too fast. Generally these reactions become slow enough only at fairly low temperatures which necessitates the use of mixed solvents. Thus, the nonahydrate $Th(H_2O)_9^{4+}$ has been found to exist in water–acetone solutions of thorium perchlorate at −100°C[19b]. Evidently, this result only provides an indication of the formula of the hydrate existing in water at, say, 25°C.

Due to the higher charge of the central ion, these hydrates are much stronger acids than those formed by the actinide ions of lower charge. Nevertheless, the acid strength is lower than found for tetravalent ions of smaller radii, such as Ce^{4+} or Zr^{4+}. As is also the case for many other aquo acids, polynuclear complexes are extensively formed as a result of the hydrolysis. These reactions will be discussed later together with the rather remarkable trend found for the variation of the acid strength of the M^{4+} ions along the actinide series (see 2.2.1).

The penta- and hexavalent oxidation states are even more prone to hydrolysis, as is immediately apparent by the persistence of the oxygen-containing cations MO_2^+ and MO_2^{2+} even in very acidic solutions. The oxygens of the ions MO_2^{2+} do not seem to possess any basic properties at all. They do not coordinate protons, however high the hydrogen ion concentration. For ions of the type MO_2^+ this may happen at high acidities, at least in the case of PaO_2^+. It is even possible that this ion, contrary to the formally analogous UO_2^+, NpO_2^+, PuO_2^+ and AmO_2^+, should itself rather be formulated $PaO(OH)_2^+$. In the PaO_2^+,

[19b] S. F. Lincoln, *Coord. Chem. Rev.* 6 (1971) 309.

only one of the oxygen would thus be reluctant to add protons[4]. Agents forming strong complexes may replace the oxygens of MO_2^+ even in aqueous solution, especially at high acidities. Thus, strong solutions of hydrofluoric acid most probably contain U(V)[20,5] as UF_6^- and Pa(V)[4] as PaF_6^-, PaF_7^{2-} and probably also PaF_8^{2-}. The last ion is well established[21] as a discrete entity in the structure of Na_3PaF_8. For U(V), the formation of the very strong fluoride complex results in a marked stabilization of U(V) which otherwise disproportionates completely in solutions of high acidity. The oxygens of the ions MO_2^{2+} are, on the other hand, not displaced by fluoride even in concentrated hydrofluoric acid. The introduction of a solid actinide fluoride, e.g. Na_2UF_8, into such a solution results in an immediate hydrolysis[20], with the formation of UO_2^{2+} (which, however, strongly coordinates F^- to form uranyl fluoride complexes, see 2.2.2).

In aqueous solutions, the stable entities MO_2^+ and MO_2^{2+} form hydrates which act as acids. As mentioned above, the charge on the central actinide atom in these groups is higher than the net ionic charge, on account of the excess negative charge carried by the oxygens. The ions are therefore stronger acids than would be expected from their formal charge. The charge carried on M in the single-charged MO_2^+ is still so low, however, that the hydrolysis occurs only at pH values around and above 8. This has been found from measurements involving NpO_2^+ and PuO_2^+; for UO_2^+ the hydrolysis cannot be properly investigated, on account of the ready disproportionation of U(V) within the critical range of acidity, and also for AmO_2^+ the investigation may be fairly difficult. The double-charged MO_2^{2+} ions are fairly strong acids, however, giving off protons already around $pH = 3$. The hydrolysis also primarily involves polynuclear species, as is more fully discussed in section 2.2.1.

Hydrates of the MO_2^+ and MO_2^{2+} ions existing in acid solutions thus display the fairly peculiar feature of metal ion acceptors coordinating both O^{2-} and H_2O as ligands in one and the same complex. The number of ligand atoms coordinated by the ions MO_2^+ and MO_2^{2+} seems to vary both in solutions and solids. The numbers 4, 5 and 6 have been found[22,18] for MO_2^{2+}. For MO_2^+, a similar variation is probable, though the experimental data are meagre[23,24]. For chelating ligands possessing donor atoms situated suitably close to each other, the coordination number 6 is reached. This circumstance accounts, among other things, for the unusual solubility and stability of the carbonate complexes of the MO_2^{2+} ions (see 2.2.3). In the case of non-chelating ligands, six donor atoms are also sometimes coordinated to MO_2^{2+} ions, at least in solids.

As far as the hydrates are concerned, measurements of the proton magnetic resonance[19b] indicate a tetrahydrate $UO_2(H_2O)_4^{2+}$ in water–acetone solutions at −90°C. No data seem to exist for any other ions of the types MO_2^+ or MO_2^{2+}.

Including the oxygens of the actinyl groups, the coordination number of the metal atom often reaches 8, the lowest number observed being 6. In the case of 8-coordination, the six donor atoms of the ligands form a hexagon around the equators of the linear actinyl groups. In those cases where chelating ligands participate, the hexagon is generally plane, whereas it is puckered when solely non-chelating ligands are coordinated. For non-chelating ligands, the lower coordination numbers are in fact more common. When five donor atoms are coordinated, they form a pentagon normal to the axis of the actinyl group, while four donor

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[20] L. B. Asprey and R. A. Penneman, *Inorg. Chem.* 3 (1964) 727.

[21] D. Brown, J. F. Easey and C. E. F. Rickard, *J. Chem. Soc.* (A) **1969**, 1161.

[22] H. T. Evans, *Science*, **141** (1963) 154.

[23] F. H. Ellinger and W. H. Zachariasen, *J. Phys. Chem.* **58** (1954) 405.

[24] T. K. Keenan and F. H. Kruse, *Inorg. Chem.* 3 (1964) 1231.

atoms form, together with the oxygens of the actinyl group, a distorted octahedron around the metal atom. The actinyl oxygens are always closer to the metal than any other coordinated atom. In all such structures, the actinyl entities MO_2^+ and MO_2^{2+} are thus discernible. At least in aqueous solutions it appears that such a group would only be disrupted by reactions between MO_2^+ and strongly complexing agents (see above). Though the MO_2^{2+} ion always seems to survive in aqueous solution, it is by no means insensitive to the number and nature of the further ligands coordinated to the metal atom. This is plainly shown by the rather different M–O distances found in different solid actinyl complexes (see section 1.3).

The heptavalent oxidation states Np(VII) and Pu(VII) exist preferably in alkaline solutions[8] where their oxidizing properties are rather modest, at least as far as Np(VII) is concerned (Tables 18 and 19). In the acid range media, on the other hand, they act as very powerful oxidants, fairly rapidly releasing oxygen from water[9]. The ions present in acid solutions are unknown; in alkaline solutions ions of the empirical formula MO_5^{3-} are formed[8,25a]. From spectral evidence it has been concluded[25b] that these ions are in fact hexagonal bipyramids, of formula $MO_2(OH)_6^{3-}$. Thus also for this oxidation state a MO_2 group would appear to persist, viz. the ion MO_2^{3+}, coordinating six other groups around its equator.

In the solvates discussed, the solvent molecules serving as ligands may generally be exchanged for other donors present in the solution, to an extent depending upon the relative affinities of the central ion for the competing donors. In this way species known as inner sphere complexes are formed. The solvates themselves should of course also be regarded as such complexes. Often, however, the other ligand present cannot actually compete with the solvent molecules for the sites of the inner coordination sphere. Ligands which are ions or dipoles may nevertheless become attached to the solvated ion by electrostatic attraction. In such cases outer sphere complexes are formed.

For convenience, the solvent molecules are generally omitted from the reaction formulae, especially as their number is often unknown. For actinide ions, the state of solvation is even more obscure than for many other ions as should be evident from the discussion above. It must nevertheless always be remembered that the formation of a complex implies a disturbance of the solvation of the acceptor, resulting in the case of an inner sphere complex in the disruption of the inner solvate shell. It should further be remembered that the hydrolysis taking place in aqueous solution is due to protolytic reactions of the hydrate shell.

As is generally observed when complexes are formed by metal ions, the exchange of solvent molecules for other ligands on actinide ions usually takes place stepwise. This means that complexes containing more ligands are formed successively as the ligand concentration increases. Several complexes in such a series often coexist in solution in appreciable amounts. If the affinity of the central ion for the particular ligand is strong enough, however, a limiting complex is finally formed where the ligand has completely displaced the solvent from the inner coordination sphere. For ligands of very high affinity this will occur at very low concentrations of free ligand. When strong complexes are formed, virtually all ligands present in the solution may thus be coordinated to the central ion. The methods employed for the investigation of systems of consecutively formed complexes will be discussed further in section 2.1.

A particular ligand has, as a rule, rather different affinities for different oxidation states

[25a] A. J. Zielen and D. Cohen, *J. Phys. Chem.* 74 (1970) 394.

[25b] C. K. Jørgensen, *Chem. Phys. Letters*, 2 (1968) 549.

of the actinides. This will influence the redox conditions in such a manner that the states preferred will be stabilized relative to the others. The effect will become very considerable in the case of ligands which form strong complexes preferentially with one particular oxidation state. In the presence of strongly discriminating complexing agents, the picture given above of the relative stability of the various oxidation states may thus be drastically changed. States which otherwise readily disproportionate may for example be quite stable. This is the case with U(V) in strong fluoride solutions. Further examples are provided by the stabilization of Pu(IV) by sulphate and also, though to a much smaller extent, by nitrate. The difference in effect between the two ligands is due to the widely different strength of the complexes formed in the two cases (see section 2.2.3). The stabilization of Pu(IV) achieved in strong nitrate solutions is nevertheless of considerable importance in the recovery of plutonium from irradiated uranium. In the process most commonly employed (Purex process), Pu(IV) is extracted from a nitric acid solution by means of tributyl phosphate dissolved in an organic diluent (see section 4.8). Of the other oxidation states, Pu(VI) is rather poorly extracted, and Pu(V) and Pu(III) hardly at all. The stabilization of Pu(IV) due to the nitrate medium is therefore essential for the feasibility of the process. Naturally enough, sulphate ions also stabilize the tetravalent states of other actinides, such as U(IV) and Np(IV) (see section 3.2).

The formation of strong complexes by a particular state will also reduce its oxidizing properties. In this way, an oxidation state which would not otherwise be stable in, for example, aqueous solution may be stabilized by addition of suitable ligands. This is exemplified by the stabilization of Am(IV) and Cm(IV) achieved in fluoride solutions (see sections 1.1 and 3.1).

The non-aqueous solutions of actinide compounds are of great general interest for the elucidation of the chemistry of the actinides. Many non-aqueous solutions are also very important from a practical point of view, especially because of their extensive use in nuclear fuel processing[26]. Much work has therefore been done on complexes which are soluble in non-aqueous solvents, and on the extraction of actinides in various oxidation states from aqueous solutions by means of ligands forming such complexes. A detailed discussion of this field is given in section 4.

In spite of the extensive use of other solvents, water is nevertheless the most widely used solvent for actinide compounds. Consequently, aqueous solutions have on the whole attracted more attention than non-aqueous ones. The bulk of detailed quantitative knowledge of actinide solution chemistry therefore refers to aqueous systems.

1.3. Ionic dimensions

For the actinide ions of the types M^{3+} and M^{4+} which possess spherical symmetry the conventional crystal ionic radii can be estimated (Table 2). These have been found from interatomic distances in fluorides and oxides which are presumed to be approximately ionic compounds. For the radii of F^- and O^{2-}, the values 1·33 and 1·46 Å have been chosen, respectively. The metal ion radii thus obtained have further been corrected so as to refer to an octahedral coordination. For higher coordination numbers, the effective radii increase, on account of the increased repulsive forces between the ligand ions. Coordination numbers of 8 or 9 which are evidently the common ones for the tri- and tetravalent actinides in

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[26] J. J. Katz and G. T. Seaborg, *The Chemistry of the Actinide Elements*, Methuen, London (1957).

solution will presumably mean an increase of 5–10% to the values for 6-coordination listed in Table 2[18,27].

The very concept of radius is somewhat ill-defined for objects such as atoms or ions which have no sharp boundary. It is further often questionable whether the inter-atomic distances measured really refer to bonds which are essentially ionic. Even if this condition is fulfilled, it may be discussed how to divide the distance found between the two ions. In spite of this, the values of Table 2 should nevertheless give a fairly realistic estimate of the size of the naked central ions.

As already pointed out above, M^{5+} and M^{6+} do not exist as solvated ions in solutions. Ionic radii for the naked ions may nevertheless be calculated in the same way as for the lower oxidation states, i.e. from crystallographic data on the solid fluorides[27]. For comparison, these radii are included in Table 2.

For the rod-shaped ions MO_2^+ and MO_2^{2+} which are the ordinary mode of appearance of the penta- and hexavalent states in solution, the concept of ionic radius has evidently to be further qualified. For these ions, the distance of closest approach between the central atom M and further ligand atoms is certainly the most interesting feature as far as solutions are concerned. Direct determinations of such distances for complexes in solution are generally not possible, but reasonably safe estimates may be obtained from data referring to solid structures. In some cases, the inferences made from solids have been confirmed by direct determinations of solution structures.

Naturally enough, most data are available for the uranyl(VI) ion, UO_2^{2+}. Fluoride ions are coordinated to this ion at a distance of 2·24 Å from the uranium atom[18]. The radius of action of the uranium atom in a uranyl(VI) fluoride complex is thus ≃0·9 Å, i.e. not much larger than the formal ionic radius of U^{6+} (Table 2). Oxygen atoms in water, as well as in nitrate and acetate ions, are generally coordinated at 2·4–2·5Å. In the polynuclear complexes formed on hydrolysis of the uranyl ion, the oxygens present as hydroxo- and oxo-bridges are 2·3–2·4 and ≃2·2 Å from the uranium atoms, respectively[18,22,28]. With a radius of O^{2-} equal to 1·46 Å, the radius of action of the hexavalent uranium atom thus emerges as ≃0·8 Å, i.e. about the same as the ionic radius of U^{6+}. For the hydrolytic complexes, the results of the determinations of the solid structures are corroborated by structure determinations of solutions[28]. Only the distances between the uranium atoms joined by the bridges can then be determined, but these fit very well with the corresponding distances in the solids. It may therefore safely be postulated that also the distances to the bridging atoms are the same.

As already pointed out, the oxygens of the uranyl group are always much closer to the uranium atoms than oxygens or other ligand atoms coordinated equatorially, though the actual distance depends on the nature and arrangement of the other ligands[18,22,29]. In the 8-coordinated complexes where the equatorial ligand atoms form a hexagon it is 1·71 ± 0·05 Å. In 7-coordinated complexes, with a pentagonal arrangement of further ligand atoms, a longer distance is generally found, 1·80 ± 0·05 Å, and in 6-coordinated complexes a still longer one, 1·9–2·0 Å. This reflects a decrease of bond order[30] from ≃2 at a distance of 1·70 Å to ≃1·6 at 1·80 Å and finally to ≃1·25 at 1·95 Å. The reason why the strength of the bonds within the uranyl group decreases with the number of equatorially bonded ligand

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[27] W. H. Zachariasen, *The Actinide Elements*, Nat. Nucl. Energy Series Div. IV, Vol. 14A, p. 769, G. T. Seaborg and J. J. Katz (Eds.), McGraw-Hill, New York (1954).

[28] M. Åberg, *Acta Chem. Scand.* **23** (1969) 791; **24** (1970) 2901; **25** (1971) 368.

[29] G. Bergström and G. Lundgren, *Acta Chem. Scand.* **10** (1956) 673.

[30] W. H. Zachariasen and H. A. Plettinger, *Acta Cryst.* **12** (1959) 526.

atoms is certainly that a lower number is connected with a closer approach to the central atom, i.e. with stronger bonds between uranium and the equatorial ligands. But the higher the order of these bonds, the lower that of the uranyl, or generally the actinyl, oxygens, and the longer the corresponding inter-atomic distances. The data pertaining to other actinyl(VI) ions than UO_2^{2+} are still extremely scarce, however.

So is also the information available about actinyl(V) ions. The distance of closest approach of carbonate ligands to NpO_2^+, PuO_2^+ and AmO_2^+ is $\simeq 2 \cdot 55$ Å, however, which is $\simeq 0 \cdot 1$ Å more than would be expected for the corresponding actinyl(VI) ions[24]. This difference is of the same order of magnitude as the difference between the ionic radii of M^{5+} and M^{6+} ions (Table 2).

The distances between metal and oxygen within the actinyl(V) ions are considerably longer than for actinyl(VI) ions (Table 2). This is to be expected, in view of the lower charge on the central ion in the lower oxidation state.

1.4. Enthalpies and entropies of hydration, and of formation of actinide ions

In all cases where a strong solvation takes place, i.e. when the solvent molecules are coordinated to the metal ion by strong bonds, the formation of a solvate generally results in a large stabilization relative to the gaseous ion. A direct measure of this stabilization is provided by the free energy change, ΔG_s, for the solvation reaction $M^{z+}(g) \rightarrow M^{z+}(solv)$.

The change of free energy depends upon the changes of enthalpy, ΔH_s, and of entropy, ΔS_s, taking place during the solvation ($\Delta G_s = \Delta H_s - T \cdot \Delta S_s$). The formation of the ordered solvate structure generally implies a rather large negative value of ΔS_s. The entropy term will thus counteract the reaction. The formation of strong bonds between the metal ion and the solvent molecules is, on the other hand, a strongly exothermic process, i.e. ΔH_s is very strongly negative. The enthalpy term will thus favor the solvation. Moreover, it will heavily outweigh the entropy term, thereby causing a large negative value of ΔG_s and hence the strong stabilization of the solvated ion generally found.

The functions ΔG_s, ΔH_s and ΔS_s refer to changes of state of individual ions. It is therefore not possible to devise any method to determine these functions by direct experiment. Instead, semi-empirical approaches are used for their calculation from various quantities accessible to measurement. It is generally possible, however, to choose the inevitable assumptions in such a way that the sets of thermodynamic functions calculated for a series of ions become consistent, i.e. even if their absolute values are not very certain, the differences between the values should nevertheless be reliable[6,31].

For polyatomic, non-spherical ions, such as the actinyl ions, these semi-empirical approaches are not applicable, however. Consequently, no values of the changes of enthalpy or entropy on solvation are available for these ions.

For ions of the types M^{3+} and M^{4+}, on the other hand, solvation enthalpies and entropies have been calculated, but only for aqueous solution[6] (Table 3). The values of the hydration enthalpies ΔH_h are very high. They are, moreover, much higher for M^{4+} than for M^{3+}, as should be expected from the stronger attractive forces exerted by the more highly charged ions. In addition, the ordering influence of the ions on the solvent increases with the charge and hence the values of the hydration entropies $-\Delta S_h$. In spite of the fairly high values of $-\Delta S_h$, however, the entropy term $T \cdot \Delta S_h$ is only $\simeq 3\ \%$ of the enthalpy term at the standard temperature of 25°C which has been used for the compilation of Table 3.

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[31] D. F. C. Morris, *Structure and Bonding*, Vol. 4, p.63, Springer Verlag, Berlin (1968).

TABLE 3. HYDRATION ENTHALPIES (kJ mole^{-1}) AND ENTROPIES (J K^{-1} mole^{-1}) FOR ACTINIDE IONS AT 25°C[a]

	M^{3+}		M^{4+}	
Element	$-\Delta H_h$	$-\Delta S_h$	$-\Delta H_h$	$-\Delta S_h$
Ac	3385	329·5		
Th			6420	500·5
Pa			6550	511·5
U	3415	339	6670	521·5
Np	3420	342·5	6720	525
Pu	3435	346	6820	534·5
Am	3480	361·5	6840	535·5
Cm	3495	366	6880	539·5
Bk	3525	377	6920	542
Cf	3540	381		
Es	3555	386·5		
Fm	3565	389		
Md	3575	391·5		
No	3575	393·5		
Lr	3575	393·5		

[a] Ref. 6.

The enthalpy term thus essentially determines the magnitude of the free energy change of solvation. The values of both $-\Delta H_h$ and $-\Delta S_h$ increase along the actinide series for both types of ions as expected as a consequence of the decreasing ionic radius. The resulting strengthening of the electric field will cause both a stronger bonding and a more ordered structure; the enthalpy and entropy changes will, therefore, both become more negative.

The lanthanide ions are all smaller than the corresponding actinide ions (Fig. 1). Consequently, the thermodynamic functions for their solvation should be more negative. This is illustrated by a comparison between the values of $-\Delta S_h$ for the two series (Fig. 1).

Even if the enthalpies of hydration cannot be determined for the actinyl ions, their enthalpies of formation, ΔH_f, from the elements in their standard states are still available. As these include, *inter alia*, the ionization potential, and also the lattice energy of the metal, they do not, of course, give any immediate information about the thermodynamics of the hydration process. Nevertheless, it is possible to draw certain conclusions about the relative stabilities of the various ions in aqueous solution as is evident from a scrutiny of the data

TABLE 4. ENTHALPIES OF FORMATION, $-\Delta H_f$, FOR ACTINIDE IONS IN AQUEOUS SOLUTION AT 25°C (kJ)[a]

Element	M^{3+}	M^{4+}	$MO_2{}^+$	$MO_2{}^{2+}$
Th		770		
U	513	612		1046
Np	528	554	977	860
Pu	593	536	920	828
Am	679	485	869	715
Cm	589			

[a] J. Fuger, *MTP Intern. Rev. Science, Inorg. Chem. Series One*, Vol. 7, p. 157. *Lanthanides and Actinides*, K. W. Bagnall (Ed.), Butterworth, London (1972.

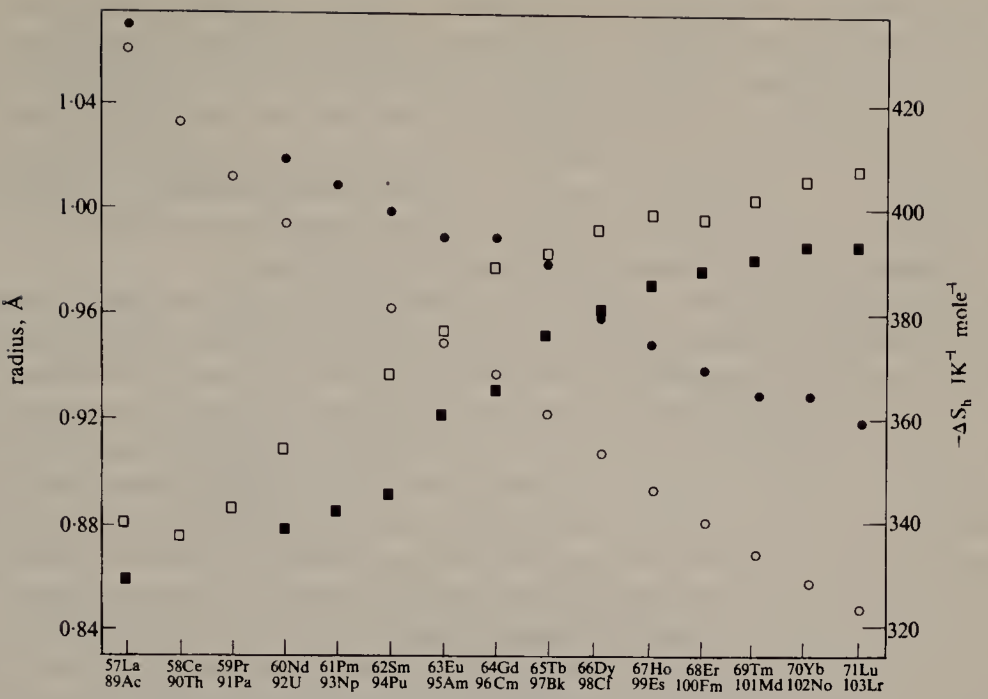

FIG. 1. Radii (left ordinate, circles) and hydration entropies (right ordinate, squares) of trivalent actinide and lanthanide ions as functions of the atomic number. Filled and open signs refer to the actinide and lanthanide ions, respectively.

listed in Table 4. The values of $-\Delta H_f$ for the higher oxidation states decrease monotonously along the series. This decrease is, moreover, more rapid the higher the oxidation state. For the trivalent state, on the other hand, an increase of $-\Delta H_f$ is observed except for the last element, curium. These trends clearly reflect the increasing stability of the lower oxidation states relative to the higher ones along the series.

The reason for the exceptional behavior of curium is no doubt the considerable increase of metallic lattice energy that takes place between americium and curium, as evidenced by the large rise in melting point observed between these two metals[2]. The high stability of Cm(III) relative to the higher oxidation states of this element indicates that the values of $-\Delta H_f$ for these states would in fact be lower than for Cm(III).

1.5. Color and spectra

Solutions of actinide ions generally possess a large number of absorption bands in the near ultraviolet, visible and infrared regions. The many bright colors due to selective absorption of visible light is certainly one of the most striking characteristics of actinide solutions, and one which has from the beginning attracted much attention.

The absorption bands are due to electronic transitions[32,33]. These are of three different types. First, transitions may occur between two f levels of different angular momentum, i.e. within an inner electron shell. Such transitions are not much disturbed by influences from the environment and the absorptions bands are therefore quite narrow. The differences

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[32] C. K. Jørgensen, *Absorption Spectra and Chemical Bonding in Complexes*, Pergamon Press, Oxford (1962); *Progr. Inorg. Chem.* Vol. 12, p. 101. S. J. Lippard (Ed.), Interscience, New York (1970).

[33] J. L. Ryan, *MTP Intern. Rev. Science, Inorg. Chem. Series One*, Vol. 7, p. 323. *Lanthanides and Actinides*, K. W. Bagnall (Ed.), Butterworths, London (1972).

between the different energy levels are of such an order of magnitude that bands due to $5f \rightarrow 5f$ transitions appear in the ultraviolet, visible and near infrared regions. As the transitions occur between orbitals of the same sub-shell, they are generally Laporte-forbidden. The probabilities of the transitions are therefore low and the absorption bands consequently not very intense, with maximum molar absorption coefficients typically in the range 10–50 $\mathrm{cm^{-1}\ M^{-1}}$. Generally, only $5f \rightarrow 5f$ transitions involving no change of the spin multiplicity are observable. A change of spin implies that the transition becomes doubly forbidden, and its probability will then be practically zero.

The energy levels involved in the $5f \rightarrow 5f$ transitions are further split by spin–orbit interactions and ligand field effects. The total number of theoretically possible energy levels is therefore quite large, especially for oxidation states involving many *f* electrons. Not all of these are in fact observed, especially not in solution spectra, but for each electronic transition quite a few energy levels are as a rule so well populated, and separated, that they give rise to resolvable bands. The number of bands observed is therefore often quite large.

Electronic transitions may also occur between the 5*f* and 6*d* shells. As an outer shell takes part, these $5f \rightarrow 6d$ transitions are much more disturbed by influences from the environment than are the $5f \rightarrow 5f$ transitions. The absorption bands are therefore broad, and no fine structure can as a rule be detected. The energy differences are generally larger so that the bands mostly appear in ultraviolet. As the transitions take place between orbitals of different azimuthal quantum number, they are Laporte-allowed. The absorption is therefore often very intense, with molar absorption coefficients well over 1000 $\mathrm{cm^{-1}\ M^{-1}}$.

For electronic transitions occurring between the 5*f* shell and orbitals of coordinated ligands the nature of the ligands is obviously of paramount importance, as the very possibility of the transitions depends upon peculiar features of the electronic configuration of the ligands. The transitions are, moreover, markedly affected by environmental influences. The resulting absorption bands, called charge transfer, or electron transfer bands, are therefore broad and devoid of all fine structure. Their position depends very much upon the ligand participating. As a rule, however, the energy differences involved correspond to an absorption in the ultraviolet region though often extended well into the visible. The absorption is also generally quite intense. The deep and vivid colors characteristic of many actinide complexes in solution are generally due to charge transfer bands. Mostly, these bands are less intense than those resulting from $5f \rightarrow 6d$ transitions. The latter are, however, to a larger extent situated within the ultraviolet region and they will therefore produce less color.

The absorption spectra of actinide solutions have been widely used for two principal purposes. First, as should be evident from the above discussion, important conclusions about the structure and bonding of actinide complexes can be drawn from the number, appearance, energy and intensity of the absorption bands. In this way, information has been obtained about the electronic configuration of the actinide atoms, about the coordination number and stereochemistry of complexes formed, and about the nature of the bonds involved. In addition the variation of the absorption with the concentration of ligands present in the solutions can also be utilized for the determination of the stability of the various complexes formed. The electron transfer bands are especially useful for this purpose. As they are so directly connected with the coordination reaction, their position and intensity will vary strongly as the complex formation proceeds. Naturally enough, this does not occur to the same extent with the bands arising from transitions within the actinide electron shells, and especially not for bands arising from $5f \rightarrow 5f$ transitions.

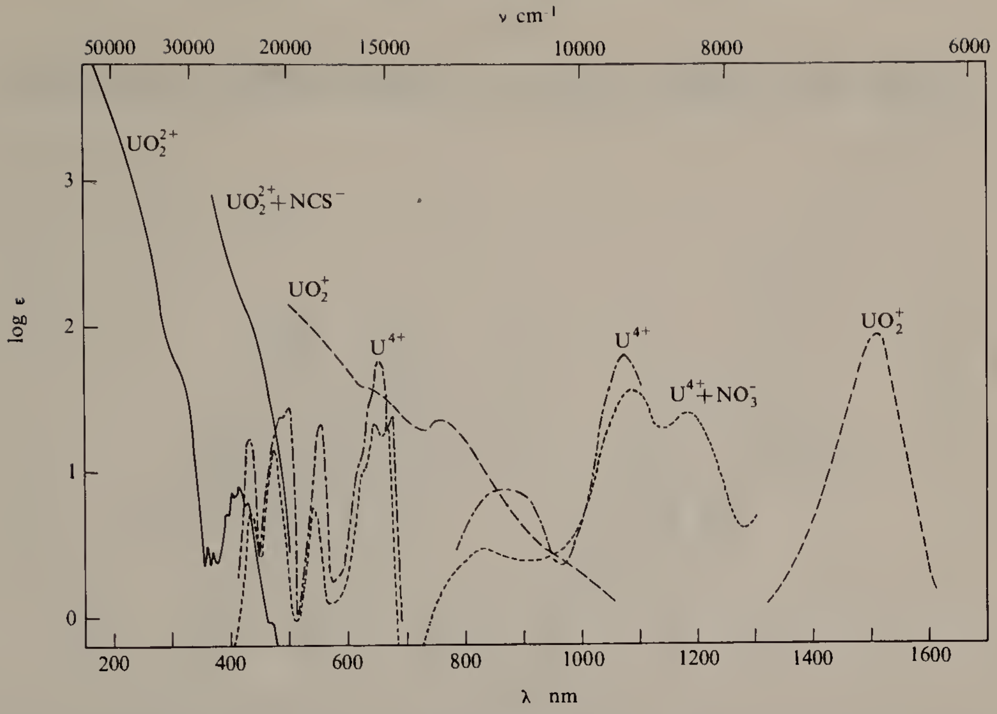

FIG. 2. Absorption spectra of uranyl(VI), uranyl(V) and uranium(IV) in acid aqueous solutions at 25°C. The curves refer to: (1) UO_2^{2+}, unhydrolysed, in aqueous perchloric acid solutions of $I = 3$ M (full-drawn; from J. T. Bell and R. E. Biggers, *J. Molec. Spectrosc.* **22** (1967) 262; **25** (1968) 312). (2) $UO_2^{2+}+NCS^-$, in an unhydrolysed perchlorate solution of $I = 1$ M, containing 0·25 M thiocyanate (second full-drawn curve; from S. Ahrland, *Acta Chem. Scand.* 3 (1949) 1067). (3) UO_2^+, in a DMSO solution containing perchlorate to $I = 0{\cdot}5$ M (dashed curve; from G. Gritzner and J. Selbin, *J. Inorg. Nucl. Chem.* **30** (1968) 1799). (4) U^{4+}, virtually unhydrolysed acid perchlorate solutions of I=1–2 M (dots and dashes; from refs. 34, 35). (5) U^{4+}, in 4 M nitric acid (dotted curve; from W. E. Keder, J. L. Ryan and A. S. Wilson, *J. Inorg. Nucl. Chem.* **20** (1961) 131). In this figure, as well as in the following Figs. 3–5, a logarithmic scale has been used for the molar absorption coefficients, in order to accommodate all the absorption bands on the same plot, in spite of their widely different intensities. The lower abscissae give wavelengths, the upper ones wavenumbers.

For the f^0 states Ac(III), Th(IV), Pa(V), U(VI) and Np(VII), no $5f \rightarrow 5f$ or $5f \rightarrow 6d$ transitions can possibly occur. In these cases, the absorption taking place in the ultraviolet and visible regions is therefore due to electron transfer processes. For the states present as simple hydrated ions, these bands are connected with a transfer of charge from the hydrate shell. Such a transfer gives rise to an absorption far out in the ultraviolet and the solutions are consequently colorless. For the uranyl(VI) ion, an electron transfer also takes place within the ion, from the oxygens of the uranyl group to the central uranium atom. This transfer involves much less energy so that part of the absorption moves into the visible region (Fig. 2), resulting in the characteristic yellow color of uranyl(VI) compounds and solutions. An even stronger absorption in the visible characterizes the ions (section 1.2) formed by heptavalent neptunium, especially the quite stable species present in alkaline solutions[8]. These solutions are green, the color being due to two fairly intense absorption bands, with maxima at 410 and 625 nm. The unstable acid solutions of Np(VII) are also strongly colored[9], on account of two broad and intense bands with maxima at 360 and 420 nm. This absorption results in a brown color.

The coordination of ligands which are very prone to transfer electrons to e.g. the uranyl

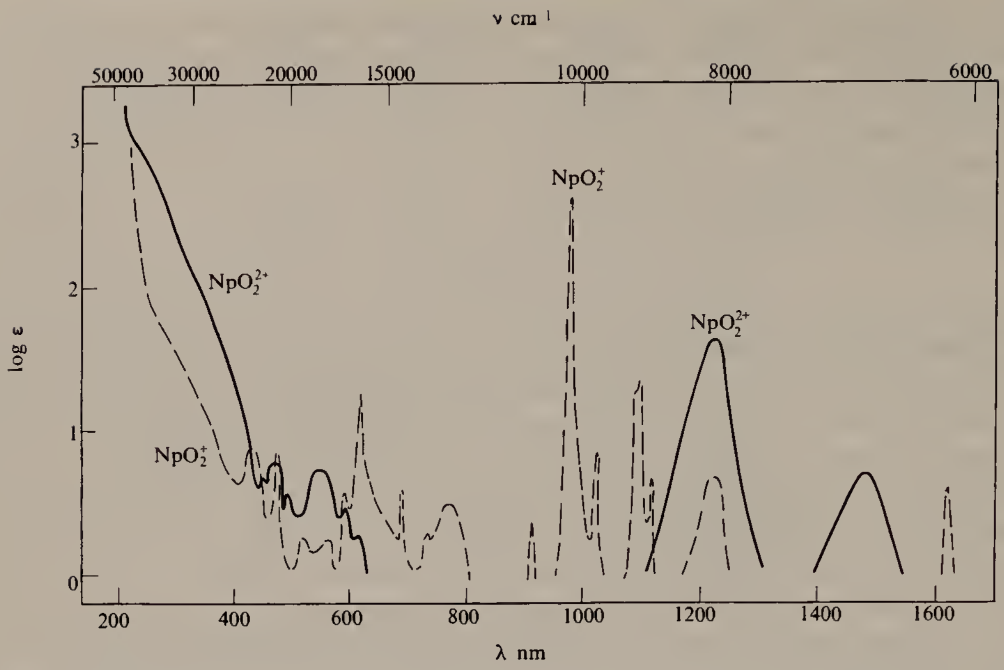

FIG. 3. Absorption spectra of neptunyl(VI) (fulldrawn) and neptunyl(V) (dashed) at 25°C. The measurements refer to unhydrolysed perchloric acid solutions in ordinary or heavy water (see text). The data are from R. Sjoblom and J. C. Hindman, *J. Amer. Chem. Soc.* **73** (1951) 1744 (especially for the ultraviolet region); P. G. Hagan and J. M. Cleveland, *J. Inorg. Nucl. Chem.* **28** (1966) 2905; and W. C. Waggener, *J. Phys. Chem.* **62** (1958) 382 (especially for the infrared region).

(VI) ion will cause the electron transfer bands to move even further into the visible spectrum. Such an effect is brought about by the thiocyanate ion which gives an intensely yellow color with uranyl solutions, caused by a strong absorption extending to wavelengths well over 500 nm (Fig. 2).

For the f^1 states Pa(IV), U(V), Np(VI) and Pu(VII), the possibility of $5f \rightarrow 5f$ and $5f \rightarrow 6d$ transitions exists. New bands consequently appear, though the number is still small. For yl ions of configuration f^1, such as UO_2^+ and NpO_2^{2+}, the electron transfer bands are still prominent, and their spectra therefore have many features in common with that of UO_2^{2+}. On account of the disproportionation of UO_2^+ in water, reliable spectra of this ion can only be measured in non-aqueous media, e.g. in dimethylsulphoxide (Fig. 2). A new band, assigned to a $5f \rightarrow 5f$ transition, appears in the near infrared, besides the intense electron transfer band at lower wavelengths. For NpO_2^{2+}, the main new bands appear in the infrared region, and at wavelengths so high that the absorption due to water is already considerable. The most detailed and reliable absorption spectra of NpO_2^{2+} have, therefore, been obtained in heavy water. In spectral regions where reliable measurements are possible both in ordinary and in heavy water, the same absorptivities have been found in both cases, as would be expected. Measurements from both solvents have therefore been merged for the construction of the absorption curve of NpO_2^{2+} given in Fig. 3.

For the f^2 states U(IV), Np(V) and Pu(VI), the spectra have already become more complicated, reflecting the increasing number of existing energy levels. This is evident from the absorption curves of the ions U^{4+} and NpO_2^+ (Figs. 2 and 3).

For U^{4+}, curves obtained both in perchloric and nitric acid media are presented (Fig. 2). The hydrolysis is suppressed in both cases, but an extensive formation of nitrate complexes

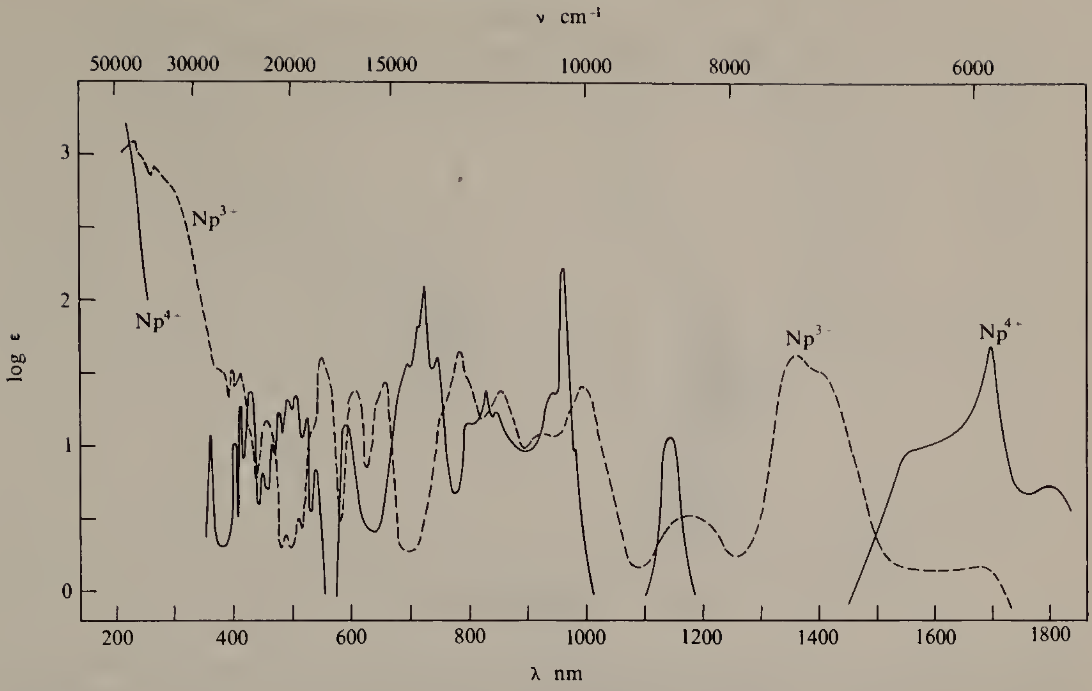

FIG. 4. Absorption spectra of Np(IV) (fulldrawn) and Np(III) (dashed) at 25°C. The measurements refer to unhydrolysed perchloric acid solutions in ordinary or heavy water and are from the same sources as those of Fig. 3.

takes place in the fairly concentrated nitric acid. The many narrow bands observed throughout the spectrum are due to $5f \rightarrow 5f$ transitions. They very much resemble the lanthanide bands due to $4f \rightarrow 4f$ transitions, though with the important difference that the absorption is much more intense. The $5f \rightarrow 5f$ transitions are thus much more probable than the $4f \rightarrow 4f$ transitions. The coordination of nitrate ions to U^{4+} causes a general decrease of the intensities of all the bands (Fig. 2). This decrease becomes more marked as the complex formation proceeds and when the final (presumably the hexanitrato) complex has been formed, all peaks have been very severely reduced. A similar depression of the intensity of the absorption is brought about by the hydrolysis of U^{4+}. In this case drastic changes are observed already after the dissociation of the first proton[34,35].

As would be expected, the spectrum of PuO_2^{2+} is very similar to that of NpO_2^+, both with regard to the number and intensity of the bands[36]. For the highest of the narrow peaks due to $5f \rightarrow 5f$ transitions, a maximum absorptivity of 550 cm^{-1} M^{-1} (at 803 nm) is found for PuO_2^{2+}, as against 395 cm^{-1} M^{-1} (at 980 nm) for the corresponding NpO_2^+ peak (Fig. 3).

For the f^3 states, represented by U(III), Np(IV), Pu(V) and Am(VI), and the f^4 states, represented by Np(III), Pu(IV) and Am(V), the spectra are becoming increasingly complex[36,37]. The increase in number and complexity of the absorption bands with the number of f electrons is illustrated by the spectra of the hydrated ions Np^{4+} and Np^{3+} (Fig. 4).

With increasing number of f electrons, the disturbances of the $5f \rightarrow 5f$ transitions from

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[34] K. A. Kraus and F. Nelson, *J. Amer. Chem. Soc.* **72** (1950) 3901.

[35] H. A. C. McKay and J. L. Woodhead, *J. Chem. Soc.* **1964**, 717.

[36] D. Cohen, *J. Inorg. Nucl. Chem.* **18** (1961) 211.

[37] R. A. Penneman and T. K. Keenan, *The Radiochemistry of Americium and Curium*, NAS-NS 3006, U.S. Department of Commerce, Washington D.C. (1960).

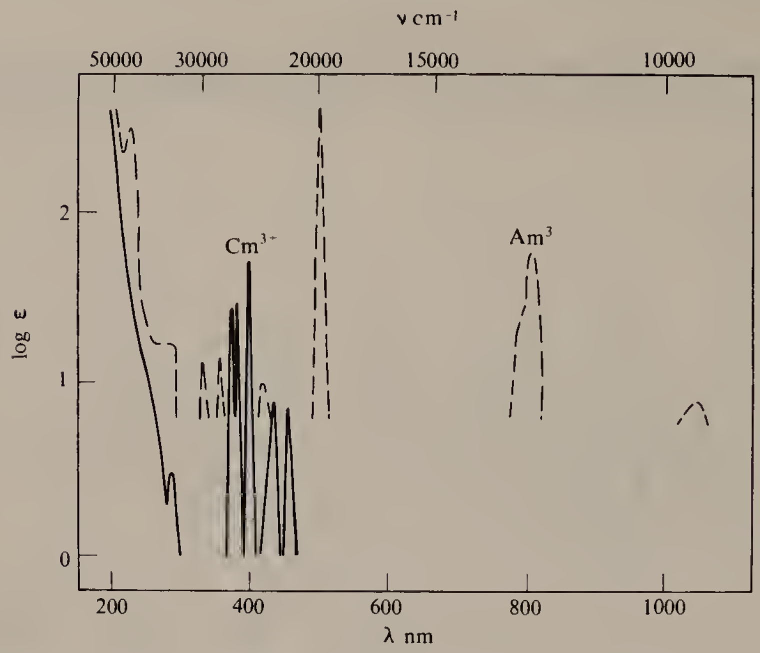

FIG. 5. Absorption spectra of Am(III) (dashed) and Cm(III) (fulldrawn) at 25°C, in perchloric acid solutions which have been measured immediately after their preparation. The spectra should thus apply to the unhydrolysed ions Am^{3+} and Cm^{3+} and should moreover be free from interferences due to products of radiolysis. The figure has been adapted from ref. 37.

outside the atom become even smaller, and the spectra are therefore more like those of the lanthanides, with extremely narrow peaks. This is illustrated by the spectra of the hydrated Am^{3+} and Cm^{3+} (electron configurations $5f^6$ and $5f^7$, respectively) which are presented in Fig. 5.

Recording the solution spectra of americium and curium is beset by difficulties due to the scarcity of material and, even more, to the radiolytic reactions taking place as a consequence of the α-decay of the actinide nuclides[37]. The decomposition products thus building up in the solutions often possess quite a high absorption. The actinide spectra will thus be superposed on a background which often becomes quite disturbing after rather a short time. For the actinides heavier than curium, with nuclides of shorter half-lives, these difficulties become even more serious. Nonetheless, it has been possible to record a detailed solution spectrum of einsteinium[38].

Almost pure $^{253}_{99}Es$, an α-emitter with $t_{1/2} = 20{\cdot}5$ days, was used for these experiments which were all conducted within 56 hr of the separation of the nuclide from its daughter $^{249}_{97}Bk$. The total amount of einsteinium used in one experiment was as little as ~3 μg, but as extremely small volumes of solution could be used, down to 3 nl, high concentrations could nevertheless be achieved and even low absorptivities thus recorded. Chemically, the $5f^{10}$ state Es(III) was present, dissolved in 3–6 M hydrochloric acid. The spectrum (Fig. 6) thus presumably refers to a mixture of the hydrated ion Es^{3+} and its chloride complexes, apart from the heavy background due to radiolytic decomposition products such as Cl_2, H_2O_2, etc. Eighteen absorption bands are observed between 373 and 690 nm. Further bands do not exist in the region observed, i.e. from 340 to 1060 nm. The intensities are

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[38] D. K. Fujita, B. B. Cunningham, T. C. Parsons and J. R. Peterson, *Inorg. Nucl. Chem. Letters*, 5 (1969) 245.

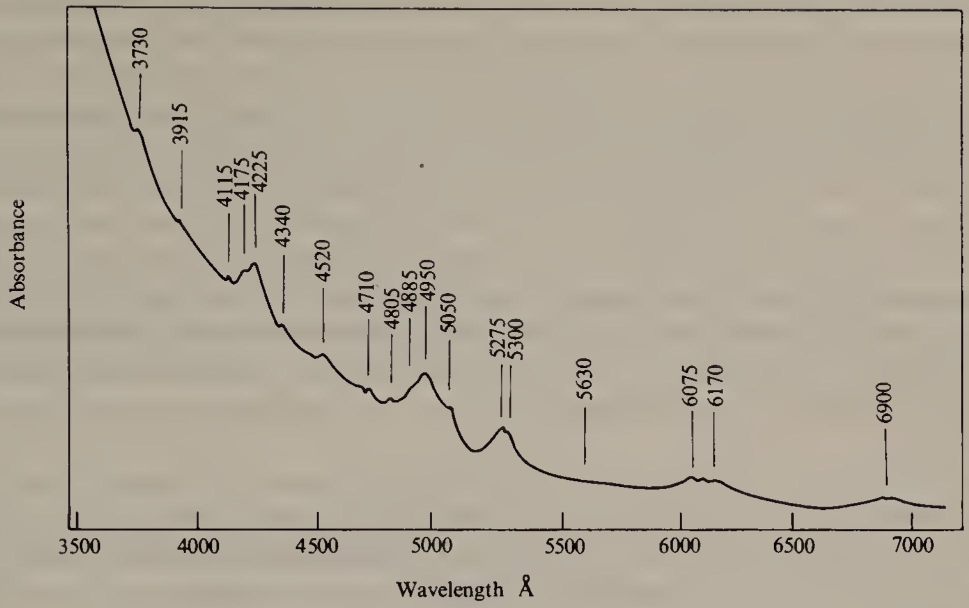

FIG. 6. Absorption spectrum of Es(III) in hydrochloric acid solution, over a heavy background due to products of radiolysis (from ref. 38).

throughout quite low, the most prominent peak, at 495 nm, having a maximum molar absorption coefficient of only $\simeq 5\ \mathrm{cm}^{-1}\ \mathrm{M}^{-1}$.

2. EQUILIBRIA IN AQUEOUS SOLUTION

2.1. Methods of measurement

2.1.1. *General Principles for the Determination of Equilibrium Constants*

As pointed out in section 1.2, several complexes generally coexist in solutions of actinide salts. In order to determine reliably the constants for all these interwoven equilibria, it is necessary to collect a large body of data, as free as possible from systematic as well as random errors. This means that the data have to be both accurate and precise, especially if polynuclear complexes are formed, as is the case for the important hydrolytic reactions (see 2.2.1).

Most of the procedures used for the identification of complexes in solution can be characterized as equilibrium methods. By such methods, some quantity is measured which depends in a known manner upon the concentrations of the species participating in the existing equilibria. By applying the law of mass action it will then be possible not only to identify the complexes present, but also to determine their equilibrium constants and hence their absolute and relative concentrations in solutions of given compositions[39,40].

In order to apply successfully the law of mass action on complicated ionic equilibria, it is necessary to maintain at least approximately constant activity conditions in all solutions.

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[39] F. J. C. Rossotti and H. Rossotti, *The Determination of Stability Constants*, McGraw-Hill, New York (1961).

[40] S. Fronaeus, *Technique of Inorganic Chemistry*, Vol. 1, p. 1. H. B. Jonassen and A. Weissberger (Eds.), Interscience, New York (1963).

This is achieved by measuring in a virtually constant ionic medium. Most often a perchlorate medium is used, as the perchlorate ion seems to be among the ones least prone to form metal ion complexes in aqueous solution. The constants found will be concentration constants, strictly valid only for the medium chosen. They will vary both with the ionic strength, I, of the medium and also with the ions employed to create it. The variation with I also depends much upon the nature of the ions participating in the equilibrium, and especially upon their charges. For all types of ions, however, the activity coefficients, and hence the equilibrium constants, vary rapidly with I both at very low and very high ionic strengths. In an intermediate range of I, however, very roughly between 0·2 and 2 M, the variation is generally modest and constants determined for a value of I within these limits may be considered as fairly representative for the whole range. The individualities of various ions becomes more prominent, the higher their concentrations. They are very noticeable already for values of I around 1 M.

By determining the constants for low and decreasing values of I, values of the thermodynamic constants may be obtained by a Debye–Hückel extrapolation to $I = 0$. This procedure will evidently be most successful in cases where constants can be reliably determined even at quite low ionic concentrations. The best results will therefore be obtained for strong complexes.

The equilibria may be described by the gross or overall stability constants, β_{mn}, for the formation of the complex M_mL_n out of the actinide ion M and the ligand L (charge signs omitted) according to

$$m\mathrm{M}+n\mathrm{L} \rightleftharpoons \mathrm{M}_m\mathrm{L}_n \tag{2.1a}$$

$$\beta_{mn} = [\mathrm{M}_m\mathrm{L}_n][\mathrm{M}]^{-m}[\mathrm{L}]^{-n} \tag{2.1b}$$

where the square brackets denote the concentrations of the respective species. In the simplest case which also often occurs, only mononuclear complexes ($m = 1$) are formed, with overall stability constants

$$\beta_n = [\mathrm{ML}_n][\mathrm{M}]^{-1}[\mathrm{L}]^{-n} \tag{2.2}$$

As already mentioned (section 1.2), the complexes are generally formed stepwise. It is therefore often desirable to discuss the consecutive stability constants, K_n, characterizing the equilibrium between a complex and the next higher one. In the mononuclear case these are thus defined according to

$$K_n = [\mathrm{ML}_n][\mathrm{ML}_{n-1}]^{-1}[\mathrm{L}]^{-1} \tag{2.3}$$

2.1.2. *Stability Constants from Potentiometric Measurements*

Among the equilibrium methods, potentiometric determination of either the free ligand concentration, [L], or the free metal ion concentration, [M], have been the classical methods. They are still both the most used and most precise methods available.

The value of [L] is most often found by measurements of pH, nowadays as a rule determined by a glass electrode. This is a good method in most cases where L is also a base of suitable strength. In fluoride solutions which are important in actinide chemistry the glass electrode fails, but in many cases the quinhydrone electrode may then be used. If the ligand is not sufficiently basic, other indicator electrodes are used, e.g. the Fe^{3+}/Fe^{2+} redox electrode for fluoride systems. Often [L] can be directly determined by the recently developed anion-sensitive membrane electrodes. This method may even yield a more precise value of [L] than any of the other methods available[41a].

[41a] S. Ahrland and L. Kullberg, *Acta Chem. Scand.* **25** (1971) 3457.

From the values of [L] measured and the total concentrations of ligand, C_L, and metal ion, C_M, the ligand number $\bar{n}$, defined according to

$$\bar{n} = (C_L - [\mathrm{L}])/C_M \tag{2.4}$$

can be calculated. For the simplest case of a system of mononuclear complexes

$$C_L = [\mathrm{L}] + \sum_{n=1}^{N} n[\mathrm{ML}_n] \quad \text{and} \quad C_M = [\mathrm{M}] + \sum_{n=1}^{N} [\mathrm{ML}_n],$$

where N is the highest number of ligands that can be coordinated. After introduction of the appropriate stability constants, the complex formation function is obtained

$$\bar{n} = \frac{\sum_{n=1}^{N} n\beta_n[\mathrm{L}]^n}{X} \tag{2.5}$$

where

$$X = 1 + \sum_{n=1}^{N} \beta_n[\mathrm{L}]^n \tag{2.6}$$

If only mononuclear complexes are present, $\bar{n}([\mathrm{L}])$ (i.e. 2.5) is evidently independent of [M], and hence of the value of C_M chosen. From this function, all the constants β_n of complexes existing in perceptible amounts within the range of [L] covered can be calculated without too much difficulty[39,40].

If, on the other hand, polynuclear complexes are formed, $\bar{n}([\mathrm{L}])$ will depend upon [M]. Series of different C_M will then result in a family of formation functions, as exemplified by the measurements of the hydrolysis of UO_2^{2+} (presented in Fig. 9a). From these functions, it is at least in principle possible to find not only the composition of all the complexes present, but also their stability constants β_{mn}. Even when the complexes formed are not too many or too large, this generally takes a lot of computing. As a first step, it is as a rule helpful to identify some of the complexes formed. An example of such a procedure is given in Fig. 9b. As the numbers m and n grow, however, the differences between the alternatives presented by adjacent complexes become quite small so that the actual possibilities to decide between them become rather precarious in view of the unavoidable experimental errors. This difficulty to discern between different highly polynuclear complexes is common to all equilibrium methods (see further 2.1.5).

Most potentiometric determinations of [M] have been performed by amalgam electrodes. The original, and still most often preferred, technique has been to employ stationary electrodes, but in later years polarography has also been used fairly frequently. The actinides do not readily form amalgams, however, and another technique has therefore to be applied in their case, viz. measurements of the redox potential set up between two oxidation states present in the solution.

If only mononuclear complexes are formed, the determination of [M] allows a direct calculation of the function X which in such a case is $= C_M/[\mathrm{M}]$. If, moreover, the complexes are not too strong (i.e. $\beta_1 \lesssim 1500\ \mathrm{M}^{-1}$), values of [L] corresponding to computed values of X may be found by an extrapolation to $C_M = 0$ where $[\mathrm{L}] = C_L$. From the function $X([\mathrm{L}])$ (i.e. 2.6) thus determined, the constants β_n are easily calculated. When stronger complexes are formed the values of [L] are initially too low to be determined by such an extrapolation procedure. They may nonetheless be computed by a different approach[40].

If polynuclear complexes are also formed, the ratio $C_M/[M]$ will no more be independent of [M]. From the more complicated functions then obtained, the constants β_{mn} may in principle be calculated. Such calculations are generally fairly laborious and, as remarked above, the outcome tends to become uncertain when large aggregates are involved. In such cases a safer interpretation is possible if both [M] and [L] are measured.

2.1.3. *Stability Constants from Distribution Measurements*

In other very useful equilibrium methods the distribution of M between the aqueous solution and a second phase is measured as a function of [L]. These methods include extraction into a solvent which is immiscible with water, sorption on ion exchangers and measurements of the solubility in the presence of a solid phase. Distribution measurements have been especially valuable for the elucidation of actinide equilibria, partly because of the restrictions experienced in the use of the generally more precise potentiometric methods, but also because they have in fact turned out to be quite versatile tools for this task. Among the distribution methods, solvent extraction has been especially widely used, on account of the great number of suitable extractants which have become available (see further section 4). Recently, the use of solvent extraction for equilibrium investigation has become still more attractive with the introduction of highly automatized measuring equipment[41b].

In the simplest case, one of a series of mononuclear complexes ML_n formed in the aqueous phase is extractable. Such a complex has to be uncharged. If the ratio between the charge z of the central ion and the charge y of the ligand is denoted by i the formula will thus be ML_i. The complex must also be coordinatively saturated. Further conditions for its extractability are given in section 4. The measured quantity is the distribution ratio, $D = C_{M,org}/C_M$ where $C_{M,org}$ is the total concentration of M in the solvent. In this case $C_{M,org} = [ML_i]_{org}$, i.e. the concentration of ML_i in the solvent phase. For the uncharged complex, Nernst distribution law demands

$$\lambda_i = [ML_i]_{org}/[ML_i] \tag{2.7}$$

If the mass action law is introduced to express the concentrations in the aqueous phase, $[ML_i]_{org} = \lambda_i\beta_i[M]\,[L]^i$ and hence

$$D = \frac{C_{M,org}}{C_M} = \frac{\lambda_i\beta_i[L]^i}{X([L])} \tag{2.8}$$

From corresponding values of D and [L], all the constants β_n, as well as λ_i, can be determined. The value of D is as a rule best measured radiometrically if a suitable radioactive isotope of the element is available, as is the case for all actinides. On account of the high sensitivity of the radiometric method even very extreme values of D can be precisely determined and C_M may, moreover, be chosen so low that $[L] \simeq C_L$ which considerably simplifies the evaluation of the measurements. A further advantage of the radiometric method is its independence of the chemical composition of the solutions while much attention must often be paid to the presence of interfering agents when other methods of analysis are employed. Equation (2.8) is further discussed in section 4.6.2.

Even when no complex in the system to be investigated is extractable, the solvent extraction method can be applied. An auxiliary ligand, A, able to form an extractable complex with M, is then added. The simplest conditions will prevail if both this ligand and the complex it forms are virtually insoluble in the aqueous phase. The ligand is generally added to the solvent in the form of the corresponding acid. In the simplest case, which is

[41b] H. Reinhardt and J. Rydberg, *Chem. Ind.* **1970**, 488.

also common in practice, this acid is monobasic (i.e. $i = z$) and the complex formation implies the displacement of the proton from the acid HA

$$M^{z+}(aq) + zHA(org) \rightleftharpoons MA_z(org) + zH^+(aq) \tag{2.9}$$

If the constant for this equilibrium is denoted by K_D the following expression is valid for the measured distribution ratio

$$D = K_D \left(\frac{[HA]_{org}}{[H]}\right)^z \frac{1}{X([L])} \tag{2.10}$$

From corresponding values of D, $[HA]_{org}$, [L] and [H] (= the hydrogen ion concentration of the aqueous phase) all the unknown constants (K_D and β_n) can be calculated.

Cases where the solvent extraction follows more complicated patterns than the simple ones delineated above are frequent, however. Partly protonated complexes $ML_z(HL)_x$ or $MA_z(HA)_x$ are often formed when the simple uncharged species ML_z and MA_z would not have the right coordination number. Different ligands which may originally be present either in the aqueous phase or in the solvent may combine to form an extractable mixed complex which may also be partly protonated.

The extractability also depends very much on both the dielectric and the solvating properties of the solvent. Solvent molecules are often attached to the extracted actinide ion, in order that its preferred coordination number should be reached. Several such cases will be treated in section 4.

Sorption of actinide ions on cation exchangers, combined with their elution by suitable complexing agents, has been extensively used for both identification and separation. This very process has in fact been of decisive importance for the discovery of all transcurium elements. With the exception of No, these elements are all exclusively, or at least predominantly, trivalent (Table 1) and the sorption and elution processes mentioned have therefore mainly been concerned with M^{3+} ions. All the types of ions formed by the actinides are sorbed, however, though their affinity for the ion exchanger depends very much upon the effective ionic charge[26]. The M^{4+} ions are by far most strongly sorbed, the M^{3+} and MO^{2+}, of about equal and still quite high affinity, come next, while M^{2+} and MO_2^+ are rather weakly sorbed. The very different sorption characteristics of M^{3+} and M^{2+} ions have been utilized, e.g. for the distinction between No(III) and No(II), and the estimation of the standard oxidation potential of the No(III)/No(II) redox couple[16].

When complexes are formed with anions, the ionic charge decreases and hence the affinity of the actinide species for the cation exchanger decreases. Solutions of complex forming anions may thus act as eluants. The order of elution will depend upon the balance between the affinities of the various actinides for the ion exchanger and the anions offered (see also section 2.2.3).

Measurements of the sorption of an actinide on the ion exchanger as a function of the concentration of a complexing agent in the outer solution can in fact be arranged so as to yield quantitative information about the equilibria involved. This method has the great advantage of being almost generally applicable for all systems of complexes formed between cations and anions. As most actinide complexes in aqueous solution are of this type, cation exchange has been widely used for their investigation.

Some complications inherent in the method must, however, be taken into account if a correct result is to be obtained[40]. First, though the sorption rapidly decreases with the charge, the sorption of positively charged complexes is nevertheless not negligible in comparison with that of the free ion M^{z+}. In particular the sorption of the first complex is often quite considerable. Another, often more troublesome, complication is that the cation exchangers are not quite monofunctional, but contain sites of different affinity for the species to be sorbed. The constants characterizing the sorption equilibria will then depend upon the load on the exchanger. At least certain types of the modern sulphonated polystyrene resins now generally used for the present purposes are almost monofunctional, however.

2.1.4. *Stability Constants from Spectrophotometry and Formally Analogous Methods*

As pointed out in section 1.5, the charge transfer bands of the actinide spectra change considerably both in wavelength and intensity when complexes are formed. This variation can be utilized for the investigation of the complex equilibria.

The absorption coefficient, a, of a complex solution at a given wavelength is the sum of the absorption coefficients of all the species present. According to Beer's law, these coefficients are proportional to the concentrations. In the simplest case when mononuclear complexes are formed with a ligand which does not itself absorb any light at the actual wavelength, this is expressed by

$$a = \epsilon_0[\mathrm{M}] + \sum_{n=1}^{N} \epsilon_n[\mathrm{ML}_n] \qquad (2.11)$$

where ϵ_0 and ϵ_n are the molar absorption coefficients for the free (= hydrated) actinide ion and the complexes, respectively. Introduction of a formal mean molar absorption coefficient $\epsilon_\mathrm{M} = a/C_\mathrm{M}$, and expressions for the concentrations $[\mathrm{ML}_n]$ according to the law of mass action, results in

$$\epsilon_\mathrm{M} = \frac{\epsilon_0 + \sum_{n=1}^{N} \epsilon_m \beta_n [\mathrm{L}]^n}{X} \qquad (2.12)$$

where the quantity ϵ_M can be measured experimentally. The fractional function (2.12) is reminiscent of the complex formation function (2.5), but with the important difference that the coefficients of the numerator are not integers but a set of unknown constants. The number of unknowns to be determined has thus doubled, which puts correspondingly higher demands on the accuracy and precision of the data. These demands are often difficult to meet, especially as the values of ϵ_n tend to become increasingly the same for the higher complexes which means that the variation of ϵ_n with [L] generally becomes quite slight as the complex formation proceeds. Under such circumstances, it is of course basically very difficult to decide whether a certain complex is really converted into a higher one with increasing [L]. For that reason, it is also important to select for the measurements a wavelength where the variation of ϵ_M with [L] is as large as possible. If polynuclear complexes are also formed, ϵ_M will be a function of [M] as well as of [L] which will further complicate the function.

The best way of evaluating a set of mononuclear constants from (2.12) is generally to apply the principle of corresponding solutions[39,40]. This method utilizes the fact that in such a case ϵ_M is a function of [L] only, independent of the value of C_M chosen. The value of [L] corresponding to a measured ϵ_M may then be found from an extrapolation to $C_\mathrm{M} = 0$. Once [L] has been found, the ligand number $\bar{n}$ can be calculated, and hence the constants found from the complex formation function (2.5). By this treatment, the relatively simple function (2.5) ensues instead of the more complicated (2.12) which considerably lessens the

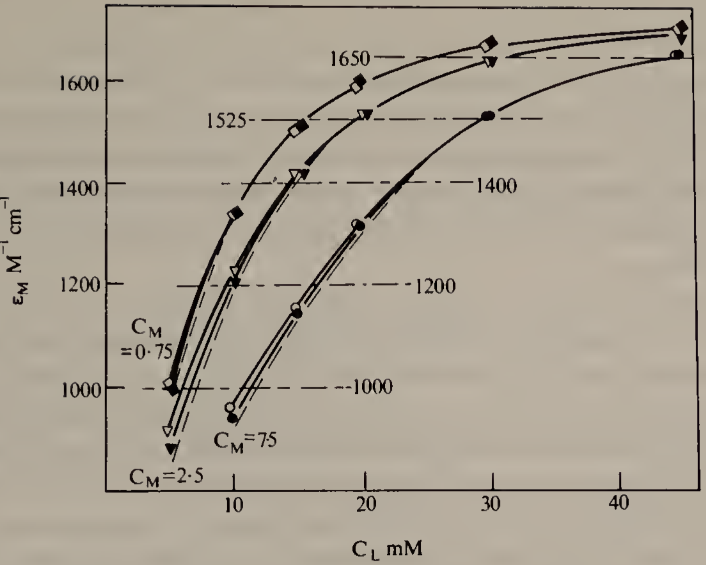

FIG. 7. Determination of the stability constants of the uranyl acetate system from spectrophotometric measurements, by means of the method of corresponding solutions (S. Ahrland, *Acta Chem. Scand.* 5 (1951) 199). The outcome of the first extrapolations, performed in order to remove the influence of hydrolytic reactions taking place at low values of [L], is indicated by the dashed lines. The functions $\epsilon_M(C_L)$ have been cut at several values of ϵ_M, each corresponding to a certain value of [L] and hence to a certain value of $\bar{n}$, as is evident from the eqns (2.12) and (2.5). The functions $C_L(C_M)$ for constant ϵ_M are therefore straight lines [cf. eqn (2.4)] with an intercept on the ordinate axis = [L] and a slope = $\bar{n}$.

strain upon the experimental data. The method is illustrated in Fig. 7, which refers to a determination of the stability constants of the uranyl acetate system. In this case an initial extrapolation has been necessary in order to remove the influences of hydrolytic reactions perceptible at low values of [L].

When polynuclear complexes are formed, the method of corresponding solutions cannot be applied and this considerably limits the usefulness of spectrophotometry. This drawback of course also applies to methods formally analogous with spectrophotometry. Among such methods, the polarimetric one is also based on an optical property. If the coordinated ligand is asymmetric, the optical rotatory power of the system will be the sum of the contributions from the ligand and the various complexes. According to the law of Biot, analogous to that of Beer, the contributions will be proportional to the respective concentrations. An expression similar to (2.12) will therefore result, though with the difference that, besides the complexes, the free ligand, but not the hydrated actinide ion, possesses optical rotatory power. The values of the molar optical rotary powers α_n, corresponding to ϵ_n of the spectrophotometric method, may moreover be negative as well as positive.

The total enthalpy of reaction for the formation of a set of complexes also follows a function formally analogous to (2.12). On account of their great interest from both theoretical and practical points of view (see 2.3), reaction enthalpies have been measured more and more extensively during later years. From the reasoning above, it should be obvious that it is often very difficult, or at least not very advantageous, to determine simultaneously both the β_n values of the various complexes and the enthalpy changes accompanying their formation from a formula analogous to (2.12). As a rule, therefore, the values of β_n are determined separately by any of the methods mentioned above, and the calorimetric measurements are utilized only for the determination of the reaction enthalpies (see 2.1.6).

2.1.5. *Methods yielding the Average Mass or Size of Solute Particles*

As pointed out above (2.1.2), the difficulties in discerning between different complexes by means of equilibrium methods become very marked as the complexes M_mL_n become highly polynuclear[42,43]. Even when the condensation is still not very far advanced, several pairs m,n (of the same, or approximately the same, ratio m/n) fit about equally well to the data obtained[44]. Evidently, even the identity of the complexes formed cannot be safely determined in such cases.

On the other hand, valuable information can be obtained by methods which are not primarily sensitive to the number of particles, as is the characteristic common feature of all equilibrium methods, but rather to their mass or size. Among such methods, ultracentrifugation[45,46] and light scattering[47] have been successfully applied to the investigation of the complexes formed in hydrolysed actinide solutions. In the later stages of the hydrolysis, the complexes are so highly polynuclear that their identification by means of equilibrium methods becomes virtually impossible. Even for solutions where complexes of an intermediate degree of polymerization still prevail, particle size determinations have contributed much towards the elucidation of the equilibria involved, in spite of the fact that no equilibrium constants can be calculated from these measurements.

2.1.6. *Enthalpy Changes of Complex Formation Reactions*

The standard free energy changes can be calculated from the stability constants in the general case according to:

$$\Delta G^\circ = -RT \ln \beta_{m,n} \tag{2.13}$$

The function ΔG° provides a measure of the tendency of the complex to be formed; the more negative ΔG°, the more complete the formation of M_mL_n from its components M and L. In the special case of a step in a system of mononuclear complexes, equation (2.13) becomes

$$\Delta G_n{}^\circ = -RT \ln K_n \tag{2.14}$$

where ΔG° measures the tendency of formation of ML_n from its predecessor ML_{n-1}. The standard free energy change is made up by contributions from the changes of enthalpy and entropy according to

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{2.15}$$

Stable complexes are thus formed in strongly exothermic reactions and/or if their formation involves a large gain of entropy, i.e. a large loss of order in the solution. It turns out that these two terms play very different roles in the formation of complexes of different types, depending upon the nature of the bonds involved (see section 2.3). It is therefore of great interest to determine not only ΔG°, via β_{mn}, but also ΔH° and ΔS°. In practice, ΔH° is measured, and ΔS° then calculated from equation (2.15).

[42] F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.* **10** (1956) 957.
[43] N. Ingri, *Acta Chem. Scand.* **17** (1963) 597.
[44] C. F. Baes, Jr., N. J. Meyer and C. E. Roberts, *Inorg. Chem.* **4** (1965) 518.
[45a] R. M. Rush and J. S. Johnson, *J. Phys. Chem.* **67** (1963) 821.
[45b] R. M. Rush, J. S. Johnson and K. A. Kraus, *Inorg. Chem.* **1** (1962) 378.
[46] F. C. Hentz, Jr., and J. S. Johnson, *Inorg. Chem.* **5** (1966) 1337.
[47] F. C. Hentz, Jr. and S. Y. Tyree, Jr., *Inorg. Chem.* **4** (1965) 873.

Values of ΔH° have been determined either by direct calorimetric measurements, or from the temperature coefficients of the stability constants of the relevant complexes. Of these methods, the calorimetric one is generally much more precise, and also more accurate[48,49], especially if the required stability constants are determined separately (see 2.1.4)[50]. For a system of mononuclear complexes, the reaction heat per mole (after deduction of heats of dilution etc.), Δh, is related to the total enthalpy changes, $\Delta H_{\beta n}$, for the formation of the consecutive complexes between M and L according to

$$\Delta h = \frac{\sum_{n=1}^{N} \Delta H^\circ_{\beta n}\, \beta_n [\mathrm{L}]^n}{X} \tag{2.16}$$

where $\Delta H_{\beta n}$ is the sum of the stepwise enthalpy changes

$$\Delta H^\circ_{\beta n} = \sum_{k=1}^{n} \Delta H_k^\circ \tag{2.17}$$

The function Δh is independent of [M] when only mononuclear complexes are formed while terms containing [M] enter on the formation of polynuclear complexes[51,52].

Though very small amounts of heat can be very precisely measured by modern calorimeters[52–54], most types nevertheless demand for a good result that at least about 0·1 mmole of metal ion reacts. The species involved must therefore not be too slightly soluble. Moreover, the reaction must not be too slow.

For reactions where these conditions cannot be realized, the determination of ΔH° from the van't Hoff equation for the temperature dependence of the equilibrium constant is generally to be preferred[49,55]. If ΔH_n° does not vary appreciably within the range of T used and if K_n is measured very precisely over a not too small range of T (which involves a lot of work) good, or at least usable, values of ΔH_n° are obtained also by this method.

2.2. Complexes formed by actinide ions

2.2.1. *Complexes formed on Hydrolysis*

As pointed out in section 1.2, the hydrated actinide ions act as Brönsted acids. The tendency to split off protons generally increases with the ionic charge, being strongest for the tetravalent ions. It should be remembered, however, that the actual charges on the actinide atoms in the actinyl(VI) and actinyl(V) ions are in fact much higher than the formal ionic charges of +2 and +1, respectively, and, therefore, that such ions are much stronger acids than ions of the same charge possessing spherical symmetry[56]. On the dissociation of protons, the residual species often condense into polynuclear complexes, a rather general

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[48] S. Ahrland, *Helv. Chim. Acta*, **50** (1967) 306.

[49] R. G. de Carvalho and G. R. Choppin, *J. Inorg. Nucl. Chem.* **29** (1967) 737.

[50] R. Arnek, *Arkiv Kemi*, **24** (1965) 531.

[51] I. Leden and T. Ryhl, *Acta Chem. Scand.* **18** (1964) 1196.

[52] R. Arnek, *Acta Chem. Scand.* **23** (1969) 1986.

[53] P. Gerding, I. Leden and S. Sunner, *Acta Chem. Scand.* **17** (1963) 2190.

[54] I. Grenthe, H. Ots and O. Ginstrup, *Acta Chem. Scand.* **24** (1970) 1067.

[55] L. Drougge, L. I. Elding and L. Gustafson, *Acta Chem. Scand.* **21** (1967) 1647.

[56] R. E. Connick and Z. Z. Hugus, Jr., *J. Amer. Chem. Soc.* **74** (1952) 6012.

feature of hydrolytic reactions involving metal ions[57–59]. The mean number of actinide atoms in these complexes generally increases with pH and with the total concentration of actinide, C_M. Various complexes may moreover coexist in appreciable amounts in the same solution. These circumstances often make the disentanglement of the various equilibria quite an arduous task. If the complexes formed are highly polynuclear, it may even be practically impossible to find their exact composition (section 2.1)[44–46].

Another difficulty in the investigations of these hydrolytic equilibria is that precipitates are often formed after addition of even fairly small amounts of alkali, when the number of protons split off per actinide ion is still low. This is especially likely to occur when the value of C_M is not very low. As reasonably accurate determination of equilibria of the present kind demands a rather large variation of both pH and C_M, such an early precipitation of products of hydrolysis often complicates evaluation of the results.

It might be imagined that the formation of very high-molecular polymers in the solutions normally precede the precipitation. Such giant polymers are also well established as important constituents of highly hydrolysed solutions, especially of the tetravalent actinide ions. The earliest indication of their formation was given by the slow reactions which were generally observed to take place in the later stages of the hydrolysis of solutions of these ions. More direct evidence about the nature of the products formed was later obtained from ultracentrifugation experiments, and from measurements of the light-scattering of the solutions. As pointed out in section 2.1, these techniques yield the average degree of polymerization which is practically impossible to determine for high polymers by measurement of ionic equilibria.

Especially for Th(IV) but also for Pu(IV), the high polymers formed in the later stages of the hydrolysis have been rather thoroughly investigated[46,60,61]. For Th(IV), complexes of a fairly low degree of polymerization predominate until $\simeq 2 \cdot 5$ protons have been split off per thorium atom. As discussed below, it is also possible, in this range, to identify the species formed by pH measurements. As the hydrolysis proceeds, however, the degree of polymerization starts to increase very rapidly and before the number of protons split off per thorium has reached 3, the complexes seem to contain on the average well over 100 thorium atoms. In this range, the kinetics also becomes very slow, the degree of polymerization increasing for weeks without attaining equilibrium. In the case of plutonium, the slow reactions taking place when Pu(IV) is extensively hydrolysed have created serious problems for the plutonium processing industry. High polymers once formed do not readily disperse in solutions of acidities that would certainly prevent their formation. This has often led to wrong conclusions about the ionic state of the plutonium present, with consequences which have proved troublesome or even dangerous.

The precipitates formed on hydrolysis are generally amorphous and their structures therefore not well defined. In several cases, however, where it has been possible to obtain, or rather induce, the products of hydrolysis into a crystalline state, the atoms are, as would be expected, ordered in some infinite arrangement[18,22,29,62]. On the other hand, several structures do contain finite hydrolysed species of a low degree of polymerization. Their

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[57] L. G. Sillén and A. E. Martell, *Stability Constants of Metal-ion Complexes*, 2nd ed., 1964, and Supplement No. 1, 1971, Special Publications Nos. 17 and 25, The Chemical Society, London.

[58] L. G. Sillén, *Quart. Rev.* **13** (1959) 146.

[59] G. Biedermann, *Svensk. Kem. Tidskr.* **76** (1964) 362.

[60] A. Brunstad, *Ind. Eng. Chem.* **51** (1959) 38.

[61] O. Wick, *Plutonium Handbook*, vol. 1, Gordon & Breach, New York (1967).

[62] G. Lundgren, *Svensk. Kem. Tidskr.* **71** (1959) 200.

composition generally agrees with that of some complex existing in solution[28, 63]. If such a complex is apt to form a solid phase together with other species present, this phase will of course precipitate even if no high polymers are present.

Due to the amorphous character of the fresh precipitates, few solubility products have been determined for compounds formed by the hydrolysis of actinide ions. Not only the structures but also the compositions of the precipitates are often ill defined. Large variations are found when the concentrations of the various components of the solutions are varied. In most cases, these variations are certainly due to the ion exchange properties exhibited by many hydroxide compounds, especially those of high valent ions[64]. In these compounds, the hydrogens of the hydroxide groups are often exchangeable for other cations. As for all ion exchange processes involving the replacement of H^+, the present reactions take place more extensively the higher the value of pH. The amounts of other ions taken up moreover depend upon their concentration and, perhaps even more important, on their affinity for the ion exchanger. It is therefore not surprising that many conflicting statements about the composition of the products of hydrolysis are found in the literature. It may safely be said that several of the solubility products reported have little physical significance.

The determination of true solubility products is further complicated by the intricate composition of the solutions in equilibrium with the various precipitates.

For reasons given in section 1.2, only few data referring to the solution chemistry of the trivalent actinide ions are available. As far as hydrolytic equilibria are concerned, the only constant determined which refers to an equilibrium in solution seems to be that associated with the formation of the first mononuclear product of hydrolysis of trivalent plutonium, $PuOH^{2+}$. For the acid dissociation constant of Pu^{3+}, referring to the reaction $Pu^{3+} + H_2O \rightleftharpoons PuOH^{2+} + H^+$, a value of $pK_1^* = 6{\cdot}95$ was found in the early days of plutonium solution chemistry[57]. For the lighter lanthanides, the values of this constant are found to be considerably higher, viz. in the range $8{\cdot}5 < pK_1^* < 10{\cdot}1$. This is certainly rather surprising as one would presume that the lanthanide ions would have the stronger acidity on account of their smaller radii. Further experimental evidence is obviously needed to clarify this point.

Many investigations have, on the other hand, been devoted to the hydrolysis of the tetravalent actinide ions[57]. As already mentioned, this especially applies to Th^{4+} whose availability and stability towards oxidation and reduction allow very thorough studies without the expenditure of excessive amounts of time and effort[44,46,65]. These studies have revealed an intricate pattern of polynuclear complexes besides the first two mononuclear ones. For the other tetravalent ions which have been investigated, up to and including Pu^{4+}, polynuclear complexes are also certainly formed. In those cases, however, the measurements so far do not warrant any reasonably detailed, or even safe, conclusions about any complex other than the first mononuclear one (Table 5). The more complete results reported for the hydrolysis of Th^{4+} are listed in Table 6.

As seen from Table 5, the tetravalent ions are quite strong acids. The values of pK_1^* are around 2, or lower, with the exception of Th^{4+} where pK_1^* is considerably higher. Only to a minor part, however, does this increase reflect a weaker tendency of Th^{4+} to split of protons, as compared with the subsequent M^{4+} ions. Except at very low Th(IV)

[63] G. Johansson, *Acta Chem. Scand.* **22** (1968) 389, 399.

[64] K. A. Kraus, H. O. Phillips, T. A. Carlson and J. S. Johnson, *Proc. 2nd U.N. Intern. Conf. Peaceful Uses Atomic Energy*, Vol. 28, p. 3 (P/1832), Geneva (1958).

[65] S. Hietanen and L. G. Sillén, *Acta Chem. Scand.* **22** (1968) 265.

TABLE 5. HYDROLYSIS OF TETRAVALENT ACTINIDE IONS. (Formation of the first mononuclear complex at 25°C in ionic media of different strength *I*. Sodium perchlorate/perchloric acid have been used as supplementary electrolytes, if not otherwise stated.)[a]

$I\rightarrow$	0·5	1	2	3	2[d]
M^{z+}	pK_1^*				
Th^{4+}		4·23		5·0[b]	
Pa^{4+}				0·14[c]	
U^{4+}	1·47	1·56	1·68	2·0	1·74
Np^{4+}			2·30		2·50
Pu^{4+}	1·60	1·51	1·73		1·94

[a] The values have been selected from the compilation of L. G. Sillén and A. E. Martell (ref. 57).

[b] In sodium chloride/hydrochloric acid.

[c] In lithium perchlorate/perchloric acid.

[d] In heavy water, refs. 66 and 67.

concentrations, the monomer has no great share in the complex formation, not even at low degrees of hydrolysis. For a wide range of intermediate concentrations, the dimer predominates in the earlier stages of hydrolysis, the constant for the dimerization reaction $2Th(OH)^{2+} \rightleftharpoons Th_2(OH)_2^{6+}$ being $10^{3\cdot 85}$ M^{-1} in 1 M perchlorate medium at 25°C (cf. Table 6). If not too low concentrations are considered, the hydrolysis of Th^{4+} for a given value of pH will therefore not be much less than for the following M^{4+} ions, though the dimer, and not the monomer, will be the main species formed initially. This is illustrated in Fig. 8 where the relative amounts of the various species present are given for 0° and 95°C. The initial strong predominance of the dimer for $C_M = 0\cdot 1$ M is evident, though the value of the dimerization constant for both 0° and 95°C is lower than for 25°C, viz. $10^{3\cdot 03}$ and $10^{1\cdot 91}$, respectively. At the low value of $C_M = 0\cdot 001$ M, however, the monomer is initially the predominant species, especially at 95°C[44].

For those solutions where the equilibrium measurements, carried out as pH titrations, indicate the predominance of a dimer, such a complex is also found from direct X-ray investigations of the solutions[63]. The Th–Th distance in this complex is 3·94 Å which is very close to the corresponding distance, 3·99 Å, in the crystalline compound $Th_2(OH)_2(NO_3)_6(H_2O)_8$, where the two thorium atoms joined by a double hydroxo-bridge form a discrete complex. It is likely that a similar bridged complex occurs in the solution. The presence of the tetrameric complex which becomes prominent as the hydrolysis proceeds is also clearly indicated by the X-ray investigations on solutions.

At least at 95°C, $ThO_2(s)$ may be brought into equilibrium with perchloric acid solutions. From measurements of the amount of thorium dissolved, combined with the measurements referred to above yielding the composition of the solution, the solubility product $K_{so}^* = [M]/[H]^4$ referring to the reaction $ThO_2(s) + 4H^+ \rightleftharpoons Th^{4+} + 2H_2O$ can be calculated. A value of $K_{so} = 10^{4\cdot 26}$ M^{-3} is found at 95°C for 1 M perchlorate medium[44].

For Pa^{4+}, the value of pK_1^* listed in Table 5 seems quite low when compared with the values reported for its neighbors. The hydrolysed species $PaOH^{3+}$ would thus have an unexpected strong tendency to form. Considering the large experimental difficulties involved in the investigation of protactinium solutions, it may be wise, however, to await further

TABLE 6. HYDROLYSIS OF THORIUM(IV) AND URANYL(VI) IN VARIOUS IONIC MEDIA, AT TEMPERATURES STATED. (Constants $\beta^*_{m,n}$ refer to the acid dissociation equilibria $mM^{z+}+nH_2O \rightleftharpoons M_m(OH)_n^{(zm-n)+}+nH^+$.)

M^{z+}	m, n	$p\beta^*_{m,n}$			
Th^{4+}	t°C →	0[a]	25	95[a]	25
	I →	1[b]	1[b]	1[b]	3[c]
	1, 1	4·31	4·23	2·25	5·0
	1, 2	8·46	7·69	4·51	
	2, 2	5·59	4·61	2·59	4·76
	2, 3				8·94
	2, 5				16·99
	3, 1				1·36
	3, 3				6·83
	4, 8	22·80	19·16	10·44	21·11
	6, 14				36·58
	6, 15	43·81	37·02	20·61	
	10, 25				65·35

M^{z+}	m, n	$p\beta^*_{m,n}$							
UO_2^{2+}	t°C →	25							
	I →	0·5[d]	1[e]	1[f]	1[g]	3[h]	3[i]	3[k]	5[k]
	1, 1	5·7						5·38	5·53
	2, 2	5·92	5·94	6·17	5·96	6·02	6·64	6·34	6·52
	3, 4			12·33	12·8		12·54		
	3, 5	16·22	16·41	17·00	16·21	16·54	18·07	17·37	17·76
	4, 6						20·0		
	4, 7						24·9		

[a] The constants referring to these temperatures are on the molality scale (cf. Fig. 8).
[b] Sodium perchlorate/perchloric acid, ref. 44.
[c] Sodium chloride/hydrochloric acid, ref. 65.
[d] Potassium nitrate/nitric acid, ref. 70.
[e] Sodium perchlorate/perchloric acid, ref. 45a.
[f] Sodium chloride/hydrochloric acid, ref. 45b.
[g] Potassium nitrate/nitric acid, ref. 68.
[h] Sodium perchlorate/perchloric acid, ref. 69.
[i] Sodium chloride/hydrochloric acid, ref. 68.
[k] Magnesium nitrate/nitric acid, ref. 71.

experimental evidence on this point before attempting a theoretical interpretation. On the other hand, Np^{4+} is certainly a markedly weaker acid than its neighbors. This rather unexpected circumstance will be discussed in section 2.3. A variation of the ionic strength within the range $0·5 \leq I \leq 3$ M does not cause very drastic changes of K_1^*, though a decrease of the acid strength is clearly discernible, as the value of I is increased above 1 M. This is in keeping with the general trend for the variation of equilibrium constants with I (see 2.1.1).

For U^{4+}, Np^{4+} and Pu^{4+}, the dissociation in heavy water has also been investigated. A slight decrease of the acid strength as compared with ordinary water is found in all cases[66,67].

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[66] J. C. Sullivan and J. C. Hindman, *J. Phys. Chem.* 63 (1959) 1332.
[67] S. W. Rabideau and R. J. Kline, *J. Phys. Chem.* 64 (1960) 680.

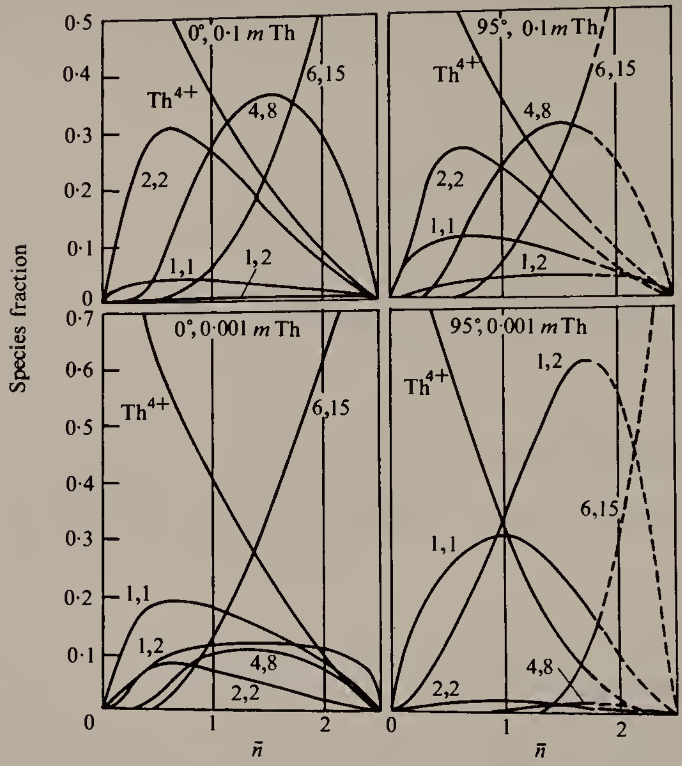

FIG. 8. Species fractions in Th(IV) solutions as a function of the number of hydroxide ions bonded per thorium atom (= $\bar{n}$) for two highly different values of C_M, at 0° and 95°C. In these measurements (ref. 44), the concentrations have been expressed in molalities, m (= mole/kg solvent, in this case water). A 1 M perchlorate medium has been employed.

For the actinyl(V) ions of formal charge +1, the actual charge on the actinide atom is so low that the tendency to split off protons from the hydration shell is still quite weak. Measurements of the hydrolysis of NpO_2^+ and PuO_2^+ have yielded values of pK_1^* around 9 or 10.

In the actinyl(VI) ions, with a formal charge of +2, the central actinide atoms have, on the other hand, an actual charge large enough to make ions of this type to fairly strong acids. Consistent quantitative results seem to be available only for UO_2^{2+}, however. The schemes arrived at for this ion in different media are included in Table 6. In all cases, the dimer $(UO_2)_2(OH)_2^{2+}$ and the trimer $(UO_2)_3(OH)_5^+$ are very important products of the hydrolysis. In perchlorate media,[45a,68,69] they even seem to be the only species existing in appreciable amounts. In chloride media[45b,68], however, another trimer, $(UO_2)_3(OH)_4^{2+}$, is also prominent while the monomer UO_2OH^+ seems to be well established in nitrate media[70,71]. An example of the experimental results is given in Fig. 9. Though fairly high, the tendency for hydrolysis is still lower for actinyl(VI) ions than for the tetravalent ions. Even Th^{4+}, the weakest acid among the tetravalent ions, is still more easily hydrolysed than e.g. UO_2^{2+}, as is evident from a comparison of the constants β_{22}, referring to the formation of the dimers predominating in the early stages of hydrolysis of each ion. In 1 M perchlorate medium at

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[68] H. S. Dunsmore, S. Hietanen and L. G. Sillén, *Acta Chem. Scand.* **17** (1963) 2644, 2657.
[69] R. Arnek and K. Schlyter, *Acta Chem. Scand.* **22** (1968) 1331.
[70] C. F. Baes, Jr. and N. J. Meyer, *Inorg. Chem.* **1** (1962) 780.
[71] U. Schedin and M. Frydman, *Acta Chem. Scand.* **22** (1968) 115.

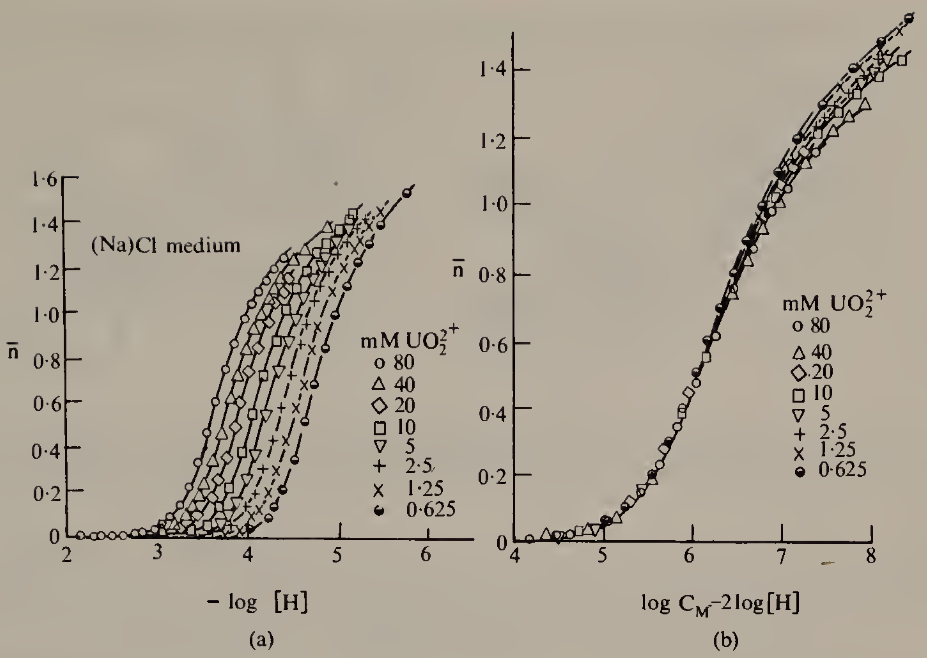

FIG. 9. (a) The number of hydroxide ions bonded per uranyl group ($= \bar{n}$) as a function of $-\log [H]$, for different values of C_M. The dependence of $\bar{n}$ on C_M indicates formation of polynuclear complexes. (b) If all the polynuclear complexes M_mL_n had had $n = 2(m-1)$, i.e. belonged to the series M_2L_2, M_3L_4, M_4L_6, etc., then all the curves $\bar{n}(\log C_M - 2 \log [H])$ would have coincided. They do in their lower parts where M_2L_2 and M_3L_4, both belonging to the series, predominate, but not in their upper parts where especially M_3L_5, not belonging to the series, becomes important. The measurements (ref. 68) refer to a chloride medium of $I = 3$ M, and 25°C.

25°C, the value of $p\beta_{2,2}$ found for Th^{4+} is $\simeq 1{\cdot}3$ units lower than that found for UO_2^{2+}; in 3 M chloride medium the difference is even higher, $\simeq 1{\cdot}9$ units.

The existence of the uranyl(VI) dimer indicated by the equilibrium measurements has also been confirmed by X-ray investigations of the solutions[28]. A crystalline compound containing such a dimer as part of a discrete uncharged complex, viz. $(UO_2)_2(OH)_2Cl_2(H_2O)_4$, is also known (Fig. 10). In this complex, the uranium atoms, 3·944 Å apart, are joined by a double hydroxo bridge, i.e. the arrangement is analogous to that found for the thorium atoms in the dimeric Th(IV) complex mentioned above. The U–U distance in the dimer present in solution is 3·86 Å; this species is therefore most probably arranged in the same way as the complex found in the crystalline compound.

The existence of complexes containing more than two uranium atoms is also indicated by the X-ray investigations of solutions. Most probably a trimer is present, in keeping with the results of the equilibrium data. So far it has not been possible to prepare a crystalline compound containing a discrete trimeric complex. On the other hand, a tetramer has been found in a solid phase crystallized from a highly hydrolysed solution. This is, of course, in accordance with the general experience that very much depends upon the lattice energy when a crystalline compound is formed. A species present in large amounts in the solution may be very unsuitable as a building stone in an ordered structure, while another one present in too small an amount to be detected by the equilibrium analysis may fit so well that a slightly soluble compound is readily formed.

For some of the actinide ions, viz. Th^{4+}, U^{4+} and UO_2^{2+}, the enthalpy changes $\Delta H°$ accompanying the hydrolytic reactions have also been measured. In only one of these

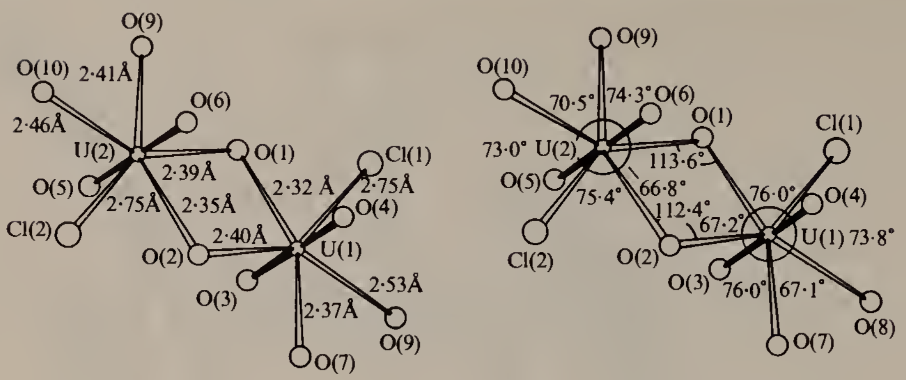

FIG. 10. Structure of the dimeric complex $(UO_2)_2(OH)_2Cl_2(H_2O)_4$ present in crystalline phase and most probably also in hydrolysed solutions of high chloride concentrations (from ref. 28).

investigations[69], however, has $\Delta H°$ been found calorimetrically; in all other cases the values have been calculated from the temperature coefficient of the equilibrium constant[44,70,72,73]. As mentioned above, the latter method is generally less accurate, but in the present cases the results still give a coherent picture of the thermodynamic characteristics of the reactions (Table 7).

Though fairly acidic, the actinide ions listed in Table 7 still have acid dissociation constants <1 on the molar scale. The standard free energy changes, $\Delta G°$, of the dissociation reactions will therefore be >0. Nevertheless, they are all less than the corresponding values of $\Delta H°$. The entropy changes are consequently also all >0. The entropy term therefore always favors the dissociation, in many cases to a considerable extent, while the endothermic enthalpy term counteracts it.

For the polynuclear complexes formed by Th^{4+} and UO_2^{2+}, the values of both $\Delta H°$ and $\Delta S°$ per proton split off are strikingly constant for each of the acceptors (Table 7). Both quantities, and especially $\Delta S°/n$, are much higher for the more highly charged Th^{4+} than for UO_2^{2+}. The formation of mononuclear complexes of Th^{4+} involves lower values of both $\Delta H°/n$, and, particularly, $\Delta S°/n$ than the formation of polynuclear complexes of the same acceptor. The very large increase of $\Delta S°/n$ between Th^{4+} and U^{4+} makes the latter ion the very much stronger acid, in spite of the fact that its dissociation is considerably more endothermic.

The positive values of $\Delta G°$ indicate that the hydrolysis would be far from complete in the presence of no stronger base than H_2O. This even applies to the strongest acid U^{4+} if its concentration is not extremely low ($C_M \lesssim 0{\cdot}3$ mM for $\gtrsim 99\%$ hydrolysis). In the presence of stronger bases, e.g. OH^-, the hydrolysis easily proceeds to completion, as is evident from the strongly negative values of $\Delta G°$ found for the reactions $m\mathrm{M}^{z+} + n\mathrm{OH}^- \rightleftharpoons \mathrm{M}_m\mathrm{OH}^{(mz-n)+}$ (Table 8). These reactions are favored both by highly positive values of $\Delta S°$ and, moreover, by negative values of $\Delta H°$. The contributions from the enthalpy and entropy terms to the decrease of the free energy are in fact of the same order of magnitude, except for the formation of UOH^{3+} where the entropy term is still very predominant. The constancy of $\Delta H°/n$ and $\Delta S°/n$ observed for the formation of the polynuclear complexes by acid dissociation reactions naturally remains when the hydrolyses are looked upon as reactions with hydroxide ions.

[72] K. A. Kraus and F. Nelson, *J. Amer. Chem. Soc.* 77 (1955) 3721.

[73] R. H. Betts, *Canad. J. Chem.* 33 (1955) 1775.

TABLE 7. THERMODYNAMICS OF THE PROTOLYTIC REACTIONS $mM^{z+}+nH_2O \rightleftharpoons M_m(OH)_n^{(mz-n)+}+nH^+$ FOR ACTINIDE IONS AT 25°C (ΔG° and ΔH° in kJ; ΔS° in JK^{-1})

m, n	I	Method[a]	ΔG°	ΔH°	ΔS°	$\Delta H^\circ/n$	$\Delta S^\circ/n$
			$M^{z+} = Th^{4+}$				
1, 1	1	T[b]	23·4	24·7	3·8	24·7	3·8
1, 2			44·7	58·2	46·0	29·1	23·0
2, 2			26·4	61·9	118·8	30·9	59·4
4, 8			108·4	241·4	446·0	30·2	55·8
6, 15			209·6	454·0	819	30·3	54·7
			$M^{z+} = U^{4+}$				
1, 1	0·5	T[c]	8·4			46·9	130
	0·19	T[d]	6·7			44·8	172
	0	T[c]	3·9			49·0	151
			$M^{z+} = UO_2^{2+}$				
2, 2	3	C[e]	34·3	39·7	18·0	19·8	9·0
3, 5			94·6	102·1	25	20·4	5
1, 1	0·5	T[f]	32·6			(46)	(46)
2, 2			33·8	42·6	29·7	21·3	14·9
3, 5			92·5	105·0	42	21·0	8

[a] The values of ΔH° have been determined calorimetrically (C) or by the temperature coefficient method (T); in the latter case between the temperature limits stated in the following notes.
[b] 0–95; ref. 44.
[c] 10–43; ref. 72.
[d] 15–25; ref. 73.
[e] ref. 69.
[f] 25–94; ref. 70.

The connexion between these thermodynamic features and the nature of the bonds existing in the complexes will be discussed in section 2.3, together with the pertinent material related to other complexes.

2.2.2. *Complexes formed with Halide Ions*

The equilibria between actinide ions of various types and halide ions have been extensively investigated. A representative selection of the results is presented in Table 9. In order to avoid the complications due to hydrolysis the measurements have often been performed in strongly acid solutions. This applies especially to investigations involving the easily hydrolysed M^{4+} ions. Under such conditions, the fluoride ligand is present as the undissociated hydrofluoric acid, HF. The constants listed in the original papers therefore often refer to equilibria such as

$$M^{4+}+nHF \leftrightharpoons MF_n^{4-n}+nH^+$$

$$MF_{n-1}^{5-n}+HF \rightleftharpoons MF_n^{4-n}+H^+$$

characterized by their respective constants

$$\beta_n^* = [MF_n][H]^n[M]^{-1}[HF]^{-n} \qquad (2:18)$$

$$K_n^* = [MF_n][H][MF_{n-1}]^{-1}[HF]^{-1} \qquad (2.19)$$

TABLE 8. THERMODYNAMICS OF THE HYDROLYSIS $m\text{M}^{z+} + n\text{OH}^- \rightleftharpoons \text{M}_m(\text{OH})_n^{(mz-n)+}$ FOR ACTINIDE IONS AT 25°C (cf. Table 7)

m, n	I	$\Delta G°$	$\Delta H°$	$\Delta S°$	$\Delta H°/n$	$\Delta S°/n$
			$\text{M}^{z+} = \text{Th}^{4+}$			
1, 1	1[a]	−55·1			−31·4	79·7
1, 2		−113·0	−54·0	197·8	−27·0	98·9
2, 2		−131·0	−50·3	270·6	−25·2	135·3
4, 8		−522·1	−207·4	1053·2	−25·9	131·7
6, 15		−971·3	−387·5	1958	−25·8	130·5
			$\text{M}^{z+} = \text{U}^{4+}$			
1, 1	0·5[b]	−70·4			−9·6	204
			$\text{M}^{z+} = \text{UO}_2{}^{2+}$			
2, 2	3[c]	−127·1	−69·9	192	−34·9	96
3, 5		−310·3	−172·0	464	−34·4	93

[a] Ref. 44.
[b] Ref. 72.
[c] Ref. 69.

In this equilibria, HF, and not F$^-$, is regarded as the reacting ligand species. A fair comparison between the affinities of the actinide acceptors for various halide donors presumes, however, that constants of analogous reactions are considered. The constants β_n^* and K_n^* have thus to be recalculated to β_n and K_n, respectively. This is possible if the association constant of the hydrofluoric acid

$$K_1(\text{H}) = [\text{HF}][\text{H}]^{-1}[\text{F}]^{-1} \tag{2.20}$$

is known for the actual medium and temperature. For the compilation of Table 9, the pertinent values of K_1(H) have been taken from refs. 74 and 75.

As seen from Table 9, all actinide acceptors form strong complexes with fluoride ions in aqueous solution, though the differences between acceptors of different types are considerable. By far the strongest affinity for F$^-$ is shown by the M^{4+} ions followed by MO_2^{2+} and M^{3+}. The comparison between these is made difficult by the fact that data are not available for both types formed by the same element, but it seems certain nevertheless that the fluoride complexes of MO_2^{2+} ions are markedly stronger than those of M^{3+}. The complexes formed by MO_2^+ are even weaker though no quantitative information is available for these.

In striking contrast, the complexes formed by the heavier halides are all very weak. Such measurements mostly refer to chlorides, but in a few instances bromide complexes have also been investigated. In all cases, the strength of the complexes decreases as the size of the halide ion increases. Iodide systems have not been measured because the complexes formed are extremely weak and the systems are often not stable due to rapid oxidation of I$^-$ by the actinide ions.

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[74] H. N. Farrer and F. J. C. Rossotti, *J. Inorg. Nucl. Chem.* **26** (1964) 1959.
[75] S. Ahrland and L. Brandt, *Acta Chem. Scand.* **22** (1968) 1579.

TABLE 9. STABILITY OF ACTINIDE HALIDE COMPLEXES IN AQUEOUS SOLUTION (The values refer to perchlorate media and 25°C, if not otherwise stated[a]).

M^{z+}	I	Fluoride			
		log K_n			
$n \rightarrow$		1	2	3	4
Am^{3+}	0·5[b]	3·39	2·72	2·89	
	1	2·93			
Cm^{3+}	0·5[b]	3·34	2·83	2·90	
Cf^{3+}	1	2·99			
Th^{4+}	0·5[c]	7·56	5·72	4·42	
	4[d,e]	8·12	6·44		
Pa^{4+}	3	7·87	6·67		
U^{4+}	4[d,e,f]	8·98	6·62	5·40	
Np^{4+}	4[d,f]	8·26	6·13	5·78	4·7
UO_2^{2+}	1[g]	4·54	3·43	2·45	1·46
NpO_2^{2+}	1[f]	3·86	3·11		
PuO_2^{2+}	1[h]	5·06	4·99	4·88	3·17
		Chloride		Bromide	
		log K_n		log K_n	
$n \rightarrow$		1	2	1	
Ac^{3+}	1	−0·10	−0·52	−0·25	
Pu^{3+}	1[i]	~0·0			
Am^{3+}	0·5[i]	0·24			
	1	−0·05			
	4	−0·15	−0·54		
Cm^{3+}	0·5	0·18			
Th^{4+}	1	0·18			
U^{4+}	1[d]	0·30		0·18	
Np^{4+}	1[d]	−0·04			
Pu^{4+}	1	0·14			
UO_2^{2+}	1[d]	−0·10		−0·30	
	2	−0·06			
NpO_2^{2+}	2	−0·21			
PuO_2^{2+}	4	0·02			

[a] For this table, as well as for the following ones, the values have mainly been selected from the extensive compilation of Sillén and Martell (ref. 57) and from the review of Jones and Choppin (ref. 6). The latter contains specifically stability constants and enthalpy changes pertaining to the formation of actinide complexes. Values not to be immediately found in any of these compilations (as a rule from investigations too recent to be included) are commented upon in special notes.

[b] A. Aziz and S. J. Lyle, *J. Inorg. Nucl. Chem.* **31** (1969) 3471.

[c] Calculated from the values of K_n^* reported by Dodgen and Rollefsen (ref. 76), with log $K_1(H) = 2·91$, from ref. 74.

[d] Temperature 20°C.

[e] Calculated from the values of K_n^* reported by B. Noren, *Acta Chem. Scand.* **23** (1969) 931, with log $K_1(H) = 3·44$, from ref. given in note f.

[f] S. Ahrland and L. Brandt, *Acta Chem. Scand.* **22** (1968) 1579.

[g] Ref. 41.

[h] Calculated from the values of K_n^* reported by V. N. Krylov, E. V. Komarov and M. F. Pushlenkov, *Radiokhimiya*, **10** (1968) 717, with log $K_1(H) = 2·95$, from ref. 74.

[i] M. Ward and G. A. Welch, *J. Inorg. Nucl. Chem.* **2** (1956) 395; in hydrochloric acid medium.

The strength of the complexes varies with the effective charge on the central ion, and with the size of the halide ion in such a way as would be expected if the complex formation is due essentially to the electrostatic attraction between the central ion and the ligand. Consequently, an increase of the stability of the complexes along the actinide series would also be expected, since the contraction of the ionic radii along the series for all oxidation states present in solution (see Table 2) should imply a stronger electrostatic attraction. The precision of the measurements allows such a comparison only for the fluoride complexes. Generally, these do become stronger along the actinide series, as expected, but exceptions occur, most notably for Np^{4+} and NpO_2^{2+}. Other factors than the simple electrostatic interaction between acceptor and donor are evidently also of importance, as will be discussed in section 2.3.

The simple fluorides MF_3 and MF_4 are relatively insoluble compounds. Few determinations of their solubility products have been carried out, however, and the values published have often been calculated without due consideration to the complexes formed in the solution. For ThF_4, however, a reliable determination of the equilibrium constant for the reaction

$$ThF_4 \cdot 4H_2O(s) + 2H^+ \rightleftharpoons ThF_2^{2+} + 2HF + 4H_2O$$

has been performed[76]. Combination of this constant with K_1^* and K_2^* determined in the same investigation and $K_1(H)$ from ref. 74 yields solubility product K_{so} for the reaction

$$ThF_4 \cdot 4H_2O(s) \rightleftharpoons Th^{4+} + 4F^- + 4H_2O$$

In a perchlorate medium of $I = 0{\cdot}5$ M, $pK_{so} = 26{\cdot}3$ at 25°C.

For a neutral complex such as ThF_4 or UF_4, the concentration in solution in equilibrium with a solid phase of the same stoichiometry has to be a constant. This follows from the Nernst distribution law (cf. section 2.1.3) which may be considered as a corollary of the law of mass action. Such a complex thus possesses a certain constant solubility, independent of the concentration of ligand present. Nor does the solubility depend much on I, as the activity coefficient of a neutral species does not change very much with the ionic medium.

For UF_4, the solubility in a $0{\cdot}12$ M perchlorate medium at 25°C has been found[77] to be $= 1{\cdot}09 \times 10^{-4}$ M. For the calculation of K_{so}, the constants K_1 to K_4 are needed. Of these, only K_3 and K_4 have been determined in the actual medium while K_1 and K_2 values are known only for $I = 4$ M (listed in Table 9). These constants vary considerably with the medium, and the use of the present values therefore implies a rather crude approximation. If they are nevertheless applied, a value of $pK_{so} \simeq 28$ results, i.e. of the same order of magnitude as that found for ThF_4, only somewhat higher. This result seems very reasonable, in view of the higher affinity for F^- displayed by U^{4+}, as compared with Th^{4+} (see Table 9).

Fluorides of the actinyl ions are very soluble in water as are the heavier halides of all the oxidation states of the actinides. For these, however, hydrolytic reactions are always prone to occur when the solutions are not sufficiently acidic (see 2.2.1). The fluoride solutions are, on the other hand, relatively well protected against hydrolysis by the strong complex formation occurring.

For the fluoride complexes of Th^{4+} and UO_2^{2+}, reliable determinations of the changes of enthalpy and entropy accompanying the complex formation are also available (Table 10).

[76] H. W. Dodgen and G. K. Rollefsen, *J. Amer. Chem. Soc.* **71** (1949) 2600.
[77] A. W. Savage, Jr., and J. C. Browne, *J. Amer. Chem. Soc.* **82** (1960) 4817.

TABLE 10. THERMODYNAMICS OF THE STEPWISE FORMATION OF ACTINIDE FLUORIDE COMPLEXES $MF_{n-1}^{z-n+1} + F^- \rightleftharpoons MF_n^{z-n}$, AT 25°C[a, b] ($\Delta G_n^\circ$ and ΔH_n° in kJ; ΔS_n° in JK^{-1})

M^{z+}	I	ΔG_1°	ΔH_1°	ΔS_1°	ΔG_2°	ΔH_2°	ΔS_2°
Th^{4+}	0	−48·16	−5·0	145	−37·8	−3·3	115
UO_2^{2+}	1	−25·89	1·7	92·5	−19·65	0·4	67·2
		ΔG_3°	ΔH_3°	ΔS_3°	ΔG_4°	ΔH_4°	ΔS_4°
Th^{4+}	0	−27·1	−3·3	80	−19·2	−3·8	52
UO_2^{2+}	1	−13·91	0·3	47·5	−8·4	−2·1	21

[a] Values for Th^{4+} from E. W. Baumann, *J. Inorg. Nucl. Chem.* **32** (1970) 3823. Values of ΔH_n° determined from the temperature coefficient of log K_n between 0° and 45°C. Values of ΔS_n° recalculated by the present authors from the values of log K_n and ΔH_n° given by Baumann.

[b] Values for UO_2^{2+} from S. Ahrland and L. Kullberg, *Acta Chem. Scand.* **25** (1971) 3471; calorimetric determination of ΔH_n° .

The high stabilities of the complexes are almost exclusively due to the high positive values of ΔS_n°. In all cases, the value of ΔH_n° is small. For the first three steps of the UO_2^{2+} system, it even counteracts the complex formation, being >0. These features which are also typical for the formation of other actinide complexes in solution, are discussed in section 2.3.

2.2.3. *Complexes formed with Ligands Coordinating via Oxygen and/or Nitrogen*

Prominent among the complexes coordinating via oxygen are the hydrates and the hydroxo complexes. On account of the fundamental importance of these complexes in the chemistry of the actinides in aqueous solution, they have been treated separately in earlier sections (see 1.2, 1.4, and 2.2.1). It was pointed out that the enthalpies of hydration (Table 3) are indeed very high, indicating that strong bonding forces operate between the actinide ions and the oxygen donor atom of the water molecule. As just discussed (section 2.2.2), however, fluoride ions readily displace the water of the hydrate shell even in dilute aqueous solutions and form fluoride complexes. On the other hand, the affinities of the heavier halides for actinide acceptors are so much weaker that high concentrations of, for example, hydrochloric acid are necessary (involving a high activity of chloride ions and a markedly lowered activity of water) before any extensive displacement of water by chloride ions takes place.

The question then arises to what extent the hydrate water may be replaced by ligands coordinating via donor atoms belonging to the chalcogen and nitrogen groups. In the first place the affinity of ligands coordinating via the lightest donor atom of each group, viz. oxygen and nitrogen, should be considered.

An important difference exists between halogen donor atoms and those belonging to the other groups mentioned, viz. the former are present in aqueous solutions as monoatomic ions, while the latter are not (except S^{2-} and its homologs in strongly alkaline media). The chalcogen and nitrogen donors are generally part of a polyatomic ligand the composition of which extensively influences the coordinating properties of the donor atoms. This must, of course, always be remembered when the affinities of various donor atoms are compared. Such comparisons are only valid between structurally similar ligands.

When donor atoms are built into a more or less complicated molecule or ion, two or more may be present in the same species. These donor atoms may, or may not, be of the same kind. They may coordinate to the same actinide ion, forming chelate complexes, or to different ions, forming bridged complexes whose polynuclearity may vary within wide limits.

After the hydroxide and oxide ions, the peroxide ion, O_2^{2-}, may be regarded as the simplest oxygen donor forming complexes with actinide ions. The two closely connected oxygens are very prone to form bridged complexes. These may be highly polynuclear, but complexes evidently containing few bridges are also known. The former are presumably chain polymers whereas a cyclic arrangement has been proposed for the latter. The peroxide ion may also be present in mononuclear complexes, however, presumably acting as a chelating ligand[26,78,79].

The highly polynuclear complexes are only slightly soluble. A well-known example is the light-yellow peroxide $UO_4 \cdot 4H_2O$ which is precipitated from moderately acid solutions ($pH \simeq 2$) of uranyl(VI) salts by hydrogen peroxide. At 90°C this compound is dehydrated to $UO_4 \cdot 2H_2O$ without loss of peroxide oxygen. In strongly acid solutions it decomposes with evolution of oxygen. In alkaline media, on the other hand, it is converted into peroxyuranate ions. As the alkalinity increases, a depolymerization takes place which may finally, for $pH \gtrsim 12$, result in a complete dissolution. An orange-red solution is then obtained, seemingly by formation of the ion $UO_2(O_2)_3^{4-}$. This entity gives easily soluble salts with many cations. In contrast to the "uranates" formed on the hydrolysis of uranyl(VI) with hydroxides, the peruranates may thus exist as discrete, monomeric ions.

Hydrogen peroxide causes precipitation of an insoluble peroxide when added to an acid solution of Pu(IV). The same green Pu(IV) peroxide is also obtained when solutions of trivalent or hexavalent plutonium are treated, due to oxidation and reduction reactions, respectively. Part of the plutonium is not precipitated, however, but stays in the solution as soluble peroxide complexes, as is immediately evident from the remarkable color changes observed. The solution first turns deep-brown and, on addition of more peroxide, red. Two complexes are formed, both presumably cyclic dimers.

The common inorganic anions NO_3^-, SO_4^{2-}, CO_3^{2-} and PO_4^{3-}, all coordinating via oxygen, react very differently with actinide ions. With NO_3^-, the complexes formed are very weak, no stronger in fact than those of the heavy halide ions (Table 11). Extensive complex formation only occurs at quite high nitrate concentrations[35]. Much stronger complexes are formed by SO_4^{2-}, mainly because of its higher charge, which implies a stronger electrostatic interaction (Table 11). Among the actinide ions, M^{4+} forms the strongest complexes with SO_4^{2-}. Those formed by ions of the types M^{3+} and MO_2^{2+} are considerably weaker. They are, moreover, of about the same strength, as might be expected from the fact that the effective charge is much the same (cf. sections 1.2 and 2.2.1). For all types of ions, the complexes generally become stronger as the ionic radius decreases, though exceptions occur, notably for the neptunium ions. The trivalent ions of the elements in the middle of the series form sulphate complexes of much the same strength. On the whole, the trends described are evidently similar to those found for the fluoride complexes (section 2.2.2).

The addition of not too large amounts of the strong base CO_3^{2-} causes hydrolysis in actinide solutions, with the formation of precipitates. The exact nature of these is not known. As CO_3^{2-} may act as a bridging ligand, just as OH^- or O^{2-}, it is most likely, however, that they are mixed hydroxy-carbonato or oxo-carbonato complexes. Mixed peroxo-carbonato

[78] J. A. Connor and E. A. V. Ebsworth, *Advances in Inorganic Chemistry and Radiochemistry*, Vol. 6, p. 279, H. J. Emeleus and A. G. Sharpe (Eds.), Academic Press, New York (1964).

[79] H. Martin-Frere, *Bull. Soc. Chim. France*, **1965**, 2860, 2868.

TABLE 11. STABILITY OF ACTINIDE SULPHATE AND NITRATE COMPLEXES IN AQUEOUS SOLUTION (The values refer to perchlorate media and 25°C, if not otherwise stated.)

M^{z+}	I	Sulphate		Nitrate
		log K_1	log K_2	log K_1
Ac^{3+}	1	1·20	0·65	0·12
Am^{3+}	0·5	1·85	0·99	
	1	1·57	1·09	0·25
	2	1·43	0·42	
Cm^{3+}	0·5	1·86	0·89	
	2	1·34	0·52	
Cf^{3+}	2	1·36	0·71	
Th^{4+}	2	3·30[a]	2·42	
U^{4+}	2	3·65[a]	2·43	0·06
Np^{4+}	2	3·51[a]	2·12	
UO_2^{2+}	1	1·81[b]	0·95	−0·30
NpO_2^{2+}	1	1·80[c]	0·77	

[a] For these sulphate systems, K_n has been calculated from K_n^* with log K_1(H) = 1·08, from E. L. Zebroski, H. W. Alter and F. K. Heumann, *J. Amer. Chem. Soc.* 73 (1951) 5646. The values of K_n^* have been taken from: Th^{4+}, A. J. Zielen, *J. Amer. Chem. Soc.* **81** (1959) 5022; U^{4+}, R. A. Day, Jr, R. N. Wilhite and F. D. Hamilton, *J. Amer. Chem. Soc.* 77 (1955) 3180; Np^{4+}, J. C. Sullivan and J. C. Hindman, *J. Amer. Chem. Soc.* 76 (1954) 5931.

[b] S. Ahrland and L. Kullberg, *Acta Chem. Scand.* **25** (1971) 3677.

[c] Temperature 21°C. Calculated from K_n^* reported in ref. 75, with log K_1(H) = 1·01. This value has been calculated from log K_1(H) = 1·06 and ΔH_1° = 23·47 kJ found for I = 1 and 25°C by Ahrland and Kullberg (note b).

complexes have in fact been identified[80]. At higher concentrations of CO_3^{2-}, a depolymerization takes place and soluble carbonato complexes are formed, most readily by the MO_2^{2+} ions. In this case, mononuclear tricarbonato complexes $MO_2(CO_3)_3^{4-}$ are finally formed[57]. Solid phases containing such ions, e.g. $Ca_2[UO_2(CO_3)_3]$, are also well known. Structure determinations of such phases[22] show that the carbonate ions are coordinated as bidentate ligands. The six coordinating oxygen atoms are situated at the corners of a plane hexagon, all at the same distance from U. The complex probably has the same structure in solution.

The PO_4^{3-} ion acts preferably as a bridge, forming slightly soluble precipitates with the actinide ions. Generally several different phases may be formed, each one stable between certain limits of phosphate concentration and acidity of the supernatant solution. Thus, for U(IV), $U(HPO_4)_2 \cdot 6H_2O$ is stable in contact with phosphoric acid of a concentration <9·8 M while for acid concentrations >9·8 M $U(HPO_4)_2 \cdot H_3PO_4 \cdot H_2O$ is formed[81]. For U(VI) three phases have been identified, viz. $(UO_2)_3(PO_4)_2 \cdot 6H_2O$, $UO_2HPO_4 \cdot 4H_2O$ and $UO_2(H_2PO_4)_2 \cdot 3H_2O$, stable in equilibrium with low (<0·014 M), intermediate and high (>6·1 M) phosphoric acid concentrations, respectively[82].

These phosphates generally possess structures which are open enough to allow a

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[80] P. Souchay and H. Martin-Frere, *Bull. Soc. Chim. France*, **1965**, 2874.

[81] J. M. Schreyer, *J. Amer. Chem. Soc.* 77 (1955) 2972.

[82] J. M. Schreyer and C. F. Baes, Jr., *J. Amer. Chem. Soc.* 76 (1954) 354.

TABLE 12. STABILITY OF ACTINIDE CARBOXYLATE COMPLEXES IN AQUEOUS PERCHLORATE MEDIA, COMPARED WITH THE BASICITY OF THE LIGANDS[a] (Temperature 20° or 25°C (see note b))

M^{z+}	I	log K_n			log $K_1(H)$
$n \rightarrow$		1	2	3	
		Acetate			
Pu^{3+}	2[c]	2·02	1·32		4·80
Am^{3+}	0·5[d]	1·99	1·28		
	2[b,e]	1·96			4·80
Cm^{3+}	0·5[d]	2·06	1·04		
	2[b,e]	2·03			
Bk^{3+}	2[b,e]	2·05			
Cf^{3+}	2[b,e]	2·12			
UO_2^{2+}	1[f]	2·38	1·98	1·98	4·59
NpO_2^{2+}	1[f]	2·31	1·92	1·77	4·61
PuO_2^{2+}	1[f]	2·05	1·49	1·42	4·63
	0·1[b,g]	2·31	1·49		
		Propionate			
UO_2^{2+}	1[h]	2·53	2·15	1·64	
NpO_2^{2+}	1[f]	2·44	2·02	2·04	4·72
		Monochloroacetate			
UO_2^{2+}	1[f]	1·44	0·85	0·51	2·66
NpO_2^{2+}	1[f]	1·33	0·77		2·66
PuO_2^{2+}	1[f]	1·16	0·45		
		Glycolate			
Am^{3+}	0·5[d]	2·82	2·04		
Cm^{3+}	0·5[d]	2·85	1·90		
UO_2^{2+}	1[i]	2·42	1·54	1·24	3·60
PuO_2^{2+}	1[k]	2·16	1·29	0·82	3·63
	0·1[b,l]	2·43	1·36		3·65
		Oxalate			
Am^{3+}	0·5[b,m]	4·82	3·78		
	1[b,n]	4·63	3·72	2·80	3·54[r]
Cm^{3+}	0·5[b,m]	4·80	3·82		
Th^{4+}	1[b,p]	8·23	8·54	6·00	
Np^{4+}	1[b,q]	7·47	6·22	5·68	
UO_2^{2+}	1[h]	4·63	4·05	3·31	

[a] Determined in the same investigations as K_n.

[b] Investigations performed at 25°C, all other data refer to 20°C.

[c] L. Magon, A. Cassol and R. Portanova, *Inorg. Chim. Acta*, **2** (1968) 285.

[d] I. Grenthe, *Acta Chem. Scand.* **16** (1962) 1695; **17** (1963) 1814.

[e] G. R. Choppin and J. K. Schneider, *J. Inorg. Nucl. Chem.* **32** (1970) 3283.

migration of ions from the solution into the solid phase[18]. If cations thus entering the solid phase have a sufficiently high affinity for phosphate, they will displace the hydrogen ions attached to the phosphate groups in many of these compounds. Insoluble phosphates of this type will thus act as ion exchangers[83-85]. The actual composition of the solid phase will then evidently depend upon the concentrations of sorbable cations in the solution. Any extensive displacement of hydrogen ions is, moreover, likely to involve a change of structure of the solid phase. When high-valent ions are taken up, drastic changes occur even at low loads. After such a change, the compound does not generally revert to the original structure even if exclusively loaded with hydrogen ions.

With increasing acidity, the hydrogen ions become more and more efficient competitors for the oxygen donor atoms of the phosphate ions. The bridging properties of the ligand therefore decline and, instead of the large polymers, monomeric protonated complexes are formed. These are more or less easily soluble. Thus, for U(VI), a maximum solubility of not less than $\simeq 2$ M is reached in 6·1 M phosphoric acid[82]. For U(IV), solubilities of the same order of magnitude are reached at high concentrations of phosphoric acid[81].

Carboxylate ligands have a strong affinity for actinide ions, especially if they contain several carboxylate groups and hence are able to form chelates. This is evident from Table 12, where the stabilities of the actinide complexes formed by some representative carboxylate ligands are listed. For comparison, the values of the proton association constants are also given.

Reliable data on actinide acetate complexes exist only for ions of the types M^{3+} and MO_2^{2+}. The first complex formed is of about the same stability for all the systems. This is in keeping with the behavior of the fluoride and sulphate ions which also form complexes of not very different strength with M^{3+} and MO_2^{2+} ions (Tables 9 and 11). The higher acetate complexes are formed much more readily for MO_2^{2+} ions than for M^{3+} ions, however. For the former ions, they are in fact so strong that even at rather modest concentrations of free ligand, practically all of the central ion is present as the coordinatively saturated triacetato complex. Such complexes form crystalline salts with many cations, e.g. $Na[UO_2(OOCCH_3)_3]$. In this salt, the acetate ion acts as a bidentate ligand, the six oxygens forming a plane hexagon around the uranyl group[30]. The arrangement is thus analogous to that found for the tricarbonato complexes. No doubt it also persists in solution.

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[83] C. B. Amphlett, *Inorganic Ion Exchangers*, Elsevier Publishing Co., Amsterdam (1964).

[84] V. Pekárek and M. Benešová, *J. Inorg. Nucl. Chem.* **26** (1964) 1743.

[85] V. Veselý and V. Pekárek, *J. Inorg. Nucl. Chem.* **27** (1965) 1419.

Notes to Table 12 (*cont.*)

[f] A. Cassol, L. Magon, G. Tomat and R. Portanova, *Inorg. Chim. Acta*, **3** (1969) 639.

[g] S. H. Eberle, J. B. Schaefer and E. Brandau, *Radiochim. Acta*, **10** (1968) 91.

[h] C. Miyake and H. W. Nürnberg, *J. Inorg. Nucl. Chem.* **29** (1967) 2411.

[i] S. Ahrland, *Acta Chem. Scand.* **7** (1953) 485.

[k] R. Portanova, A. Cassol, L. Magon and G. Tomat, *J. Inorg. Nucl. Chem.* **32** (1970) 221.

[l] S. H. Eberle and J. B. Schaefer, *Inorg. Nucl. Chem. Letters*, **4** (1968) 283.

[m] A. Aziz, S. J. Lyle and S. J. Naqvi, *J. Inorg. Nucl. Chem.* **30** (1968) 1013.

[n] T. Sekine, *J. Inorg. Nucl. Chem.* **26** (1964) 1463.

[p] $\log K_4 = 4{\cdot}4$; A. I. Moskvin and L. N. Essen, *Russ. J. Inorg. Chem.* **12** (1967) 359.

[q] B. M. L. Bansal and H. D. Sharma, *J. Inorg. Nucl. Chem.* **26** (1964) 799.

[r] $\log K_2(H) = 1{\cdot}0$.

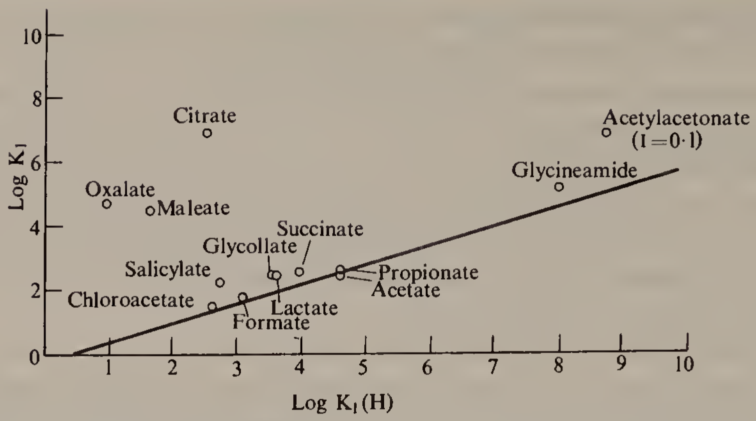

FIG. 11. The stability of the first uranyl(VI) complex as a function of the basicity of the ligand, for ligands of various coordination patterns (C. Miyake and H. W. Nürnberg, *J. Inorg. Nucl. Chem.* **29** (1967) 2411).

The propionate ion forms somewhat stronger complexes than the acetate ion with both MO_2^{2+} and H^+, while the opposite is true for monochloroacetate (Table 12). For ligands containing just one carboxylate group, a linear relation appears to exist between log K_1 and log K_1(H), e.g. with UO_2^{2+} (Fig. 11). Ligands containing, in addition to the carboxylate group, other groups which may coordinate to the actinide ions, e.g. hydroxycarboxylates, do not generally fall on this line, however. Nor do ligands containing two or more carboxylate groups. In the latter cases, the deviations may become very large (Fig. 11). The deviations always indicate a stabilization of the actinide complex relative to the acid. This stabilization is evidently due to the fact that the existence of several functional groups permit the formation of chelate complexes with the actinide ions. This involves a stability increment which may become very large for ligands whose donor atoms fit nicely into the coordination figure of the actinide ion. For the hydrogen ion, on the other hand, the possibility of a chelate formation does not exist.

As an example of a hydroxycarboxylate, information on the glycolate ion is included in Table 12, as reliable data exist for quite a few actinide systems with this ligand. With M^{3+} ions it forms much stronger complexes than does acetate, in spite of its considerably lower basicity. The chelate effect is thus considerable. With MO_2^{2+} ions, the first complex formed is of about the same strength for both ligands, while the higher complexes are stronger in case of acetate. Though still marked, the chelate effect is evidently much smaller for MO_2^{2+} than for M^{3+}. This is to be expected from the fact that MO_2^{2+} ions also form chelate complexes with the acetate ion whereas M^{3+} ions do not (cf. refs. 86, 87). A more versatile chelating ligand should therefore have a larger effect on M^{3+} ions than on MO_2^{2+} ions.

Hydroxycarboxylates have been very widely used as eluting agents in ion exchange processes used for the identification and separation of actinide elements (cf. 2.1.3)[26]. Ammonium citrate or ammonium lactate solutions were originally used for this purpose since both provided more favorable separation factors than did glycolate. It was later found that α-hydroxyisobutyrate is superior to all other eluants tried. With this agent very sharp separations are achieved (Fig. 12).

With all the eluents used, the heavier actinides are eluted first. An analogous order of elution is found for the lanthanide elements[26]. Generally two effects combine to bring about

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[86] I. Grenthe, *Acta Chem. Scand.* **23** (1969) 1752.

[87] J. Albertsson, *Acta Chem. Scand.* **24** (1970) 3527.

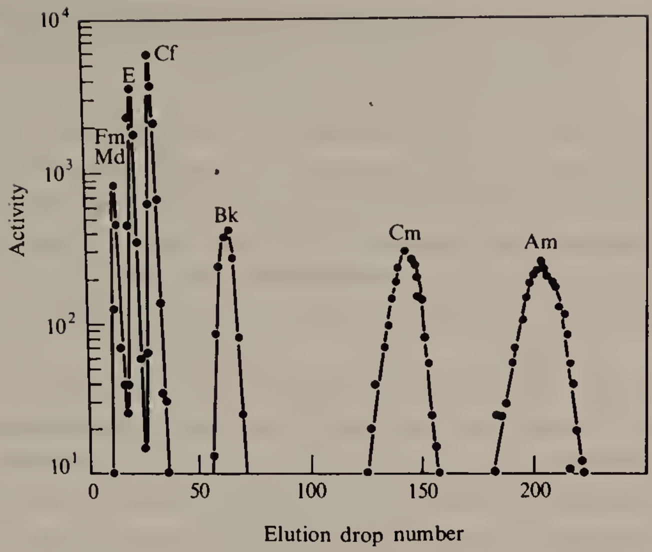

FIG. 12. Separation of the trivalent oxidation states of the transplutonium elements Am–Md by elution from the cation exchange resin Dowex-50 (sulphonated polystyrene; 12% crosslinked) with ammonium α-hydroxyisobutyrate at 87°C (G. R. Choppin, B. G. Harvey and S. G. Thompson, *J. Inorg. Nucl. Chem.* **2** (1956) 66).

this order. First, on organic cation exchangers of the sulphonated cross-linked polystyrene type, ordinarily used for these operations, the M^{3+} ions are more weakly sorbed the higher the atomic number[88]. Second, the affinity for the hydroxycarboxylate ions generally increases in the same order. The unusually good separations achieved by α-hydroxyisobutyrate evidently depend on the fact that the affinities of this ion for adjacent actinide(III) or lanthanide(III) ions differ appreciably. For the lanthanides, this has been verified experimentally, but the data pertaining to actinide systems are still quite few[57].

Among the dicarboxylate complexes, those formed by the oxalate ion are best known. In spite of its fairly low basicity, this ion forms stronger complexes than the monocarboxylates and the glycolate ion (Table 12 and Fig. 11). Evidently the formation of a five-membered chelate ring contributes to the stability of the oxalate complexes. Ions of the types M^{3+} and MO_2^{2+} again form complexes of much the same strength, while the complexes of M^{4+} are appreciably stronger. Slightly soluble oxalate phases are formed by the M^{3+} and M^{4+} ions.

The actinide malonate complexes are of about the same strength as the oxalate complexes. If the carbon chain between the carboxylate groups is further lengthened, however, the chelate effect rapidly drops[57]. Even the complexes formed by the succinate ion are not much more stable than those formed by a monocarboxylate of the same basicity (Fig. 11).

While simple dicarboxylates do not form polynuclear complexes even at fairly high actinide concentrations[89], such complexes are readily formed by dicarboxylates also containing hydroxy groups, viz. malate and tartrate[90], and also by the citrate ion, a hydroxytricarboxylate[91]. With UO_2^{2+} a dimer is formed by all these ions. The constant for the dimerization reaction which might be written $2ML \rightleftharpoons (ML)_2$ for malate and $2MHL \rightleftharpoons$

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[88] J. P. Surls, Jr. and G. R. Choppin, *J. Amer. Chem. Soc.* **79** (1957) 855.
[89] K. S. Rajan and A. E. Martell, *J. Inorg. Nucl. Chem.* **29** (1967) 523.
[90] K. S. Rajan and A. E. Martell, *J. Inorg. Nucl. Chem.* **26** (1964) 1927.
[91] K. S. Rajan and A. E. Martell, *Inorg. Chem.* **4** (1965) 462.

$(MHL)_2$ for tartrate and citrate is quite high for all three ions, viz. $10^{3\cdot35}$, $10^{3\cdot24}$ and $10^{3\cdot96}$ M^{-1}, respectively, in 1 M nitrate medium at 25°C. This means that the dimer predominates over the monomer except in extremely dilute solutions.

The actinides form much stronger complexes with carboxylate ions than with several other oxygen donors. Thus the acetate complexes are much stronger than those with nitrate (Tables 11 and 12) in spite of the fact that the two ions have the same charge and much the same size. They are even stronger than the complexes formed by the divalent sulphate ion. As may certainly be expected, more factors than the electrostatic interaction between ligand and central ion are evidently important for the complex formation; this is discussed in section 2.3.

Strong complexes with actinide ions are formed by several other ligands coordinating exclusively or mainly via two or more oxygen atoms. Representative among those chelating ligands are acetylacetonate, $CH_3\cdot CO\cdot CH_2\cdot C(O^-)\cdot CH_3$, benzohydroxamate, $C_6H_5\cdot CO\cdot NHO^-$, and ethylenediaminetetraacetate (EDTA), $(OCO\cdot CH_2)_2\cdot NH\cdot CH_2\cdot CH_2\cdot NH(CH_2\cdot COO)_2^{4-}$ (Table 13). Acetylacetonate forms very stable six-membered rings especially with M^{4+} ions with at least the first Np^{4+} complex again being weaker than expected (cf. also 2.2.2). The benzohydroxamate certainly coordinates via the two oxygen atoms, thus forming a five-membered ring. The complexes are even stronger than the acetylacetonates. EDTA forms extremely strong complexes with most actinide ions. In general these are probably hexadentates, the ligand coordinating via four oxygens and two nitrogens. As usual, the strongest complexes are formed by the M^{4+} ions, again with the complex of Np^{4+} weaker than that of U^{4+}. The strength of the M^{3+} complexes increases steadily from Pu^{3+} to Cf^{3+}. The stereochemistry of the MO_2^{2+} ions are certainly not very favorable for EDTA. For a ligand of this structure, it must be almost impossible to conform to the plane or somewhat puckered hexagons preferred by these acceptors. Thus, EDTA will tend to act as a bridging ligand with such ions, giving rise to polynuclear complexes. The monomers formed are readily protonated, indicating that the chelate is coordinated via less than six donor atoms.

Ligands coordinating merely via nitrogen atoms cannot, as a rule, displace the hydrate water of actinide ions to any measurable degree. The affinities between actinide acceptors and nitrogen donors are *per se* small. Moreover, the nitrogen donors are often so basic that they coordinate the protons of the hydrate water instead of the actinide ion, thus causing the formation of hydrolysed species. This happens, for example, on addition of ammonia or ammines. Only for nitrogen ligands of unusually low basicity[57], such as SCN^- (with a value of $\log K_1(H)$ probably rather much less than 0) and N_3^- (with $\log K_1(H) = 4\cdot44$ in 1 M sodium perchlorate at 25°C), have actinide complexes been found. In the latter case, they have been claimed only for UO_2^{2+}, however. The more numerous and more reliable data refer to SCN^- (Table 14).

It should be pointed out that the linear species SCN^- may coordinate via either the S or N atom. There is no doubt, however, that coordination to all actinide (as well as lanthanide) ions occurs via N. This has been conclusively proved by measurements of the infrared absorption of the complexes[92,93]. This is to be expected from the general affinity rules which are discussed in section 2.3.

The thiocyanate complexes are all weaker than the corresponding carboxylate or sulphate complexes. The pattern found for the affinity to actinide ions of different charge types is very similar to that found for the ligands discussed previously.

[92] S. Fronaeus and R. Larsson, *Acta Chem. Scand.* 16 (1962) 1447.

[93] J. L. Burmeister, S. D. Patterson and E. A. Deardorff, *Inorg. Chem. Acta*, 3 (1969) 105.

TABLE 13. STABILITY OF ACTINIDE COMPLEXES OF SOME TYPICAL CHELATE LIGANDS, COORDINATING VIA O AND/OR N ATOMS, IN AQUEOUS SOLUTION (The values refer to perchlorate media and 25°C, if not otherwise stated.)

M^{z+}	I	$\log K_n$			
		1	2	3	4
		Acetylacetonate			
Th^{4+}	0·1[a]	8·00	7·48	6·00	5·30
U^{4+}	0·1[b]	9·02	8·26	6·52	5·60
Np^{4+}	1[b]	8·58	8·65	6·71	6·28
Pu^{4+}	0·1[b]	10·5	9·2	8·4	5·91
UO_2^{2+}	0·1[c]	6·8	6·3		
		Benzohydroxamate[d]			
Th^{4+}	0·025[e]	9·60	10·21	8·95	
U^{4+}	0·01	9·89	8·1	8·3	6·62
Pu^{4+}	1[e]	12·73			
UO_2^{2+}	0·1	8·72	8·05		
		Ethylenediaminetetraacetate (EDTA)			
Pu^{3+}	0·1[f]	18·07[g]			
Am^{3+}	0·1[h]	18·16			
Cm^{3+}	0·1[h]	18·45			
Bk^{3+}	0·1[h]	18·88			
Cf^{3+}	0·1[h]	19·09			
Th^{4+}	0·1[i]	23·29			
U^{4+}	0·1[k]	25·83			
Np^{4+}	1[l]	24·55			
PuO_2^{2+}	0·1[f,m]	16·39			

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[a] J. Rydberg, *Acta Chem. Scand.* **15** (1961) 1723.

[b] J. O. Liljenzin and J. Stary, *J. Inorg. Nucl. Chem.* **32** (1970) 1357.

[c] J. Rydberg, *Arkiv Kemi*, **8** (1955) 113.

[d] A. Barocas, F. Baroncelli, G. B. Biondi and G. Grossi, *J. Inorg. Nucl. Chem.* **28** (1966) 2961.

[e] Nitrate medium.

[f] Chloride medium.

[g] Calculated by J. Fuger and B. B. Cunningham, *J. Inorg. Nucl. Chem.* **27** (1965) 1079, from a value determined for 20°C by J. K. Foreman and T. D. Smith, *J. Chem. Soc.* **1957**, 1752.

[h] J. Fuger, *J. Inorg. Nucl. Chem.* **5** (1958) 332; **18** (1961) 263.

[i] At 20°C; see ref. 6.

[k] N. N. Krot, N. P. Ermolaev and A. D. Gel'man, *Russ. J. Inorg. Chem.* **7** (1962) 1062; cf. ref. 57 (supplement).

[l] S. H. Eberle and M. T. Paul, *J. Inorg. Nucl. Chem.* **33** (1971) 3067.

[m] At 20°C; J. K. Foreman and T. D. Smith, *J. Chem. Soc.* **1957**, 1752.

For ligands coordinating via oxygen, the formation of more or less stable complexes with actinide ions in aqueous solution is exclusively, or at least mainly, due to a large gain of entropy, just as found for the fluoride complexes (Table 10). This is evident from the thermodynamic functions for the stepwise formation of sulphate, acetate and EDTA complexes listed in Table 15. In the case of sulphate and acetate, the enthalpy changes are positive, generally fairly strongly so, with the third step of the uranyl acetate system as the only exception. Generally the enthalpy term thus counteracts the coordination of these ions. For EDTA, the enthalpy change is negative, though of minor importance. The large contribution to the stability still comes from the entropy gain. For the thiocyanate ion, coordinating via nitrogen, very different conditions prevail. Here the formation of the uranyl complexes is mainly due to a negative enthalpy change while the entropy term is of minor importance for the first step and negative, and hence counteracting, for the second.

An interpretation is given in section 2.3 of the thermodynamic patterns found for the formation of various actinide complexes in aqueous solution.

TABLE 14. STABILITY OF ACTINIDE THIOCYANATE COMPLEXES IN AQUEOUS PERCHLORATE MEDIA, AT 25°C (mainly from ref. 6)

M^{z+}	I	log K_n 1	2	3
Pu^{3+}	1	0·46	0·29	
Am^{3+}	1	0·50	0·34	
Cm^{3+}	1	0·43	0·41	
Cf^{3+}	1	0·48		
Th^{4+}	1[a]	1·08		
U^{4+}	1	1·49	0·62	
$UO_2{}^{2+}$	1[b]	0·75	−0·03	0·5

[a] W. C. Waggener and R. W. Stoughton, ORNL-795, 1950 (as quoted in ref. 57).

[b] S. Ahrland and L. Kullberg, *Acta Chem. Scand.* **25** (1971) 3677.

2.2.4. *Complexes formed between Actinyl(V) Ions and Other Cations, especially Actinyl(VI) Ions*

Actinyl(V) ions form, in non-complexing perchlorate solutions, complexes with several other cations. Such complexes, of the compositions $M'O_2^+ \cdot M''O_2^{2+}$ and $M'O_2^+ \cdot M^{3+}$, have so far been found with $M' = U$ and Np, $M'' = U$ and $M^{3+} = $ Cr and Rh (Table 16). In these complexes, the ion $M'O_2^+$ presumably takes the place of a water molecule in the hydrate shell of MO_2^{2+} or M^{3+}, coordinating via one of its negatively charged oxygens. As seen from Table 16, the complexes are all fairly weak, especially compared with the dimers formed, e.g. on the hydrolysis of UO_2^{2+} or Th^{4+} (section 2.2.1). In spite of this, complexes of these types may nevertheless serve as important intermediates in many redox reactions. Such a formation of complexes between cations of different oxidation states has in fact been postulated as a rather general feature of redox reactions (section 3.8)[94].

[94] F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions*, 2nd ed., J. Wiley & Sons, New York (1967).

Table 15. Thermodynamics of the Stepwise Formation of Actinide Complexes with Ligands Co-ordinating via O and/or N Atoms (ΔG_n° and ΔH_n° in kJ: ΔS_n° in JK$^-$)

M^{z+}	I	Method[a]	ΔG_1°	ΔH_1°	ΔS_1°	ΔG_2°	ΔH_2°	ΔS_2°
				Sulphate				
Am^{3+}	2	T[b]	−8·4	18·4	90			
Cm^{3+}	2	T[b]	−7·5	17·2	83			
Cf^{3+}	2	T[b]	−7·9	18·8	90			
Th^{4+}	2	C[c]	−18·8	20·9	133	−13·8	19·5	112
Np^{4+}	2	T[d]	−20·0	18·3	128			
UO_2^{2+}	1	C[e]	−10·3	18·2	96	−5·4	16·9	75
				Acetate				
Am^{3+}	2	T[f]	−11·2	18·0	98			
Cm^{3+}	2	T[f]	−11·7	18·0	100			
Bk^{3+}	2	T[f]	−11·7	18·4	101			
Cf^{3+}	2	T[f]	−12·0	15·9	94			
UO_2^{2+}	1	C[e]	−13·8	10·5	82	11·4	9·7	71
				Ethylenediaminetetraacetate (EDTA)				
Pu^{3+}	0·1	C[g]	−103·1	−17·7	287			
Am^{3+}	0·1	C[g]	−103·6	−19·5	282			
				Thiocyanate				
UO_2^{2+}	1	C[e]	−4·3	−3·2	4	0·2	−5·7	−20

[a] The values of ΔH_n° determined calorimetrically (C) or by the temperature coefficient method (T), between the temperature limits stated in the following notes.

[b] 0–55°C; R. G. de Carvalho and G. R. Choppin, *J. Inorg. Nucl. Chem.* **29** (1967) 737.

[c] Calculated from A. J. Zielen, *J. Amer. Chem. Soc.* **81** (1959) 5022.

[d] 10–35°C; calculated from J. C. Sullivan and J. C. Hindman, *J. Amer. Chem. Soc.* **76** (1954) 3931, combined with data for the formation of HSO^- from A. J. Zielen (see note c).

[e] S. Ahrland and L. Kullberg, *Acta Chem. Scand.* **25** (1971) 3677; in the acetate system the functions for the third step are $\Delta G_3^\circ = -11{\cdot}3$, $\Delta H_3^\circ = -4{\cdot}0$, $\Delta S_3^\circ = 25$.

[f] 0–55°C (for Bk^{3+} 0–40°C); G. R. Choppin and J. K. Schneider, *J. Inorg. Nucl. Chem.* **32** (1970) 3283.

[g] J. Fuger and B. B. Cunningham, *J. Inorg. Nucl. Chem.* **27** (1965) 1079.

2.3. Factors governing the formation of actinide complexes in aqueous solution

From the review of the coordination chemistry of the actinides in aqueous solution given in the previous section, some very striking features emerge.

First, strong complexes are formed with the fluoride ion, and with a wide variety of ligands coordinating via oxygen. Only very weak complexes are formed with the heavier halides. In addition, in aqueous solution the actinide ions have practically no affinity for

TABLE 16. STABILITY OF COMPLEXES FORMED BETWEEN ACTINYL(V) IONS AND OTHER CATIONS IN PERCHLORATE MEDIA AT 25°C

Reaction	I	log K
$UO_2^+ + UO_2^{2+} \rightleftharpoons UO_2^+ \cdot UO_2^{2+}$	2	1·20[a]
$NpO_2^+ + UO_2^{2+} \rightleftharpoons NpO_2^+ \cdot UO_2^{2+}$	3	−0·15[a]
$NpO_2^+ + Cr^{3+} \rightleftharpoons NpO_2^+ \cdot Cr^{3+}$	8	0·42[a]
$NpO_2^+ + Rh^{3+} \rightleftharpoons NpO_2^+ \cdot Rh^{3+}$	8	0·52[b]

[a] T. W. Newton and F. B. Baker, *Inorg. Chem.* **4** (1965) 1166.

[b] R. K. Murmann and J. C. Sullivan, *Inorg. Chem.* **6** (1967) 892.

ligands coordinating via the heavier chalcogens (S and homologs). Nor are the heavier donors of the nitrogen group coordinated, while a modest affinity exists for nitrogen.

Second, the strength of the complexes increases in the order $MO_2^+ < M^{3+} \simeq MO_2^{2+} < M^{4+}$, i.e. with the effective charge on the acceptor atom. For ions of the same charge, an increase with decreasing radius is generally observed in the beginning of the actinide series; later the trend becomes less regular. In spite of these minor irregularities, however, the increase of stability of actinide complexes with the ratio of effective charge to radius is unmistakable.

Third, the complexes are generally formed in endothermic reactions, their stabilities being due to a large gain of entropy which outweighs the unfavorable direction of the enthalpy change.

These features are characteristic of metal ions (and of acceptors generally) which have been classified as hard (or belonging to class (a))[95,96]. Their counterparts are the soft, or class (b), acceptors which generally possess opposite characteristics. They thus prefer the heavier donors of each group and the strength of the complexes does not primarily depend upon the charge-to-radius ratio of the acceptor. In fact, the heavy donors often show a strong affinity for large acceptors of low charge. Complexes of this type are, moreover, always formed in exothermic reactions[96]. Their stability is thus exclusively, or at least mainly, due to a favorable enthalpy term, while the entropy term counteracts the reaction, sometimes quite strongly, or is at least of minor importance.

The two classes of acceptors were originally characterized by the affinity sequences listed in Table 17, embodying the first feature discussed above. It turns out, however, that the two further characteristics are always linked to the first one.

From the characteristics of hard acceptors it is immediately evident that the electrostatic interaction between the central ion and the ligand is of crucial importance for the complex formation. For soft acceptors, showing the opposite characteristics, this cannot possibly be the case. Here the formation of an essentially covalent bond to the ligand must be the main factor. In order to participate in the electron sharing characterizing such a bond, a metal ion acceptor has apparently to possess two important properties, viz. a well-filled *d* shell and a high polarizability. Acceptors with these characteristics are formed by elements situated in a roughly triangular, rather restricted area of the periodic system. Thus, mono-

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[95] R. G. Pearson, *J. Amer. Chem. Soc.* **85** (1964) 3533; *J. Chem. Educ.* **45** (1968) 581, 643.

[96] S. Ahrland, *Helv. Chim. Acta*, **50** (1967) 306; *Structure and Bonding*, Vol. 5, p. 118, Springer-Verlag, Berlin (1968).

TABLE 17. CHARACTERISTIC AFFINITY SEQUENCES OF ACCEPTORS OF THE CLASSES (a) OR HARD, AND (b) OR SOFT, FOR VARIOUS DONOR GROUPS

Donor group	Oxidation state	(a) or hard	(b) or soft
7 B	−I	$F \gg Cl > Br > I$	$F \ll Cl < Br < I$
6 B	−II	$O \gg S > Se > Te$	$O \ll S < Se \simeq Te$
5 B	−III	$N \gg P > As > Sb$	$N \ll P > As > Sb$

valent copper, silver and gold of the electron configuration d^{10}, and with very high polarizabilities, are the most typical group of soft acceptors. Mercury and the platinum metals are also very soft in their various oxidation states[96,97].

Hard acceptors, on the other hand, lack either a well-filled *d* shell or a high polarizability, or both. As to the actinide ions, their polarizabilities seem to be of the same order of magnitude as those of most soft acceptors[98]. This also applies to the lanthanide ions. On the other hand, their *d* shells are empty, or almost empty. This evidently means that they possess no orbitals of energies well compatible with those of the ligand orbitals. They are, therefore, not prone to the formation of covalent bonds and hence display a typically hard character.

Such very hard acceptors, with a high effective charge, are very strongly hydrated in aqueous solution (see section 1.4 and Table 3). So also are those ligands of high charge-to-radius ratio which they prefer. The formation of a complex therefore involves the breaking of strong bonds within the hydrate shells of both the acceptor and the ligand. This takes large amounts of energy which are evidently not fully regained on the formation of the acceptor-to-ligand bond. Consequently the overall reaction becomes endothermic. On the other hand, the liberation of the water molecules from the highly ordered hydrate structures means an increase of freedom, implying a large gain of entropy. For strongly hydrated ions, this gain is nowhere near compensated by the loss due to the formation of the acceptor-to-ligand bond. A considerable net gain of entropy results, which on balance brings about a large decrease of free energy, and hence the formation of a strong complex, in spite of the positive net enthalpy change.

In contrast to this, typically soft acceptors, generally of low charge, are only weakly hydrated and so also are the ligands they prefer. The breaking of their hydrate structures therefore does not take much energy. A lot of energy is gained, however, by the formation of a strong covalent bond between acceptor and ligand. Consequently, the overall reaction becomes exothermic. On the other hand, little or no gain of entropy occurs as a result of the dehydration. On balance, a strong complex is formed in an exothermic reaction, with the entropy term often counteracting the reaction, as is in fact observed[96].

3. REDOX REACTIONS IN AQUEOUS SOLUTIONS

3.1. Stability and preparation of the various oxidation states

The small differences between the energy levels of the 5*f* and 5*d* electrons and the poor shielding within the actinide series gives rise to a wide range of oxidation states for the

[97] S. Ahrland, *Structure and Bonding*, Vol. 1, p. 207, Springer-Verlag, Berlin (1966).
[98] C. K. Jørgenson, *Rev. Chim. Minerale*, **6** (1969) 83.

TABLE 18. PREPARATION METHODS AND STABILITY OF ACTINIDE IONS IN AQUEOUS SOLUTIONS

Ion	Stability and method of preparation
Md^{2+}	Slow oxidation to Md^{3+}.[a,b,c]
No^{2+}	Stable.[c,d,e]
Ac^{3+}	Stable.[f,g]
U^{3+}	Slow oxidation by water, rapid oxidation by air, to U^{4+}. Prepared by electrolytic reduction (Hg cathode).[f,h]
Np^{3+}	Stable to water, rapid oxidation by air to Np^{4+}. Prepared by electrolytic reduction (Hg cathode) or by reduction by H_2(g) with Pt catalyst.[f,i,j,k]
Pu^{3+}	Stable to water and air. Oxidizes by action of its own α-radiation to Pu^{4+}. Prepared by reduction by SO_2, Zn, U^{4+} or H_2(g) with Pt catalyst.[f,l,m,n]
Am^{3+}	Stable. Difficult to oxidize.[f,o,p,q]
Cm^{3+}	Stable.[f,o,p,q]
Bk^{3+}	Stable. Can be oxidized to Bk^{4+}.[f,o,r]
Cf^{3+}	Stable.[f,s]
Es^{3+}	Stable.[f,t,u]
Fm^{3+}	Stable.[u,v]
Md^{3+}	Stable. Can be reduced to Md^{2+}.[c,u,w]
No^{3+}	Stable? Can be reduced to No^{2+}.[c,d,e,v]
Lw^{3+}	Stable.[e,v]
Th^{4+}	Stable.[a,f]
Pa^{4+}	Stable to water. Rapid oxidation by air to Pa(V). Prepared by electrolytic reduction (Hg cathode) and by the action of Zn-amalgam, Cr^{2+} or Ti^{3+} in hydrochloric acid.[b,f,x,y]
U^{4+}	Stable to water. Slow oxidation by air to UO_2^{2+}. Oxidation in nitrate media catalyzed by U.V. light. Prepared by oxidation of U^{3+} by air or electrolytic reduction of UO_2^{2+} (Hg cathode) and reduction of UO_2^{2+} by Zn or H_2(g) with Ni catalyst.[f,h,u]
Np^{4+}	Stable to water. Slow oxidation by air to NpO_2^{+}. Prepared by oxidation of Np^{3+} by air or reduction of higher oxidation states by Fe^{2+}, SO_2, I^- or H_2(g) with Pt catalyst.[f,i,j,k,u,z]
Pu^{4+}	Stable in concentrated acids, e.g. 6 M HNO_3. Disproportionates to Pu^{3+} and PuO_2^{+} at lower acidities. Prepared by oxidation of Pu^{3+} by BrO_3^-, Ce^{4+}, $Cr_2O_7^{2-}$, HIO_3 or MnO_4^- in acid solution or by reduction of higher oxidation states by HNO_2, NH_3OH^+, I^-, 3 M HI, 3 M HNO_3, Fe^{2+}, $C_2O_4^{2-}$ or HCOOH in acid solution.[f,l,m,u]
Am^{4+}	Not stable in water. Most stable in 15 M NH_4F or NH_4F+2 M $K_4P_2O_7$ as the complex ion AmF_6^{2-}. Reduced by I^-. Prepared by electrolytic oxidation (Pt anode) of Am^{3+} in 12 M H_3PO_4.[f,u,A]
Cm^{4+}	Known as CmF_6^{2-}. Stable only 1 hr at 25°C.[f,o,p,q,u,B]
Bk^{4+}	Stable to water. Slow reduction to Bk^{3+}. Prepared by oxidation of Bk^{3+} by $Cr_2O_7^{2-}$ or BrO_3^-.[f,o,r,C]
PaO^{3+} or PaO_2^{+}	Stable. Difficult to reduce.[b,f,x,y]
UO_2^{+}	Disproportionates to U^{4+} and UO_2^{2+}. Most stable at pH 2·5. Prepared by electrolytic reduction of UO_2^{2+} (Hg cathode) and by reduction of UO_2^{2+} by Zn amalgam or H_2(g). pH around 2·5 used.[f,h,u,D]
NpO_2^{+}	Stable. Disproportionates only at high acidities. Prepared by oxidation of lower oxidation states by Cl_2 or ClO_4^- and by reduction of higher oxidation states by NH_2NH_2, NH_2OH, HNO_2, H_2O_2/HNO_3, Sn^{2+} or SO_2.[f,i,j,k,u]
PuO_2^{+}	Disproportionates to Pu^{4+} and PuO_2^{2+}. Most stable at low acidities. Prepared by reduction of PuO_2^{2+} by I^- or SO_2 at pH 2.[f,l,m,u]
AmO_2^{+}	Disproportionates in strong acids to Am^{3+} and AmO_2^{2+}. Reduces at low acidities to Am^{3+} by action of its own α-radiation. Prepared by electrolytic oxidation (Pt anode) of Am^{3+} in 2 M $LiIO_3+0{\cdot}7$ M HIO_3 at pH 1·47.[f,o,p,q,u,A]
UO_2^{2+}	Stable. Difficult to reduce. Prepared by oxidation of lower states by Fe^{3+}/H_2SO_4, MnO_2, Cl_2, Br_2, ClO_4^- or air.[a,h,k,u]
NpO_2^{2+}	Stable. Easy to reduce. Prepared from lower oxidation states by oxidation by Ce^{4+}, MnO_4^-, Ag^{2+}, Cl_2 or BrO_3^-.[f,i,j,k,u]
PuO_2^{2+}	Stable. Fairly easy to reduce. Reduces slowly under the action of its own α-radiation. Prepared by oxidation of lower oxidation states by BiO_3^-, HOCl or Ag^{2+}.[f,l,m]
AmO_2^{2+}	Stable. Reduces fairly rapidly under action of its own α-radiation. Prepared by electrolytic oxidation (Pt anode) in 5 M H_3PO_4 or by $S_2O_8^{2-}$ in the presence of Ag^+.[f,o,p,q,u,E,F]
NpO_5^{3-}	Stable in alkaline solution. Prepared by oxidation of NpO_2^{2+} in alkaline solution by O_3, $S_2O_8^{2-}$, ClO^-, BrO^- or BiO_3^-.[G,H,I]
PuO_5^{3-}	Stable in alkaline solution. Prepared by oxidation of PuO_2^{2+} in alkaline solution by O_3, $S_2O_8^{2-}$, ClO^- or BrO^-.[I]

actinide ions (see Table 1). A general discussion of the electronic structure and its relation to the occurrence and stability of the various ions is given in section 1.1. The relative stabilities of the oxidation states also depends on the nature of the medium surrounding the ions. Ions very unstable in aqueous solution can be found as relatively stable species in other solvents. Such effects will be treated in the section on non-aqueous solutions (p. 615).

The stabilities and the preparation methods used for the actinide valence states in aqueous solution are summarized in Table 18. Only the most common methods of preparing the various oxidation states are listed. For complete details the reader should consult the original articles.

For elements with more than one oxidation state in solution, two effects interact to complicate their aqueous chemistry. Firstly, complex formation usually favors one of the oxidation states. This gives a stabilization of one of the oxidation states at the expense of others (see Fig. 19). Thus the species which are stable in non-complexing aqueous acid solution may not be those dominating when other reagents, e.g. complexing agents, are present in the solution. This is discussed further in section 3.4. Secondly, no oxidation state can be kept completely free of the others as this would demand infinitely large oxidation or

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Notes to Table 18

[a] L. I. Katzin, Natl. Nucl. Energy Series Div. IV, Vol. 14A, p. 66 (1954).

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[h] H. R. Hoeckstra and J. J. Katz, *ibid.* p. 130.

[i] B. B. Cunningham and J. C. Hindman, *ibid.* p. 456.

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reduction potentials. It is known that even small amounts of a more reactive oxidation state may result in a greatly increased total reaction rate, e.g. the well-known catalytic effect of Cr^{2+} on the reaction between Cr^{3+} and EDTA. The change in relative concentrations occurring when the redox potential is varied is discussed in detail below (section 3.5).

3.2. Formal and standard potentials

Every redox reaction can be split into two half-reactions—an oxidation reaction which liberates electrons, e^-, and a reduction reaction which consumes electrons. For example, the reduction of neptunyl(V) by iron(II) in acid solution

$$NpO_2{}^+ + Fe^{2+} + 4H^+ \rightleftharpoons Np^{4+} + Fe^{3+} + 2H_2O \qquad (1)$$

can be split into the two half-reactions (2) and (3)

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^- \quad \text{(oxidation)} \qquad (2)$$

$$NpO_2{}^+ + 4H^+ + e^- \rightleftharpoons Np^{4+} + 2H_2O \quad \text{(reduction)} \qquad (3)$$

According to the IUPAC convention, all reactions involving electrons (half-reactions) should be written as reduction reactions,

$$\text{ox} + ne^- \rightleftharpoons \text{red} \qquad (4)$$

with a corresponding equilibrium constant K defined as

$$K = \frac{\{\text{red}\}}{\{\text{ox}\}\{e^-\}^n} \qquad (3.1)$$

where { } is used to denote activities. The standard potential $E°$ is then defined as

$$E = E° + \frac{RT}{nF} \ln \frac{\{\text{ox}\}}{\{\text{red}} \qquad (3.2)$$

where E is the reduction potential relative to the standard hydrogen electrode, R is the gas constant, T is the absolute temperature and F is the Faraday constant[98a].

The standard free energy change $\Delta G°$ is similarly related to the activities.

$$\Delta G = \Delta G° + RT \ln \frac{\{\text{red}\}}{\{\text{ox}\}} \qquad (3.2a)$$

With these definitions and conventions the following relation between the equilibrium constant and the standard potential is obtained[99].

$$\ln K = \frac{nE°F}{RT} \qquad (3.3)$$

When more than one redox system is present in the same solution their redox potentials must be the same. This condition allows the calculation of equilibrium constants for any redox reaction when the standard potentials are known for the corresponding reduction reactions. The reduction of NpO_2^+ by Fe^{2+} (see reaction 1) will be used again as an example. The two reduction reactions are $Fe^{3+} + e^- = Fe^{2+}$ with $E° = 0{\cdot}771$ V and $NpO_2^+ + 4H^+ + e^- = Np^{4+} + 2H_2O$ with $E° = 0{\cdot}7391$ V.

[98a] W. Nernst, *Z. für physikalische Chemie*, **4** (1889) 129.

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The requirement that these reactions must have equal potentials gives rise to the following equation

$$E = 0{\cdot}771 + \frac{RT}{F}\ln\frac{\{\mathrm{Fe^{3+}}\}}{\{\mathrm{Fe^{2+}}\}} = 0{\cdot}7391 + \frac{RT}{F}\ln\frac{\{\mathrm{NpO_2^+}\}\{\mathrm{H^+}\}^4}{\{\mathrm{Np^{4+}}\}\{\mathrm{H_2O}\}^2}$$

which after rearrangement of terms becomes

$$\ln\frac{\{\mathrm{Fe^{3+}}\}\{\mathrm{Np^{4+}}\}\{\mathrm{H_2O}\}^2}{\{\mathrm{Fe^{2+}}\}\{\mathrm{NpO_2^+}\}\{\mathrm{H^+}\}^4} = \frac{0{\cdot}7391-0{\cdot}771}{RT/F} = \ln K$$

where K is the equilibrium constant to be calculated. At 25°C the value for $RT/F \ln 10$ is 0·05916. Using this value $\log K = -0{\cdot}539$ or $K = 0{\cdot}29$ is obtained.

Standard and formal potentials for the actinide ions are given in Table 19. To give a complete picture of these redox systems some estimated potentials are included in the table for species that obviously will not occur in aqueous solutions, as they would oxidize or reduce the water molecules instantaneously. For each element the reactions and potentials are given for increasing oxidation states, and for each couple the reaction in acid solution is given first and then the reaction in alkaline solution. The formal potentials for 1 M perchloric acid are more accurate than the standard potentials at zero ionic strength as the latter are extrapolated values or calculated from thermodynamic data. On the other hand, most of the formal potentials in 1 M NaOH or the standard potentials in alkaline solution are generally more uncertain as few of them are based on direct measurements. They are usually calculated from the standard potential in acid solution and the solubility products of the hydroxides. The uncertainty introduced comes mainly from the solubility data, which often are known only within a few powers of ten.

TABLE 19. FORMAL AND STANDARD POTENTIALS FOR THE ACTINIDE ELEMENTS

Element	Oxidation numbers	Reaction	Formal potential E (volt) (1 M $HClO_4$ or 1 M NaOH)	Standard potential $E°$ (volt) ($I = 0$)
Ac	III–0	$Ac^{3+}+3e^- = Ac(s)$	−2·62	−2·58
Th	IV–III	$Th^{4+}+e^- = Th^{3+}$	−2·4	−2·4
	IV–0	$Th^{4+}+4e^- = Th(s)$	−1·8	−1·9
		$Th(OH)_4+4e^- = Th(s)+4OH^-$	−2·46	−2·48
Pa	V–IV	$PaO_2^++4H^++e^- = Pa^{4+}+2H_2O$	−0·29*	~−0·1
	V–0	$PaO_2^++4H^++5e^- = Pa(s)+2H_2O$	−0·97	−1·0
U	VI–V	$UO_2^{2+}+e^- = UO_2^+$	0·063	0·080
	VI–IV	$UO_2^{2+}+4H^++2e^- = U^{4+}+2H_2O$	0·338	0·319
		$UO_2^{2+}+2e^- = UO_2(s)$	0·427	0·447
	VI–III	$UO_2^{2+}+4H^++3e^- = U^{3+}+2H_2O$	0·015	0·014
		$UO_2(OH)_2+2H_2O+2e^- = U(OH)_4+2OH^-$	−0·600	−0·620
	V–IV	$UO_2^++4H^++e^- = U^{4+}+2H_2O$	0·613	0·558
	V–III	$UO_2^++4H^++2e^- = U^{3+}+2H_2O$	−0·009	−0·019
	IV–III	$U^{4+}+e^- = U^{3+}$	−0·631	−0·596
		$U(OH)_4+e^- = U(OH)_3+OH^-$	−2·13	−2·14
	III–0	$U^{3+}+3e^- = U(s)$	−1·85	−1·80
		$U(OH)_3+3e^- = U(s)+3OH^-$	−2·14	−2·17
Np	VII–VI	$NpO_2^{3+}+e^- = NpO_2^{2+}$	>2·07	>2·1
		$NpO_5^{3-}+e^-+H_2O = NpO_4^{2-}+2OH^-$	0·5281	0·538
	VI–V	$NpO_2^{2+}+e^- = NpO_2^+$	1·1364	1·153
		$NpO_2(OH)_2+e^- = NpO_2(OH)+OH^-$	0·49	0·48

TABLE 19 (*cont.*).

Element	Oxidation numbers	Reaction	Formal potential E (volt) (1 M $HClO_4$ or 1 M NaOH)	Standard potential E° (volt) ($I = 0$)
	VI–IV	$NpO_2^{2+}+4H^++2e^- = Np^{4+}+2H_2O$	0·9377	0·918
		$NpO_2(OH)_2+2H^++2e^- = Np(OH)_4$	0·45	0·43
	VI–III	$NpO_2^{2+}+4H^++3e^- = Np^{3+}+2H_2O$	0·6769	0·676
	V–VI	$NpO_2^++4H^++e^- = Np^{4+}+2H_2O$	0·7391	0·684
		$NpO_2(OH)+2H_2O+e^- = Np(OH)_4+OH^-$	0·40	0·39
	V–III	$NpO_2^++4H^++2e^- = Np^{3+}+2H_2O$	0·4471	0·437
	IV–III	$Np^{4+}+e^- = Np^{3+}$	0·1551	0·190
		$Np(OH)_4+e^- = Np(OH)_3+OH^-$	−1·75	−1·76
	III–0	$Np^{3+}+3e^- = Np(s)$	−1·83	−1·83
		$Np(OH)_3+3e^- = Np(s)+3OH^-$	−2·22	−2·25
Pu	VII–VI	$PuO_5^{3-}+H_2O+e^- = PuO_4^{2-}+2OH^-$	0·847	0·857
	VI–V	$PuO_2^{2+}+e^- = PuO_2^+$	0·9164	0·933
		$PuO_2(OH)_3^-+e^- = PuO_2(OH)+2OH^-$	0·27	0·26
	VI–IV	$PuO_2^{2+}+4H^++2e^- = Pu^{4+}+2H_2O$	1·0433	1·024
		$PuO_2(OH)_3^-+2H_2O+2e^- = Pu(OH)_4+3OH^-$	0·52	0·51
	VI–III	$PuO_2^{2+}+4H^++3e^- = Pu^{3+}+2H_2O$	1·0228	1·022
		$PuO_2(OH)_3^-+2H_2O+3e^- = Pu(OH)_3+4OH^-$	0·03	0·02
	V–IV	$PuO_2^++4H^++e^- = Pu^{4+}+2H_2O$	1·1702	1·115
		$PuO_2(OH)+2H_2O+e^- = Pu(OH)_4+OH^-$	0·77	0·76
	V–III	$PuO_2^++4H^++2e^- = Pu^{3+}+2H_2O$	1·0761	1·066
		$PuO_2(OH)+2H_2O+2e^- = Pu(OH)_3+2OH^-$	−0·09	−0·10
	IV–III	$Pu^{4+}+e^- = Pu^{3+}$	0·9819	1·017
		$Pu(OH)_4+e^- = Pu(OH)_3+OH^-$	−0·94	−0·95
	III–0	$Pu^{3+}+3e^- = Pu(s)$	−2·08	−2·03
		$Pu(OH)_3+3e^- = Pu(s)+3OH^-$	−2·39	−2·42
Am	VI–V	$AmO_2^{2+}+e^- = AmO_2^+$	1·60	1·62
		$AmO_2(OH)_2+e^- = AmO_2(OH)+OH^-$	1·1	1·1
	VI–IV	$AmO_2^{2+}+4H^++2e^- = Am^{4+}+2H_2O$	1·38	1·36
		$AmO_2(OH)_2+2H_2O+2e^- = Am(OH)_4+2OH^-$	0·9	0·9
	VI–III	$AmO_2^{2+}+4H^++3e^- = Am^{3+}+2H_2O$	1·70	1·70
		$AmO_2(OH)_2+2H_2O+3e^- = Am(OH)_3+3OH^-$	0·7	0·7
	V–IV	$AmO_2^++4H^++e^- = Am^{4+}+2H_2O$	1·16	1·10
		$AmO_2(OH)+2H_2O+e^- = Am(OH)_4+OH^-$	0·7	0·7
	V–III	$AmO_2^++4H^++2e^- = Am^{3+}+2H_2O$	1·75	1·74
		$AmO_2(OH)+2H_2O+2e^- = Am(OH)_3+2OH^-$	0·6	0·6
	IV–III	$Am^{4+}+e^- = Am^{3+}$	2·34	2·38
		$Am(OH)_4(s)+e^- = Am(OH)_3(s)+OH^-$	0·5	0·5
	III–II	$Am^{3+}+e^- = Am^{2+}$	−2·93	−2·9
	III–0	$Am^{3+}+3e^- = Am(s)$	−2·42	−2·38
		$Am(OH)_3(s)+3e^- = Am(s)+3OH^-$	−2·68	−2·71
Cm	IV–III	$Cm^{4+}+e^- = Cm^{3+}$	3·24	3·28
	III–II	$Cm^{3+}+e^- = Cm^{2+}$	−5·0	−5·0
	III–0	$Cm^{3+}+3e^- = Cm(s)$	−2·31	−2·29
Bk	IV–III	$Bk^{4+}+e^- = Bk^{3+}$	1·64	1·68
	III–II	$Bk^{3+}+e^- = Bk^{2+}$	−3·4	−3·4
Cf	IV–III	$Cf^{4+}+e^- = Cf^{3+}$	>1·60	>1·64
	III–II	$Cf^{3+}+e^- = Cf^{2+}$	−1·9	−1·9
	III–0	$Cf^{3+}+3e^- = Cf(s)$	−2·32	−2·28
Es	III–II	$Es^{3+}+e^- = Es^{2+}$	−1·60	−1·57
Fm	III–II	$Fm^{3+}+e^- = Fm^{2+}$	−1·3	−1·3
Md	III–II	$Md^{3+}+e^- = Md^{2+}$	−0·15	−0·12
No	III–II	$No^{3+}+e^- = No^{2+}$	1·45	1·48

* 6 M HCl.

3.3. Graphical presentation of redox equilibria

When several oxidation states of an element are encountered in solution, graphical presentations of the various relationships are very useful and greatly facilitate the understanding of these systems.

The most simple graph is the Latimer diagram (see Fig. 13), which only relates potentials and oxidation states. The sum of the potential times the number of electrons must be the same and independent of the way used in the Latimer diagram for any two oxidation states spanning one or more intermediate states. This is quite useful as an aid in evaluating potentials indirectly from other measured potentials, e.g. the PuO_2^+/Pu^{3+} potential from the PuO_2^+/Pu^{4+} and Pu^{4+}/Pu^{3+} potentials. In this example the relation $2 \cdot E°_{V/III} = 1 \cdot E°_{V/IV} + 1 \cdot E°_{IV/III}$ was used.

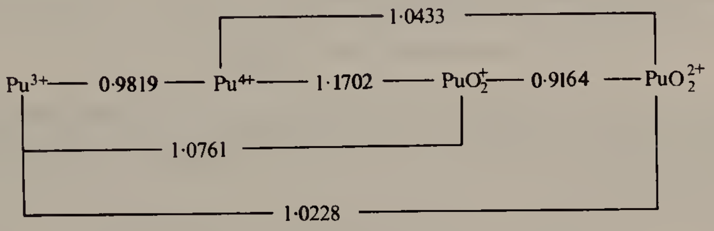

FIG. 13. The Latimer diagram for the plutonium formal potentials in 1 M $HClO_4$ (data from Table 19). Values in bold type are measured, the others are calculated from the measured potentials.

Activity ratio potential diagrams are very often used because of their simplicity (see Figure 14). However, as they use one of the oxidation states as reference basis they are not easy to use in predicting redox equilibria when more than one redox system is present in a solution.

Relative concentration potential diagrams are generally more useful in predicting

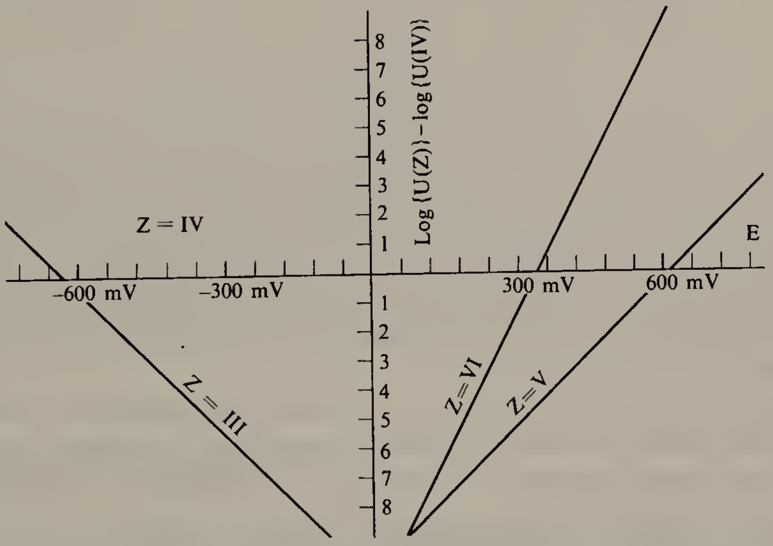

FIG. 14. Conventional redox diagram for uranium in 1 M $HClO_4$. U^{4+} is used as the reference state (horizontal line) in the diagram.

redox equilibria[100]. Here the total concentration, C_M, is used as a common reference instead of one of the oxidation states.

In mass balance calculations it is necessary to use concentration instead of activities. In order to translate activities into concentrations in a simple way, activity factors f are defined as follows[101]

$$\{X\} = f_x[X] \tag{3.4}$$

where [ ] is used to denote concentrations. The total amount C_M of an element M in its different ions M^{z+} is then

$$C_M = \sum_{z=z_l}^{z_h} [M^{z+}] = \sum_{z=z_l}^{z_h} \{M^{z+}\}/f_z \tag{3.5}$$

where z_l is the lowest and z_h is the highest oxidation state in the solution. The equation for the redox potential (3.2) can be written as follows

$$\{ox\} = \{red\}\cdot\exp\left(\frac{(E-E^\circ)nF}{RT}\right) \tag{3.6}$$

Remembering that E will be the same for all reactions in the same solution and considering consecutive oxidation states, each one unit higher than the preceding one, the total amount, C_M, can now be expressed as

$$C_M = \sum_{z=z_l}^{z_h} \frac{1}{f_z}\{M^{z_l+}\}\prod_{n=z_l}^{z} \exp\left(\frac{F(E-E_n^\circ)}{RT}\right) \tag{3.7}$$

From equation (3.7) we obtain the relative activity $\{M^{z_l+}\}/C_M$ in the form

$$\frac{\{M^{z_l+}\}}{C_M} = \frac{1}{\sum_{z=z_l}^{z_h} \frac{1}{f_z}\prod_{n=z_l}^{z} \exp\left(\frac{F}{RT}(E-E^{\text{o}}{}_n)\right)}$$

The product of exponentials in this equation can be transformed to the exponential of a sum which simplifies the numerical evaluation

$$\frac{\{M^{z_l+}\}}{C_M} = \frac{1}{\sum_{z=z_l}^{z_h} \frac{1}{f_z}\exp\left(\sum_{n=z_l}^{z} \frac{F}{RT}(E-E_n^\circ)\right)} = \frac{f_{z_l}[M^{z_l+}]}{C_M} \tag{3.8}$$

Equation (3.8) is used to calculate the relative activity and relative concentration for any potential, E. The relative activities and relative concentrations for the remaining oxidation states are then calculated from eqns. (3.6) and (3.4). The values obtained are plotted in a logarithmic form with the logarithm of the relative concentration versus potential. It is very convenient to use a potential scale where 1 unit of length is $RT \ln 10/F$, a "pE" scale, as all lines then will have integral slopes except in the immediate vicinity of any formal (or standard) potential (see Figure 15).

These diagrams can be used as follows to evaluate the equilibrium composition when two different redox systems are mixed: The appropriate redox diagrams are selected and the potential scales are aligned and the concentration scales moved so that the actual total

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[100] T. S. Lee and L. G. Sillén, *Chemical Equilibrium in Analytical Chemistry*, p. 307. Interscience, New York (1959).

[101] A. A. Noyes and W. C. Bray, *J. Am. Chem. Soc.* **33** (1911) 1646.

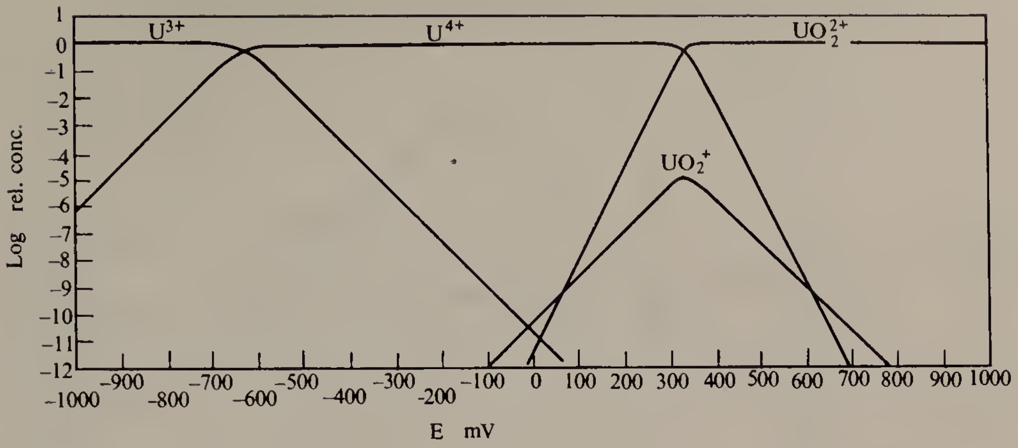

FIG. 15. The redox diagram for uranium in 1 M $HClO_4$ and 25°C (data from Table 19). Observe that the crossing U^{4+}/UO_2^+ is at a higher potential than the crossing of UO_2^+ and UO_2^{2+}. Compare also the behavior of neptunium (Fig. 21).

concentration ratio is given by the difference in the logarithmic concentration scales. The equilibrium concentrations of the different ions then corresponds to the point of intersection of the ion lines with a vertical line drawn through the intersection of the two lines representing the products formed. This can be exemplified using the reduction of NpO_2^+ by Fe^{2+}. Assume that a solution is prepared which initially contains 0·001 M NpO_2^+ and 0·2 M Fe^{2+} in 1 M acid, what will the equilibrium composition be?

The actual redox diagrams are shown in Fig. 16 shifted according to the concentrations. The products formed are Fe^{3+} and Np^{4+}, which will be produced in equal amounts (see reaction 1). A vertical line through the intersection of the Fe^{3+} and Np^{4+} lines shows that the equilibrium concentrations will be $[Fe^{2+}] \simeq 0{\cdot}2$ M, $[Fe^{3+}] = [Np^{4+}] \simeq 9 \times 10^{-6}$ M and the redox potential will be 610 mV.

Using the same kind of diagrams, with total concentrations of each valence state plotted instead of the concentrations of the free ions, it is possible to treat cases of combined complex formation and redox reaction, provided that changes in the concentration of free ligand, acidity, etc., are negligible (see section 3.4) or duly considered.

To facilitate these calculations the potentials of some common redox systems are given in Table 20. Figure 16 is a model diagram with potentials relative to $E°$ and containing curves corresponding to the typical redox systems given in Table 20.

For many practical purposes a potential pH diagram is very useful[102]. Figure 26 is an example of this type of diagram in which isoconcentration lines are used to show the composition at any pH and potential. Concentrations below 50 % are usually not shown as they would make the diagram too difficult to read. When constructing such diagrams it is important to include all relevant effects, i.e. pH-dependent potentials, hydrolysis and ionic medium effects.

3.4. Factors affecting redox equilibria

From eqn (3.8) it is evident that the relative concentration of a particular ion will

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[102] G. L. Silver, *Radiochem. Radioanal. Lett.* 7 (1971) 1. See also: M. Pourbaix, Atlas d'Equilibres Électrochimiques, Gauthier-Villars, Paris (1963).

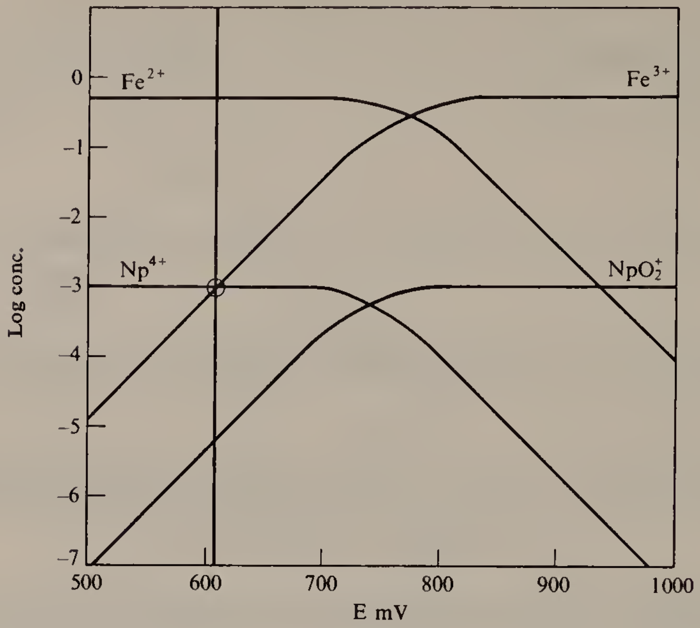

FIG. 16. Redox equilibrium after the reduction of 0·001 M Np(V) with 0·2 M Fe(II) in 1 M acid.

increase when its activity factor decreases. The mean activity factor $f_\pm$ in an ionic medium can be calculated from an extended Debye–Hückel equation[103,104].

$$\log f_\pm = \frac{a|z_1 z_2|\sqrt{I}}{1+b\sqrt{I}} + cI \tag{3.9}$$

In this equation a, b and c are adjustable parameters which are used to fit the equation to experimentally determined activity factors[105], z_1 and z_2 are the charges of the cation and anion of the neutral salt used and I is the ionic strength calculated from eqn. (3.10).

$$I = \frac{1}{2}\sum_i c_i z_i^2 \tag{3.10}$$

Here c_i is the total concentration of the ith ion with charge z_i and the summation is made over all types of ions in the solution.

Following Debye and Hückel[103] it is possible to assign individual activity factors f_z to the ions of charge z. Then for the purpose of estimation of f_z, f_z may be computed from eqn (3.11), which was derived from the assumption of an ionic medium, consisting of a 1:1 electrolyte, dominating the solution.

$$\log f_z = z^2 \log f_\pm \tag{3.11}$$

The validity of eqn (3.11) is questionable at high ionic strength, but lacking any better relation it has been used throughout section 3 for calculation of individual activity factors for ions.

From these equations it is evident that the activity factors will change more with the ionic strength the higher the ionic charge. Secondly the individual activity factors will

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[103] P. Debye and E. Hückel, *Physik. Z.* **24** (1923) 185.
[104] E. A. Guggenheim, *Phil. Mag.* **19** (1935) 588.
[105] R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, Butterworths, London (1959).

TABLE 20. STANDARD POTENTIALS FOR SOME COMMON REDOX REAGENTS
(The type given refers to the curves in Fig. 17. Data from refs. a and b.)

Reagent pair	Reaction	$E°$ (volt) ($I = 0$)	Type
O_3/O_2	$O_3(g)+2H^++2e^- = O_2(g)+H_2O$	2·07	const.
$S_2O_8{}^{2-}/SO_4{}^{2-}$	$S_2O_8{}^{2-}+2e^- = 2SO_4{}^{2-}$	2·01	special
Ce^{4+}/Ce^{3+}	$Ce(OH)^{3+}+H^++e^- = Ce^{3+}$	1·62	A+B
$BrO_3{}^-/Br_2$	$BrO_3{}^-+6H^++5e^- = \frac{1}{2}Br_2(l)+3H_2O$	1·52	H
$MnO_4{}^-/Mn^{2+}$	$MnO_4{}^-+8H^++5e^- = Mn^{2+}+4H_2O$	1·51	~H
$ClO_3{}^-/Cl_2$	$ClO_3{}^-+6H^++5e^- = \frac{1}{2}Cl_2(g)+3H_2O$	1·47	H
Cl_2/Cl^-	$\frac{1}{2}Cl_2(g)+e^- = Cl^-$	1·354	F
$NH_3OH^+/NH_4{}^+$	$NH_3OH^++2H^++2e^- = NH_4{}^++H_2O$	1·35	C+D
O_2/H_2O	$\frac{1}{2}O_2(g)+2H^{++}2e^- = H_2O$	1·229	const.
$IO_3{}^-/I_2$	$IO_3{}^-+6H^++5e^- = \frac{1}{2}I_2(s)+3H_2O$	1·195	H
Br_2/Br^-	$\frac{1}{2}Br_2(g)+e^- = Br^-$	1·0652	F
HNO_2/NO	$HNO_2+H^++e^- = NO(g)+H_2O$	1·00	K
$NO_3{}^-/N_2O_4$	$NO_3{}^-+2H^++e^- = \frac{1}{2}N_2O_4(g)+H_2O$	0·80	K
Fe^{3+}/Fe^{2+}	$Fe^{3+}+e^- = Fe^{2+}$	0·7701	A+B
I_2/I^-	$\frac{1}{2}I_2(s)+e^- = I^-$	0·0536	F
$SO_4{}^{2-}/SO_2$	$SO_4{}^{2-}+4H^++2e^- = H_2SO_3+H_2O$	0·17	C+D
Sn^{4+}/Sn^{2+}	$Sn^{4+}+2e^- = Sn^{2+}$	0·154	C+D
H^+/H_2	$H^++e^- = \frac{1}{2}H_2(g)$	0·0000	K
Ti^{4+}/Ti^{3+}	$Ti(OH)^{3+}+H^++e^- = Ti^{3+}+H_2O$	−0·055	A+B
Sn^{2+}/Sn	$Sn^{2+}=2e^- = Sn(s)$	−0·1406	J
Ti^{3+}/Ti^{2+}	$Ti^{3+}+e^- = Ti^{2+}$	−0·37	A+B
Cd^{2+}/Cd	$Cd^{2+}+2e^- = Cd(s)$	−0·4025	J
Cr^{3+}/Cr^{2+}	$Cr^{3+}+e^- = Cr^{2+}$	−0·41	A+B
Zn^{2+}/Zn	$Zn^{2+}+2e^- = Zn(s)$	−0·7628	J

[a] L. G. Sillén and A. E. Martell, *Stability Constants of Metal-ion Complexes*, Special publication No. 17, The Chemical Society, London (1964).

[b] L. G. Sillén and A. E. Martell, *Stability Constants of Metal-ion Complexes*, Supplement No. 1, Special publication No. 25, The Chemical Society, London (1970).

decrease at increasing but low ionic strength which results in a stabilization of the ions having the highest charge. Thus M^{4+} is favored at the expense of M^{3+}, MO_2^+ and MO_2^{2+}. As a result the relative amount of MO_2^+ decreases because both M^{4+} and MO_2^{2+} are more stabilized than MO_2^+. However, for many ionic media the last term in eqn (3.9) dominates at higher ionic strength and thus the activity factors increase again at higher ionic strength reversing the mentioned effects; M^{4+} then diminishes in importance and MO_2^+ gains in importance as does M^{3+}.

When -yl ions take part on one side in the reaction the potential of the reaction will depend on pH.

$$MO_2{}^++4H^++e^- \rightleftharpoons M^{4+}+2H_2O \tag{5}$$

The potential, $E_a°$, at $\{H^+\} = a$ and unit activities of MO_2^+, M^{4+} and H_2O is then

$$E_a° = E°+\frac{RT}{F}\ln a^4 \tag{3.12}$$

$E_a°$ can then be treated as a new standard potential for reaction (5), but valid only at the given hydrogen ion activity. This effect is illustrated in Fig. 18.

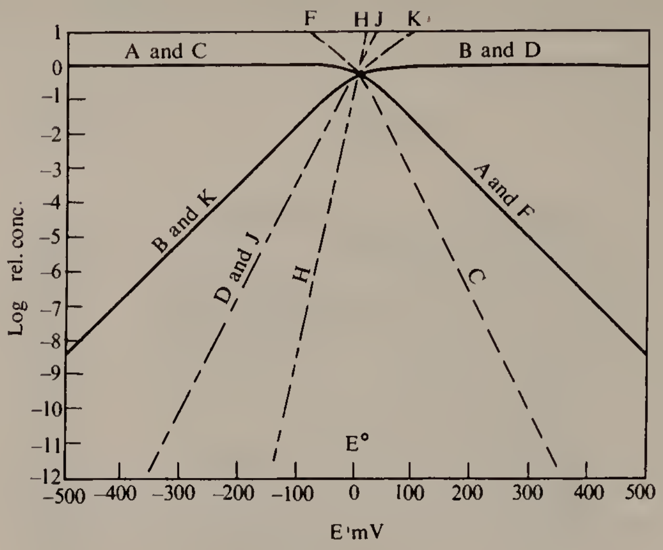

FIG. 17. Typical redox curves for some common reagents. The letters refer to Table 20.

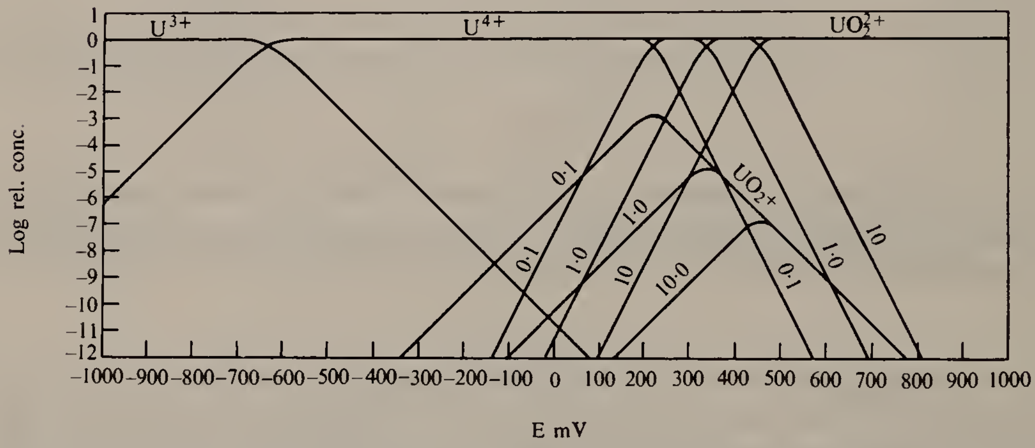

FIG. 18. Redox diagram for uranium showing the effect of hydrogen ion on the relative concentration of the free ions. $\{H^+\} = 0{\cdot}1,\ 1{\cdot}0,\ 10{\cdot}0$ M. At the lowest hydrogen ion concentration and at the highest concentration minor corrections were omitted for hydrolysis of U^{4+} and ionic strength respectively.

Besides ionic medium and pH effects there will be a tendency in most solutions for the formation of various complexes between the actinide ions and other chemical species present. This can be expressed by the general reaction (2.1), with its corresponding equilibrium constant β_n ($\beta_0 = 1$) expressed in concentration units. A series of complexes with n ranging from 1 to some upper limit N will be formed. N is determined by the coordination properties of L and the maximum coordination number of M. The total amount, $C_{M,z}$, of all forms in the valence state M^{z+} is then

$$C_{M,z} = [M^{z+}]X_z \tag{3.13}$$

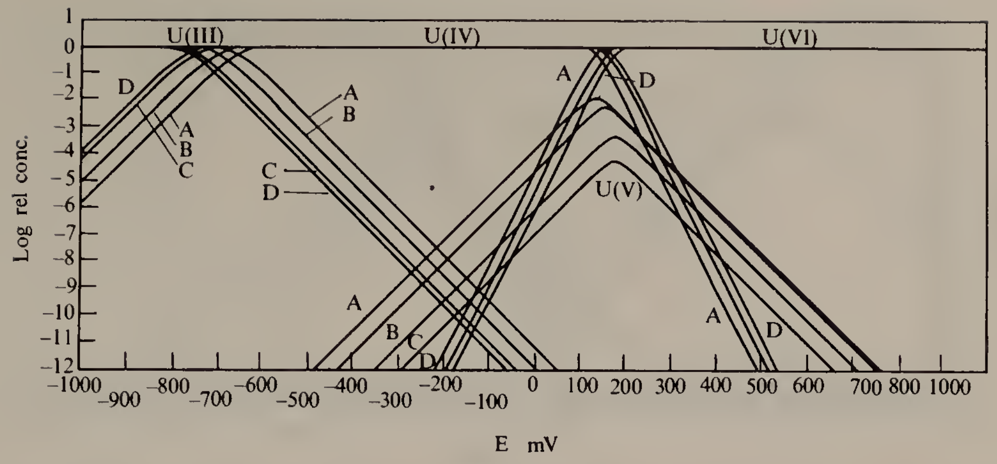

FIG. 19. The redox diagram for uranium (total concentrations) at pH = 2, $I = 1$ and $[SO_4^{2-}]$ = 0 (A), 0·01 (B), 0·1 (C), 0·33 M (D). The addition of sulphate increases the total amount of U^{4+} in various complexes at the expense of U^{3+}, UO_2^{+} and UO_2^{2+}. The effect would have been larger if the preferential hydrolysis of U^{4+} had not stabilized U(IV) even in the absence of sulphate. Data from Table 19 and refs. 37, 105, 118.

When this relation is introduced in eqn (3.8), the following expression for $\{M^{z_l+}\}/C_M$ is obtained

$$\frac{\{M^{z_l+}\}}{C_M} = \frac{1}{\sum_{z=z_l}^{z_h} \frac{X_z}{f_z} \exp\left(\sum_{n=z}^{z} \frac{F}{RT}(E-E_n^{\circ})\right)} \tag{3.14}$$

It is now evident that the formation of complexes affects the total amount of any ion involved in such a way that ions forming stronger complexes will increase in relative amount. Naturally the activity of the free ion will change in the opposite way. Figure 19 shows the stabilization of U(IV) which occurs when sulphate is added to the solution.

Solvent extraction and ion-exchange processes can be treated in a way similar to complex formation simply by introducing additional terms in the expression for X_z.

Earlier X_z was defined according to eqn (2.2). Assuming a second phase with a volume θ times the aqueous phase

$$\theta = V_{org}/V_{aq} \tag{3.15}$$

and partition constants for each species, λ_n, the expression for X_z will be

$$X_z = \sum_{n=0}^{N} (\theta\lambda_n + 1)\beta_n[L]^n = \sum_{n=0}^{N} \beta_n'[L]^n \tag{3.16}$$

Thus an extraction or ion-exchange process can be considered as a change in the relative magnitude of apparent stability constants, β_n', defined as

$$\beta_n' = (\theta\lambda_n + 1)\beta_n \tag{3.17}$$

Again redox diagrams constructed with total concentrations of each valence state can be used to predict the equilibrium composition. Figure 20 illustrates the combined effects of complex formation and solvent extraction.

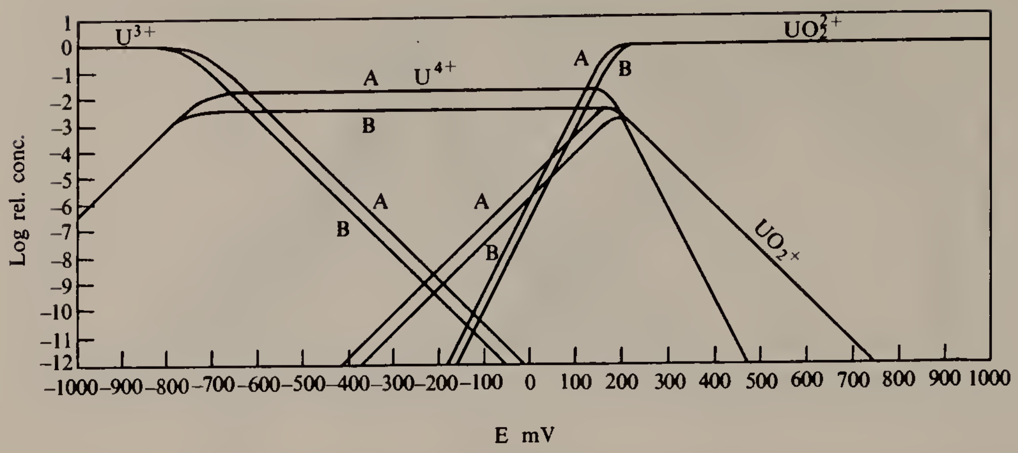

FIG. 20. The redox diagram for uranium (free ions in water) at pH = 2, $I = 1$ and in the presence of 0·2 M acetylacetone in the aqueous phase (A). When an equal amount of benzene (containing the appropriate amount of acetylacetone) is added to the aqueous phase, the new two-phase equilibria changes the redox equilibria to the curve marked B. As U^{4+} is preferentially extracted, its concentration in the aqueous phase decreases, but the potential range increases slightly. Data from Table 19 and refs. 37, 105, 118.

3.5. Redox diagrams

Using data from Table 19 a series of logarithmic redox diagrams have been constructed (Figs. 15 and 21–24 incl.). These will be of help in estimating the equilibrium composition in solutions of known redox potential or containing known amounts of other redox systems.

The effect of hydrogen ion concentration, complex formation, ionic medium and two-phase systems on the redox equilibria is discussed in section 3.4 above.

The redox diagrams for Pa, Bk, Md and No are quite simple with two oxidation states, of which one is completely dominant for acid solutions in equilibrium with air ($E \sim 1{\cdot}2$ in 1 M acid and $\sim 0{\cdot}36$ in 1 M NaOH). For this reason they are not given here.

The redox diagram for uranium (Figs. 15 and 26) shows clearly that UO_2^{2+} is the only stable species in aerated solution. It is also evident that the pentavalent ion UO_2^+ only occurs in minute amounts in acid solution. However, when the acidity of the solution decreases, the UO_2^+ ion will be more stable (see Fig. 18). For low acidities this tendency will change again as the hydrolysis of uranium will introduce new complexes stabilizing the more easily hydrolysed U^{4+} and UO_2^{2+} ions. This is the reason why UO_2^+ exhibits maximum stability around pH 2·5 in aqueous solutions free of other complexing agents. The tetravalent uranium ion U^{4+} has a fairly large range of redox potential and pH where it dominates in solution. It has, due to the high z/r, the strongest tendency among the uranium ions to form complexes with hard ligands. For this reason U^{4+} is, in most cases, greatly stabilized when complexing agents are present in the solution. U^{3+} is a sufficiently strong reducing agent to evolve hydrogen from water. To prepare solutions of U^{3+} the hydrogen ion concentration should thus be as low as possible to avoid H_2 formation and the activity of the U^{3+} ions reduced by the presence of strong complexing agents. The complexing agents must be chosen carefully as excessive complex formation with U^{4+} must be avoided and the pH must be sufficiently low to prevent hydrolysis (see Figure 26).

Neptunium occurs predominantly as NpO_2^+ in aqueous solutions that have been in contact with air for a long time (see Fig. 21). However, depending on the method of preparation, fresh solutions may also contain Np^{4+} or NpO_2^{2+}. Because of the comparatively

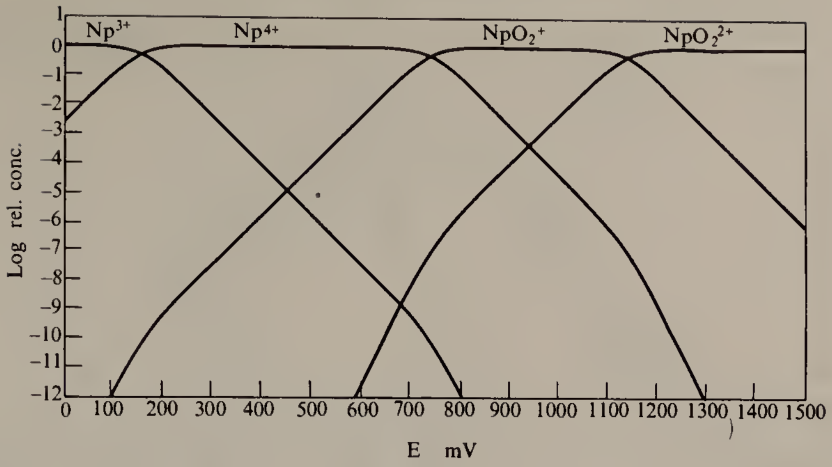

FIG. 21. The redox diagram for neptunium in 1 M $HClO_4$ and 25°C. Data from Table 19.

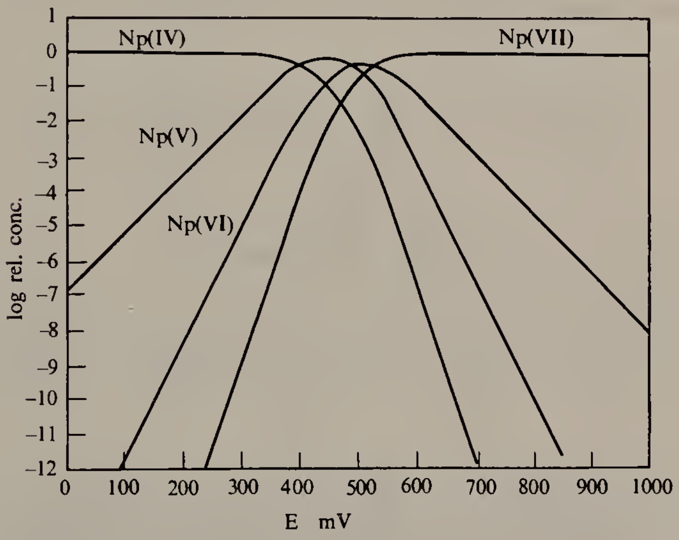

FIG. 22. The redox diagram for neptunium in 1 M NaOH and 25°C. Data from Table 19. Under these conditions the ions are strongly hydrolysed, precipitations may form etc. Np(VII) exists mainly as the anion NpO_5^{-3}.

slow reaction with air it will take a considerable time to convert Np^{4+} to NpO_2^+. As in the case of uranium, the stabilities and ranges of existence for NpO_2^+ and Np^{4+} depend on the acidity (see Fig. 27). The stability of NpO_2^+ is appreciably reduced in alkaline solution, where Np^{4+} is the most stable form, partly due to the different oxidizing ability of oxygen and partly due to the potential shift for the redox couple Np^{4+}/NpO_2^+, both caused by the large amount of OH^- ions present (see Fig. 22). Np^{3+} is more readily prepared than U^{3+} in acid solution; it is highly unstable in alkaline solution.

The plutonium ion expected to dominate in oxygenated 1 M acid aqueous solutions is Pu^{3+} (see Fig. 23). However, the closeness of the formal potentials in the Pu system makes the composition very sensitive to changes in acidity and to complex formation. Thus Pu^{3+} is the most stable ion in 1 M perchloric acid, but the presence of even a moderate amount of sulphate ions makes Pu^{4+} a more stable species. Hydrogen peroxide formed by radiolysis

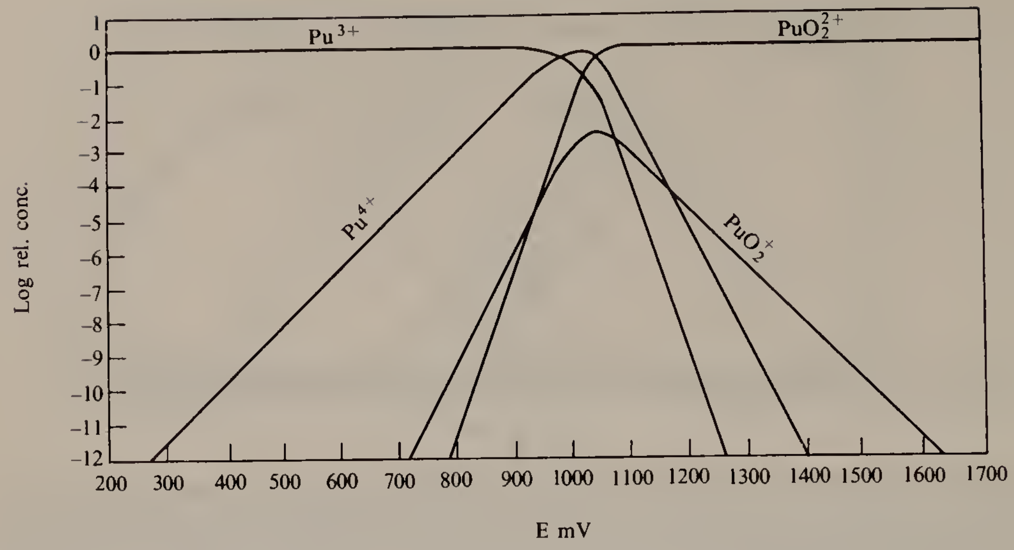

FIG. 23. The redox diagram for plutonium in 1 M $HClO_4$ and 25°C. Data from Table 19.

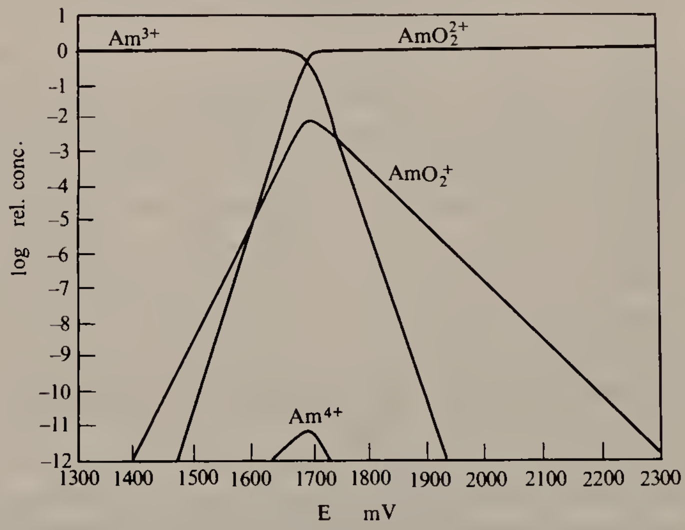

FIG. 24. The redox diagram for americium in 1 M $HClO_4$ and 25°C. Data from Table 19.

of water usually oxidizes some Pu^{3+} to Pu^{4+}. PuO_2^{2+} is less strongly oxidizing than NpO_2^{2+} but stronger than UO_2^{2+}. PuO_2^{2+} disproportionates to Pu^{4+} and PuO_2^{2+} in acid solution. It is more stable at low acidities (see Fig. 28). Pu^{4+} is stable in concentrated acids, but disproportionates to Pu^{3+} and PuO_2^{+} at lower acidities. Pu^{3+} is more stable (a weaker reducing agent) than both Np^{3+} and U^{3+}.

Americium exists in acid solutions in the absence of strong oxidizing agents, as Am^{3+}, which is the most stable oxidation state of americium (see Fig. 24 and cf. section 1.1). In the presence of strong oxidizing agents the ion AmO_2^{2+} predominates. AmO_2^{+} is only stable at lower acidities and never dominates in solution. At higher acidities AmO_2^{+} rapidly disproportionates to Am^{3+} and AmO_2^{2+}. Am^{4+} is not known in aqueous solutions, except as in the complex ion AmF_6^{2-}. As can be seen from Fig. 24, the maximum equilibrium fraction present as Am^{4+} is about 10^{-11}.

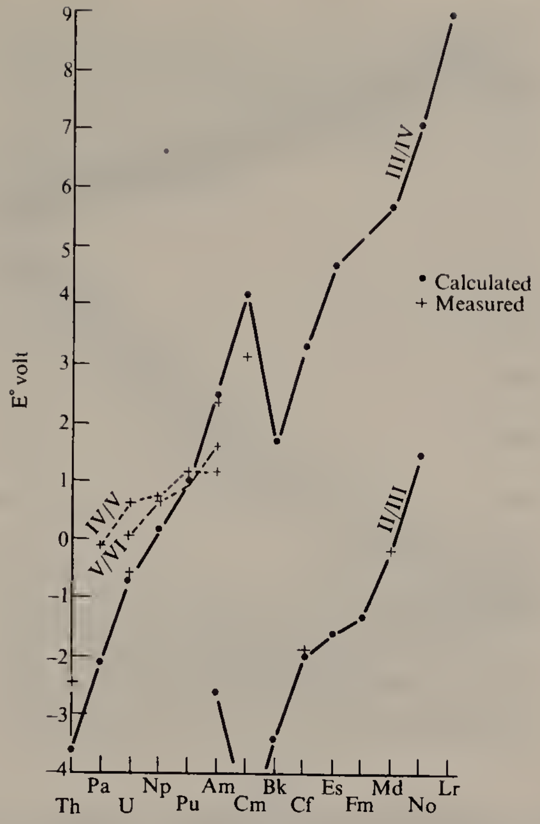

Fig. 25. Variation in redox potentials along the actinide series. (Measured values from Table 19. Calculated values from L. V. Nugent, R. D. Baybars and J. L. Burnett, *J. Phys. Chem.* **73** (1969) 1177 and from L. J. Nugent, R. D. Baybarz, J. L. Burnett and J. L. Ryan, *J. Inorg. Nucl. Chem.* 33 (1971) 2503.)

Thus there is an increasing stability of the M^{3+} ion along with the actinide series from protactinium to americium. This is shown in Fig. 25 where the formal potential of the M^{4+}/M^{3+} couple is plotted for these elements.

3.6. Potential pH diagrams

It has already been pointed out that hydrogen ions have a great influence on the composition of a solution at a given potential. This is due to a combination of three effects.

(a) The potential for one of the reactions changes with pH (see eqn 3.12).

(b) The ions involved hydrolyse to a different degree (see section 2.2.1). This changes the X_zs in eqn (3.14) and hence changes the relative amounts of the different oxidation states.

(c) The substitution of cations, e.g. H^+ for Na^+, in the ionic medium changes the activity factors, f_z, to some degree as the adjustable parameters a, b and c in eqn (3.9) changes slightly between an acid and its salt. The importance of this effect depends on the ionic strength and on the anion used in the ionic medium. When the f_zs change, the relative amounts of the different oxidation states change correspondingly according to eqn (3.14).

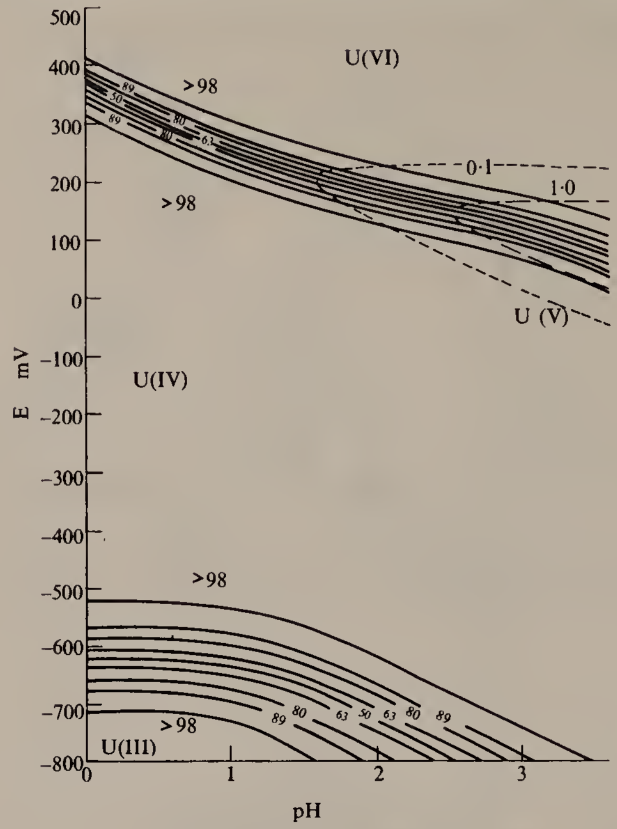

FIG. 26. The potential–pH diagram for uranium in 1 M (H,Na)ClO$_4$. Isoconcentration curves are drawn at 98, 89, 80, 63, 50, 1 and 0·1 % of the total concentration. Data from Table 19, and refs. 37, 105, 118. Hydrolysis data for U^{3+} are estimated from the lanthanides and from Pu^{3+}.

It is possible to construct a series of redox diagrams at a series of pH values with due consideration of the three effects mentioned and assuming a sufficiently low value for C_M so that polynuclear hydrolysis products are avoided. (If polynuclear species were included, C_M would have to be given a fixed value.) The results can be regarded as a three-dimensional potential concentration–pH diagram which gives excellent information about the composition at any potential and pH. Such diagrams are, however, generally not suited to presentation as two-dimensional projections, but with the sacrifice of some of the detail they can be reproduced as potential–pH diagrams with isoconcentration lines (see Figs. 26–28). In these diagrams isoconcentration lines have been drawn at 98, 89, 80, 63 and 50 % of C_M as indicated by the numbers on the curves. The 50 % lines separate areas where the indicated oxidation states dominate. For U(V) in Fig. 26, two dotted lines are drawn at 0·1 and 1 %, as this oxidation state never passes 10 % in this pH range.

The hydrolysis of U^{4+} prohibits the formation of larger amounts of U(V) as the pH dependence of the 50 % line between U(IV) and U(VI) becomes smaller. The hydrolysis of U^{4+} also decreases the amount of U(III), which is less prone to undergo hydrolysis.

Similar phenomena are observed in the neptunium system (Fig. 27) where they result in a narrow stability ridge for Np(IV) in an area of the diagram where Np(III) and Np(V) otherwise would have been the main constituents.

In the plutonium system, Pu(IV) does not undergo sufficient hydrolysis to make it the dominating species except in a very small area at low pH.

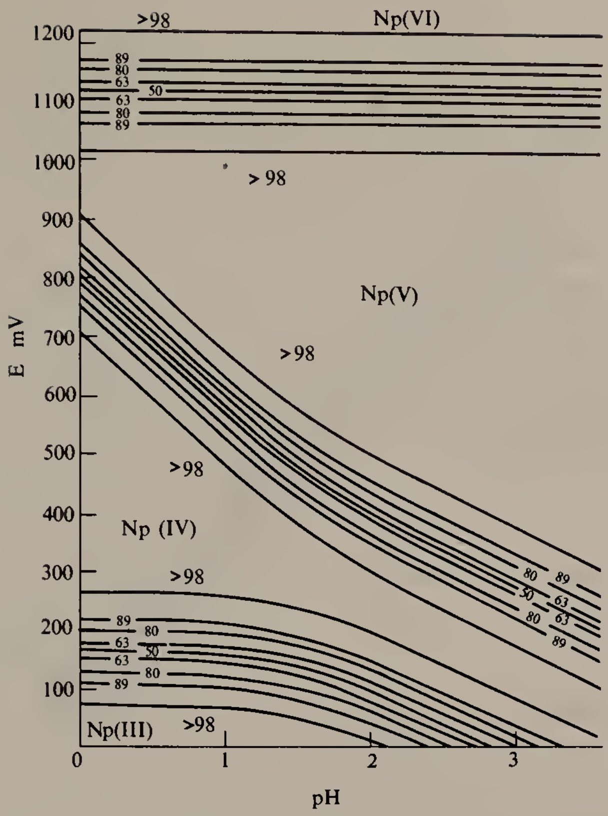

FIG. 27. The potential–pH diagram for neptunium in 1 M (H,Na)ClO$_4$. Isoconcentration curves are drawn at 98, 89, 80, 63 and 50% of the total concentration. Data from Table 19 and refs. 37, 105, 118.

3.7. Disproportionation

For some oxidation states disproportionation reactions occur. Equilibrium constants for these reactions are collected in Table 21. These constants can also be computed from the appropriate standard potentials given in Table 19.

The disproportionation tendencies in acid solutions are easily seen in Figs. 29a and b, where the free energy change from the metallic state is plotted against the oxidation number[106]. In these diagrams, oxidation states unstable to disproportionation lie above the tieline between any pair of lower and higher oxidation states. To show the importance of the hydrogen activity the free energy changes at four different hydrogen ion activities are given for each element. Hydrolysis effects are neglected in Figs. 29a and b, but they will not change the reasoning given below.

For uranium it can be seen that UO_2^+ is unstable with respect to disproportionation to U^{4+} and UO_2^{2+} even at pH 2. Above this pH the hydrolysis of U^{4+} and UO_2^{2+} will change the redox potentials in such a manner that a simple extrapolation to higher pH values is improper (see Figure 26).

The situation for neptunium is quite different. Only below a pH of −1 does the point representing NpO_2^+ fall above the tieline between Np^{4+} and NpO_2^{2+}. Thus NpO_2^+ is unstable to disproportionation in strong acids, but stable in more dilute acids. One would also expect that Np^{4+} was instable to disproportionation at pH > 3. But, as is the case with uranium, hydrolysis will interfere (see Fig. 27).

[106] E. A. V. Ebsworth, *Education in Chemistry*, 1 (1964) 123.

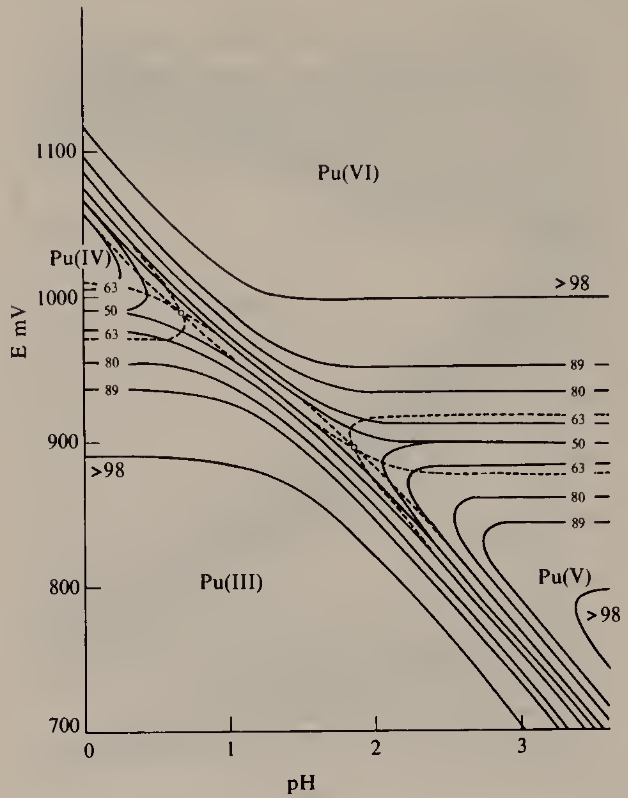

FIG. 28. The potential–pH diagram for plutonium in 1 M (H,Na)ClO_4. Isoconcentration curves are drawn at 98, 89, 80, 63, 50 and 33% of the total concentration. Data from Table 19 and refs. 13, 37, 105, 118. The two small circles indicate the two points where three of the oxidation states exist in equal amounts.

TABLE 21. DISPROPORTIONATION REACTIONS IN AQUEOUS SOLUTION

Element	Oxidation numbers	Reaction	Equilibrium constant at 25°C
U	V = IV+VI	$2UO_2^+ + 4H^+ = U^{4+} + UO_2^{2+} + 2H_2O$	log K = 9·30
Np	V = IV+VI	$2NpO_2^+ + 4H^+ = Np^{4+} + NpO_2^{2+} + 2H_2O$	log K = −6·72
Pu	V = IV+VI	$2PuO_2^+ + 4H^+ = Pu^{4+} + PuO_2^{2+} + 2H_2O$	log K = 4·29
	V = III+VI	$3PuO_2^+ + 4H^+ = Pu^{3+} + 2PuO_2^{2+} + 2H_2O$	log K = 5·40
	IV+V = III+VI	$Pu^{4+} + PuO_2^+ = Pu^{3+} + PuO_2^{2+}$	log K = 1·11
	IV = III+VI	$3Pu^{4+} + 2H_2O = 2Pu^{3+} + PuO_2^{2+}$	log K = −2·08
Am	IV+V = III+VI	$Am^{4+} + AmO_2^+ = Am^{3+} + AmO_2^{2+}$	log K = 12·5
	IV = III+VI	$3Am^{4+} + 2H_2O = 2Am^{3+} + AmO_2^{2+} + 4H^+$	log K = 32·5
	IV = III+V	$2Am^{4+} + 2H_2O = Am^{3+} + AmO_2^+ + 4H^+$	log K = 19·9

At high acidities PuO_2^+ can disproportionate both to Pu^{4+} and PuO_2^{2+} and to Pu^{3+} and PuO_2^{2+} as the point for PuO_2^+ (pH = −1) lies above the tielines between Pu^{3+} or Pu^{4+} and PuO_2^{2+}. When the pH is around 1 not only PuO_2^+ but also Pu^{4+} is unstable. Pu^{4+} can disproportionate to Pu^{3+} and PuO_2^+ or PuO_2^{2+}. In this very rare situation, we will have comparable amounts of four oxidation states of one element in one solution. At still higher

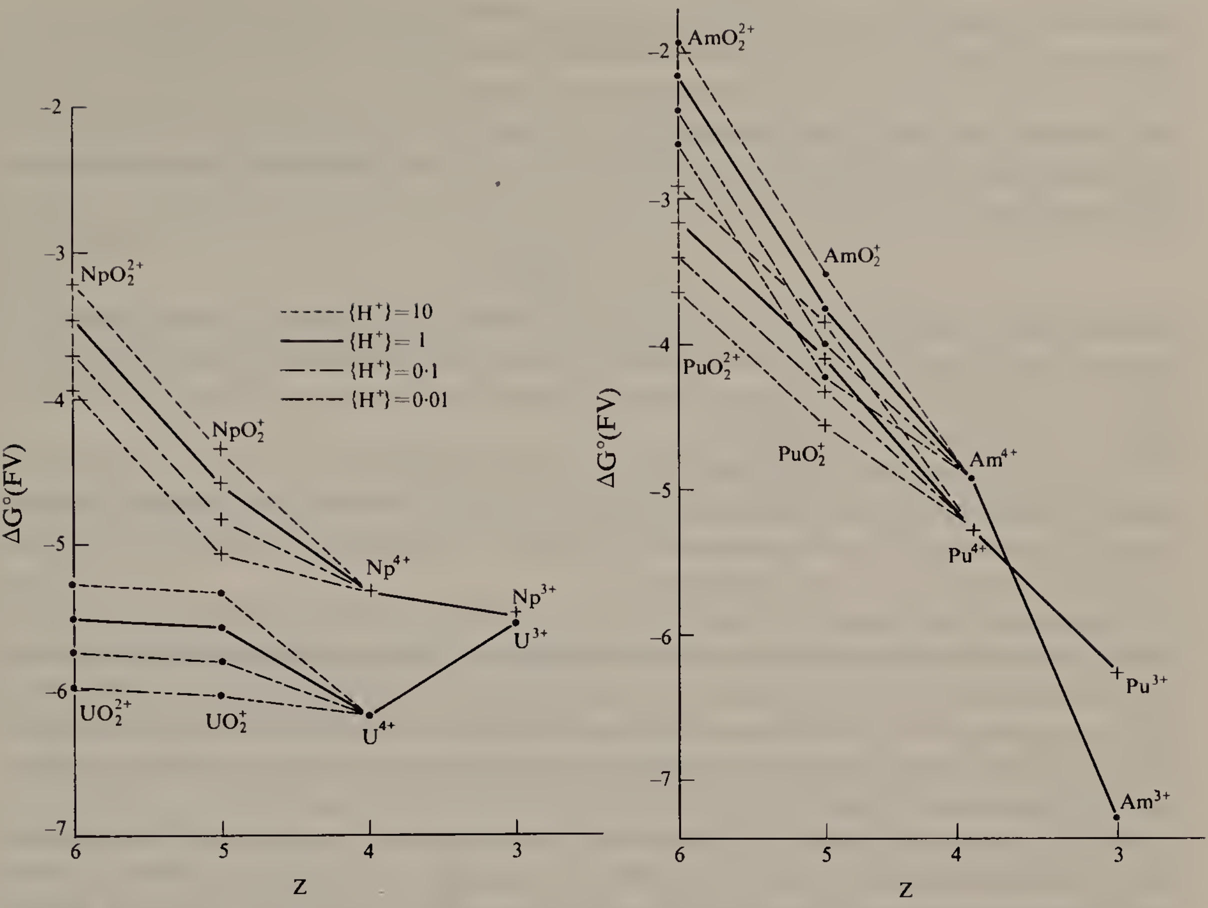

FIG. 29. Free energies of the half-reactions $M^0 \rightleftharpoons ze^- + M^{(z+)}$ in aqueous solution of different hydrogen ion activities at 25°C.

pH only Pu^{4+} can disproportionate to Pu^{3+} and PuO_2^+ or PuO_2^{2+}. Even at pH 2 hydrolysis becomes important for Pu^{4+}[107] (see Figure 28).

AmO_2^+ will disproportionate to AmO_2^{2+} and Am^{3+} at pH below ~ 1·5. Am^{4+} always disproportionates completely in acid solutions as it lies well above the corresponding tie-lines.

3.8. Redox kinetics and mechanisms

The transition from a starting composition to the equilibrium state in a redox system is a complicated process. It involves the formation of a special configuration, an activated complex, within which the charge transfer can occur. Afterwards the activated complex (A.C.) splits into the products of the reaction[108]. The activated complex often includes solvent molecules, hydrogen ions, and anions, besides the reacting metal ions. As the existence of this reacting structure is usually brief and consequently its concentration small, its composition cannot be directly determined, except in rare cases. The composition must

[107] O. Wick, *Plutonium Handbook*, Vol. I, p. 405. Gordon & Breach, New York (1967).

[108] S. Glasstone, K. J. Laidler and H. Eyring, *The Theory of Rate Processes*, McGraw-Hill, New York (1941).

therefore be elucidated from the form of the governing rate law. If we assume a reaction between A, B and C this may be formulated as follows[109].

$$aA + bB + cC = [A.C.] + dD + eE \tag{6}$$

The products D and E are thus assumed to separate in a time which is short compared to the existence of the activated complex. The rate of this reaction will then be proportional to the concentration

$$\text{rate} = \frac{k \cdot [A]^a[B]^b[C]^c}{[D]^d[E]^e} \tag{3.18}$$

Formulated in another way, a rate law (eqn 3.18) may be translated into an underlying reaction (reaction 6). However, even if the logical path from reaction to rate law is correct, the reverse procedure is not perfectly proved. Hence, care must be exercised when drawing chemical conclusions from rate laws.

Two types of activated complexes have to be considered. The first is the outer-sphere complex (see section 1.2) where the coordination shells are left intact. For reactions proceeding through outer-sphere complexes the rate of reaction usually increases when the reaction is more exothermic (ΔG° more negative)[110].

The second type is the inner-sphere complex, where the ligands of one of the reactants penetrates the coordination shell of the other reactant. These complexes are in some cases so long-lived that their existence can be proved by direct measurement as in the case of Cr(II) reduction of U(VI). When solutions of Cr(II) and U(VI) are mixed a green intermediate rapidly forms and then slowly decomposes into the reaction products, with an apparent half-time of several minutes[111].

In general, the M^{3+}–M^{4+} and MO_2^+–MO_2^{2+} reactions are reversible and rapid as they involve no bond changes. The rate is dependent on the type of reducing or oxidizing reagent used. Reagents where the reaction proceeds by two-electron or bond-breaking changes usually give a lower rate than simple one-electron reagents[112].

The M^{3+}–MO_2^+, M^{3+}–MO_2^{2+}, M^{4+}–MO_2^+ and M^{4+}–MO_2^{2+} reactions involve the formation and rupture of a metal–oxygen bond. This is the reason why they are not reversible and have lower rates than the simpler one-electron transfer reactions. Hydrogen ions are released in many of these reactions.

Some observed rate laws, rate constants and activation energies are collected in Table 22. It is evident from this table that the exponents for the hydrogen ion dependence found in the different rate laws usually differ from the number of hydrogen ions participating in the gross reaction. The oxidation of U^{4+} by PuO_2^{2+} involves the gross reaction

$$U^{4+} + 2PuO_2{}^{2+} + 2H_2O \rightleftharpoons UO_2{}^{2+} + 2PuO_2{}^{+} + 4H^+ \tag{7}$$

which would imply an inverse fourth power hydrogen ion dependence and a second order plutonyl(VI) dependence in the rate law. In fact only an inverse first-order dependence is found for hydrogen ions and a direct first-order dependence is found for PuO_2^{2+} [113]. This discrepancy is explained by assuming the formation of an activated complex according to reaction (8).

$$U^{4+} + PuO_2{}^{2+} + 2H_2O \rightleftharpoons [A.C.]^{5+} + H^+ \tag{8}$$

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[109] H. Taube, p. 1 in *Advances in Inorganic Chemistry and Radiochemistry*, Vol. 1, Academic Press, New York (1959).

[110] R. A. Marcus, *J. Phys. Chem.* **67** (1963) 853.

[111] T. W. Newton and F. B. Baker, *Inorg. Chem.* **1** (1962) 368.

[112] G. T. Seaborg, *Man-Made Transuranium Elements*, p. 87. Prentice-Hall, N.J. (1963).

[113] T. W. Newton, *J. Phys. Chem.* **62** (1958) 943.

Due to its high charge, the activated complex hydrolyses promptly, releasing the hydrogen ion as shown in reaction (8). The activated complex then exists as a binuclear metal complex for some time before the final break-up into the reaction products. By choosing suitable conditions it has been possible to show the existence of such binuclear complexes by spectrophotometric and EMF methods[114]. Thus the U(V)·U(VI), Np(V)·U(VI), Np(V)·Fe(III), U(V)·Cr(III) and Np(V)·Cr(III) entities have been identified (see section 2.2.4). This supports the conclusions about the binuclear activated complexes drawn from kinetic data.

However, as an alternative to reaction (8), a scheme has to be considered which involves hydrolysed U^{4+} species, e.g. reactions (9) and (10).

$$U^{4+} + H_2O \rightleftharpoons U(OH)^{3+} + H^+ \tag{9}$$

$$U(OH)^{3+} + PuO_2{}^{2+} + H_2O \rightleftharpoons [A.C.]^{5+} \tag{10}$$

Here the hydrogen dependence is explained as determining the concentrations of one of the reacting species, and there is no loss of hydrogen ions from the activated complex itself[115,116].

At present there is no strong evidence in favor of an interpretation according to reaction (8) or to reactions (9) and (10). In spite of the fact that much of the available experimental data have been interpreted and discussed in terms of reactions similar to (8), the second approach has some advantages and seems logically attractive.

Firstly it is known from fast kinetic studies that the exchange rate of the coordinated water molecules increases when the first complex has been formed between a metal ion and a ligand other than water[117]. Hence the rate of reaction (8) ought to be smaller than the rate of reaction (10) even when it is recognized that the two water molecules appearing on the left side of reaction (8) belong to the hydration shell of the reacting ions. It is also known that the presence of sulphate increases the rate, which further supports this mechanism. Secondly it is well known that the tetravalent cations, like U^{4+}, are hydrolysed to a considerable extent even at low pH. For example, about 25% of U(IV) is present as $U(OH)^{3+}$ at pH 1[118]. Reactions like (9) can be studied separately permitting prediction of the hydrogen dependence in the rate law.

In many cases non-integral hydrogen ion dependences are found. These are interpreted in terms of parallel or serial reactions involving the formation of more than one activated complex[114]. When only a single activated complex exists, only one reaction has to be considered. When two activated complexes occur, two different reaction patterns have to be considered, two parallel or two consecutive series of reactions. For three activated complexes four possible reaction patterns must be considered, for four activated complexes ten possible reaction patterns, etc. The multitude of alternatives obviously makes interpretation difficult for reactions with more than two activated complexes[119,120].

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[114] T. W. Newton and F. B. Baker, p. 268 in *Lanthanide/Actinide Chemistry*, Advances in Chemistry Series 71, American Chemical Society, Washington D.C. (1967).

[115] D. Benson, *Mechanisms of Inorganic Reactions in Solution*, McGraw-Hill, London (1968).

[116] J. C. Sullivan, A. J. Zielen and J. C. Hindman, *J. Am. Chem. Soc.* **82** (1960) 5288.

[117] H. Diebler, M. Eigen, G. Ilgenfritz, G. Maass and R. Winkler, *Proc. XIth Int. Conf. on Coord Chem.*, p. 95. Butterworths, London (1969).

[118] L. G. Sillén and A. E. Martell, *Stability Constants of Metal-ion Complexes*, Special publication No. 17, The Chemical Society, London (1964).

[119] L. G. Sillén and A. E. Martell, *Stability Constants of Metal-ion Complexes*, Suppl. No. Special Pub. No. 25, Chem. Soc. London (1970).

[120] O. Wick, *Plutonium Handbook*, Vol. I, p. 405. Gordon & Breach, N.Y. (1967).

TABLE 22. OBSERVED RATE LAWS, RATE CONSTANTS, ACTIVATION ENERGIES AND PROBABLE MECHANISMS (Data from ref. a)

Process	Reactant	Rate law	Rate const. k 1 M H^+, 25°C (in M and sec)	Activation energy kcal/mole	Mechanism
Oxidations of U(IV), $-d[U(IV)]/dt =$	U(VI)	$k[U(IV)]^{0\cdot93}[U(VI)]^{0\cdot92}[H^+]^{-3\cdot03}$	$2\cdot1\times10^{-7}$	38·0	$U^{4+}+UO_2^{2+}+2H_2O = 2UO_2^++4H^+$ $U^{4+}+UO_2^{2+}+2H_2O = [*]^{3+}+3H^+$ $U^{4+}+UO_2^{2+}+2H_2O = [*]^{3+}+3H^+$ $U^{4+}+UO_2^{2+} = UO_2^{2+}+U^{4+}$ $2U^{4+}+UO_2^{2+}+2H_2O = [*]^{6+}+4H^+$
	Np(IV)	$k[U(IV)][Np(IV)][H^+]^{-2\cdot5}$	$5\cdot0\times10^{-5}$	16·0	$Np^{4+}+U^{4+}+2H_2O = Np^{3+}+UO_2^++4H^+$ $Np^{4+}+U^{4+}+H_2O = [*]^{6+}+2H^+$
	Np(V)	$k[U(IV)][Np(V)][H^+]^{-2}$	$8\cdot0\times10^{-6}$	33·0	$NpO_2^++U^{4+} = Np^{4+}+UO_2^+$ $NpO_2^++U^{4+}+H_2O = [*]^{3+}+2H^+$
	Np(VI)	$k[U(IV)][Np(VI)][H^+]^{-0\cdot97}$	22·0	18·8	$U^{4+}+NpO_2^{2+}+2H_2O = UO_2^++NpO_2^+ +4H^+$ $U^{4+}+NpO_2^{2+}+H_2O = [*]^{5+}+H^+$
	Pu(IV)	$k[U(IV)][Pu(IV)][H^+]^{-1\cdot93}$	31·5	24·8	$U^{4+}+Pu^{4+}+2H_2O = UO_2^++Pu^{3+}+4H^+$ $U^{4+}+Pu^{4+}+H_2O = [*]^{6+}+2H^+$
	Pu(VI)	$k[U(IV)][Pu(VI)][H^+]^{-1\cdot2}$	3·1	19·1	$U^{4+}+PuO_2^{2+}+2H_2O = UO_2^++PuO_2^+ +4H^+$ $U^{4+}+PuO_2^{2+}+H_2O = [*]^{5+}+H^+$ $U^{4+}+PuO_2^{2+}+H_2O = [*]^{4+}+2H^+$
	V(V)	$k[U(IV)][V(V)][H^+]$	$2\cdot0\times10^4$	13·0	
	Ce(IV)	$k[U(IV)][Ce(IV)][H^+]^{-1\cdot2}$	$8\cdot7\times10^3$	15·4	$U^{4+}+CeOH^{3+}+H_2O = UO_2^++Ce^{3+}+ 3H^+$ $U^{4+}+CeOH^{3+}+H_2O = [*]^{6+}+H^+$
	ClO_2^-	$k[U(IV)][ClO_2^-][H^+]^{-0\cdot13}$	19·0	11·0	
	Fe(III)	$k[U(IV)][Fe(III)][H^+]^{-1\cdot81}$	12·8	23·6	$U^{4+}+Fe^{3+}+2H_2O = UO_2^++Fe^{2+}+4H^+$ $U^{4+}+Fe^{3+}+H_2O = [*]^{6+}+H^+$ $U^{4+}+Fe^{3+}+H_2O = [*]^{5+}+2H^+$
	H_2O_2	$k[U(IV)][H_2O_2][H^+]^{-0\cdot21}$(approx.)	$0\cdot8-2\cdot3$	16–19	
	BrO_3^-	$k[U(IV)][BrO_3^-][H^+]^{0\cdot43}$ or $[U(IV)][BrO_3^-](k_0+k_2[H^+]^2)$	$2\cdot6\times10^{-1}$ $2\cdot1\times10^{-1}$ (k_0) $5\cdot3\times10^{-2}$ (k_2)	27·2	$U^{4+}+BrO_3^- = [*]^{3+}$ $U^{4+}+BrO_3^-+2H^+ = [*]^{5+}+H_2O$
	Tl(III)	$k[U(IV)][Tl(III)][H^+]^{-1\cdot39}$	$3\cdot9\times10^{-2}$	22·5	$U^{4+}+Tl^{3+}+2H_2O = UO_2^{2+}+Tl^++4H^+$ $U^{4+}+Tl^{3+}+H_2O = [*]^{6+}+H^+$ $U^{4+}+Tl^{3+}+H_2O = [*]^{5+}+2H^+$
	O_2	$k[U(IV)][O_2][H^+]^{-1}$	$2\cdot4\times10^{-2}$	22·4	
	$S_2O_8^{2-}$	$k[U(IV)][S_2O_8^{2-}][H^+]^0$	$7\cdot2\times10^{-3}$	—	
	ClO_3^-	$k[U(IV)][ClO_3^-][H^+]^{+1}$	$2\cdot9\times10^{-3}$	—	
	Br_2	$k[U(IV)][Br_2][Br^-]^0[H^+]^{-2}$	$5\cdot3\times10^{-4}$	—	

Oxidations of U(V), $-d[\text{U(V)}]/dt =$	U(V)	$k[\text{U(V)}]^2[\text{H}^+]^{0\cdot82}$	$2\cdot4\times10^{2}$	$9\cdot0$	
	Fe(III)	$k[\text{U(V)}][\text{Fe(III)}]$	$5\cdot0\times10^{4}$	—	
	V(IV)	$k[\text{U(V)}][\text{V(IV)}][\text{H}^+]^{0\cdot2}$	$2\cdot5\times10^{4}$	—	
Reductions of U(VI), $-d[\text{U(VI)}]/dt =$	V(II)	$k[\text{U(VI)}][\text{V(II)}][\text{H}^+]^{0\cdot01}$	$7\cdot4\times10^{1}$	$7\cdot8$	$\text{UO}_2^{2+}+\text{V}^{2+} = \text{UO}_2^{+}+\text{V}^{3+}$ $\text{UO}_2^{2+}+\text{V}^{2+} = [*]^{4+}$
	V(III)	$k[\text{U(VI)}][\text{V(III)}][\text{H}^+]^{-1\cdot8}$	$2\cdot8\times10^{-1}$	$22\cdot1$	$\text{UO}_2^{2+}+\text{V}^{3+}+\text{H}_2\text{O} = \text{UO}_2^{+}+\text{VO}^{2+}+2\text{H}^+$ $\text{UO}_2^{2+}+\text{V}^{3+}+\text{H}_2\text{O} = [*]^{4+}+\text{H}^+$ $\text{UO}_2^{2+}+\text{V}^{3+}+\text{H}_2\text{O} = [*]^{3+}+2\text{H}^+$
	Sn(II)	$k[\text{U(VI)}][\text{Sn(II)}][\text{HCl}]^{-3\cdot5}$	$1\cdot7\times10^{-5}$	$18\cdot0$	
Oxidation of Np(III), $-d[\text{Np(III)}]/dt =$	Fe(III)	$k[\text{Np(III)}][\text{Fe(III)}][\text{H}^+]^{-0\cdot95}$	$6\cdot8\times10^{2}$	$15\cdot0$	$\text{Np}^{3+}+\text{Fe}^{3+} = \text{Np}^{4+}+\text{Fe}^{2+}$ $\text{Np}^{3+}+\text{Fe}^{3+}+\text{H}_2\text{O} = [*]^{5+}+\text{H}^+$
Reduction of Np(IV), $-d[\text{Np(IV)}]/dt =$	Cr(II)	$k[\text{Np(IV)}][\text{Cr(II)}][\text{H}^+]^{-1\cdot27}$	$4\cdot3$	$18\cdot0$	$\text{Np}^{4+}+\text{Cr}^{2+} = \text{Np}^{3+}+\text{Cr}^{3+}$ $\text{Np}^{4+}+\text{Cr}^{2+}+\text{H}_2\text{O} = [*]^{5+}+\text{H}^+$ $\text{Np}^{4+}+\text{Cr}^{2+}+\text{H}_2\text{O} = [*]^{4+}+2\text{H}^+$
Oxidations of Np(IV), $-d[\text{Np(IV)}]/dt =$	Np(V)	$k[\text{Np(IV)}]^{1\cdot5}[\text{Np(V)}]^{0\cdot5}[\text{H}^+]^{-2}$ $+k'[\text{Np(V)}]^2[\text{H}^+]$	$6\cdot45\times10^{-8}$ $1\cdot1\times10^{-5}$ (k')	$37\cdot4$ $18\cdot2$	$\text{Np}^{4+}+\text{NpO}_2^{+} = \text{NpO}_2^{+}+\text{Np}^{4+}$ $\text{Np}^{4+}+\text{NpO}_2^{2+}+\text{H}_2\text{O} = [*]^{4+}+2\text{H}^+$ $2\text{NpO}_2^{+}+\text{H}^+ = [*]^{3+}$
	Fe(III)	$k[\text{Np(IV)}][\text{Fe(III)}][\text{H}^+]^{-3}$	$5\cdot7\times10^{-2}$	$35\cdot0$	$\text{Np}^{4+}+\text{Fe}^{3+}+2\text{H}_2\text{O} = \text{NpO}_2^{+}+\text{Fe}^{2+}+4\text{H}^+$ $\text{Np}^{4+}+\text{Fe}^{3+}+2\text{H}_2\text{O} = [*]^{4+}+3\text{H}^+$
Reductions of Np(V), $-d[\text{Np(V)}]/dt =$	Np(III)	$k[\text{Np(V)}][\text{Np(III)}][\text{H}^+]^{1\cdot05}$	$4\cdot3\times10^{1}$	$6\cdot4$	
	Cr(II)	$k[\text{Np(V)}][\text{Cr(II)}][\text{H}^+]^{-1}$	$1\cdot1\times10^{3}$	—	
	V(III)	$[\text{Np(V)}][\text{V(III)}][\text{H}^+]^{0}$ $\times(k+k'[\text{Np(IV)}][\text{H}^+]^{-1\cdot5}/[\text{V(IV)}])$	$3\cdot0\times10^{-1}$ $6\cdot0\times10^{-2}$ $1\cdot6\times10^{-1}$ (k')	$15\cdot2$	$\text{NpO}_2^{+}+\text{V}^{3+}+2\text{H}^+ = \text{Np}^{4+}+\text{VO}^{2+}+\text{H}_2\text{O}$ $\text{NpO}_2^{+}+\text{V}^{3+} = [*]^{4+}$
	I	$k[\text{Np(V)}]^{0\cdot86}[\text{I}^-]^{1\cdot55}[\text{H}^+]^{2\cdot61}$	$1\cdot7\times10^{-3}$	$28\cdot3$	
Oxidations of Np(V), $-d[\text{Np(V)}]/dt =$	Np(VI)	$k[\text{Np(V)}][\text{Np(VI)}][\text{H}^+]^{0\cdot13}$	$9\cdot0\times10^{1}$	$10\cdot6$	$\text{NpO}_2^{+}+\text{NpO}_2^{2+} = \text{NpO}_2^{2+}+\text{NpO}_2^{+}$ $\text{NpO}_2^{+}+\text{NpO}_2^{2+} = [*]^{3+}$
	Cr(VI)	$k[\text{Np(V)}][\text{Cr(VI)}][\text{H}^+]^{-1\cdot6}/$ $(1+k'[\text{Np(VI)}][\text{H}^+]^{-1\cdot8}/[\text{Np(V)}])$	$4\cdot3$	$11\cdot6$	$\text{NpO}_2^{+}+\text{HCrO}_4^{-} = \text{NpO}_2^{2+}+\text{Cr(V)}$ $\text{NpO}_2^{+}+\text{HCrO}_4^{-}+2\text{H}^+ = [*]^{2+}+\text{H}_2\text{O}$ $2\text{NpO}_2^{+}+\text{HCrO}_4^{-}+4\text{H}^+ = [*]^{3+}+\text{NpO}_2^{2+}+2\text{H}_2\text{O}$
	V(V)	$k[\text{Np(V)}][\text{V(V)}][\text{H}^+]^{2\cdot3}$	$2\cdot0$	$11\cdot7$	
	NO_2^{-}–NO_3	$k[\text{Np(V)}][\text{H}^+]^{-4}$	$1\cdot0\times10^{-5}$	$12\cdot0$	

TABLE 22 (*cont.*)

Process	Reactant	Rate law	Rate const. k 1 M H^+, 25°C (in M and sec)	Activation energy kcal/mole	Mechanism
Reductions of Np(VI), –*d*[Np(VI)]/*dt* =	Np(IV)	$k[\text{Np(VI)}][\text{Np(IV)}][H^+]^{-2\cdot14}$	$4\cdot9\times10^{-2}$	25·5	$Np^{4+}+NpO_2^{2+}+2H_2O = 2NpO_2^{+}+4H^+$ $Np^{4+}+NpO_2^{2+}+H_2O = [*]^{4+}+2H^+$ $Np^{4+}+NpO_2^{2+}+H_2O = [*]^{4+}+2H^+$ $Np^{4+}+NpO_2^{2+}+H_2O = [*]^{3+}+3H^+$
	V(III)	$k[\text{Np(VI)}][\text{V(III)}][H^+]^{-1\cdot47}$	$2\cdot45\times10^{1}$	19·0	$NpO_2^{2+}+V^{3+}+H_2O = NpO_2^{+}+VO^{2+}+2H^+$ $NpO_2^{2+}+V^{3+} = [*]^{5+}$ $NpO_2^{2+}+V^{3+}+H_2O = [*]^{4+}+H^+$
	H_2O_2	$k[\text{Np(VI)}][H_2O_2][H^+]^{-1}/(1+k'[\text{Np(V)}]/[\text{Np(VI)}])$	8·9 1·9 (k')	12·4	$NpO_2^{2+}+H_2O_2 = NpO_2^{+}+HO_2+H^+$ $NpO_2^{2+}+H_2O_2 = [*]^{+}+H^+$ $2NpO_2^{2+}+H_2O_2 = [*]^{2+}+NpO_2^{+}+H^+$
Oxidations of Pu(III), –*d*[Pu(III)]/*dt* =	Pu(IV)	$k[\text{Pu(III)}]^{\sim1}[\text{Pu(IV)}]^{\sim0\cdot8}[H^+]^{-1}$	$1\cdot0\times10^{3}$	5·0	$Pu^{3+}+Pu^{4+} = Pu^{4+}+Pu^{3+}$ $Pu^{3+}+Pu^{4+}+H_2O = [*]^{6+}+H^+$
	Pu(V)	$k[\text{Pu(III)}][\text{Pu(V)}][H^+]^{0\cdot97}$	$4\cdot5\times10^{-2}$	—	
	Pu(VI)	$k[\text{Pu(III)}][\text{Pu(VI)}][H^+]^{0}$	2·7	5·4	
	O_2	$[\text{Pu(III)}]^2[O_2]^{1\cdot05}[H^+]^{-0\cdot1}$ $\times(k[SO_4^{2-}]^2+k'[SO_4^{2-}]^3)$	$6\cdot0\times10^{3}$ $1\cdot9\times10^{5}$ (k')	19·0	
	XeO_3	$k[\text{Pu(III)}][XeO_3][H^+]^{0}$	$1\cdot6\times10^{-2}$	—	
	Cl_2	$k[\text{Pu(III)}][Cl_2]^{0}[HCl]^{0}$ (?)	$7\cdot0\times10^{-6}$	15·0	
Reductions of Pu(IV), –*d*[Pu(IV)]/*dt* =	Pu(IV)	$k[\text{Pu(IV)}]^2[H^+]^{-3\cdot14}$	$5\cdot4\times10^{-5}$	—	$Pu^{4}+Pu^{4+}+2H_2O = PuO_2^{+}+Pu^{3+}+4H^+$ $Pu^{4+}+Pu^{4+}+2H_2O = [*]^{5+}+3H^+$
	Ti(III)	$k[\text{Pu(IV)}][\text{Ti(III)}][H^+]^{-1\cdot09}$	$6\cdot6\times10^{1}$	17·3	$Pu^{4+}+Ti^{3+}+H_2O = Pu^{3+}+TiO^{2+}+2H^+$ $Pu^{4+}+Ti^{3+}+H_2O = [*]^{6+}+H^+$
	V(III)	$k[\text{Pu(IV)}][\text{V(III)}][H^+]^{-1\cdot43}$	$6\cdot2\times10^{1}$	21·2	$Pu^{4+}+V^{3+}+H_2O = Pu^{3+}+VO^{2+}+2H^+$ $Pu^{4+}+V^{3+}+H_2O = [*]^{6+}+H^+$ $Pu^{4+}+V^{3+}+H_2O = [*]^{5+}+2H^+$
	Fe(II)	$k[\text{Pu(IV)}][\text{Fe(II)}][H^+]^{-0\cdot92}$	$4\cdot7\times10^{1}$	19·6	$Pu^{4+}+Fe^{2+} = Pu^{3+}+Fe^{3+}$ $Pu^{4+}+Fe^{2+}+H_2O = [*]^{5+}+H^+$
	Sn(II)	$k[\text{Pu(IV)}][\text{Sn(II)}][H^+]^{0}[Cl^-]^{1\cdot9}$	$1\cdot7\times10^{1}$	20·0	$Pu^{4+}+Sn^{2+}+5Cl^- = [*]^{+}$ $Pu^{4+}+Sn^{2+}+4Cl^- = [*]^{2+}$
Reductions of Pu(V), –*d*[Pu(V)]/*dt* =	Pu(V)	$k[\text{Pu(V)}]^2[H^+]^{1\cdot1}$	$8\cdot0\times10^{-3}$	19·6	
	Fe(II)	$k[\text{Pu(V)}][\text{Fe(II)}][H^+]^{\sim1}$	$3\cdot0\times10^{1}$	—	

Reductions of Pu(VI), $-d[\mathrm{Pu(VI)}]/dt =$	Fe(II)	$k[\mathrm{Pu(VI)}][\mathrm{Fe(II)}][\mathrm{H^+}]^{-0\cdot36}$	$1\cdot66\times10^3$	7·5	$PuO_2^{2+}+Fe^{2+} = PuO_2^{+}+Fe^{3+}$ $PuO_2^{2+}+Fe^{2+} = [*]^{4+}$ $PuO_2^{2+}+Fe^{2+} = [*]^{4+}$ $PuO_2^{2+}+Fe^{2+}+H_2O = [*]^{3+}+H^+$
	Ti(III)	$k[\mathrm{Pu(VI)}][\mathrm{Ti(III)}][\mathrm{H^+}]^{-1\cdot05}$	$1\cdot1\times10^2$	10·9	$PuO_2^{2+}+Ti^{3+}+H_2O = PuO_2^{+}+TiO^{2+}+2H^+$ $PuO_2^{2+}+Ti^{3+}+H_2O = [*]^{4+}+H^+$
	Sn(II)	$k[\mathrm{Pu(VI)}][\mathrm{Sn(II)}][\mathrm{H^+}]^{0}[\mathrm{Cl^-}]^{1\cdot46}$	$6\cdot7\times10^1$	10·6	$PuO_2^{2+}+Sn^{2+}+4Cl^- = [*]^0$ $PuO_2^{2+}+Sn^{2+}+3Cl^- = [*]^+$
	V(III)	$k[\mathrm{Pu(VI)}][\mathrm{V(III)}][\mathrm{H^+}]^{-1\cdot3}$	$2\cdot24$	16·1	$PuO_2^{2+}+V^{3+}+H_2O = PuO_2^{+}+VO^{2+}+2H^+$ $PuO_2^{2+}+V^{3+}+H_2O = [*]^{4+}+H^+$ $PuO_2^{2+}+V^{3+}+H_2O = [*]^{3+}+2H^+$
Reductions of Am(V), $-d[\mathrm{Am(V)}]/dt =$	Am(V) H_2O_2	$k[\mathrm{Am(V)}]^2[\mathrm{H^+}]^{2\cdot5}$ $k[\mathrm{Am(V)}][\mathrm{H_2O_2}][\mathrm{H^+}]^{-2}$	$5\cdot7\times10^{-4}$ $4\cdot1\times10^{-3}$		

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[a] T. W. Newton and F. B. Baker, p. 268 in *Lanthanide/Actinide Chemistry*, Advances in Chemistry Series 71, American Chemical Society, Washington D.C. (1967).

4. SOLVENT EXTRACTION

Solvent (or liquid–liquid) extraction is defined as the transfer of one or more solutes between two immiscible or partly miscible liquid phases[121]. Our *solutes* are the actinide ions. As liquid phases we shall in this section consider only the combination of an aqueous and an organic phase. Other combinations, such as molten salts and liquid metals, are treated elsewhere in this monograph. For simplicity we shall introduce the expression "inorganic (solvent) extraction" to define our area of interest, i.e. the distribution of inorganic solutes between water and organic solvent.

Because most inorganic species are only slightly soluble in inert organic solvents, the extraction can be carried out only through interaction with an organic molecule, the *extracting agent*. The organic phase may either be a pure extracting agent, or the agent may be dissolved in an inert organic *diluent*, such as kerosene or carbon tetrachloride. The term *extractant* is used both for the pure extracting agent and its organic solution[121]. Except for industrial processes, we shall here reserve the term extractant for the extracting agent only.

Inorganic solvent extraction may be carried out for preparative purposes, in which case the aim is to obtain the solute in a pure and concentrated form, the starting solution (the *feed*) normally being a dilute and impure aqueous solution. In analytical chemistry, using solvent extraction, the end product may be the solute in the organic phase (the *extract*), e.g. for colorimetric determination. The solute may be obtained from the organic phase by e.g. evaporation.

The evaporation step is often unsuitable in industrial extraction, and therefore the extract is washed with an aqueous *strip* solution, giving an aqueous solution containing the desired solute in a pure and concentrated form (section 4.8).

Solvent extraction is also used to investigate the species formed in the two phases. The *distribution ratio D* of the solute (defined by eqn 4.1) is then measured as a function of different variables, as for example the concentration of the metal ion or of the extractant. From the distribution curves (D as a function of some variable) conclusions can be drawn concerning the species present and their equilibrium constants can be determined (section 4.6).

Solvent extraction of actinides has been extensively used for both these purposes. This has in fact elevated inorganic solvent extraction from a little known analytical procedure to an important technique for studying inorganic solution chemistry as well as to an efficient unit process in industrial inorganic chemistry. The historically important relation between solvent extraction and actinide chemistry motivates a somewhat general treatment of the subject of inorganic solvent extraction.

4.1. Early inorganic extraction and the Nernst distribution law

The prime requirement for solvent extraction is the availability of only partially miscible solvents. Around 1800 the common solvents were water, alcohol, ether and "etheric oils". It is difficult to trace organic solvents much further back in history, although the requisites for producing a rather large variety of them had been at hand for almost ten centuries—water, bitumen, fat, oils, acids and distillation equipment. The reason for this difficulty

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[121] *Proc. Int. Solv. Extr. Conf., The Hague*, 1971, XXV. Chem. Ind., London (1971).

may simply be that the organic compounds obtained by distillation of mixtures of natural products were found to be rather uninteresting, because they had no practical value, nor could they be used to produce gold.

The early nineteenth century saw an enormous development in chemistry. Not only were numerous inorganic and organic compounds synthesized, they were also characterized through skillful analyses. Pure compounds, so necessary for the analyst, were identified from measurements of melting and boiling points, densities, refraction and crystal structure. It was then found that many inorganic salts, such as the chlorides of iron, mercury and gold, dissolved in, and could be recrystallized from, alcohols and ethers.

Inorganic extractions seem to have come into practical use without any great notice. Although E. Peligot in 1842 reported that uranyl nitrate could be recrystallized from ether[122], he never mentioned extraction of this salt from aqueous solutions. In textbooks from 1870, however, it is mentioned in passing that "ether even can withdraw sublimate" ($HgCl_2$) "from an aqueous solution"[123]. In 1867 W. Skey[124] had noticed that thiocyanates of some metals—among them uranium—are soluble in organic solvents, and proposed the use of solvent extraction to separate these metals from each other and from other elements. The technique was applied some years later by H. Vogel[125], who observed that cobalt thiocyanate is weakly extracted by ether, better by amyl alcohol, but much better by an equal mixture of both. This may be the first account of a *synergistic extraction* (see section 4.5.3), although that term was not introduced in solvent extraction until 1957[126,127,128].

The practical use of solvent extraction for separation and purification of different substances led E. M. Berthelot and E. C. Jungfleisch[129] to investigate the distribution of a large number of organic and inorganic compounds between ether, or carbon disulphide, and water. On the basis of these results Berthelot in 1872 proposed a law $D_X = a + b\,[X]$, where D_X (*coefficient de partage*) is the measured distribution ratio of the compound X between the organic and the aqueous phase (the *distribution factor*):

$$D_X = \frac{C_{X,org}}{C_{X,aq}} \tag{4.1}$$

where C_X refers to the concentration of all species of X in the phase indicated. Because a and b are constants, which are different for each system, much futile work was carried out to find connections between these constants and the kind of solutes extracted. About 20 years later W. Nernst realized that one had to take into account the different reactions of the solute in each phase, such as dimerization in the organic phase and dissociation in the aqueous phase. If the solute, however, had the same molecular weight (*Molekulargrosse*) in the organic and aqueous phases, the distribution should be independent of the concentration of the solute. Thus in 1891, W. Nernst[130] arrived at the much simpler relation

$$K_d = \frac{[X]_{org}}{[X]} \tag{4.2}$$

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[122] E. M. Peligot, *Ann. Chim.* **5** (1842) 5.

[123] N. J. Berlin and C. W. Blomstrand, *Oorganisk kemi*, Lund (1870).

[124] W. Skey, *Chem. News*, **16** (1867) 201.

[125] H. Vogel, *Ber. Chem. Ges.* **12** (1879) 2312.

[126] J. M. Schmitt, reported by K. B. Brown, C. F. Coleman, D. J. Crouse and A. D. Ryan, in USAEC Report ORNL-2346 (1957).

[127] H. Irving, ref. 128, p. 91.

[128] D. Dyrssen, J. O. Liljenzin and J. Rydberg (Eds.), *Solvent Extraction Chemistry*, North-Holland, Amsterdam (1967).

[129] E. M. Berthelot and E. C. Jungfleisch, *Ann. Chim. Phys.* **26** (1872) 396; E. M. Berthelot, *ibid.* 508.

[130] W. Nernst, *Z. phys. chem.* **8** (1891) 110.

where 'org' refers to the organic phase. Nernst proved his equation to be valid for the extraction of a number of organic acids, which either dimerized in the organic phase or dissociated in the aqueous phase, the dimerization and dissociation being determined from vapor pressure and conductivity measurements. For acetic acid, HA, in the two-phase system benzene–water, he could write the expression

$$D_A = \frac{[HA]_{org}+2[H_2A_2]_{org}}{[HA]+[A^-]} \tag{4.3}$$

Introducing

$$K_d = [HA]_{org}/[HA] \tag{4.4}$$

and

$$K_a = [H^+][A^-]/[HA] \tag{4.5}$$

and

$$k' = [H_2A_2]_{org}/[HA]_{org}^2 \tag{4.6}$$

for the distribution, dissociation and dimerization of acetic acid, one arrives at the expression

$$D_A = \frac{K_d(1 + 2k' \cdot K_d[HA])}{(1 + K_a[H^+]^{-1})} \tag{4.7}$$

Having determined k' and K_a separately, Nernst could verify this expression although he did not write out eqn (4.7) *in extenso*.

The validity of the Nernst eqn (4.2) was extended to metal salts in 1902. From measurements of the distribution of divalent mercury between toluene and water of various Hg^{2+} and Cl^- concentrations, H. Morse[131] determined the formation constants (β_1 and β_2) of $HgCl^+$ and $HgCl_2$, as well as the distribution constant of the neutral complex $HgCl_2$ (K_d).

The Nernst distribution law can be derived from thermodynamic considerations using the free energy concept[132]. At equilibrium, the chemical potential μ_X of a solute X must be the same in both phases of a two-phase liquid–liquid system, e.g. water (aq) and organic solvent (org):

$$\mu_X(aq) = \mu_X(org) \tag{4.8}$$

Because

$$\mu_X = \mu_X^\circ + RT \ln a_X \tag{4.9}$$

for each phase, one obtains

$$\mu_X^\circ(aq) + RT \ln a_X(aq) = \mu_X^\circ(org) + RT \ln a_X(org) \tag{4.10}$$

where the reference standard states μ°_X are different in the two phases, and a_X is the chemical activity of X, defined by

$$a_X = f_X[X] \tag{4.11}$$

where f is the activity factor. Simplifying eqn (4.10) and introducing eqn (4.11) gives

$$a_X(org)/a_X(aq) = \exp\,[\mu_X^\circ(aq) - \mu_X^\circ(org)]/RT = K_d^* \tag{4.12}$$

Although the ratio activities of X in the two phases must be constant, the K_d^* value depends on the choice of standard states, and can be given any constant value, in principle. Of practical importance, however, is the relation between K_d^* and the commonly measured

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[131] H. Morse, *Z. phys. chem.* **41** (1902) 709.

[132] G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*. McGraw-Hill, New York (1923).

(concentration) distribution constant K_d

$$K_d = K_d^* \cdot f_X(\text{aq})/f_X(\text{org}) \tag{4.13}$$

as obtained through the relations (4.11), (4.12) and

$$K_d = \frac{[X]_{org}}{[X]_{aq}} \tag{4.14}$$

the last equation being identical to (4.4). It is important to observe in eqn. (4.13) that K_d is proportional to the inverse ratio of the activity coefficients in the two phases.

4.2. Development of metal extractants

In the early nineteenth century it was observed that many metals reacted with organic compounds to form colored complexes, which were soluble in organic solvents. In these complexes—later to be called *chelates*[133]—the metal atom is bound to at least two donor atoms (O, O; O, N; S, N; etc.) linked together through a hydrocarbon chain. The specific significance of the cyclic structure of metal chelates was discussed in 1904 by H. Ley[134]. Chelating agents can be made highly selective for certain metals through variation of donor atoms, donor strength and ring structure (section 4.5.3). This has led to their extensive use in analytical chemistry for separating different metals, which is the subject of several excellent monographs[135–139].

The first publication on chelate extraction was probably that of P. Cazeneuve in 1900[138,140], who extracted aqueous Cr(III) by a solution of diphenylcarbazide in benzene. Important new chelating agents have been introduced successively: cupferron in 1917[141], dithizone in 1933[142], and thenoyltrifluoroacetone (HTTA) in 1950[143]. The latter reagent was developed specifically for extracting actinides from solutions acidic enough to avoid hydrolysis of the metals.

In the early works the analytical application of chelate extractions was the main interest, and optimal extraction or separation conditions were obtained empirically. The first quantitative description of metal chelate extraction was given in 1941 by Kolthoff and Sandell[144] for the system Zn(II)–dithizone–water–chloroform. Further developments towards a general mathematical description of chelate extraction were provided by Connick and McVey[145], Furman, Mason and Pekola[146], Rydberg[147,148] and Irving, Rossotti and Williams[149]. This theory is outlined in section 4.6.2. It will be shown that from studies of the

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[133] G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.* **117** (1920) 1456.

[134] H. Ley, *Z. Elektrochemie*, **10** (1904) 954.

[135] A. E. Martell and M. Calvin, *Chemistry of the Metal Chelate Compounds*, Prentice-Hall, New York (1952).

[136] G. H. Morrison and H. Freiser, *Solvent Extraction in Analytical Chemistry*, Wiley & Sons, New York (1957).

[137] J. Stary, *Extraction of Metals*, Pergamon Press, Oxford (1964).

[138] Yu. A. Zolotov, *Extraction of Chelate Compounds*, Humprey Science Publ., Ann Arbor (1970).

[139] A. K. De, S. M. Khopkar and R. A. Chalmers, *Solvent Extraction of Metals*, Van Nostrand/Reinhold, London (1970).

[140] P. Cazeneuve, *Compt. Rend.* **131** (1900) 346.

[141] O. Bandish and R. Fürst, *Chem. Ber.* **50** (1917) 234.

[142] H. Fischer, *Angew. Chemie*, **46** (1933) 442; **47** (1934) 685.

[143] J. C. Reid and M. Calvin, *J. Am. Chem. Soc.* **72** (1950) 2948.

[144] I. M. Kolthoff and E. B. Sandell, *J. Am. Chem. Soc.* **63** (1941) 1906.

[145] R. Connick and W. McVey, *J. Am. Chem. Soc.* **71** (1949) 3182.

[146] N. H. Furman, W. B. Mason and J. S. Pekola, *Anal. Chem.* **21** (1949) 1325.

[147] J. Rydberg, *Acta Chem. Scand.* **4** (1950) 1503.

[148] J. Rydberg, *Arkiv Kemi*, **8** (1955) 101, 113.

[149] H. Irving, R. J. P. Williams and F. J. C. Rossotti, *J. Chem. Soc.* **1955**, 1906.

dependence of D upon the concentration of the metal, the extractant, pH, etc., it is possible to identify the metal species in the two phases. The equilibrium constants can then be obtained by different graphical or numerical methods[150,151].

Because of the usually low solubility of metal chelates both in water and in organic solvents, radioactive tracers have been used extensively in these studies. In order to extend the results from trace to macro-concentrations, one must be certain that the Nernst distribution law holds throughout the whole concentration range. This was proved by Grahame and Seaborg[152] in 1938 for the extraction of the $^{67+68}$Ga(III) chloride complex into diethylether in the concentration range C_{Ga} 10^{-12} to 10^{-3} M.

Radiotracer work is particularly suitable for solvent extraction because the distribution ratio D is easily determined by measurement of the radioactivity of each phase. The simplicity of the technique and its validity both for trace and macro-concentrations are probably the main reasons why solvent extraction has been so widely used in actinide research.

The first large-scale industrial solvent extraction process was used in the production of ton amounts of high-purity uranium in 1942 by the Mallinckrodt Chemical Company in St. Louis, where ether was employed to extract uranyl nitrate selectively from impure aqueous solutions[153]. Ether was later replaced by dibutylcarbitol (DBC, butex) and methylisobutylketone (MIBK, hexone) for uranium purification[154], and the same solvents were subsequently used in the Redox and Butex processes for plutonium isolation[155,156] (section 4.8).

The continued search after the war for improved extractants led to the development of two new types of extracting reagents, the organophosphorus compounds and the alkylamines.

The organophosphorus extractants were introduced by Warf[157] in 1945, who found that Ce(IV), Th(IV) and U(VI) in nitric acid could be extracted by an organic phase consisting of pure tributylphosphate (TBP). TBP was not only found to be chemically more resistant than the previously used ether, it also had superior extracting properties as compared to most ethers, ketones and other extractants with carbon bonded oxygen donor atoms. TBP was almost immediately employed for separation of U(VI) and Pu(IV) from fission products (the Purex process)[158,159]. This compound and other types of organophosphorus compounds, such as trioctylphosphine oxide (TOPO) and di-2-ethylhexyl-phosphoric acid (HDEHP), have been developed and intensively studied, e.g. by Moore[160], Mason and Peppard[161], Siddall[162] and others of the U.S. Atomic Energy Commission's research

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[150] F. J. C. Rossotti and H. Rossotti, *The Determination of Stability Constants*, McGraw-Hill, New York (1961).

[151] M. T. Beck, *Chemistry of Complex Equilibria*, Van Nostrand/Reinhold, London (1970).

[152] D. Grahame and G. Seaborg, *J. Am. Chem. Soc.* **60** (1938) 1027; *Phys. Rev.* **60** (1941) 909.

[153] R. G. Hewlett and O. E. Andersson, *The New World, 1939/1946*, The Pennsylvania State University Press, University Park (1962).

[154] D. E. Ferguson and E. L. Nicholson, USAEC Report ORNL-715 (1950).

[155] F. L. Culler, *Proc. Int. Conf. Peaceful Uses of Atomic Energy*, Vol. 9, p. 464, Geneva (1956).

[156] O. J. Wick (Ed.), *Plutonium Handbook*, Gordon & Breach, New York (1967).

[157] J. C. Warf, *J. Am. Chem. Soc.* **71** (1949) 3257.

[158] D. E. Ferguson and T. C. Runion, USAEC Report ORNL-260 (1949).

[159] J. R. Flanary, *Proc. Int. Conf. Peaceful Uses of Atomic Energy*, Vol. 9, p. 528, Geneva (1956).

[160] R. L. Moore, USAEC Report AECD-3196 (1947); Report ORNL-1314 (1952).

[161] G. W. Mason and D. Peppard, *Nucl. Sci. Eng.* **17** (1963) 247; see also D. Peppard, *Adv. Inorg. Radiochem.* **9** (1966) 1.

[162] T. H. Siddall, *Proc. Int. Conf. Peaceful Uses of Atomic Energy*, Vol. 17, p. 339, Geneva (1959).

laboratories[156,163], by McKay[164] and co-workers at the U.K. Atomic Energy Research Establishment at Harwell, by Shevchenko and Russian co-workers[165,166], and others[156,163,167].

The large organic cationic alkylamine extracting reagents were introduced by Smith and Page[168] in 1948 and developed particularly for industrial uranium recovery by research groups at the Oak Ridge National Laboratory[169]. Almost simultaneously, Tribalat[170] showed the extraction properties of the similar tetraphenylphosphonium and tetraphenylarsonium cations. These compounds are all known as liquid anion exchangers, because they form ion pairs with exchangeable anions, including anionic metal complexes, which are soluble in organic solvents. Trioctylamine (Alamine 336 and Adogen 364) dissolved in kerosene is now the principle extractant for uranium recovery from sulphuric acid-leached ores[171], and the same or other amines are increasingly used in the separation of actinides from fission products[172].

4.3. Solvent properties

Some common organic solvents used for the extraction of metal complexes are listed in Table 23. They all have a low solubility in water; the low polar (low dipole moment and low dielectric strength) solvents, which do not contain oxygen atoms (which may form hydrogen bonds with water), have the lowest solubility, and also dissolve less water than the other solvents. For similar solvents, like diethylether and di-i-propyl ether, the one with the higher molecular weight usually has the lower solubility in water, and also dissolves less water. This size effect is probably related to hydrophobic bonding[173], which is a structuring of water molecules around organic hydrocarbon molecules because of H_2O–H_2O interaction and H_2O–hydrocarbon non-interaction. This lowers ΔS, and thus requires energy ($\Delta G > 0$). Consequently hydrophobic bonding opposes the dissolution of large organic molecules more than the dissolution of small organic molecules.

Many attempts have been made to systematize solvent (liquid) properties. Ewell, Harrison and Berg[174] divide liquids into five classes:

Class 1: Liquids capable of forming three-dimensional networks of strong hydrogen bonds, e.g. water, poly- and amino-alcohols, hydroxy acids, etc.

Class 2: Other liquids having both active hydrogen atoms and donor atoms (O, N, F),

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[163] J. T. Long, *Engineering for Nuclear Fuel Reprocessing*, Gordon & Breach, New York (1967).

[164] H. A. C. McKay, *Proc. Int. Conf. Peaceful Uses of Atomic Energy*, Vol. 7, p. 314, Geneva (1956); ref. 128, p. 185; H. A. C. M. and T. V. Healy, *Process Chemistry*, **2** (1958) 546.

[165] K. A. Petrov, V. Shevchenko, *et al.*, *Russ. J. Inorg. Chem.* **5** (1960) 237.

[166] A. V. Nikolaeva (Ed.), *Ekstraktsiya Neorganischeskib Veshchestv*, Izdatetstvo Nauka, Novosibirsk (1970).

[167] Y. Marcus and S. Kertes, *Ion Exchange and Solvent Extraction of Metal Complexes*. Wiley-Interscience, London (1969).

[168] E. L. Smith and J. E. Page, *J. Chem. Soc. Ind.* (*London*), **67** (1948) 48.

[169] C. F. Coleman, K. B. Brown, J. G. Moore and D. J. Crouse, *Ind. Eng. Chem.* **50** (1958) 1756.

[170] S. Tribalat, *Anal. Chim. Acta*, **3** (1949) 113; **4** (1950) 228.

[171] J. House, General Mills Chem., Minneapolis, private communication (1971); J. W. Barnes, *Proc. Int. Conf. Peaceful Uses of Atomic Energy*, Vol. 3, p. 183, Geneva (1958).

[172] C. F. Coleman, *Process Chemistry*, **4** (1970) 233 (*Progress in Nuclear Energy*, Series III, Pergamon, Oxford).

[173] A. K. Covington and P. Jones (Eds.), *Hydrogen Bonded Solvent Systems*, Taylor & Francis Ltd., London (1968).

[174] R. H. Ewell, J. M. Harrison and L. Berg, *Ind. Eng. Chem.* **36** (1944) 871.

TABLE 23. PHYSICAL PROPERTIES OF SOME COMMON SOLVENTS

Compound	Mole weight	Density g/cm³	B.p. °C	Dipole moment	Diel. const.	Solub. vol. % Comp. in aq.	Solub. vol. % Water in org.
Water	18	1·0	100·0	1·85	81	—	—
Carbon tetrachloride	153·8	1·59	76·5	0·0	2·24	0·077	0·009
Chloroform	119·4	1·45	61·3	1·15	4·90	0·705	0·702
Dichloroethane	98·9	1·18	57·3	1·99	10·0	0·05	≤0·1
n-Butyl alcohol	74·1	0·81	117·7	1·68	16·1	7·31	20·4
n-Octyl alcohol	130·2	0·82	195·2	1·68	10·3	0·05	<5
Diethyl ether	74·1	0·72	34·6	1·15	4·33	6·04	1·26
Di-i-propyl ether	102·2	0·73	68·4	1·20	4·04	1·2	0·63
Dichloroethyl ether, CH_3CHCl_2	143·0	1·22	178·0	2·58	21·2	1·12	0·28
Dibutyl carbitol	218·3	0·89	254·6	1·83		0·3	1·4
Di-i-butyl ketone	142·2	0·81	168·1		2·74	0·06	0·45
Methyl-i-butyl ketone	100·1	0·80	115·9	2·79	13·11	1·7	1·9
Tributyl phosphate	267·0	0·97	289·0	3·0	8·0	0·04	6·4
n-Hexane	86·2	0·66	68·7	0·0	1·91	0·001	0·02
n-Octane	114·2	0·70	125·0	0·0	1·95	0·0001	
Cyclohexane	84·2	0·87	80·7	0·0	2·10	0·006	0·02
Benzene	78·1	0·88	80·1	0·0	2·28	0·178	0·072
o-Xylene	106·2	0·88	144·4	0·5	2·57	0·018	0·03
Chlorobenzene	112·6	1·11	131·7	1·56	5·62		
Nitrobenzene	123·1	1·20	210·7	3·95	34·8	0·19	0·25

e.g. alcohols, acids, primary and secondary amines, nitro compounds with α-positioned hydrogen, ammonia, etc.

Class 3: Liquids composed of molecules containing donor atoms, but no active hydrogen atoms, e.g. ethers, ketones, aldehydes, esters, tertiary amines, nitro compounds without α-hydrogen, etc.

Class 4: Liquids composed of molecules containing active hydrogen atoms but no donor atoms, e.g. $CHCl_3$ and other aliphatic halides.

Class 5: Liquids with no hydrogen bond-forming capability and no donor atoms, e.g. pure hydrocarbons, CS_2, CCl_4, etc.

This great variation in solvent properties causes great differences in the distribution ratios in the extraction of metal complexes. Some solvents, particularly those of class 3, react directly and extract some inorganic complexes without addition of any additional extractant (sections 4.5.2 and 4.7.2).

For low-polar solvents with near ideal mixing entropies ("regular solutions"), Hildebrand[175] has developed the concept of the solubility parameter, δ, being defined as the square root of the internal energy of vaporization per unit volume. The smaller the difference between the solubility parameter of the two solvents, the more nearly ideal will the mixture be, and the greater the difference the less will their mutual solubility be. The solubility parameter concept is sometimes useful for predicting distribution factors (see sections 4.5.3 and 4.7.2). The total parameter term may be resolved into partial terms, each one corresponding to a particular type of solute–solvent interaction, as indicated in the classification above.

[175] J. H. Hildebrand and R. L. Scott, *The Solubility of Non-electrolytes*, Dover Publ. Inc., New York (1964).

Solvent systems are extensively treated in a number of monographs[175–179]. Criteria for industrial use of a particular solvent are, in addition to low price non-inflammability, low vapor pressure at working temperature, low viscosity, non-toxicity, reproducible qualities, etc. Data of this kind are collected in the different standard tables and monographs.

4.4. General aspects of metal extraction

The metal species are characterized by their ionic charge $z+$ and maximum coordination number N. In the aqueous phase the uncomplexed ion is $M(H_2O)_n^{z+}$. The water of hydration is assumed to form an inner coordination sphere; this is indicated by an extra parenthesis around the complex, when necessary, thus $(M(H_2O)_N)^{z+}$. Much of the following reasoning is based on the assumption that the inner coordination sphere is always filled. This is expected because the actinide ions can act as acceptors for Lewis bases (electron pair donors). Such bases are always present in solvent extraction, either as inorganic anions, e.g. Cl^-, NO_3^-, SO_4^{2-}, or as uncharged inorganic or organic species, notably the oxo-compounds (see Table 24). As discussed in section 1, the coordination numbers of the actinide ions with respect to oxygen are probably 7–9 for the trivalent state, 8 (eventually 9) for the tetravalent state and 4–6 for the penta- and hexavalent states in the -yl groups. The coordination number may vary somewhat for ligands of greatly different size (cf. section 1.2). The anionic ligands are denoted by L^- (or A^- or L^{2-}, when necessary) and the neutral (Lewis bases) adduct molecules by B. The neutral and coordinatively saturated complex between M^{3+}, L^- and B will thus be MB_5L_3 for $N = 8$ (monodentate L^- and B). B may be H_2O or any other neutral Lewis base.

TABLE 24. BASICITY (ELECTRON-PAIR DONATING TENDENCY) OF SOME IONS AND MOLECULES
(R is an alkyl or aryl group)

Basicity of some common anions relative to the actinide cations
$ClO_4^- < I^- < Br^- < Cl^- < NO_3^- < SCN^- <$ acetate $< F^-$

Basicity of some organic molecules		
Amine compounds		R_3N[a] $<$ R_2NH[b] $<$ RNH_2[c] $< NH_3$
Arsine compounds		R_3As
Phosphine compounds		R_3P
Oxo-compounds	Phosphoryls	$(RO)_3PO$[d] $<$ $R'(RO)_2PO$[e] $<$ $R_2'(RO)PO$[f] $<$ $R_3'PO$[g]
	Arsenyls	R_3AsO[h]
	Carbonyls	$RCHO < R_2CO$ ($\lesssim R_2O < ROH < H_2O$)[j]
	Sulphuryls	$(RO)_2SO_2$[k] $<$ R_2SO_2[l] $<$ $(RO)_2SO$[m] $<$ R_2SO[n]
	Nitrosyls	RNO_2[p] $<$ RNO[q]

Substitutions causing basicity decrease of oxo-compound
$(CH_3)_2CH— < CH_3(CH_2)_n— < CH_3— < CH_3O— < ClCH_2—$

[a–c] Tertiary, secondary and primary amines. [d] Tri-R phosphate. [e] Di-R-R′ phosphonate. [f] R-di-R′ phosphinate. [g] Tri-R′ phosphine oxide. [h] Arsine oxide. [j] Ether and hydroxo-compounds. [k] Sulphates. [l] Sulphones. [n] Sulphites. [m] Sulphoxides. [p] Nitro compounds. [q] Nitroso compounds.

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[176] E. Hecker, *Verteilungsverfahren im Laboratorium*, Verlag Chemie, GmbH, Weinheim/Bergst. (1955).
[177] R. E. Treybal, *Liquid Extraction*, McGraw-Hill, New York (1963).
[178] J. A. Riddick and W. B. Bunger, *Organic Solvents*, Wiley-Interscience, New York (1970).
[179] I. Mellan, *Industrial Solvents Handbook*, Noyes Data Corp., Park Ridge, N.J. (1970).

The hydrated metal ions always prefer the aqueous phase to the organic, because of hydrogen bonding and dipole interaction in the aqueous phase. Therefore a *prime requirement* for extraction into an organic low-polar solvent is partial or complete dehydration of the metal species. A *second requirement* is that the species entering the organic phase is electrically neutral. The *third requirement* is that the metal complex must be organophilic, i.e. the neutral complex must have an inert organic surface appearance if the organic solvent is inert, or be able to form a solvate with the organic solvent molecules.

These requirements can be met in three ways (assuming monodentate ligands L^-):

(1) by increasing the ligand concentration of L^- so that the negatively charged metal complex ML_N^{z-N} is formed, which is then extracted by large organic cations RB^+ (see section 4.5.1) in the form of the ion pair $(RB^+)_{N-z}(ML_N)^{z-N}$,

(2) by replacing the water in the inner coordination sphere by uncharged organic molecules B (see section 4.5.2), thus forming the ion MB_N^{z+}, which is extracted in the form of the ion association complex $(MB_N)^{z+}L_z^{z-}$, or compound $MB_{N-z}L_z$ (or $ML_z \cdot (N-z)B$), or

(3) by replacing the ligand L^- by (preferably polydentate) organic anions A^- (see section 4.5.3), which leads to the formation of an extractable neutral complex MA_z.

We have at this stage omitted some details and modifications of the extraction processes, as well as combinations between them. This will be discussed later. One theoretically possible mode of extraction has been omitted purposely, that is the extraction with large monodentate organic anions. Examples of such are the anions of α-naphthol, $C_{10}H_7OH$ (pK_a 3·7), and thiophenol, C_6H_5SH (pK_a 7·9). However, no extraction of actinides has been reported with such anions. Polynuclear complexes have been omitted also. Few such complexes of the classical type containing –M–O–M– bonds are known to be extracted. However, some specific reagents may be able to add more than one metal atom per molecule, or form large aggregates (micelles) in a polynuclear-like manner. Such cases are discussed in section 4.7.1.

The *extractants* can thus be divided simply into three main groups, large organic cations RB^+, neutral organic molecules B, and polydentate organic anions A^-[167,180]. Each extractant group is discussed below, first with respect to its general properties (section 4.5), then in more detail for various actinide systems (section 4.7).

The inorganic ligand L^- in the aqueous phase plays a decisive role in the extraction according to the categories 1 and 2 above, because uncharged or negatively charged metal complexes must be formed with L^- in order for the extraction to take place. The complex formation occurs in the aqueous phase. Because it does not differ from that described in section 2, it will be considered here only in the mathematical relations describing the extraction process (section 4.6), and when discussing specific cases of actinide extraction (section 4.7).

The physical chemistry of solvent extraction has recently been reviewed in a number of publications in addition to those previously mentioned[181–183], and in some cases with particular reference to actinide extraction[180,184].

[180] D. Peppard, *Ann. Rev. Nucl. Sci.* 21 (1971) 364.

[181] A. Kettrup and H. Specker, *Fortschritte chem. Forsch.* **10** (1968) 238.

[182] H. A. C. McKay, T. B. Healy, I. L. Jenkins and A. Naylor (Eds.), *Solvent Extraction Chemistry of Metals*, Macmillan, London (1966).

[183] A. M. Rozen, ref. 128, p. 195.

[184] E. K. Hulet and D. D. Bodé, p. 1 in *Lanthanides and Actinides*, K. W. Bagnall (Ed.), Butterworths, London (1972).

4.5. Extractant properties

In most practical solvent extraction studies, when tracer or microgram amounts of actinide salts are used, the overall behavior of the system will not differ significantly from that of the simpler system containing the aqueous acid (acid in order to avoid metal hydrolysis) and the organic solvent only, and perhaps a non-extractable electrolyte. The behavior of such systems can in most cases be regarded as a common feature for the extraction of any metal, at least as far as the physical properties of the phases and the nature of the acid–solvent interaction are concerned. Because of this bearing on the actinide extraction, it is relevant to discuss in some detail the general properties of the extractants in their common environment.

4.5.1. Cationic Extractants; Liquid Anion Exchange

The cationic extractants are formed through the reaction

$$R^+ + B \rightleftharpoons RB^+ \tag{1}$$

where R^+ is a Lewis acid and B a Lewis base.

In order to extract actinide anions into organic solvents, RB^+ must be a large organic cation. The only organic Lewis bases B, which can form adducts with the acid R^+ (either H^+ or an organic aliphatic or aromatic radical) are the alkyl or aryl substituted amines, phosphines, arsines and stibines (cf. Table 24). Only for the amines are all combinations $R_{4-n}H_nN^+$ $(0 \leq n \leq 4)$ stable towards water, a necessary requirement in our case. Of the others, only the highly substituted aryl compounds (e.g. $(C_6H_5)_4X^+$, where X is P, As or Sb) have any application, although not for the actinides. The discussion will therefore be limited to the amines.

The primary and secondary short-chain ($\lesssim$ four carbon atoms) amines, B, are very soluble in water and therefore not suitable as extractants. The water-solubility decreases, and solubility in non-polar solvents increases, with increasing organic substitution and carbon chain length in the amines, up to about ten carbon atoms, after which the solubility in the organic phase again decreases. The most commonly used amines contain eight to twelve carbon atoms per chain. The common trioctylamine (TOA) and tridodecyl (lauryl) amine (TLA) dissolve to $<0{\cdot}0005$ vol.% in water.

The C_8–C_{12} tertiary amines are liquids at room temperature and infinitely soluble in non-polar solvents. It has been observed that several amines, and especially the tertiary ones, interact with carbon tetrachloride and chloroform[167,185]. Kerosene is the common organic diluent for amines in industrial applications; its composition is close to that of octane (see Table 23). The solutions are usually rather dilute, rarely exceeding 20% by volume of amine, because at higher amine concentrations the organic phase becomes rather viscous. Because of the high molecular weight of the most commonly used amines (the mol. wt of TOA is 353) the molarity in the organic phase is usually <1.

The solution of amine in a water-immiscible organic solvent will dissolve some water. It has been suggested that a primary amine salt may be hydrated by three, a secondary by two and a tertiary amine by one water molecule. Water is also introduced into the organic phase by quaternary ammonium salts.

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[185] R. Foster, *Chem. Ind.* (*London*), **1960**, 1354.

Because we are concerned with organic aqueous two-phase systems, reaction (1) must be written

$$B(org) + H_3O^+ + L^- \rightleftharpoons BH^+L^-(org) + H_2O \qquad (2a)$$

except for the quaternary ammonium salts, R_4NL, which are formed through direct synthesis between R_3N and the alkyl or aryl halide RL. (RB^+ refers to all ammonium ions, but BH^+ only to the primary, secondary and tertiary ones.) In their ability to extract a proton from water the primary (RH_2N), secondary (R_2HN) and tertiary (R_3N) amines are much stronger bases than the two other main groups of neutral extractants, the carboxo and phosphoryl compounds, which are discussed in subsequent sections. The equilibrium constant for reaction (2a) shall be denoted K_{DA} (for distribution of acid). A few values are given in Table 25 (see otherwise ref. 167).

TABLE 25. EXTRACTION OF HBr BY 0·1 M TRILAURYLAMINE, AND OF HCl AND UO_2^{2+} (FROM 6 M HCl) BY 0·1 M TRIOCTYLAMINE, DISSOLVED IN DIFFERENT ORGANIC DILUENTS (K_{DA} is defined by reaction (2) and D_U by eqn (4.1))

Diluent	ϵ	log K_{DA}(HBr)[a]	log K_{DA}(HCl)[b]	D_U[c]
Cyclohexane	2·10	2·2	−3·0	130
Benzene	2·28	5·1		47
Toluene	2·38		−1·2	30
Chloroform	4·90	7·6		0·09
Nitrobenzene	35	7·7	2·6	

[a] W. Muller and R. M. Diamond, *J. Phys. Chem.* **70** (1966) 3469.
[b] W. E. Keder and A. S. Wilson, *Nucl. Sci. Eng.* **17** (1963) 287; *J. Inorg. Nucl. Chem.* **24** (1962) 561.
[c] T. Sato, *J. Inorg. Nucl. Chem.* **28** (1966) 1461.

The amine salts are less soluble in organic solvents, usually being <0·5 M in inert diluents. The solubility decreases in the order $SO_4^{2-} > Cl^- > NO_3^-$ and tertiary > secondary > primary amine[169]. The solubility usually increases with branching.

The amines are used as extractants for metals in the form of the ammonium salt, RB^+L^- (R = H or organic radical), where L is usually choosen to be the same ligand as in the metal complex, e.g. ML_n^{z-n}.

In the two-phase organic aqueous acidic system, the amines extract excess acid over the 1:1 amine:acid mole ratio indicated by reaction (2a). According to Fig. 30 the excess acid is linearly proportional to the aqueous acid concentration. The question of whether this excess acid is bound to the amine in a complex like $RBNO_3 \cdots HNO_3$ or is molecularly dissolved HNO_3 has been widely considered. The relation

$$RB^+L^-(org) + HL \rightleftharpoons RB^+L^-HL(org) \qquad (2b)$$

where HL is undissociated acid in the aqueous phase, has been found to hold over rather large amine and acid concentrations[187–189]. The equilibrium constant K_{DEA} (for *e*xcess *a*cid) for this reaction was found to be ~0·3 for triisooctyl amine in xylene (TiOA) and HNO_3, while K_{DA} for reaction (2a) was found to be $1 \cdot 4 \times 10^5$ [189]. Making allowance for

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[186] V. Bertocci and G. Rolandi, *J. Inorg. Nucl. Chem.* **23** (1961) 323.
[187] O. I. Zakharov-Nartsissov and A. V. Ochkin, *Zh. Neorg. Khim.* **6** (1961) 1936; *ibid.* **7** (1962) 665.
[188] A. S. Kertes and I. T. Platzner, *J. Inorg. Nucl. Chem.* **24** (1962) 1417.
[189] W. Knoch, *J. Inorg. Nucl. Chem.* **27** (1965) 2075.

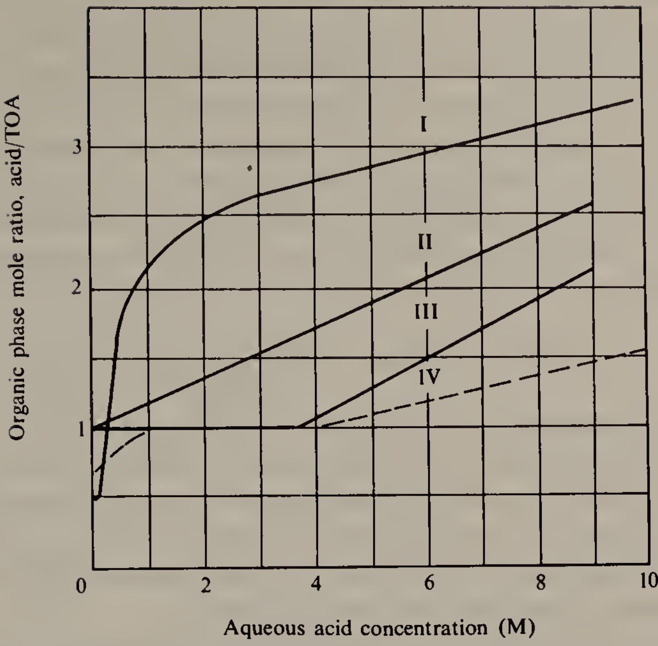

FIG. 30. Extraction of excess acid by 0·01–0·5 M trioctyl amine. I, HF; II, HNO_3; III, HCl; IV, H_2SO_4[172,186].

the HNO_3 dissociation, the excess acid is obviously more loosely bound than the acid in the amine complex RB^+L^-. It will be shown that the question concerning the state of this excess acid hinders the explanation of the metal complex extraction.

The reaction for metal extraction can be written

$$p\mathrm{RB^+L^-(org)} + \mathrm{ML}_n{}^{-p} \rightleftharpoons (\mathrm{RB^+})_p\mathrm{ML}_n{}^{p-}\mathrm{(org)} + p\mathrm{L^-} \qquad (3)$$

The equilibrium constant for this reaction will be denoted K_{DM}; $p = n - z$. The species involved (including the anions) are all hydrated or solvated. Reaction (3) is an anion exchange. The organic amines and ammonium salts are therefore commonly referred to as *liquid anion exchangers*. The trialkyl sulphonium salts, $R_3S^+L^-$, also belong to this group[190], but they have not been used for actinide extractions.

Because amines extract acids and metal complexes as ion pairs, it is useful to consider the energetics of ion dissolution and transfer. As is well known, gaseous ions dissolve more easily in polar than in non-polar solvents. This indicates a gain in energy when the ions become surrounded (solvated) by dipolar molecules (see section 1.4). Transfer of these solvated ions from a high dielectric medium like water (ϵ_1) to a low dielectric medium like the organic solvent (ϵ_2)

$$\mathrm{RB^+}(\epsilon_1) + \mathrm{L^-}(\epsilon_1) \underset{K_{\epsilon_1\to\epsilon_2}}{\rightleftharpoons} \mathrm{RB^+}(\epsilon_2) + \mathrm{L^-}(\epsilon_2) \underset{K_{\mathrm{ionp}}}{\rightleftharpoons} \mathrm{RB^+L^-}(\epsilon_2) \qquad (4)$$

will thus require energy, the amount (i.e. free energy change ΔG for one mole) according to Born[191] corresponding to

$$\Delta G_{\epsilon_1\to\epsilon_2} = \frac{\mathrm{N}\cdot e}{2}\left(\frac{1}{r_+} + \frac{1}{r_-}\right)\left(\frac{1}{\epsilon_2} - \frac{1}{\epsilon_1}\right) \qquad (4.15)$$

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[190] E. L. T. M. Spitzer and J. Radder, *Advances in Extractive Metallurgy*, Inst. of Mining and Metallurgy, London (1967).

[191] M. Born, *Z. Physik*, 1 (1920) 45.

where r is the radius of the ion, e is the electronic charge and N the Avogadro number. Although the Born equation has its defects, as discussed by Bates[192] and others, it gives results of the right order of magnitude. The Born equation "opposes" the extraction, that is the extraction of ions from water to a low-dielectric solvent requires energy ($-\mathbf{R}T \ln K_{\epsilon_1 \to \epsilon_2} = \Delta G_{\epsilon_1 \to \epsilon_2} > 0$). For reaction (4) to proceed spontaneously to the right, some energy gain must be made. These gains are of two kinds: electrostatic in the formation of ion pairs in the low-dielectric medium (equil. const. K_{ionp}) and chemical in the formation of a covalent bond. The electrostatic gain in the ion-pair formation from free ions can be described by the equation[193,194]

$$-\Delta G_{\mathrm{ionp}} = \mathrm{R}T \ln K_{\mathrm{ionp}} = \mathrm{R}T \ln \left[\frac{4\pi \mathrm{N}}{1000}\left(\frac{\mathrm{e}^2}{\epsilon \mathbf{k}T}\right)^3 Q(b)\right] \tag{4.16}$$

In refs.193–4 $Q(b)$ is tabulated, where $b = \mathrm{e}^2/d \cdot \epsilon \cdot \mathbf{k}T$; d is the distance between the center of charges of the ion pairs (thus $r_+(\mathrm{solv}) + r_-(\mathrm{solv})$, if the ions are solvated). Because $Q(b)$ is a positive regularly increasing function of b, ion-pair formation (K_{ionp}) increases with decreasing ϵ, d, and T. Thus ion pairs are stable (i.e. $\Delta G_{\mathrm{ionp}} < 0$) at 20 Å apart if $\epsilon = 2$ (e.g. octane), but only at $d < 3{\cdot}7$ Å at $\epsilon = 10$ (e.g. octanol). The gain on formation of a covalent bond cannot be predicted in a similar manner.

It follows from eqn (4.15) that the extraction of an ion pair from water into an organic solvent should be less opposed (have a lower ΔG) the higher ϵ_{org} is. Thus D should increase with ϵ. This is also found for simple acids, as is seen for HBr and HCl in Table 25, where the equilibrium constant K_{DA} is proportional to the distribution factor D of the acid (cf. eqn (4.17) below).

According to relation (2) the plots in Fig. 31 should yield straight lines. For dissociation of the ion pair in the organic phase

$$\mathrm{BH^+L^-(org)} \rightleftharpoons \mathrm{BH^+(org)} + \mathrm{L^-(org)} \tag{5}$$

and formation of polymeric ion-pair aggregates (micelles)

$$q\mathrm{BH^+L^-(org)} \rightleftharpoons \mathrm{(BHL)}_q\mathrm{(org)} \tag{6a}$$

in the organic phase, the measured extraction will follow the relation

$$C_{\mathrm{L,org}} = (g+1)\cdot K_{\mathrm{DA}}[\mathrm{B}]_{\mathrm{org}}\{\mathrm{HL}\} \qquad (4.17$$

where {HL} is the activity of the acid in the aqueous phase as obtained, for example is from emf measurements. The symbol g represents a variable: if dissociated ions are formed g is proportional to $[\mathrm{BH^+L^-}]_{\mathrm{org}}^{-\frac{1}{2}}$, but if a polymeric species is formed it is proportional to $q[\mathrm{BH^+L^-}]_{\mathrm{org}}^{q-1}$. The straight line in Fig. 31 is obtained only when $g = 0$ ($[\mathrm{L_{tot}}]_{\mathrm{org}} = [\mathrm{TLAH^+L^-}]_{\mathrm{org}}$), i.e. when only ion pairs are formed in the organic phase. The deviation for nitrobenzene at low HBr concentration indicates that free ions $\mathrm{R_3HN^+}$ and $\mathrm{Br^-}$ are formed in increasing amounts. The upwards curvature at high HBr concentration for the low-polar diluents is accordingly interpreted as being due to the formation of aggregates containing an increasing number of ion pairs[195]. In xylene the polymeric $(\mathrm{TLAHBr})_n$ species have been suggested as $n = 2$, 3 and 30. The latter value shall be interpreted as the average size of the polymer, as obtained by the particular measurement technique and method of calculation[196].

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[192] R. G. Bates, ref. 173.
[193] N. Bjerrum, *Kungl. Danske Vidensk. Selskab.* 7 (9) (1926).
[194] R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.* **55** (1933) 1019.
[195] W. Müller and R. M. Diamond, *J. Phys. Chem.* **70** (1966) 3469; ref. 128, p. 349.
[196] M. A. Lodhi and E. Högfelt, ref. 128, p. 421.

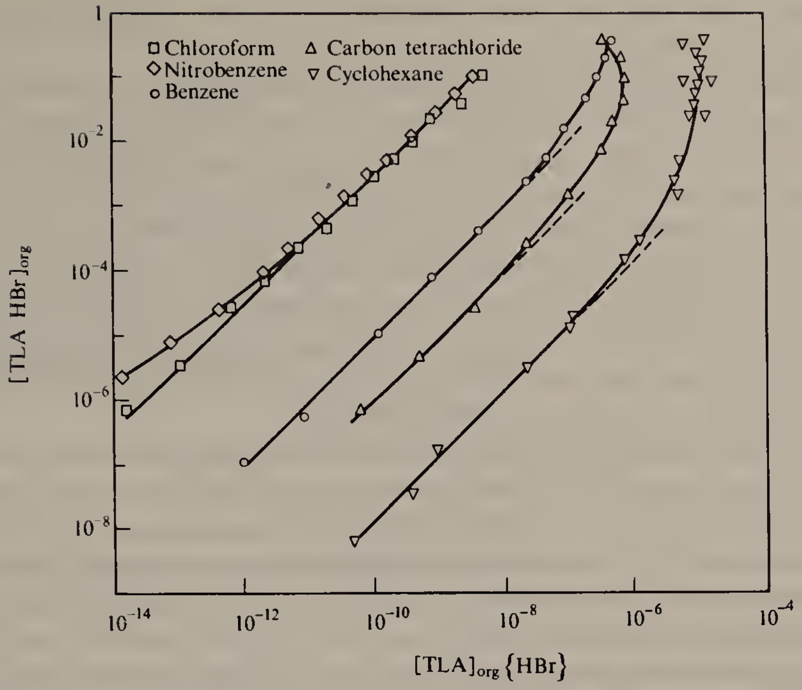

FIG. 31. Equilibrium distribution of HBr between organic solvents containing trilauryl amine (TLA) and water[195].

Although aggregation numbers (i.e. ion pairs per micelle) above 100 have been suggested, smaller aggregates may be stable over rather large concentration regions. Thus $TLAHNO_3$ is mainly trimeric in *m*-xylene at concentrations of 0·002–0·2 M, but larger aggregates are formed at higher amine concentrations[197]. These aggregates seem to behave like monofunctional species, each extracting only one actinide ion. Marcus[198] has suggested that the aggregated amine salt always is mono-ionized

$$(RB^+L^-)_q \rightleftharpoons (RB^+)_q(L^-)_{q-1}{}^+ + L^- \tag{6b}$$

and thus will exchange only one anion. The stoichiometry of the reaction will in any case be rather complicated.

Aggregation increases in the order primary < secondary < tertiary < quaternary amine in the presence of most anions except sulphate. It is particularly common for the tertiary and quaternary amines at high "loading", i.e. high ratio of anion (L^- or ML_n^{z-n}) to amine. Aggregation is less in aromatic than in aliphatic diluents, and increases with decreasing ϵ of the organic diluent.

There have been speculations about the nature of the micelles. The polar amines and ammonium salts may align themselves either parallel or antiparallel. Equation (4.16) also permits rather large singly charged ion pairs to be formed at low ϵ values. Some of these systems also show "anomalous" extraction, i.e. the distribution ratio of the metal will depend on mixing intensity, and show slow kinetics. This was first observed by Allen and McDowell[199] in the extraction of uranyl sulphate with TOA in benzene. This phenomenon,

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[197] E. Högfelt *et al., Trans. Royal Inst. Techn., Stockholm,* Nos. 226–229 (1964).

[198] Y. Marcus, *J. Inorg. Nucl. Chem.* **28** (1966) 209.

[199] K. A. Allen and W. J. McDowell, *J. Phys. Chem.* **64** (1960) 877.

which has been observed with other amines[200–202] and more recently also in other actinide extraction systems[203], is not yet well understood.

The ion-pairing is not purely electrostatic, but may involve a weak hydrogen bond between the ammonium cation and the anion. This interaction is stronger the smaller and more basic the anion is. The basicity of the more common anions with respect to the actinide ions (as Lewis acids) increases in the order indicated in Table 24; this order deviates slightly from the Brønsted basicity order, partly because of the chelating properties of NO_3^- and Ac^- (cf. section 2.2.3). These anions are, however, extracted preferentially in the opposite order (thus $ClO_4^- > I^- >$ etc.) because it is the aqueous phase interaction of the ions (hydration) and not the organic phase interaction which dominates in determining the sequence. Water is the best anion-solvating agent present, and the anions therefore leave the aqueous phase in the order of decreasing hydration[204].

Actinides can be extracted with amines as negatively charged fluoride, chloride, nitrate, sulphate, acetate, etc., complexes. The distribution ratio, D_M, will depend on the β_n values for the formation of the ML_n^{z-n} complexes, the L^- concentration, and the K_{DM} value of reaction (3). Although K_{DM} is usually $\gg 1$, the high ligand concentration required leads to high activity factors and micelle formation, which limits the physical interpretation of the metal extraction data (cf. section 4.7.1).

A further complication is that high loading of the organic phase will change its ϵ value as well as its over-all composition considerably. Thus in cyclohexane containing 0·4 M TLA, $\epsilon = 2{\cdot}02$, but with 0·4 M TLAHBr, $\epsilon = 4{\cdot}35$[195]. This change may be so large in metal extraction that the organic phase splits into two phases, one usually rich in the diluent, and the other high in amine salt concentration. The three-phase system is a particular nuisance in industrial solvent extraction, because extraction equipment is designed for two phases only. Such three-phase systems have been studied particularly by Kertes[205] who points out that the miscibility gap prevails as long as the organic phase contains high concentrations of at least two different ion pairs such as $R_3NH^+Cl^-$ and $(R_3NH^+)_2(UO_2Cl_4)^{2-}$. At low salt concentrations both ion pairs can exist together. The appearance of a third phase at high salt concentrations is probably associated with micelle formation, the micelles becoming large enough to condense into a separate phase.

The third phase can be eliminated by increasing the aromatic content of the diluent, or by addition of highly polar organic molecules (modifiers), such as long-chain alcohols (e.g. octanol, $\epsilon = 10{\cdot}3$) or phosphoryl compounds (e.g. tributyl phosphate, $\epsilon = 8{\cdot}0$). These molecules are also strong Lewis bases, and may thus solvate the ion pairs. The interplay between different factors is complicated, and no conclusive explanation has yet been given.

4.5.2. *Neutral Extractants; Solvation and Adduct Formation*

The actinide complexes which are extracted with neutral extractants B are of the type ML_nB_p. It is useful for the discussion to consider the different paths by which this complex is formed and extracted. For simplicity, it is assumed that both L^- and B are monodentate and in the inner sphere, and $N = n + p$.

[200] C. F. Coleman and J. W. Roddy, ref. 128, p. 362.

[201] W. J. McDowell and C. F. Coleman, ref. 128, p. 540.

[202] J. Desreux, *Radiochem. Radioanal. Letters*, 7 (1971) 45.

[203] J. Rydberg, H. Reinhardt and J. O. Liljenzin, *Ion exch. and solv. extr.* 3 (1973) in press.

[204] R. M. Diamond and D. G. Tuck, p. 109 in *Progress in Inorg. Chem.* F. A. Cotton (Ed.), Interscience (1960).

[205] A. S. Kertes, ref. 182, p. 377.

A. Heterogeneous reaction

$$M(H_2O)_N^{z+} + nL^- \rightleftharpoons M(H_2O)_pL_n + nH_2O \tag{7a}$$

$$M(H_2O)_pL_n + pB(org) \rightleftharpoons ML_nB_p(org) + pH_2O \tag{7b}$$

B. Homogeneous reactions, dehydration in organic phase

$$M(H_2O)_N^{z+} + nL^- \rightleftharpoons M(H_2O)_pL_n + (N-p)H_2O \tag{8a}$$

$$M(H_2O)_pL_n \rightleftharpoons M(H_2O)_pL_n(org) \tag{8b}$$

$$M(H_2O)_pL_n(org) + pB(org) \rightleftharpoons MB_pL_n(org) + pH_2O(org) \tag{8c}$$

C. Homogeneous reaction, dehydration in aqueous phase

$$B(org) \rightleftharpoons B(aq) \tag{9a}$$

$$M(H_2O)_N^{z+} + pB \rightleftharpoons M(H_2O)_nB_p^{z+} + pH_2O \tag{9b}$$

$$M(H_2O)_nB_p^{z+} + nL^- \rightleftharpoons ML_nB_p + nH_2O \tag{9c}$$

$$ML_nB_p \rightleftharpoons ML_nB_p(org) \tag{9d}$$

Reaction path A is the one most commonly assumed, though it is not always divided into two separate steps [cf. reaction (10)]. Reaction path B leads to two or more complexes in the organic phase, solvated both by H_2O and B. The reactions shown (8) involve some simplifications, i.e. for example the formation of mixed complexes of type $ML_n(H_2O)_pB_s$ is neglected. Reaction path C requires a number of differently solvated complexes in the aqueous phase, all having the same ligand number with respect to L^-. Although it is not possible from equilibrium studies to decide between the three reaction paths, separate measurements on the equilibria in the pure phases according to eqns. (8a), (8c), (9b) and (9c) will give a strong indication about the most probable one (*vide infra*). Further information must come from kinetic measurements.

The extractant B must be a neutral organic Lewis base. Of those listed in Table 24, the carboxo and phosphoryl compounds are effective for actinide extraction, in addition to the amines described in the previous section. While the corresponding amine adducts are mainly ionic in the organic phase, the oxo adducts are mostly non-ionic[206], with the exception of the combination of the most basic phosphoryl and carboxo compounds with strong acids[167]; thus HCl is reported to be almost completely dissociated in isopentanol[207].

Carboxo compounds. In the search for suitable extractants for the actinides, interest was first focused on the basic carboxo compounds. Reason for this choice was obvious: uranyl nitrate was known to dissolve in ether, amyl alcohol, acetone, etc., but not in inert solvents like carbon disulphide, benzene or chloroform (cf. ref. 208). Interest ultimately centred on diethyl ether, methyl isobutylketone and dibutylcarbitol, which were employed in early large-scale uranium purification and actinide separation.

The carboxo compounds form somewhat undefined complexes with the actinides. The extraction of uranyl nitrate by such monodentate compounds, B, should in principle give rise to a complex of type $UO_2(NO_3)_2(H_2O)_xB_{a-x}$ ($x \leq a = 2$ or 3), with all ligands in the inner sphere. With isobutyl alcohol a hexasolvated complex, $UO_2(C_4H_9OH)_6(NO_3)_2$, is reported to be formed in the organic phase[167], but only $UO_2(C_4H_9OH)_3(NO_3)_2$ crystallizes. Riskin *et al.*[209] found that the nitrato oxygens are in direct contact with the metal. The solid complex $UO_2(H_2O)_2((C_2H_5)_2O)_2(NO_3)_2$ is obtained from aqueous diethylether on

[206] I. Lindqvist, *Inorganic Adduct Molecules of Oxocompounds*, Springer Verlag (1963).

[207] L. M. Gindin, I. F. Kopp, A. M. Rozen and E. F. Kauba, *Zh. Neorg. Khim.* 5 (1960) 139.

[208] A. Seidell and W. F. Linke, *Solubilities*, Vol. II, Am. Chem. Soc., Washington (1965).

[209] Y. I. Riskin, U. P. Shvedov and A. A. Soloveva, *Zh. Neorg. Khim.* 4 (1959) 2268.

evaporation[210], although the organic solvent also is reported to contain a considerable fraction of $UO_2(H_2O)_3((C_2H_5)_2O)_3(NO_3)_2$[211]. With ligands of approximately equal basicity, the nitrate group may drift from the inner sphere to the outer sphere, thus giving the uranyl group a variable coordination number. In this case, $n+p$ in the reactions above will not be constant, implying a change in N.

The heterogeneous extraction (7b) is analogous to the amine extraction (3). The equilibrium constant will again be given as K_{DM} for this reaction, as for all heterogeneous metal extractions written in their simplest form.

It is improbable that actinide extraction with neutral adducts occur through the heterogeneous reaction, because these compounds are either rather soluble in water or extract considerable amounts of water into the organic phase, making reaction paths B and C possible. In order to discuss this matter further, the extractant properties in the acid–water–diluent system must first be considered.

The carboxo compounds are partly soluble in water, the lighter ones often completely. The solubility, which is due to their ability to form hydrogen bonds, e.g. $R_2O\cdots HOH$, decreases with increasing carbon chain length, but increases with an increasing number of oxygen atoms in the molecule (cf. Table 23).

The carboxo compound solubility in water increases slowly with increasing aqueous acidity, until most of the water is tied up as hydrate water around the proton, e.g. $H(H_2O)_4^+$, following which it increases rapidly, probably due to further solvation of the protons by the carboxo compound, e.g. $H(R_2O)_n^+$. The increase in carboxo solubility in water is accompanied by a corresponding increase in water and acid solubility in the carboxo phase, due to the increasing formation of organophilic $H(B)_nL$ ($L = Cl^-$, NO_3^-, etc.) complexes. The interaction in the organic phase between the carboxo compound, water and the acid produces stoichiometric compounds, as for example $H_2O\cdot B_n$ and $HB_n(H_2O)_pL$, but true dissolution without specific interaction may also occur.

The increasing mutual solubility leads to considerable phase volume changes at high acid concentrations (Fig. 32). This must be taken into account in actinide extraction, because the highest distribution ratios are usually observed under these conditions (see Fig. 33). At very high acid concentration a single phase may be formed, particularly for the low molecular weight adducts.

Addition of a salt to the aqueous phase has an opposite effect to that of the acid, in that the solubility of the carboxo compound in water decreases, owing to the increasing deficiency of free water molecules to which the oxo compounds can hydrogen bond. Because the metal salt provides no protons to associate with, the aqueous phase becomes increasingly organophobic. It is known that the activity factor of neutral organic compounds in aqueous solutions increases with ionic strength. The carboxo compound is therefore "salted out" of the aqueous phase cf. eqn (4.13).

Acids and extractable actinide salts are salted out in the same manner (Fig. 33). The salting-out power of a metal cation increases with its hydration, and is thus high for ions like Li^+, Ca^{2+} and Al^{3+}, and low for ions like NH_4^+ and K^+. The anion acts in the same direction, but the effect is less pronounced: thus Cl^- is a more efficient salting-out anion than NO_3^-. Because of complex formation (and technical problems like corrosion) the choice of anion for salting-out purposes is limited.

The high salt concentrations, which often are required in order to get high actinide

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[210] L. I. Katzin and J. C. Sullivan, *J. Phys. Coll. Chem.* **55** (1951) 346.

[211] V. V. Fomin, *Ektstraktziya*, **1** (1960) 104.

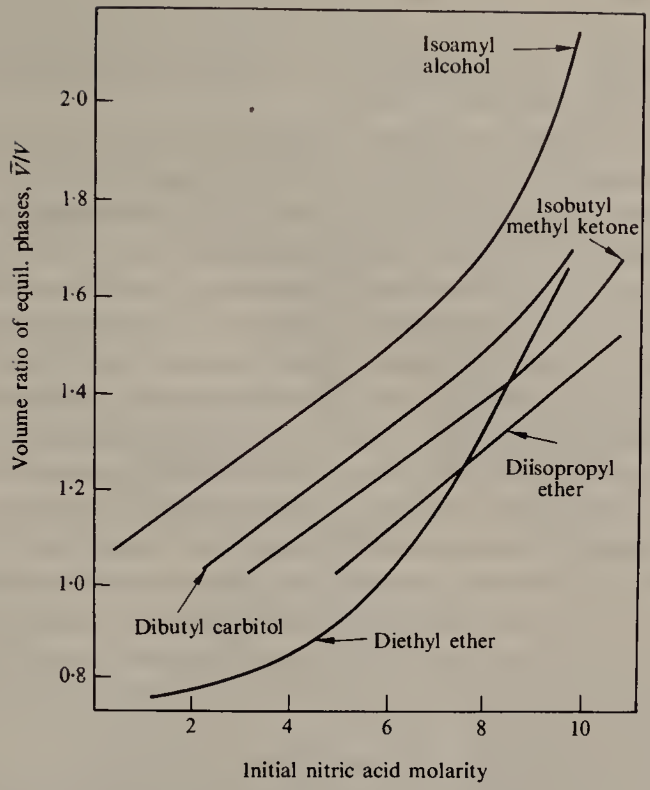

FIG. 32. Volume changes occurring on equilibration of aqueous HNO_3 solutions with some basic solvents. Initial phase volume ratio organic:water ($\bar{V}/V$) equal to one[167].

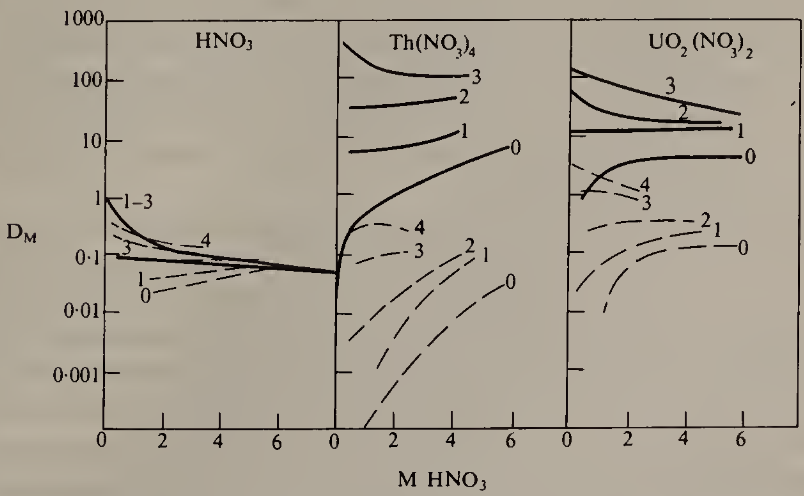

FIG. 33. Salting-out effect by $Ca(NO_3)_2$ (0, 1, 2, 3 and YM) on extraction of HNO_3, $Th(NO_3)_4$ and $UO_2(NO_3)_2$ with (a) methyl-i-butylketone (Hexone, ----)[212], and (b) tributylphosphate (TBP, ——)[213], at different HNO_3 concentrations.

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[212] J. Rydberg and B. Bernström, *Acta Chem. Scand.* **11** (1957) 86.
[213] B. Bernström and J. Rydberg, *Acta Chem. Scand.* **11** (1957) 1173.

extractions with the carboxo compounds, may lead to the formation of a third phase. The conditions are very similar to third phase formation with the amines (cf. section 4.5.1). Thus third-phase formation appears more easily with the low dielectric strength compounds, as for example diethyl ether ($\epsilon = 4\cdot3$), and can be prevened by adding another more polar compound as for example octanol ($\epsilon = 10\cdot3$).

The extraction of actinides into carboxo solvents is often accompanied by extraction of additional water, which makes reactions (8b) and (8c) plausible. Some, or total, dehydration may then occur, to yield the $ML_n(H_2O)_pB_s$ complex ($p \geq 0$). Depending on the conditions, a whole series of complexes may appear. Many authors have postulated a few species in their systems, and then tried to estimate activity factors, in order to obtain thermodynamic equilibrium constants. Unfortunately activity factors for undissociated inorganic salts in organic solvents can be obtained indirectly only, usually from partition measurements. Because the activity factors change in a very complicated way, particularly at the concentrations necessary for actinide extraction[214], comparison of equilibrium constants for actinide carboxo adducts is meaningful only for very similar extraction conditions (cf. section 4.7).

Many carboxo extractants are unstable towards solutions of high nitric acid concentration. The reaction seems to be autocatalytic, and most rapid for low-molecular-weight ethers, and may, under unfortunate circumstances, lead to violent reactions. Even when the reaction is slow, as for example with methylisobutyl ketone, decomposition products are formed which change the extraction conditions. Thus laboratory experiments must be carried out with freshly prepared solutions and with great care, and continuous purification is required in industrial processes.

Phosphoryl compounds. Although a large number of phosphoryl extractants have been studied[161,162,164,167], the outstanding reagent is tributylphosphate, $(n\text{-}C_4H_9O)_3PO$, TBP. It is a readily available compound produced for use as a plasticizer in resins. It is extensively applied as extractant for the separation of actinides from fission products, both in the laboratory and on the industrial scale, and of other metals in the non-nuclear inorganic industry. The most basic phosphoryl extractants are the trialkyl phosphine oxides, R_3BO; the most common is trioctylphosphine oxide, $(n\text{-}C_8H_{17})_3PO$, TOPO, which is a solid at room temperature (melting point 51°C). The discussion of the phosphoryl compounds will center on these two compounds. The extracting power of other phosphoryl compounds falls between them, as is illustrated for uranyl nitrate in Fig. 34. The extracting power follows approximately the basicity rules in Table 24.

The stronger basicity of the phosphoryl compounds as compared to the carboxo compounds gives them more distinctive properties. In the organic phase they usually form water-free inner-sphere complexes with the metal. These complexes have a definite structure in the solution, with the phosphoryl oxygen directly bound to the metal atom as is indicated from IR spectra. The compounds can also be crystallized. Figure 35 shows the triethylphosphate uranyl nitrate complex[216], $UO_2(NO_3)_2\cdot2(C_2H_5O)_3PO$. The uranyl group is symmetrically surrounded by two oxygens from each NO_3^- group (bidentate), and one oxygen from each $(RO)_3PO$, forming a plane hexagon. The coordination number is 6. The uranium–oxygen distances indicate that this is a non-ionic inner-sphere complex. It fits with the designation of the complex ML_nB_p in the reaction formulas.

In general, the phosphoryl compounds show regularities similar to those of the carboxo compounds. However, the stronger basicity of the phosphoryl compounds, their lower solubility in water (for TBP see Table 23; the solubility of TOPO in water is $<0\cdot001$ vol. %),

[214] H. A. C. McKay, *Chem. Ind.* **1954**, 1549.

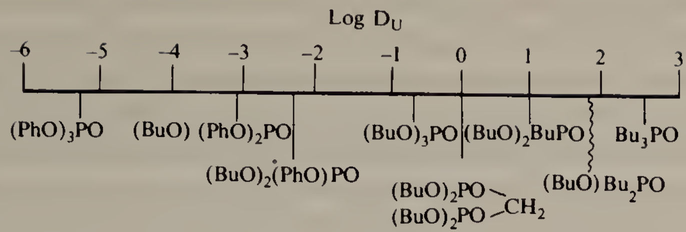

FIG. 34. The extraction (log D_U) of uranyl nitrate from 1 M HNO_3 by various phosphory compounds[215].

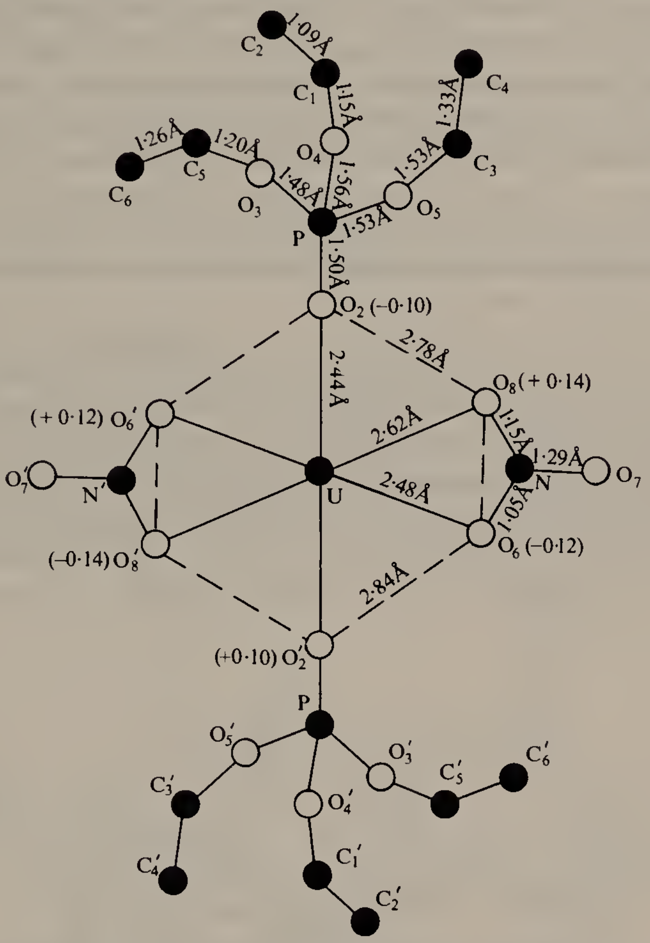

FIG. 35. Structure of $UO_2(NO_3)_2 \cdot 2(C_2H_5O)_3PO$[216]. The uranyl oxygens are situated on the normal axes through the central atom.

and the higher distribution factors obtained with metal complexes (no salting-out agent needed) make these systems more amenable to quantitative treatment.

The mole ratio H_2O:TBP is equal to one in TBP saturated with water. It was soon assumed therefore that a complex $(C_4H_9O)_3PO \cdots HOH$ is formed. The formation of

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[215] H. Irving and R. J. P. Williams, p. 1357 in *Treatise on Analytical Chemistry*, I. M. Kolthoff and P. J. Elving (Eds.), Interscience (1961).

[216] J. E. Fleming and H. Lynton, *Chem. Ind.* **1960**, 1415.

phosphoryl hydrates is supported by infrared and nuclear magnetic resonance measurements. The water solubility in the organic phase is highly temperature-dependent, decreasing for TBP from a mole ratio of 1 at room temperature to $< 0{\cdot}5$ at 50°C. When phosphoryls are diluted with inert organic solvents in organic-water two-phase systems, the concentration of the phosphoryl in water is lowered, as well as the water concentration in the organic phase.

With monobasic acids the phosphoryl compounds form a 1:1 complex, and with dibasic acids a 2:1 phosphoryl:acid complex. From dilute aqueous solutions the acids are extracted with the hydrated proton, $H(H_2O)_4^+$, as is indicated from stoichiometry and conductivity measurements. The ionic species in the organic phase have been postulated to be $(TBP\cdot H_2O\cdot H)_3O^+L^-$[167]. With nitric acid at higher concentration the organic phase probably contains the species $TBP\cdot H_2O$, $TBP\cdot HNO_3$, and $TBP(H_2O)HNO_3$. The $TBP\cdot HNO_3$ complex seems to dominate over a large concentration region, from $\lesssim 1$ M to $\gtrsim 8$ M HNO_3 (aq), the acid being undissociated. It is believed that the excess HNO_3 extracted over the 1:1 complex at very high HNO_3 concentration is due to simple dissolution of molecular HNO_3, although the existence of higher $TBP(HNO_3)_n$ complexes has also been suggested[167].

While the extraction of actinide salts by many carboxo compounds introduces more water into the organic phase, water is expelled from the organic phase when the extractant is a phosphoryl compound[167]. Thus

$$UO_2^{2+} + 2NO_3^- + 2TBP\cdot H_2O(org) \rightleftharpoons UO_2(NO_3)_2(TBP)_2(org) + 2H_2O \qquad (10)$$

The tri-, tetra- and hexavalent actinides form the stoichiometric complexes $M(NO_3)_3B_3$, $M(NO_3)_4B_2$ and $MO_2(NO_3)_2B_2$, respectively, with most phosphoryl compounds.

The phase diagram for the system H_2O–TBP–HNO_3–$UO_2(NO_3)_2$ is given in Fig. 36[166]. The lower left triangle shows that at > 80 % HNO_3 one phase is obtained in the H_2O–TBP–HNO_3 system (trace actinide). In the $UO_2(NO_3)_2$–H_2O–TBP system three hydrates free of TBP are formed, together with a $UO_2(NO_3)_2(TBP)_2$ solvate (43 % TBP) free of

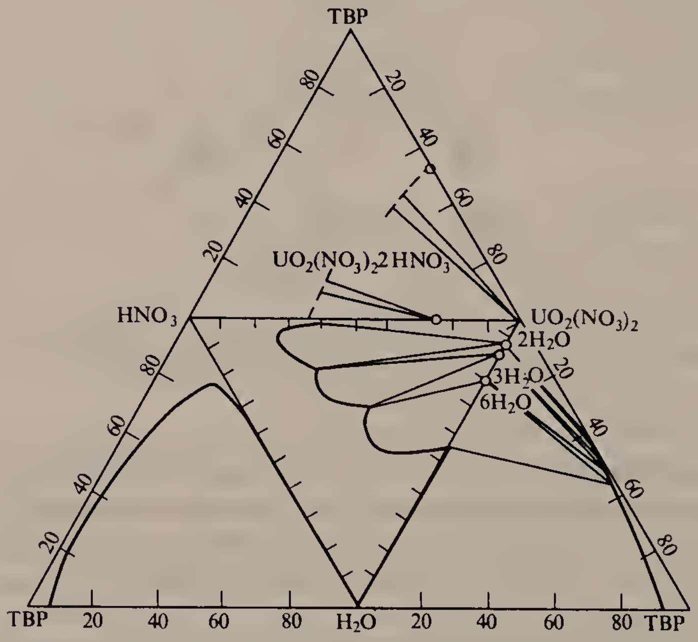

FIG. 36. Ternary phase diagrams for the four-component system H_2O–TBP–HNO_3–$UO_2(NO_3)_2$[166]. Scale in weight-%.

water; at very high TBP concentration (right lower area) a single phase is formed. The solubility of the three uranyl nitrate hydrates in water is given by the middle triangle.

The dehydration of the uranyl nitrate hydrate according to reaction (10) may take place either in the aqueous phase (reaction 9c) or in the organic phase (reaction 8c) or alternatively at the liquid–liquid interface (reaction 7b). It should be possible to distinguish between the two first reaction paths, because constants for the aqueous complexation of the cation (reaction 8a) as compared to (9c) should be different. This does not appear to have been investigated.

Metal complex and acid extraction increases with aqueous salt concentration as is seen in Fig. 33. Thus salting-out with 3·8 M $Ca(NO_3)_2$ increases the extraction of $Th(NO_3)_4$ from 1 M HNO_3 into 100 % TBP by a factor of about 800. The distribution factor also increases with the concentration of the phosphoryl compound in the organic phase.

With inert diluents third phase formation occurs at high acid and metal complex concentrations in the organic phase (cf. Fig. 36). The lighter organic phase contains mainly the diluents, while the heavier organic phase is dominated by an acid or metal solvate, e.g. $TBP(H_2O)_nHNO_3$. The third phase can be removed by raising the temperature, increasing the phosphoryl concentration or adding a modifier. A critical review of third-phase formation with particular reference to the action of modifiers is available[205].

4.5.3. *Anionic Extractants; Chelation*

The anionic extractants are formed by dissociation of the corresponding organic acid: $HA \rightleftharpoons H^+ + A^-$. They form chelates, i.e. ring-formed structures of 4–7 atoms, with the metal cation (see example in Fig. 37). In these structures the anion occupies two (bidentate) or more (multidentate) coordination positions at the metal atom, the coordination atoms usually being N, O or S. A number of representative compounds which extract actinides are

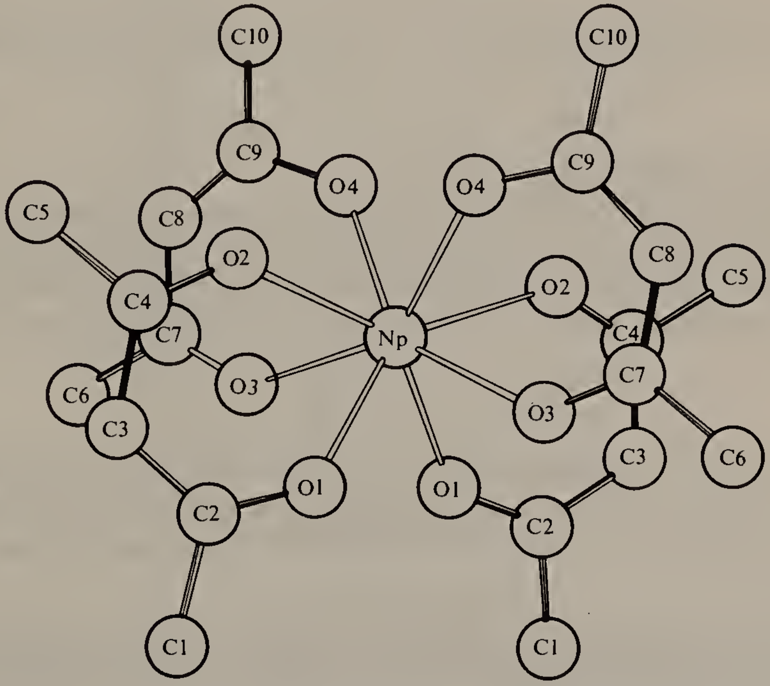

FIG. 37. Structure of neptunium(IV) acetylacetonate, $NpAA_4$[217].

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[217] B. Allard, *Acta Chem. Scand.* **26** (1972) 3792.

TABLE 26. SOME ORGANIC COMPOUNDS FUNCTIONING AS POLYDENTATE ANIONS IN METAL EXTRACTION

Chelate ring size	Acidic groups	Coord. atoms	Compound group; examples
4	1	O, O	Carboxylic acid, RCOOH; e.g. perfluorobutyric (C_3F_7COOH), salicylic ($C_6H_4(OH)COOH$), cinnamic ($C_6H_5CHCHCOOH$) acid.
4	1	O, O[a]	Di(alkyl or aryl)phosphoric and phosphinic acid, RR′PO(OH); e.g. HDEHP[b]; corresp. thioacids[a].
4	1	S, S	Dithiocarbamate, RR′NC(S)SH, xanthate, ROC(S)SH; e.g. NaDDC.[c]
4	2	O, O[a]	Mono(alkyl or aryl)phosphoric and phosphinic acid, $RPO(OH)_2$; e.g. H_2MEHP[d].
5	1	O, O	Nitrosohydroxylamine, RN(NO)OH (e.g. cupferron $R=C_6H_5$); hydroxamic acid, RC(O)NHOH.
5	1	O, N	8-Hydroxyquinoline (oxine), C_9NH_6OH.
5 (or 6)	1	S, N (or N, N)	Diphenylthiocarbazone (dithizone), $C_6H_5NHNC(SH)NNC_6H_5$.
6	1	O, O	β-Diketone, RC(O)CHC(OH)R′, e.g. acetylacetone ($R=R'=CH_3$), HTTA[e]($R=C_4SH_3$, $R'=CF_3$).
6	1	O, O	1-Nitroso-2-naphthol, $C_{10}H_6(NO)OH$.
6	2	O, O	Di(alkyl or aryl)pyrophosphate, RP(O)(OH)OP(O)(OH)R′; e.g dioctylpyrophosphate ($R=R'=C_8H_{17}O$).
>5 or 2×4	2	O, O	Dicarboxylic acids, $R(COOH)_2$.

[a] O, S or S, S for the corresponding thioacids.
[b] Di(2-ethylhexyl)phosphoric acid.
[c] Sodium diethyldithiocarbamate.
[d] Mono(2-ethylhexyl)phosphoric acid.
[e] Thenoyltrifluoroacetone.

given in Table 26. The over-all relation for metal extraction can be written (omitting solvation)

$$M^{z+} + zHA(org) \rightleftharpoons MA_z(org) + zH^+ \tag{11}$$

The corresponding equilibrium constant is K_{DM}.

It is instructive to compare the extraction of a trivalent and a tetravalent actinide ion by a mono-negative bidentate organic anion. Using the symbols M^{3+}, M^{4+} and HA for the metal ions and the acid, respectively, and assuming that a coordination number of 8 must be satisfied for both metal atoms, the formation of the neutral complexes will occur as,

$$M(H_2O)_8{}^{3+} + 3A^- \rightleftharpoons M(H_2O)_2A_3 + 6H_2O \tag{12a}$$

$$M(H_2O)_8{}^{4+} + 4A^- \rightleftharpoons MA_4 + 8H_2O \tag{13a}$$

The extractability of the complex formed with the trivalent actinide can be expected to be low because of its hydration. The tetravalent actinide complex has an all-organic surface (cf. Fig. 37), and is therefore expected to be easily extracted, the reaction being

$$MA_4 \rightleftharpoons MA_4(org) \tag{13b}$$

The expected poor extraction of $M(H_2O)_2A_3$ and good extraction of MA_4 is observed. In the system benzene–water at pH 1 and 0·1 M $[HTTA]_{org}$, <0·1 % of Am(III) is extracted but >90 % of Th(IV)[127, 218].

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[218] L. Newman, *J. Inorg. Nucl. Chem.* **25** (1963) 304.

In order for the trivalent actinide to be efficiently extracted, its complex must be dehydrated:

$$M(H_2O)_2A_3 + 2B \rightleftharpoons MB_2A_3 + 2H_2O \tag{12b}$$

$$MB_2A_3 \rightleftharpoons MB_2A_3(org) \tag{12c}$$

The adduct molecule B is, as before, an organic Lewis base. In the absence of a separate adduct molecule, the undissociated acid HA may solvate the complex[219]. It may then act either as a mono- or bidentate ligand. The simpler β-diketones form such self-adducts, as expected from their dual role of acid (in the enolic form) and Lewis base (the ketonic form). Thus with acetylacetone (HAA), U(VI) forms two extractable complexes, $UO_2AA_2(H_2O)_x$ with a distribution constant of 3·3 and UO_2AA_2HAA with a constant of 22 (chloroform–water)[148].

Such self-adducts are probably also formed in the Am(III)–HTTA system, but this has not been specifically proven[219a].

With strong bases such as TBP and TBPO (tributylphosphine oxide $(C_4H_9)_3PO$), the hydrate water is replaced, and more easily so by the more basic TBPO. Thus, when the organic phase is made 1 M in TBP, 10% Am(III) is extracted, and with 1 M TBPO over 99% is extracted[218].

The improved extraction by the addition of a second reagent (complex former, adduct molecule, etc.) is called *synergism*, the opposite effect being *antagonism*. Synergism is particularly well known for systems where hydration hampers the extraction. A further example of this phenomenon is given in Fig. 38, which illustrates U(VI) extraction with

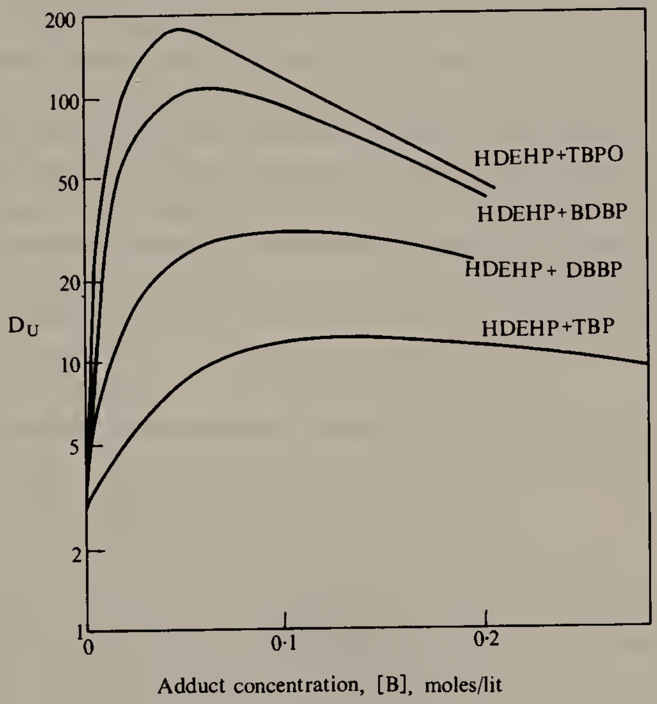

FIG. 38. Synergistic extraction of U(VI) by di-2-ethylhexyl phosphoric acid (HDEHP) and four different phosphoryl adducts. Aqueous phase 1·5 M H_2SO_4 and 0·004 M U(VI). Organic phase 0·1 M HDEHP in kerosene. TBPO = tributylphosphine oxide, $(C_4H_9)_3PO$. BDBP = butyldibutyl phosphinate, $(C_4H_9O)(C_4H_9)_2PO$. DBBP = dibutylbutylphosphonate, $(C_4H_9O)_2(C_4H_9)PO$[264].

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[219] D. Dyrssen, *Svensk kem. tidskr.* 67 (1955) 311.

[219a] H. Schreck, KFK 672, Kernforschungszentrum Karlsruhe (1967).

HDEHP (di-2-ethylhexyl phosphoric acid, $(C_8H_{17}O)_2P(O)OH = HA)$) and four different adduct formers B. The extracted complex is assumed to be $UO_2(HA_2)_2B_x$ ($x = 1$ or 2). The extraction is improved in the order of increasing basicity of B, being with TBPO almost a factor of 100 better than with no adduct former. The decrease in D with higher adduct concentration is due to interaction between the adduct former and HDEHP, which lowers the activity of the latter. An excellent review of synergism is given by Irving[127]. Synergism should not be confused with improvement in extraction due to change of diluent, provided the diluent does not directly interact with the metal ions.

It is generally assumed that the first step in metal chelate extraction is the formation of a neutral complex in the aqueous phase. This is supported by the fact that in two-phase aqueous organic systems the equilibrium constants determined for complexation in the aqueous phase are the same, independently of the organic solvents, as long as they are "inert" (e.g. benzene, carbon tetrachloride, etc.)[220].

An increase in the free ligand concentration will favor metal complexation, and consequently also metal extraction. The free ligand concentration, $[A^-]$, depends on the total concentration of A in the system, and the reactions in the organic phase (e.g. polymerization) and water (dissociation, complex formation). An example of a relation governing the distribution of an acidic reagent is given by eqns (4.3) to (4.7) for benzoic acid in benzene–water. High A^- concentration is favored by high pH, high acid dissociation constant (low pK_a) and low distribution constant (K_d). For the same group of compounds, K_a increases by the introduction of electronegative groups in the organic chain[135]. There seems to be no general relation between the K_a and K_d of the chelating agent.

The physical properties of some common chelating agents are listed in Table 27. Most of them are rather weak acids in water, with the exception of the substituted phosphoric acids. The distribution constants K_d are in most cases very high, the exceptions being low molecular weight compounds containing a relatively high amount of basic (in the Lewis sense) oxygens, such as salicylic acid and acetylacetone. With this same exception, the solubility of the compounds in water is very low. As can be seen from the table, the solubilities in organic diluents (Sorg) vary considerably, in some instances being quite low. In a saturated system with limited solubilities, K_d is of course equal to the ratio of the solubilities in the two phases.

TABLE 27. PHYSICAL PROPERTIES OF SOME ORGANIC ACIDS USED AS ACTINIDE EXTRACTANTS

Acid	Org. diluent	S_{org}(M)	log K_d	$-\log K_a$
Salicylic acid	Chloroform	0·17	0·5	2·9
Cupferron	Chloroform	0·4	2·3	4·2
8-Hydroxyquinoline (oxine)	Chloroform	2·63	2·66	9·8
Acetylacetone	Benzene	∞	0·78	9·0
Thenoyltrifluoroacetone	Benzene	5·27	1·6	6·2
1-Nitroso-2-naphthol	Chloroform	1·35	2·97	7·6
Di(2-ethylhexyl)phosphoric acid*	n-Octane	∞	3·44	1·4
Mono(2-ethylhexyl)phosphoric acid	n-Octane	∞		1·3 (k_1)

* Dimerization constant log K_2 4·47.

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[220] J. Rydberg, *Svensk kem. tidskr.* 67 (1955) 499.

The complexes formed between chelating reagents and metals are characterized by

(a) dentate number (bidentate, tridentate, etc.),
(b) chelate ring size (4-, 5-, or higher membered ring),
(c) number of acidic groups (monobasic, dibasic, etc.),
(d) metal coordinating atoms (e.g. O and O, O and N, etc.).

This division is used in arranging the compounds in Table 26. The monobasic compounds forming bidentate complexes form the largest group. The carboxylic and organophosphorus acids, and the corresponding thio-compounds, may form 4-membered rings, and all other agents in practical use form 5- or 6-membered rings. The rings are usually nearly planar. The ring formation stabilizes the complex through delocalization of electrons, which decreases the total energy in the system. The complexes with 5- and 6-membered rings usually show higher stability, as indicated from the complexity constants, than the 4- or more unusual 7-membered rings. Dimeric phosphoryl compounds may form 8-membered rings.

The formation of multidentate (i.e. more than bidentate) bonds requires bending and angular adjustment of the organic compound to fit the possible orbitals of the metal. Fewer multidentate complex formers are known, the most common ones being polybasic alkylamines like EDTA. These reagents extract actinides only weakly.

From reactions (12a) and (13a) it is seen that the total number of molecules increases in the formation of the metal chelate, and thus (at least to a first approximation) the disorder increases in the system. The corresponding increase in ΔS shifts the equilibrium to the right, because β_n of the reaction increases: $-\mathbf{R}T \ln \beta_n = \Delta G = \Delta H - T\Delta S$. The stability constants are therefore usually higher when chelation occurs, than when single bonds are formed. The stability also increases with the number of rings formed[135].

It is well known that for a particular group of organic compounds, the stability constants of the corresponding metal complexes change with the acid dissociation constant in a manner according to Fig. 11. For the same reacting atoms, and nearly the same steric configurations, only the basicity of the anion will change by substitution in the organic structure, and thus the attraction for M^{z+} and H^+ will change proportionally. The weaker acids will consequently form the stronger complexes.

The metal chelate complexes have high distribution constants, often much higher than the extractant itself. For example, the distribution constant of acetylacetone (HAA) between benzene and water is 6·0, while it is 320 for the $ThAA_4$ complex[220]. According to the theory of regular solutions[135], one would expect the distribution constant of the metal complex (λ) to be proportional to the distribution constant (K_d) of the complexant. This is also found with inert organic solvents. For example[222], $\log \lambda_4 = 4 \log K_d + \text{const.}$ for the extraction of $NpAA_4$ into a number of inert solvents (see Fig. 39).

A high distribution constant for the metal complex makes it possible to extract $\gtrsim 99\%$ of the metal in one experimental step. Unfortunately, the solubility of the metal complexes in the organic phase is often much lower than that of the extractant itself. For example, while oxine (HOx) is highly soluble in chloroform, and the distribution constant λ_4 of the complex $ThOx_4$ between chloroform and water is 430, the solubility of the metal complex in chloroform is only $0{\cdot}9 \times 10^{-3}$ M[138]. Actinide extractions with organic anions are therefore often limited to trace concentrations.

Extraction with organophosphoric acids is an exception. Both the acids themselves and the metal complexes are quite (often infinitely) soluble in organic solvents. The monobasic acids usually dimerize and the dibasic ones polymerize in non-polar solvents.

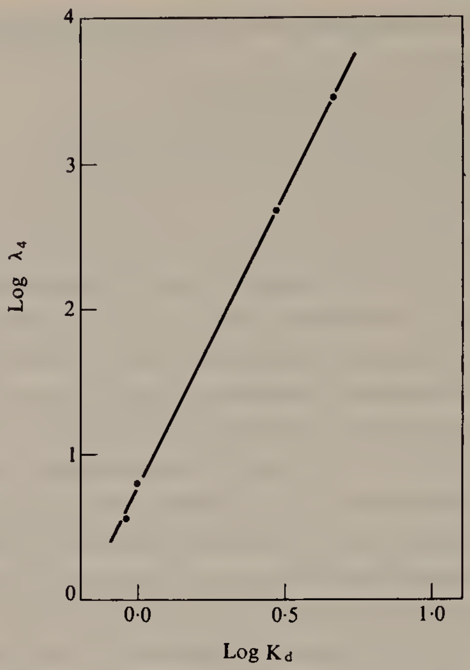

FIG. 39. The distribution constant λ_4 for $NpAA_4$ as a function of the distribution constant K_d for acetylacetone (HAA) in (from top to bottom) benzene, carbon tetrachloride, cyclohexane and n-hexane[222].

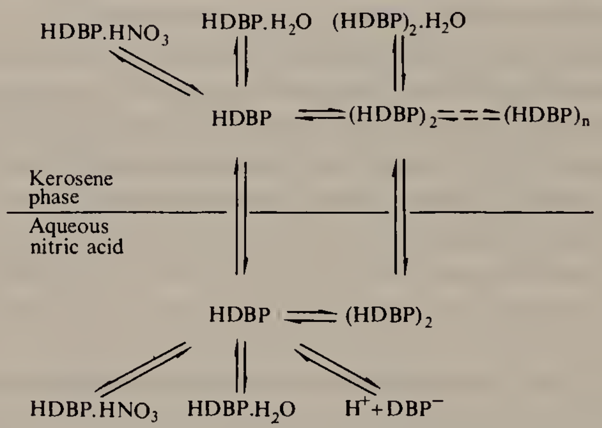

FIG. 40. Schematic diagram of equilibria in the dibutylphosphoric acid–kerosene–HNO_3 system. HDBP = $(C_4H_9O)_2P(O)OH$[257].

The degree of polymerization depends on the polarity of the diluent (Table 28). The number of extractant species which have to be considered in actinide extractions is indicated in Fig. 40. This complicates the stoichiometry of the extraction process, as is discussed in section 4.7.3.

Chelate complex formation is treated in the monographs by Martell and Calvin[135] and, with special reference to solvent extraction, by Zolotov[138]. The excellent survey of actinide extraction by Dyrssen in 1956 is still of current interest[221].

[221] D. Dyrssen, *Svensk kem. tidskr.* **68** (1956) 212.
[222] J. O. Liljenzin and J. Stary, *J. Inorg. Nucl. Chem.* **32** (1970) 1357.

TABLE 28. DEGREE OF POLYMERIZATION OF ALKYLPHOSPHORIC ACIDS IN VARIOUS DILUENTS[c]

Diluent	ϵ	HDEHP[a]	H_2MEHP[b]
n-Hexane	1·91	2·1	14·5
Carbon tetrachloride	2·24	2·0	6·5
Benzene	2·28	2·0	6·2
Chloroform	4·90	1·9	4·5
Acetone	18·5	1·7	2·0
Methylalcohol	32·6	1·0	1·0

[a] Di(2-ethylhexyl)phosphoric acid.
[b] Mono(2-ethylhexyl)phosphoric acid.
[c] J. R. Ferraro and D. F. Peppard, *Nucl. Sci. Eng.* **16** (1963) 389.

4.6. Mathematical treatment of solvent extraction equilibria

Solvent extraction of actinide species is carried out either to learn about the chemistry of the actinides (cf. section 2.1.3), or in order to prepare a pure actinide sample. These two approaches lead to two sets of equations: the fundamental equations (sections 4.6.1 and 4.6.2) which give the relation between complex formation and actinide distribution[144–151], and the applied equations (section 4.6.3) associated with the relations between actinide distribution, yield and purity[163,176,177,223]. Only the equations pertinent to actinide extraction are given here.

Because of the difficulties involved in determining the activity factors of the solutes in both phases, practically all solvent extraction equilibrium constants are based on concentration data only. In solvents so different that they are immiscible, it seems highly improbable that the activity factors run parallel. It is therefore essential that experiments are carried out at constant (preferably high) ionic strength and media[223a], and with nearly constant organic phase composition. Tracer experiments with actinides often meet these criteria.

Few examples of polynuclear complexes are known to exist in the organic phase, and they will therefore not be considered in this section.

4.6.1. *Extraction by Anion Exchange*

Assuming that only one metal complex exists in the organic phase, $(RB^+)_p(ML_i)^{p-}$, but that various ML_n^{z-n} complexes are formed in the aqueous phase (depending on the free ligand concentration $[L^-]$, eqn (2.2)), reaction (3) leads to the following relation for the metal distribution between the two phases

$$D_M = \frac{K_{DM}[RB^+L^-]^p_{org}\beta_i[L^-]^{i-p}}{\sum_0^N \beta_n[L^-]^n} \tag{4.18}$$

It follows that D_M rises with $[L^-]$, when $\bar{n}$, the average ligand number in the aqueous phase (eqn (2.4)), goes from 0 (no ML_n^{z-n} complexes) to $i-p = z$. D_M will then decrease with increasing $[L^-]$, provided $i < N$, the maximum number of ligands bound to the metal atom. Curves of this type are given in Fig. 51.

[223] L. Alders, *Liquid–Liquid Extraction*, Elsevier Publ. Co., Amsterdam (1955).
[223a] O. Ginstrup, *Acta Chem. Scand.* **27** (1970) 875.

From eqn (4.18) one can derive

$$\delta \log D_{\mathrm{M}}/\delta \log [\mathrm{RB^+L^-}]_{\mathrm{org}} = p \tag{4.19}$$

and (because $i-p = z$ for the monobasic ligand $\mathrm{L^-}$)

$$\delta \log D_{\mathrm{M}}/\delta \log [\mathrm{L^-}] = z - \bar{n} \tag{4.20}$$

According to eqn (4.19) the number of amines bound per metal atom can be determined from the slope of a plot of log D_{M} against log $[\mathrm{RB^+L^-}]_{\mathrm{org}}$. An example of this is given in Fig. 48. From eqn (4.20) it follows that a plot of log D_{M} against log $[\mathrm{L^-}]$ should also yield a straight line, provided $\bar{n}$ is constant; an example of this is given in Fig. 49.

It should be observed, that $[\mathrm{RB^+L^-}]_{\mathrm{org}}$ is the concentration of free $\mathrm{RB^+L^-}$ in the organic phase. Because the amine species dissolve only in the organic phase, the total amine concentration is given by

$$\begin{aligned} C_{\mathrm{B}} = {} & [\mathrm{RB^+L^-}]_{\mathrm{org}} + [\mathrm{B}]_{\mathrm{org}} + [\mathrm{RB^+L^-HL}]_{\mathrm{org}} + [\mathrm{RB^+}]_{\mathrm{org}} + \\ & \Sigma q[(\mathrm{RB^+L^-})_q]_{\mathrm{org}} + \Sigma p[(\mathrm{RB^+})_p\mathrm{ML}_n{}^{-p}]_{\mathrm{org}} \end{aligned} \tag{4.21a}$$

The different species have all been discussed in section 4.5.1. In an acid concentration region, where the hydrolysis of the alkylamine ion can be neglected (i.e. $[\mathrm{B}] \ll [\mathrm{RB^+L^-}]$) and no excess acid is extracted ($[\mathrm{RB^+L^-HL}] \ll [\mathrm{RB^+L^-}]$; cf. Fig. 30), and under monomeric ion-pair conditions ($[\mathrm{RB^+}] + [(\mathrm{RB^+L^-})_q] \ll [\mathrm{RB^+L^-}]$; cf. Fig. 31) one obtains for *trace* metal concentration

$$C_{\mathrm{B}} = [\mathrm{RB^+L^-}]_{\mathrm{org}} \tag{4.21b}$$

In eqns (4.18) and (4.19), C_{B} cannot replace $[\mathrm{RB^+L^-}]_{\mathrm{org}}$, unless the conditions are properly chosen. Many erroneous explanations of amine extraction systems have been made because of an incorrect application of eqn (4.21b).

$[\mathrm{L^-}]$ in eqns (4.18) and (4.20) is the free ligand concentration. In addition to the common difficulties encountered in calculating $[\mathrm{L^-}]$ from C_{L}, when the concentration of L bound in complexes cannot be neglected (cf. section 2.1), concentration values are meaningful to use only at constant gross composition. At the high ligand concentrations usually necessary for metal extraction with amines it may sometimes be more advantageous to correct for varying activity factors using the Debye-Hückel or analogous equations[167], than to try to keep constant activity factors in the experiments.

In acid-deficient primary, secondary and tertiary amine systems, the amine base B may make up a considerable fraction of C_{B} (cf. eqn (4.21b)). In such systems, the metal distribution D_{M} will be found to change proportionally with $[\mathrm{B}]^p_{\mathrm{org}}$ and $[\mathrm{H^+}]^p$.

In the case of excess acid extraction (reaction 2b), and assuming that the reaction

$$p\mathrm{RB^+L^-HL(org)} + \mathrm{ML}_i{}^{-p} \rightleftharpoons (\mathrm{RB^+})_p\mathrm{ML}_i{}^{-p}\mathrm{(org)} + p\mathrm{L^-} + p\mathrm{HL} \tag{14}$$

has an equilibrium constant K_{DMEA}, the resulting equation for the metal distribution will equal eqn (4.18) with replacement of K_{DM} by $K_{\mathrm{DMEA}} \cdot K_{\mathrm{DEA}}$ (from reaction 2b). Thus the same eqns (4.19) and (4.20) will be obtained. Consequently, the effects of excess acid extraction will not lead to any $[\mathrm{H^+}]$ dependence in the metal extraction. However, an increase in $[\mathrm{H^+}]$ or [HL] will shift reaction (2b) to the right, and lower $[\mathrm{RB^+L^-}]_{\mathrm{org}}$ at constant C_{B}, leading to a decrease in D_{M}. This is the common explanation for the fact that D_{M} for the actinides decreases with increasing acidity at constant $[\mathrm{L^-}]$.

4.6.2. *Extraction by Chelation and Solvation*

The extraction of the metal cation M^{z+} from an aqueous phase into an organic solvent containing the two reactants HA and B, defined as before, will follow the reaction (omitting hydrate water)

$$M^{z+} + nHA(org) + pB(org) \rightleftharpoons MA_nB_p(org) + nH^+ \tag{15}$$

The extracted complex is assumed to be coordinatively saturated and neutral. The equilibrium constant is K_{DM}. This equation is useful in summarizing extraction data[167].

A. Simple complexes MA_n. To understand the underlying reactions we shall first assume $p = 0$ in reaction (15); thus only MA_n complexes are formed. This case has been discussed in section 2.1.3. It was shown that the distribution factor D_M for the metal is

$$D_M = \frac{\lambda_i \beta_i [A]^i}{\sum\limits_0^N \beta_n [A]^n} \tag{4.22}$$

which is identical to eqn (2.13). λ_i is the Nernst distribution constant of the uncharged complex MA_i. A plot of log D_M against log [A] will yield the curve in Fig. 41.

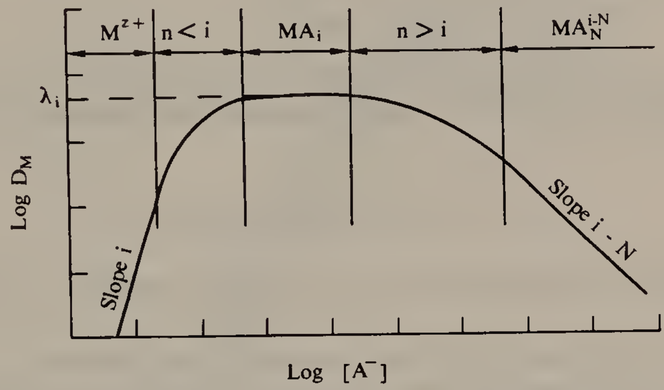

FIG. 41. Distribution curve for simple complex of type MA_n.

At low values of $[A^-]$, the denominator becomes $\beta_0 = 1$, and the curve will have a slope of i. In this region M^{z+} will dominate in the aqueous phase. If the ligand is monobasic, $i = z$, and thus the charge of the uncomplexed metal ion is obtained. This is a well-established technique for identifying the valency state of an actinide ion.

At the highest A^- concentrations, the slope will be $i-N$, which is the charge of the highest complex. If a straight line is obtained, there are good reasons to assume that the complex is coordinatively saturated. Thus the coordination number N of the actinide ion may be obtained.

At intermediate $[A^-]$ values a plateau may be encountered. From eqn (4.22) it is seen that D_M is independent of $[A^-]$ only for $i = n$, where $D_M = \lambda_i$. In this region the complex MA_i dominates in both the organic and aqueous phases. Thus the distribution constant λ_i of the neutral complex MA_i becomes known.

Finally, β_n can be determined by mathematical treatment of eqn (4.22), using either graphical (slope analysis)[147,150,224] or numerical (least squares)[225] methods. Approximate β_n values are easily obtained in the following manner: the mean ligand number $\bar{n}$ is calculated with the relation

$$\bar{n} = i - \delta \log D_M / \delta \log [A \tag{4.23}$$

From eqns (2.5) and (2.6)

$$\Sigma(\bar{n} - n)\beta_n[A]^n = 0 \tag{4.24}$$

and approximating for the two $\bar{n}$ values adjacent to $\bar{n} = 0{\cdot}5$, $1{\cdot}5$, etc., one finds that $K_1 \approx [A]^{-1}_{\bar{n}=0\cdot5}$, $K_2 \approx [A]^{-1}_{\bar{n}=1\cdot5}$, etc., where K_1, K_2, etc., are the step-wise formation constants ($\beta_n = \Pi K_n$)[147,226].

The free ligand concentration $[A^-]$ is obtained from the total amount of A in the system, the phase volumes, K_a, K_d and pH, provided the total metal concentration is much less than the total ligand concentration ($C_M \ll C_A$). This is usually the case in experiments with tracer amounts of metal. Otherwise corrections must be made for A bound in the metal complexes. Because of the simplicity of the calculations, and of the high specific radioactivity of the actinides, radioactive tracers are practically always used in extraction studies of actinides (cf. section 2.1.3).

It can easily be shown that the K_{DM} value for reaction (15) with $p=0$ is a combination of the equilibrium constants according to the relation

$$K_{DM} = \beta_i \lambda_i K_a{}^i K_d{}^{-i} \tag{4.25}$$

It can be shown further, that in the concentration range where M^{z+} dominates in the aqueous phase, the pH value for 50% extraction according to eqn (4.22) is given approximately by

$$pH_{\frac{1}{2}} = \frac{-\log K_{DM}}{i} - \log [HA]_{org} \tag{4.26}$$

K_{DM} and pH½ values are commonly used to describe extraction conditions for metal chelates.

B. Two complexes MA_n and ML_p. If the aqueous phase contains in addition to MA_n, ligands L^-, which form the complexes ML, ML_2, etc., which are non-extractable, and no mixed complexes (MA_nL_p) are produced, one can, according to section 2.1.3, derive the expression

$$D_M = K_{DM}\left(\frac{[HA]_{org}}{[H^+]}\right)^i \cdot \frac{1}{\sum\limits_{0}^{p} \beta_p[L]^p} \tag{4.27}$$

which is identical to eqn (2.10). This relation was developed by Connick and McVey[145], during their study of zirconium hydrolysis using HTTA as extractant. It has been widely used for the determination of the aqueous complexation of the actinides, and is commonly referred to as "the TTA method". The equation indicates that at constant [A] (in practice constant [HA] and pH), the distribution ratio D_M is a variable of [L] only. From the dependence of D_M (const. [HA], $[H^+]$) on [L], it is a straightforward matter to determine β_p. A good example is the investigation of Np(IV)–sulphate complexes (see Table 11).

[224] D. Dyrssen and L. G. Sillén, *Acta Chem. Scand.* 7 (1953) 663.
[225] J. Rydberg and J. C. Sullivan, *Acta Chem. Scand.* **13** (1959) 2057.
[226] J. Bjerrum, *Metal Amine Formation in Aqueous Solution.* Diss. Copenhagen (1941).

C. Mixed complexes MA_nB_p. The stability constant for the mixed complex MA_nB_p is defined by

$$\beta_{np} = \frac{[MA_nB_p]}{[M][A]^n[B]^p} \tag{4.28}$$

The uncharged, extracted complex will be identified by MA_iB_j

$$\lambda_{ij} = [MA_iB_j]_{org}/[MA_iB_j] \tag{4.29}$$

The distribution ratio of the metal will be

$$D_M = \frac{\Sigma\ \lambda_{ij}\beta_{ij}[A]^i[B]^j}{\sum^{N}\sum^{P} \beta_{np}[A]^n[B]^p} \tag{4.30}$$

Figure 42 shows how D_M may depend upon [A] and [B]. In this particular case B = HA; this, however, does not alter the reasoning. The organic phase was found to contain two different complexes $i = 2, j = 0$ and 1. The summation in the numerator must be made over all extracted uncharged complexes.

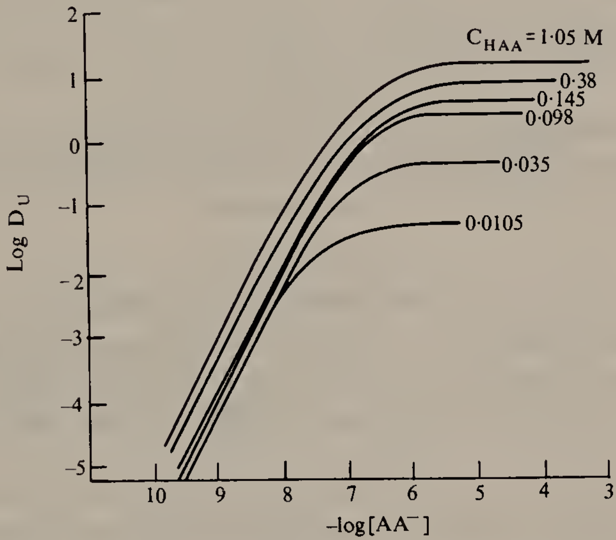

FIG. 42. Distribution of U(VI) between chloroform and water as a function of [AA⁻] and [B] (=[HAA]) where HAA is acetylacetone, in 0·1 M Na(H)ClO₄ at 25°C[148].

In Fig. 38, D_M is plotted as a function of [B]. The decrease in D_M at high [B] values is due to the interaction between the acid HA (=HDEHP) and the adduct molecule B, leading to the formation of HA·B. This decreases the concentration of free A^-, and consequently also the concentration of MA_iB_j (cf. section 4.5.2).

From (4.30) follows that

$$(\delta \log D_M/\delta \log [A])_{[B]} = i - \bar{n} \tag{4.31a}$$

and

$$(\delta \log D_M/\delta \log [B])_{[A]} = j - \bar{p} \tag{4.31b}$$

Thus, in Figure 42, where each curve represents constant [B], the slope of the curve gives the difference between the number of ligands A bound in the complex in the organic phase, i, and the corresponding average number $\bar{n}$ in the aqueous phase. When $[A] \to 0$, the slope approaches i. In an analogous manner it is possible to determine the number j of B molecules bound in the complex.

This technique was developed by Rydberg[148] for complexes of the type $MA_n(OH)_p(HA)_r$, and more generally by Irving, Rossotti and Williams[149] for complexes of type $H_hM_mL_l(H_2O)_wS_s$. From data like those in Fig. 42, β_{np} and λ_{ij} may be evaluated graphically[148] or numerically[228]. Thus, all mixed complexes and their equilibrium constants can be determined. However, the graphical approach is rather tedious. In the numerical treatment a statistical analysis must be built in, so that only significant equilibrium constants are obtained[229].

4.6.3. *Multistage Extraction*

A pure actinide product can be obtained by solvent extraction in one single equilibration (one stage) only when the distribution factor of the actinide is very high (usually $D_M \gg 10$) and the distribution factors for the undesired impurities very low (usually $D_M \ll 0{\cdot}01$). This is easily seen from the relation

$$\psi_1 = P/(P+1) \tag{4.32a}$$

where ψ_1 is the weight fraction W_{org}/W_{tot} of the solute ($W_{tot} = W_{org} + W_{aq}$) in the organic phase after one extraction and

$$P = D \cdot \theta \tag{4.33}$$

where θ is the phase volume ratio V_{org}/V_{aq}. P is called the *extraction factor.* The percentage solute extracted, commonly denoted $E(\%)$, is equal to $100 \cdot \psi_1$. Because the fraction of non-extracted actinide is φ_1, and $\psi_1 + \varphi_1 = 1$, one obtains

$$\varphi_1 = 1/(P+1) \tag{4.32b}$$

In the extraction of U(VI) with 100% TBP from 1 M HNO_3 $D_U = 20$ (Fig. 33), while for the fission product lanthanum $D_{La} = 0{\cdot}07$. If one extracts with a phase ratio of 0·5, then, according to eqns (4.32) and (4.33), $\psi_U = 0{\cdot}909$ ($E_U = 100 \cdot \psi_U = 90{\cdot}9\,\%$) and $\psi_{La} = 0{\cdot}034$ (E_{La} $3{\cdot}4\%$). This may be unsatisfactory both with respect to uranium yield and purity.

The yield can be increased by repeated extractions of the same aqueous phase (multiple extraction with one stationary phase, or "cross-current extraction"). For n such extractions one finds that

$$\varphi_n = (P+1)^{-n} \tag{4.34}$$

Suppose $n = 3$ for our example, then $\varphi_{3,U} = 0{\cdot}00075$, i.e. for the three organic phase volumes taken together $E_U = 100(1-\varphi_{3,U}) = 99{\cdot}93\%$. However, for lanthanum $\varphi_{3,La} = 0{\cdot}902$, i.e. $E_{La} = 9{\cdot}8\,\%$. Although the uranium yield is high, the lanthanum impurity may be intolerable.

A more elaborate technique must be employed in order to obtain both high yield and high purity under such conditions. Many such batch-wise laboratory techniques have been described using alternatively fresh organic (extraction) and aqueous (washing) solutions. The extractions are carried out either with a battery of test-tubes (or separatory funnels) or in special multistage equipment (Craig machines)[176].

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[227] J. C. Sullivan and J. C. Hindman, *J. Am. Chem. Soc.* **76** (1954) 5931.

[228] L. G. Sillén and N. Ingri, *Arkiv Kemi* **23** (1964) 97.

[229] J. Rydberg, *Acta Chem. Scand.* **15** (1961) 1723.

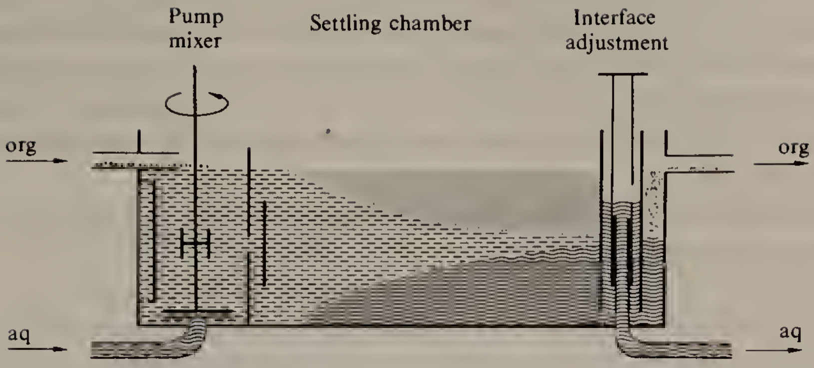

FIG. 43. Mixer-settler for continuous solvent extraction.

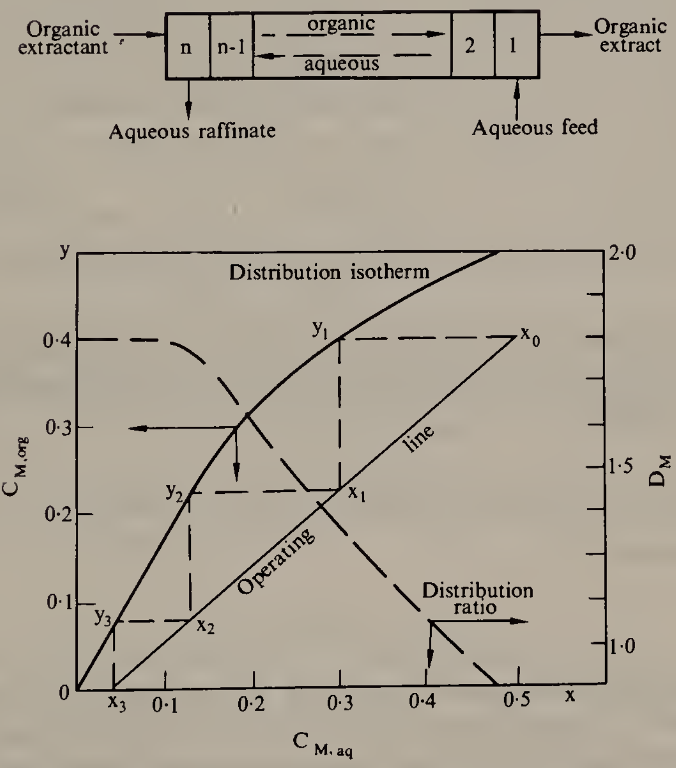

FIG. 44. Counter-current solvent extraction battery with *n* mixer-settler stages (top). Distribution isotherm and McCabe–Thiele diagram for a three-stage counter-current extraction process (bottom). C_M in the feed is x_0. After equilibration and separation in the first mixer-settler stage, the outgoing organic extract contains $C_{M,org} = y_1$ and the raffinate $C_{M,aq} = x_1$. Because the slope of the operating line is equal to the flow rate ratio aqueous:organic (θ^{-1}), the extract and raffinate leaving the second stage will have the composition y_2 and x_2, respectively, and from the third stage y_3 and x_3. The extract yield is $(x_0 - x_3)/x_0 \approx 93\%$ in the example. D_M increases from 1·37 in the first stage to 1·80 in the third stage.

Continuous processes are preferred in industry, where the most common and simple solvent extraction equipment is the mixer-settler (see Fig. 43). This type of equipment is also becoming standard in laboratories engaged in process development. In the uranium industry a single mixer-settler may hold as much as 1000 m^3. The mixer-settlers, each closely corresponding to a single ideal extraction stage, are arranged in batteries containing any number of stages. In these batteries the aqueous and organic phases flow counter-current to each other (see Fig. 44, top).

For counter-current solvent extraction, either batch-wise or continuously, one finds that for the stationary state and for n stages

$$\varphi_n = \frac{P - 1}{P^{n+1} - 1} \tag{4.35}$$

provided P is constant through all stages. In our example one obtains for $\theta = 0{\cdot}5$ (ratio of flow organic:aqueous) and $n = 3$ that $E_U = 99{\cdot}91\%$ and $E_{La} = 3{\cdot}5\%$, thus about the same yield of uranium as before, but with a somewhat lower lanthanum impurity as compared to the cross-current extraction procedure. This impurity figure can be lowered by modification of the extraction process according to Fig. 45, so that the extraction battery contains n extraction stages with the extraction factor P_1, and m washing stages with the extraction factor P_2. Then[223]

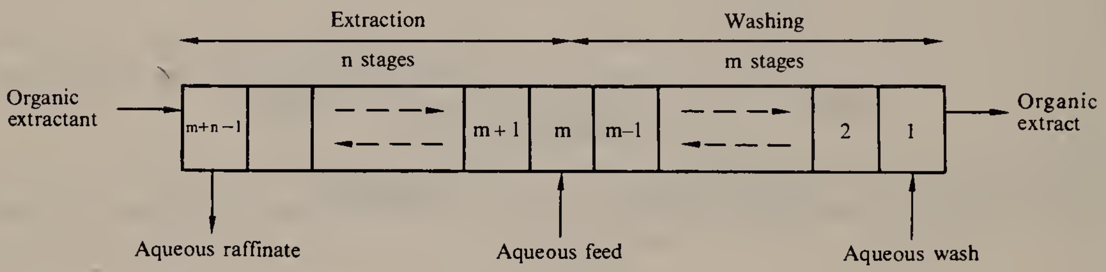

FIG. 45. Counter-current solvent extraction with intermediate feed.

$$\varphi_{m,n} = \frac{(P_1 - 1)(P_2{}^m - 1)}{(P_1{}^{n+1} - 1)(P_2 - 1)P_2{}^{m-1} + (P_2{}^{m-1} - 1)(P_1 - 1)} \tag{4.36a}$$

which for $P_1 = P_2$ reduces to

$$\varphi_{m,n} = \frac{P^m - 1}{P^{m+n} - 1} \tag{4.36b}$$

In the latter case, using three extraction stages and two washing stages, one finds for our example that E_U is $99{\cdot}91\%$ and E_{La} is $0{\cdot}12\%$. Thus both high yield and high purity are achieved with the counter-current, central or intermediate feed solvent extraction technique. This technique is extensively used in uranium production, nuclear fuel element reprocessing, and transuranium element separations (see section 4.8). Because the conditions are selected so that a high ($\gg 1$) distribution factor is obtained for the desired product, and low ones ($\gg 1$) for the impurities (e.g. fission products), high purity and good yield are often obtained in relatively few stages ($m + n \lesssim 10$).

A further industrial requirement on solvent extraction processes is high capacity, which means high concentrations of solutes in the aqueous and organic solvents ("high loading").

The extracted solute and/or the impurities may then act as (their own) salting out agents. The extraction factor P (or distribution factor D_M) will then vary from stage to stage, depending on how the extraction proceeds. Although the equations above can still be used, the calculation of the number of stages, flow ratio (θ), etc., needed in order to obtain the desired product becomes cumbersome. However, for one solute the problem is easily solved graphically with McCabe–Thiele diagrams (see Fig. 44).

4.7. Actinide extraction systems

The general principles for solvent extraction of actinides by cationic, neutral and anionic extractants have been presented in sections 4.2–4.6. In this section data are presented which emphasize the different extractabilities of the various actinide valency states, and for the same valency state the differences due to change in atomic number. In general the tetra- and hexavalent actinides are more efficiently extracted than the tri- and pentavalent states, and the heavier actinides better than the lighter ones, but many deviations exist, especially from the later rule.

The industrial requirement of high loading capacity of the organic phase has led to more investigation of the cationic (liquid anion exchangers) and neutral (carboxo and phosphoryl adducts) extractants, because they form highly soluble actinide complexes in a large number of organic solvents. In contrast, most anionic (chelating agents) extractants form complexes of very low solubility in the organic phase. However, the high metal distribution factors encountered at very low ligand concentrations in these systems (using radiotracer actinide) has made possible more precise research on the anionic extractant systems, which, therefore, are better understood than the cationic and neutral extractant systems. For the latter ones, physical methods of investigation other than distribution equilibrium data have lately provided the essential information for the interpretation of these systems.

However, the large number of variables encountered in some solvent extraction systems has made the detailed elucidation of the different reaction steps quite a difficult task. The extensive experimental data required for this purpose are probably also the reason for an almost complete lack of thermodynamic and kinetic information on solvent extraction systems, although some investigations in this field have recently been reported. The recent development of an advanced semi- or fully-automatic experimental technique ("AKUFVE") may improve the future situation[203].

4.7.1. *Liquid Anion Exchange Systems*

The extraction of actinide complexes by organic amines depends on two main factors: the complex formation in the aqueous phase and the nature of amine and diluent in the organic phase.

The complex formation in the aqueous phase has been discussed in section 2.2, where it was pointed out that the stability of a complex increases with inorganic anions in the basicity order given in Table 24. With increasing hydrogen ion concentration, the ligand anions become increasingly protonated, some anions (like F^-, Ac^-, etc.) more than others (like Cl^-, NO_3^-, etc.) leading to a reversed complex formation order. Thus, while MF_n^{z-n} complexes dominate over MCl_n^{z-n} complexes at low acidities, the MCl_n^{z-n} complexes may dominate over the MF_n^{z-n} complexes at high acidity. At the very high acidities often used for amine extraction, even the least basic anions become protonated, as for example

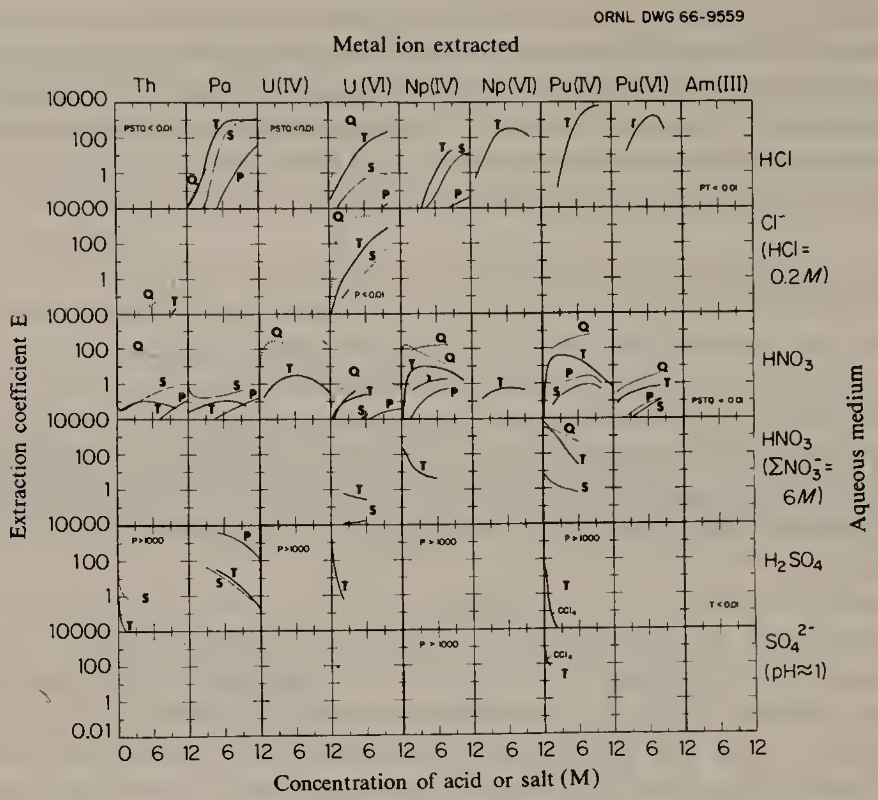

FIG. 46. Variation of extraction coefficient with acid or salt concentration and amine class for the lighter actinides. Measured at or corrected to 0·1 M amine concentration, usually in an aromatic hydrocarbon diluent. Amine classes: ---- primary amine (usually Primene JM, homologous mixture of tertiary alkyls, average molecular weight near 340); '''' secondary amine (usually Amberlite LA-1, branched dodecenyltertiary alkyl amine, average molecular weight near 360); ——— tertiary amine (usually TOA, TIOA, TLA or Alamine 336, essentially symmetrical amines with straight or slightly branched alkyls); = = = = quaternary ammonium. Points representing isolated single measurements with the respective classes are corresponding marked ., ', —, =. The notations > and <, with P, S, T and Q showing the amine classes concerned, indicate D values entirely above or entirely below the designated limit; however, the series of measurements so represented did not always extend over the entire concentration range of 0–12 M[172].

NO_3^- and Cl^-. Under such conditions a plot of log D_M against log C_{HL} will yield little information about which metal complexes are formed [cf. eqn (4.18)].

Figure 46 summarizes data on actinide amine extractions[172]. The actinides are more efficiently extracted by tertiary and quaternary amines than by primary and secondary amines from nitrate and chloride solutions. This is assumed to be due to the fact that the latter amines are more basic and therefore bind the acid more strongly, thus making it more difficult for the metal complex to replace the anion in the primary and secondary amines. However, actinide sulphates are preferentially extracted by primary and secondary amines. An explanation for this is that the extremely bulky sulphato complexes (the sulphate anion is bound monodentately to the metal complex[230]) and the tertiary and quaternary amines form a complex with charges too far apart to make a good ion pair [cf. eqn (4.16)]. Increasing ϵ_{org} would then improve the solvation and increase D_M, which is also observed[156].

The metal extraction increases with increasing amine carbon chain length up to about

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[230] M. Ross and H. T. Evans, Jr., *J. Inorg. Nucl. Chem.* **15** (1960) 338.

Table 29. Distribution of Pu(IV) between 2 M HNO_3 and Tertiary Amines (10 vol. %) in Xylene at Room Temperatures[a]

Amine	Distribution factor D_{Pu}
Tri-n-propyl	0·039
Tri-n-butyl	0·021
Tri-isobutyl	0·027
Tri-n-amyl	Formed two organic phases
Tri-isoamyl	Formed two organic phases
Tri-n-hexyl	85
Tri-n-heptyl	92
Tri-n-octyl	250
Tri-isooctyl	300
Tridecyl	115
Trilauryl (tridodecyl)	140
Triphenyl	0·0016
Tribenzyl	Amine nitrate insoluble in both phases

[a] A. S. Wilson, *Proc. Int. Conf. Peaceful Uses of Atomic Energy*, Vol. 17, p. 348, Geneva (1958).

C_{10} (see Table 29 and Fig. 51). Increased branching and aromatic substitution decreases D_M for the tertiary and quaternary amines although a certain amount of branching is often needed for good extraction[169]. That this decrease is probably due to steric hindrance (making r_+ too large) is supported by the fact that such effects are much smaller or absent with primary and secondary amines[156].

Table 25 gives the extraction of U(VI) by TOA in various diluents. D_U decreases with increasing ϵ for the diluent, which is expected according to eqn (4.16). The same order is found for the nitrate system[231]. The opposite order obtained for the extraction of acids has been discussed in section 4.5.1.

It is seen from Fig. 46 that the trivalent actinides are poorly extracted by all classes of amines under ordinary conditions. However, at very high $[Cl^-]$ and $[NO_3^-]$, tertiary and quaternary amines extract many trivalent actinides quite well (Fig. 47). The large differences in D_M values between the lanthanides and actinides, as well as between the lighter ($Z < 97$) and the heavier actinides ($Z > 97$), has led to practical application of this system in the so-called Tramex flow sheet (see section 4.8). When D_M is plotted against free amine concentration (log–log scale), a straight line of slope 2 is obtained (see Fig. 48), indicating that two amines are bound to each extracted actinide atom [cf. eqn (4.19)]. It is therefore assumed that the extracted complex is $(RB^+)_2ML_5^{2-}$. This complex is coordinatively unsaturated, and may thus contain some additional water. Van Ooyen[234] found at very high $LiNO_3$ concentration that a plot of log D_M against log $\{NO_3^-\}$ at pH 2·0 yields a line of slope 3 (Fig. 49). This fits with eqn (4.20) only if $\bar{n} = 0$, i.e. the dominating actinide species in the aqueous phase is uncomplexed (but hydrolysed) M^{3+}; this is a surprising result at these high ligand concentrations.

Moore[235] has investigated the extraction of Am(III) by various amines from 0·01 M HNO_3 in the presence of different organic acids. While no extraction was found for only

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[231] J. M. P. J. Verstegen, KR-68, Institutt for Atomenergi, Norway (1964).

[232] R. E. Leuze and M. H. Lloyd, *Process Chemistry*, 4 (1970) 597.

[233] G. Duyckaerts, J. Fuger and W. Müller, EUR 426, f, Euratom, Bruxelles (1963).

[234] J. van Ooyen, Diss. Amsterdam (1970); ref. 128, p. 485.

[235] F. Moore, *Anal. Chem.* **37** (1965) 1235.

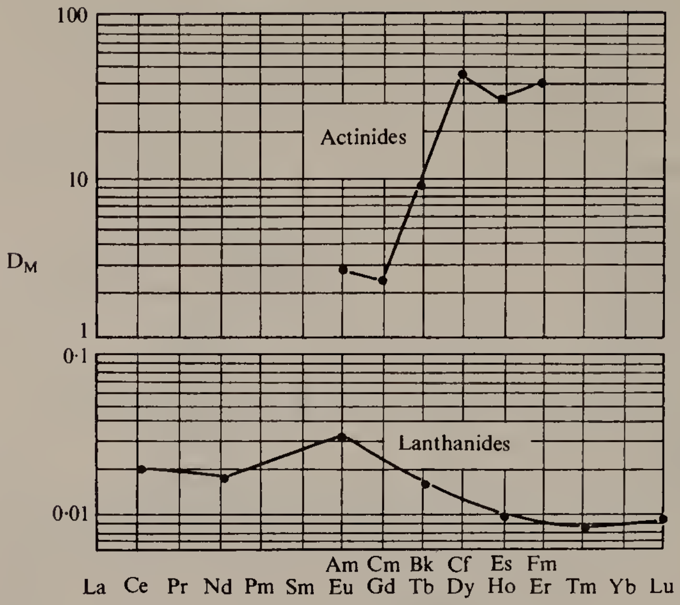

FIG. 47. Extractability of trivalent actinides and lanthanides into 0·6 M Alamin 336 (a mixture of aliphatic C_8–C_{10} tertiary amines) hydrochloride in xylene from 11 M LiCl and 0·02 M HCl[232]

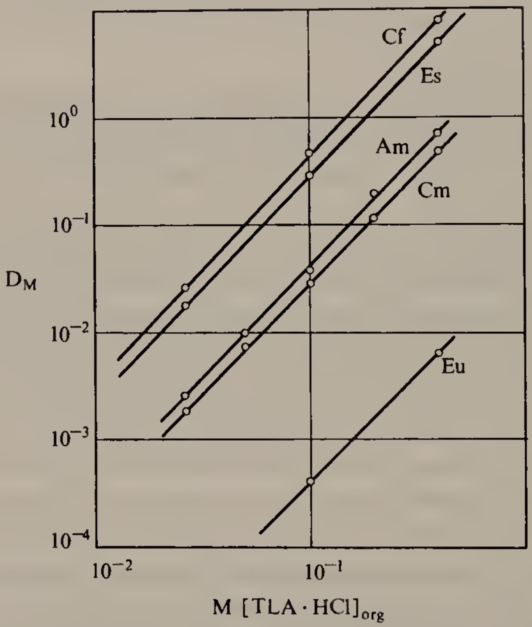

FIG. 48. The distribution of trivalent actinides and Eu(III) between TLAHCl dissolved in toluene and an aqueous phase containing 6·3 M LiCl, 2·7 M $CaCl_2$ and 0·01 M HCl. $[TLAHCl]_{org}$ is the concentration of free TLAHCl in organic phase[233]

HNO_3, $D_{Am} \gtrsim 1$ was obtained for citric, tartaric, oxalic acid and EDTA (all 0·2 M, except EDTA 0·02 M) using primary and secondary amines in xylene or hexone, and tertiary amine in hexone (except for EDTA, which however was extracted by quaternary amine) as extractants.

[236] W. E. Keder, J. C. Sheppard and A. S. Wilson, *J. Inorg. Nucl. Chem.* **12** (1960) 327.

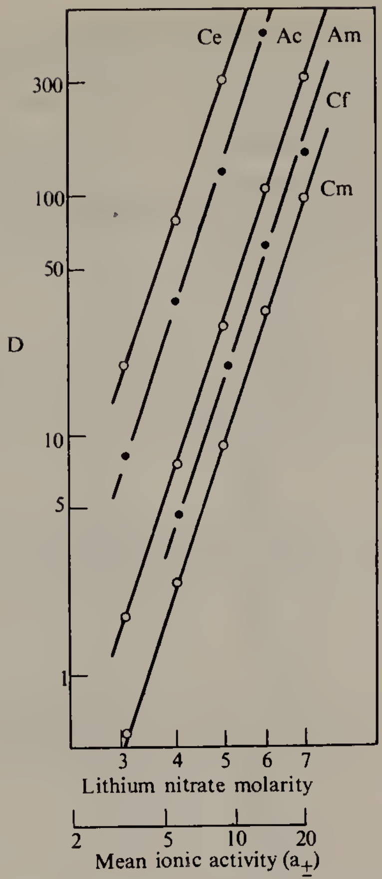

FIG. 49. Distribution factor of some of the trivalent actinides and cerium versus lithium nitrate concentration and mean ionic activity, $a_{\pm}$. All extractions at pH = 2·0. The extractant solution is 0·1 M TLMANO$_3$ in *o*-xylene[234].

The tetravalent actinides are extracted in the order of increasing Z (Th < U < Np < Pu) with the ligands Cl^- and NO_3^-, and in the order primary < secondary < tertiary < quaternary amine, as is seen from Figs. 46 and 50. For SO_4^{2-} systems the primary and secondary amines are better extractants, as discussed above. The influence of branching and substitution in tertiary amines is demonstrated by results in Fig. 51 and Table 29. From Fig. 50 it is concluded that the actinide ion-pair complex is $(TOAH^+)_2M(NO_3)_6^{2-}$. This is supported by gravimetric and spectrophotometric analyses[238]. The $(R_4N)_2M(NO_3)_6$ complexes (R_4N^+ being "Aliquat-336 ion") have been isolated by Koch *et al.*, who, from infrared measurements, conclude that the nitrato-oxygens are coordinatively attached to the actinide atom[239]. Some nitrato groups must in this case be monodentately bound to the metal atom. From Fig. 51 it is seen that the slope $\delta \log D_M$ versus $\delta \log[HNO_3]$ varies from large positive to large negative values. The decrease at high HNO$_3$ concentration has been explained as being due to the formation of less extractable $H_2M(NO_3)_6$[237], but other explanations may also be given, e.g. increasing formation of $(HB^+NO_3^-)_q$ (section 4.6.1).

The extracted chloro and sulphato complexes are assumed to be of the compositions $(RB^+)_2MCl_6^{2-}$ [234] and $(RB^+)_4M(SO_4)_4^{4-}$ [240].

[237] F. Baroncelli, G. Scibona and M. Zifferero, *J. Inorg. Nucl. Chem.* **24** (1962) 541.
[238] W. E. Keder, J. L. Ryan and A. S. Wilson, *J. Inorg. Nucl. Chem.* **20** (1961) 131.
[239] G. Koch, *Kerntechnik*, **7** (1965) 394; G. Koch and E. Schwind, *J. Inorg. Nucl. Chem.* **28** (1966) 571.
[240] V. M. Vdovenko, A. A. Lipovskii and S. A. Nikitina, *Radiokhimiya*, **3** (1961) 396.

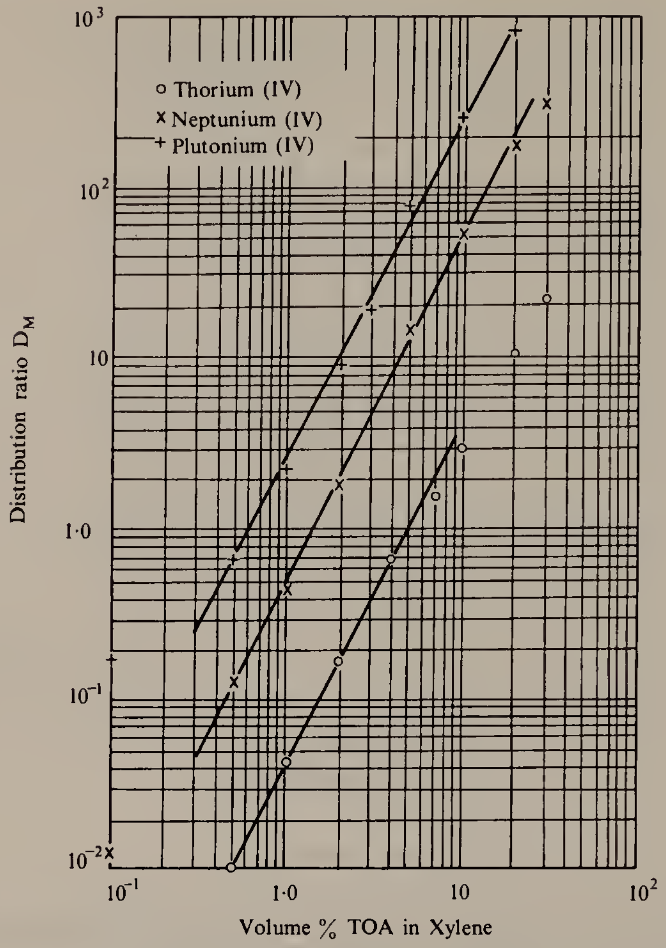

FIG. 50. The extraction of Th(IV) and Np(IV) nitrates from 4 M HNO_3, and of Pu(IV) from 2 M HNO_3, into TOA in xylene[236].

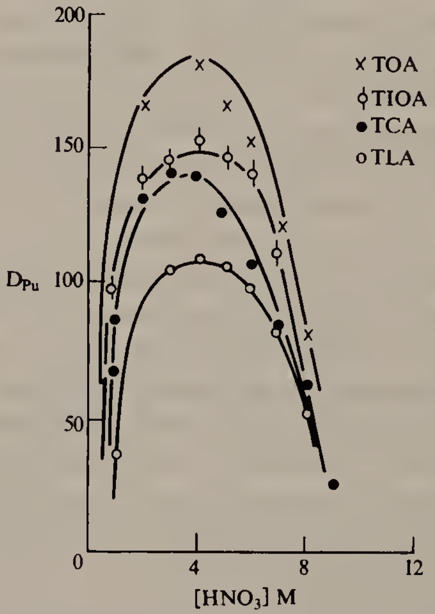

FIG. 51. Extraction of Pu(IV) by tertiary aliphatic amine nitrates (10 vol.%) in an aromatic diluent (Solvesso 100). TiOA=tri-iso-octyl amine, TCA=Alamin 336 (aliphatic chains are a mixture of n-octyls (predominating) and n-decyls) and TLA=trilauryl (tridodecyl) amine[237].

Pa(V) is efficiently extracted by all classes of amines from high concentrations of HCl and HF, but less so from HNO_3 solutions, as is seen from Fig. 46 and Table 30. The extraction is quantitative by tertiary and quaternary amines in xylene from 9 M HCl. Such systems have been used for fast and efficient separation of Pa(V) from fission products and tri- and tetravalent actinides[241]. From slope analyses the most probable complex appears to be $(RB^+)_2PaOL_5^{2-}$. Pa(V) is better extracted than Np(V).

TABLE 30. DISTRIBUTION RATIOS D_M FOR EXTRACTION OF ACTINIDES FROM NITRIC ACID WITH 10 v/o TRI-N-OCTYLAMINE (TOA)[a]

Molarity or HNO_3	Th(IV)	Pa(V)	U(IV)	U(VI)	Np(IV)	Np(V)	Np(VI)	Pu(III)	Pu(IV)	Pu(VI)	Am(III)
1·0	0·24	0·20	—	0·2	—	0·004	2·0	0·006	140	0·9	0·0004
2·0	0·48	0·28	0·6–1	0·50	45	0·010	2·8	0·032	210	1·7	0·0006
3·0	—	0·38	—	0·69	—	0·007	3·5	0·038	210	—	0·0004
4·0	0·53	0·38	—	0·99	66	0·015	5·0	0·048	250	3·8	0·0005
5·0	—	0·52	—	0·95	60	—	4·7	0·060	190	—	—
6·0	0·66	0·57	—	1·17	58	0·029	5·3	0·092	260	4·9	0·0005
7·0	—	0·65	—	1·2	55	—	—	0·095	100	—	—
8·0	0·39	0·47	—	0·78	37	0·048	4·6	0·062	80	5·0	0·0025
9·0	—	0·44	—	0·83	28	—	—	—	31	—	—
10·0	0·33	0·45	—	0·63	14	0·055	2·4	—	22	4·2	0·0010
11·0	—	—	—	1·40	—	—	—	—	8	—	—
12·0	—	—	—	0·26	—	—	—	—	4	1·7	0·0014
14·0	—	—	—	—	—	—	—	—	—	0·9	—

[a] W. E. Keder, J. C. Sheppard and A. S. Wilson, *J. Inorg. Nucl. Chem.* **12** (1960) 327.

The hexavalent actinides are extracted from HCl and HNO_3 solutions by the amines in the order primary < secondary < tertiary < quaternary, the D_M values increasing with increasing aqueous acidity. As is seen from Fig. 46, a maximum is reached for some amine–acid combinations. A more detailed comparison between U(VI), Np(VI) and Pu(VI) is presented in Fig. 52 for the extraction by TOA in xylene.

Taking into account the extraction of excess acid, Shevchenko *et al.*[242] found that $\delta \log D_{U(VI)}/\delta \log[TOAHNO_3]_{org} = 1$, and assumed the extracted complex to be $TOAH^+\text{-}UO_2(NO_3)_3^-$. Infrared measurements confirm that only the trinitrato complex is formed[238]. Slopes higher than 1, however, have been observed at high acidities and nitrate concentrations and with other diluents. This apparent violation of eqn (4.19) has been explained as being caused by the formation of the complex $(R_xH_{4-x}NNO_3)_pUO_2(NO_3)_2$ in the organic phase, where $p = 1$ for $x = 4$ (i.e. quaternary ammonium extractants), $p = 2$ for $x = 3$ and 2, and $p > 2$ for $x = 1$ (primary amines)[243]. Koch[244] has shown that the U(VI) nitrate complex extracted by tricaprylmethylammonium nitrate is $(R_3CH_3N)UO_2(NO_3)_3$.

In chloride solution the hexavalent actinides are assumed to be extracted as $MO_2Cl_4^{2-}$ complexes. From spectroscopic measurements Ryan[245] concludes that the $UO_2Cl_4^{2-}$ ion is hydrogen bonded to the tertiary ammonium chloride. The complex is probably solvated by water.

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[241] F. L. Moore, *Liquid-Liquid Extraction with High-molecular-weight Amines*, NAS-NS 3107, Nat. Acad. Sci., Washington (1960).

[242] V. B. Shevchenko, V. S. Shmidt and E. A. Nenarokomov, *Zh. Neorg. Khim.* 5 (1960) 2354.

[243] P. R. Danesi, F. Orlandini and G. Scibona, *J. Inorg. Nucl. Chem.* 27 (1965) 449.

[244] G. Koch, *Radiochim Acta*, 4 (1965) 128.

[245] J. L. Ryan, *Inorg. Chem.* 2 (1963) 348.

The extraction of U(VI) by tertiary amines from sulphuric acid solutions has been extensively studied because of its use in the industrial production of uranium. The systems show anomalous extraction (section 4.5.1) and the amines are often highly aggregated[200,201]. $D_{U(VI)}$ has a maximum around 0·015 M H_2SO_4, decreasing with increasing acidity, partly due to the formation of HSO_4^-. Distribution data suggest that there are several U(VI) sulphate species in the amine phase, $UO_2(SO_4)_n^{2-2n}$, where n may be 3 or 4[201,246,247] From studies of acid, water and metal distribution, supplemented by infrared absorption spectroscopy, thermogravimetry, differential thermoanalysis and chemical analyses

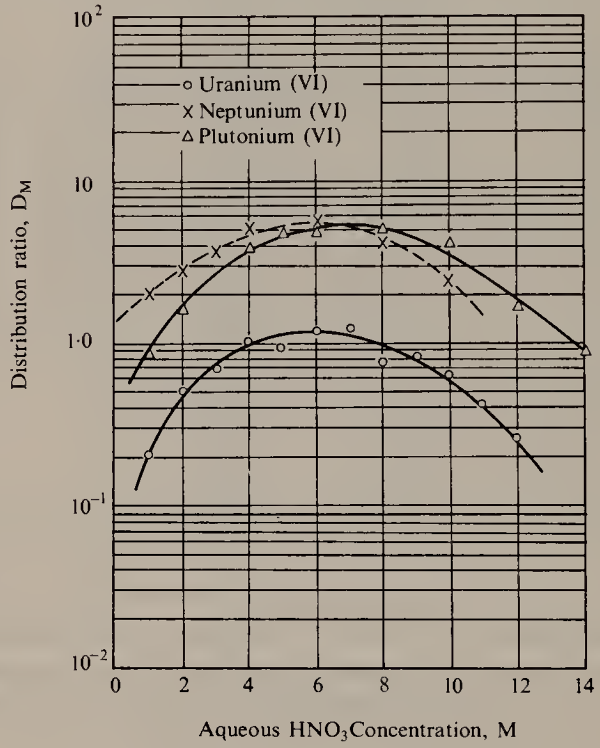


FIG. 52. The extraction of hexavalent actinide nitrates by TOA (10 vol.%) in xylene[236].

of the saturated organic phases and of the isolated complex, Sato[248] concludes that the extracted complex contains four alkylammonium ions per uranyl atom, and has the composition $(R_3NH^+)_4UO_2(SO_4)_3(H_2O)_3^{4-}$. While distribution measurements yield information about inner plus outer sphere complexes, spectroscopic measurements only refer to inner sphere complexes; thus the two techniques yield different but supplemental information.

4.7.2. *Neutral Adduct Systems*

Historically the neutral adducts have played a fundamental role in the solvent extraction of actinides. Thus uranium for the nuclear industry was first purified by extracting uranyl nitrate with diethyl ether or dibutyl carbitol (β,β′-dibutoxy diethyl ether) and later by TBP

[246] K. A. Allen, *J. Phys. Chem.* 64 (1960) 667.

[247] W. J. McDowell and C. F. Baes, Jr., *J. Phys. Chem.* 62 (1958) 777.

[248] T. Sato, *J. Inorg. Nucl. Chem.* 24 (1962) 1267; *ibid.* 25 (1963) 441; *ibid.* 26 (1964) 171; *ibid.* 26 (1964) 2229.

dissolved in hexane[232]. After the discontinuation of the precipitation process for nuclear fuel reprocessing[249], solvent extraction from nitric acid–nitrate salt solutions has been extensively used: the Redox process using methylisobutyl ketone (MIBK or hexone) in the United States[250], and the Butex process using dibutyl carbitol in Great Britain[251]. These extractants are now replaced by TBP dissolved in kerosene. Solvent extraction with neutral adducts has also been a preferred procedure in many first isolations of synthetic actinides[252].

The properties of the neutral extractants in a two-phase organic aqueous system of varying acidity and salt concentration is treated in section 4.5.2, and the equations for metal extraction in section 4.6.2.

A number of examples of actinide extraction systems have been collected in Table 31. In general the extraction efficiency for actinides increases with extractant basicity (Table 24), and is thus higher for the phosphoryl compounds than for the other oxygen donor molecules. The hexa- and tetravalent states are more easily extracted than the penta- and trivalent states from nitrate solutions, while chloride solutions promote the extraction of the hexa- and pentavalent states. While practically no extraction is obtained with sulphate or phosphate ligands (cf. [305a]) some extraction is obtained from perchlorate and chloride systems, and good extraction is observed from thiocyanate and nitrate systems. Salting out agents are effective in promoting actinide extraction for the neutral adduct system (see Fig. 33). The use of nitrate systems in the nuclear chemical industry has led to more extensive investigation of these systems than of other ligands.

The actinides are usually extracted as coordinatively saturated neutral compounds ML_zB_p where $z + p = N$. Even though definitive stoichiometric compounds have been found with some ligands, as for example NO_3^- and TBP[253–5] (see Table 32), the fact that some ligands like NO_3^- may act monodentately or bidentately makes it difficult to use the rule $z + p = N$ to predict the composition of the extracted complex, as mentioned in section 4.4.2. Thus steric factors may lower the value $p = N–z$. With the carboxo extractants the aqueous metal complex often carries some water into the organic phase. Although it is not always certain, some of this water may, together with the solvent molecules, solvate the metal in the organic phase[167]. Much careful work is necessary to establish the true composition of the complex (or complexes) in the organic phase.

The carboxo extractants are comprised of alcohols, ethers, ketones and esters. For each group, the actinide extraction power (the D_M value at constant aqueous condition) decreases with increasing carbon chain length. Thus the low molecular weight compounds would be preferable, but high water solubility limits their use. Fairly independent of molecular weight, the extraction power is found to increase with an increase in the relative number of oxygen atoms (decreasing C/O ratio) and for constant C/O ratio with increasing polarity (ϵ value), as is seen from Table 33. For the polyethers Googin *et al.*[256] found that the extraction of U(VI) nitrate also increased with increased spacing (two to six carbon atoms) between the oxygen atoms.

[249] S. G. Thompson and G. T. Seaborg, *Process Chemistry*, **1** (1956) 163.

[250] F. L. Culler, *Process Chemistry*, **1** (1956) 172.

[251] G. R. Howells, T. H. Hughes, D. R. Mackey and K. Saddington, *Proc. Int. Conf. Peaceful Uses of Atomic Energy*, Vol. 17, p. 3, Geneva (1958).

[252] J. J. Katz and G. T. Seaborg, *The Chemistry of the Actinide Elements*, John Wiley & Sons, New York (1957).

[253] T. V. Healy and H. A. C. McKay, *Rec. Trav. Chem.* **75** (1956) 730.

[254] G. F. Best, H. A. C. McKay and P. R. Woodgate, *J. Inorg. Nucl. Chem.* **4** (1957) 315.

[255] K. Alcock, G. F. Best, E. Herford and H. A. C. McKay, *J. Inorg. Nucl. Chem.* **4** (1957) 100.

[256] J. M. G. Googin, W. L. Harper, L. R. Phillips and F. W. Postma, *Nucl. Sci. Eng.* **17** (1963) 586.

TABLE 31. ACTINIDE EXTRACTION BY NEUTRAL EXTRACTANTS (For each extractant, the following information is given: composition of aqueous phase / molarity or vol. % of neutral extractant in organic phase; M(III) data // M(IV) data // M(V) data // M(VI) data; reference. For each actinide log D_M values are given for the specified conditions, or log K_{DM} according to footnote. →0 constants extrapolated to zero ionic strength.)

		Reference
Diethyl ether		
$NO_3^- \rightarrow 0/100\%$	—//—//—//U −0·94^1	a,e,f
8 NH_4NO_3, 1·4 HNO_3, C_M 0·1/100 %	—//Th −2·47//—//U 0·36; Pu 0·18	b
6 $Al(NO_3)_3$, 1·3 HNO_3, C_M 0·1/100 %	—//Th −0·5//—//U 2·32	b
Di-i-propyl ether		
$NO_3^- \rightarrow 0/100\%$	—//—//—//U −2·52^1	a,e
β,β′-Dibutoxydiethyl ether (*dibutyl carbitol, butex*), *DBC* (I)		
$NO_3^- \rightarrow 0/100\%$	—//—//—//U −0·48^{1c2}	c
3 HNO_3/100 %	Pu < −2//Pu 0·84//—//U 0·18; Pu 0·25	d
8 NH_4NO_3, 0·2 HNO_3/100 %	Pu < −2·7//Pu 0·84//—//U 0·5; Pu 0·4	d
Methyl isobutylketone (*hexone*), *MIBK* (II)		
$NO_3^- \rightarrow 0/100\%$	—//—//—//U −3·20^1	a,e
3 HNO_3/100 %	—//Th −1·8; Pu −0·2//—//U 0·0; Pu 0·1	g
2 $Ca(NO_3)_2$, 3 HNO_3/100 %	—//Th −0·4; Pu 1·2//—//U 0·6; Pu 1·0	g
i-*Amylacetate*		
$NO_3^- \rightarrow 0/100\%$	—//—//—//U −1·82^1	a,e
Di-i-butyl carbinol (III)		
0·6 $Al(NO_3)_3$, 4 HNO_3/100 %	—//—//Pa ≳ 1·7//—	h
Tributylphosphate, TBP, $(RO)_3PO$		
$NO_3^- \rightarrow 0$/Kerosene	Am 0·4^3//U 0·65^4 ($\mu = 1\cdot75$)//—//U 1·71^5	i,j,k
6 $H(ClO_4^-, NO_3^-)/C_6H_6$	—//—//Pa 0·7^6//—	l
$NO_3^- \rightarrow 0/CCl_4$	—//Pu 3·06^4//—//U 1·75;^{5} Pu 0·97^5	m,n
$NO_3^- \rightarrow 0/CHCL_3$	—//—//—//U 0·15^5	n
$NO_3^- \rightarrow 0/C_6H_6$	—//—//—//U 2·10^5	o
$NO_3^- \rightarrow 0/100\%$	—//—//—//U 1·68^5; Np −0·07^5	p,q
1 HNO_3/30 %, n-dodecane	—//Th −0·1, Np −0·1, Pu 0·5//—//U 0·95, Np 0·75, Pu 1·1	r
HCl/100 %; max. extn.	Ac −1·7 (HL 12)//Th 1·3 (HL 12)//Pa 3·4 (HL 8)// U 2·0 (HL 6)	s
HCl/100 %; max. extn.	Cf −0·2 (HL 12)//Np 2·7 (HL 9·5)//Np 2·5 (HL 10)//Np 2·8 (HL 6)	s
Dibutylbutylphosphonate, DBBP, $(RO)_2R$ PO		
$NO_3^- \rightarrow 0$/Kerosene	Am 0·87^3//—//—//—	
$NO_3^- \rightarrow 0/CCl_4$	—//Pu 4·61^4//—//U 3·46^5	i
		m,n,t,u
Butyldibutylphosphinate, BDBP, $(RO)R_2PO$		
$NO_3^- \rightarrow 0$/Kerosene	Am 2·05^3//—//—//—	
$NO_3^- \rightarrow 0/CCl_4$	—//Pu 5·75^4//—//U 5·14^5	i
		m,n,t,u
Tributyl phosphine oxide, TBPO, R_3PO		
$NO_3^- \rightarrow 0$/Kerosene	Am 3·25^3//—//—//—	i
$NO_3^- \rightarrow 0/CCly$	—//Pu 7·40^4//—// U 7·23^5	n,v,w,t,u
Tri-n-octyl phosphineoxide, TOPO, R_3PO		
$(NH_4ClO_4+HNO_3) \rightarrow O$/Kerosene	Am 3·5^3//—//—//—	x
0·6 HNO_3/Cyclohexane	—//—//—//U 8·4^5	y
6–7 HNO_3/0·1, cyclohexane	Pu ≲ −1//Pu 3//—//Pu 1·3	z,A
9–10 HCl/0·1, cyclohexane	Pu < O//Pu ~ 2·5//—//Pu ~ 2	z,B

TABLE 31 (*cont.*)

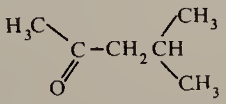
		Reference
1,2-*Bis-(di-n-hexyl-phosphinyl)-ethane*, $R_2P(O)C_2H_4P(O)R_2$		
Different inorg. acids/0·05, 1,2-dichlorobenzene	max. extn. of U(VI): 3·1 (HNO_3 1·0), 3·5 (HCl 1·5), 3·8 ($HClO_4$ 1·0)	C
Di-n-octyl sulphoxide, DOSO, R_2SO		
$NO_3^- \rightarrow 0/C_6H_6$	–//Th $4 \cdot 34^4$//–//U $3 \cdot 04^5$	D
$NO_3^- \rightarrow 0/CCl_4$	–//–//–//U $1 \cdot 96^5$	D
Trilaurylamine oxide, TLAO, R_3NO		
3 HNO_3/0·5, C_6H_6	–//Th –1·1, Pu 0·5//–//U –1·4	E

(1) log K_{DM} $MO_2^{2+} + 2\,L^- \rightleftharpoons MO_2L_2$(org).
(2) Extracted species $MO_2L_2\,(H_2O)_4$.
(3) log K_{DM} $M^{3+} + 3\,L^- + 3\,B\,(org) \rightleftharpoons ML_3B_3$ (org).
(4) log K_{DM} $M^{4+} + 4\,L^- + 2\,B\,(org) \rightleftharpoons ML_4B_2$ (org).
(5) log K_{DM} $MO_2^{2+} + 2\,L^- + 2\,B\,(org) \rightleftharpoons MO_2L_2B_2$ (org)
(6) log K_{DM} $ML_5 + 2\,B\,(org) \rightleftharpoons ML_5B_2$ (org).

Structural formulae.

I. β,β'-dibutoxydiethyl ether:
$C_4H_9OC_2H_5OC_2H_5OC_4H_9$

II. Methyl isobutylketone:



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[c] V. M. Vdovenko and E. A. Smirnova, *Radiokhimiya*, **1** (1959) 43.
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[v] K. A. Petrov *et al.*, *Zhur. Neorg. Khim.* **5** (1960) 498.
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TABLE 32. REGULARITIES IN ACTINIDE EXTRACTION FROM NITRIC ACID SOLUTIONS BY PHOSPHORYL EXTRACTANTS (B) (Under otherwise identical conditions D_M increases in the order indicated.)

Extractant: $(RO)_3PO < (RO)_2R'PO < (RO)R_2'PO < R_3'PO$
Diluent: decreasing polarity (dielectric strength ϵ)
Valency state: $M(V) \lesssim M(III) \ll M(VI) \lesssim M(IV)$
Trivalent actinides: $_{Z}M < {}_{Z+1}M$ (species $M(NO_3)_3B_3$)
Tetravalent actinides: Th < U < Np < Pu (species $M(NO_3)_4B_2$)
Pentavalent actinides: Np < Pa (species $MO(NO_3)_3B_2$)
Hexavalent actinides: Pu $\lesssim$ Np $\lesssim$ U (species $MO_2(NO_3)_2B_2$)

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[a] H. A. C. McKay, *Proc. Int. Conf. Peaceful Uses of Atomic Energy*, Vol. 7, p. 314, Geneva (1956).

[b] H. A. C. McKay and T. V. Healy, *Process Chemistry*, **2** (1958) 546.

TABLE 33. DISTRIBUTION OF U(VI) NITRATE BETWEEN WATER AND DIFFERENT ETHERS AT ROOM TEMPERATURE

Ether	Ratio C/O	Dipole moment (Debyes)	D_U	Reference
Dibutyl cellosolve[a]	5·0		0·026	e
Diethyl ether	4·0	1·15	0·14	f
Dibutyl carbitol (DBC, butex)[b]	4·0	1·83	~0·30	f,g
Hexyl ethyl carbitol[c]	4·0	2·02	0·66	g
Pentaether[d]	3·2		1·0	f

[a] $C_4H_9OC_2H_4OC_4H_9$.

[b] $C_4H_9O(C_2H_4O)_2C_4H_9$.

[c] $C_2H_5O(C_2H_4O)_2C_6H_{13}$.

[d] $C_4H_9O(C_2H_4O)_4C_4H_9$.

[e] J. M. Fletcher, *Proc. Int. Conf. Peaceful Uses of Atomic Energy*, Vol. 9, p. 459, Geneva (1955).

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[g] J. M. Googin, W. L. Harper, L. R. Phillips and F. W. Postma, U.S.A.E.C. Report Y-1408, Office of Techn. Serv., Washington D.C. (1962).

The order of actinide extractability into butex is Pu(III) $\ll$ U(VI) $\approx$ Pu(VI) < Pu(IV) (see Table 31); $D_{Pu(III)} < 0{\cdot}01$[251]. The extraction of the tetravalent actinides is shown in Figure 53. The extraction increases with increasing $[NO_3^-]$, but usually decreases with increasing $[H^+]$, the net effect being an increase in D_M with $[HNO_3]$. Because the low molecular weight ethers react with concentrated HNO_3, the extraction must be carried out at low acidity and high nitrate salt concentration. The salting out effect by aluminum nitrate on U(VI) extraction by various carboxo adducts is shown in Fig. 54. The extraction generally decreases with increasing temperature. The composition of the extracted species is not established, both acidic (e.g. $H_2M(NO_3)_6$ for tetravalent actinides) and neutral hydrated (e.g. $MO_2(NO_3)_2(H_2O)_2(R_2O)_2$ for the hexavalent actinides) complexes having been suggested[167].

The ketones are usually less effective extractants than the ethers (cf. Fig. 54). Of the ketones, methyl isobutyl ketone (MIBK, hexone) is the most used extractant. The β-diketones are acidic and will be considered in section 4.7.3.

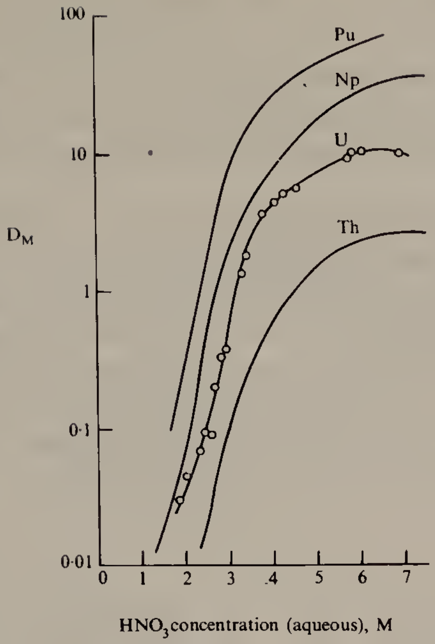

FIG. 53. Partition coefficients of the tetravalent actinide nitrates between aqueous nitric acid and dibutyl carbitol at 25°C[258].

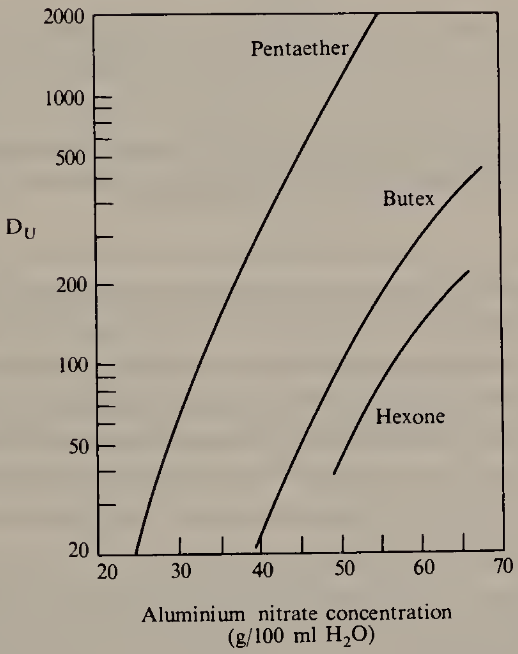

FIG. 54. Effect of aluminium nitrate in the aqueous phase on the distribution of U(VI) between aqueous and organic phases[163].

The distribution factor for U(VI) nitrate between 100% ketone and water is 0·16 for hexone[259], 0·49 for 2-pentanone[256] and 0·9 for cyclohexanone[259]. Thus hexone is by no means the most efficient ketonic extractant, but it has practical advantages, such as low cost. The extraction of trivalent actinides into hexone is very low. The extraction of Th(IV) and U(VI) is shown in Fig. 33. The tetravalent actinides are increasingly extracted in the order Th < U < Pu, whereas the order changes for the hexavalent actinides with acidity and salt concentration.

Th(IV) and U(VI) are also extracted by hexone from $HClO_4$ (D_{Th} 0·3 and D_U 0·43 at 4 M $HClO_4$) and U(VI) (but not Th(IV)) from HCl ($D_U \sim 1{\cdot}0$ at 8 M HCl) solution[260]. It should be remembered that $NaClO_4$ is not a good salt medium for the basic adduct systems because of its extractability. For 1 M $NaClO_4$(aq) the equilibrium concentration of $NaClO_4$(org) is 0·25 M in TBP and 0·01 M in hexone, increasing with increasing $[NaClO_4]$[261]. No actinide is extracted from H_2SO_4 into hexone[260]. Pa(V) is efficiently extracted from HCl solutions (but not from HNO_3, $HClO_4$ or H_2SO_4) by hexone and other ketones, as is seen from Fig. 55. Np(V) is extracted to a lesser extent than Pa(V).

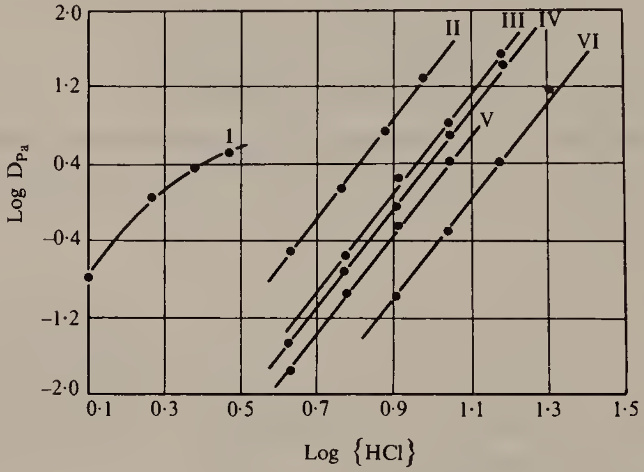

FIG. 55. Extraction of Pa(V) from hydrochloric acid solutions by different organic solvents: I, cyclohexanone; II, mesityloxide; III, diethyl ketone; IV, acetophenone; V, n-hexyl methyl ketone; VI, di-isobutyl ketone[262].

Some alcohols and esters have also been found to extract actinides, but no separation procedures or practical applications have been developed for these extractants, because of the usually low D_M values achieved. The extraction of Pa(V) from highly salted HNO_3 by di-i-butyl carbinol (Table 31) is an exception, and permits a rapid and efficient isolation of Pa(V), although small amounts of U(VI) also are extracted[263].

Some representative data for the actinide extraction by phosphoryl compounds, particularly for the commonly used nitrate systems, are also given in Table 31. The stronger

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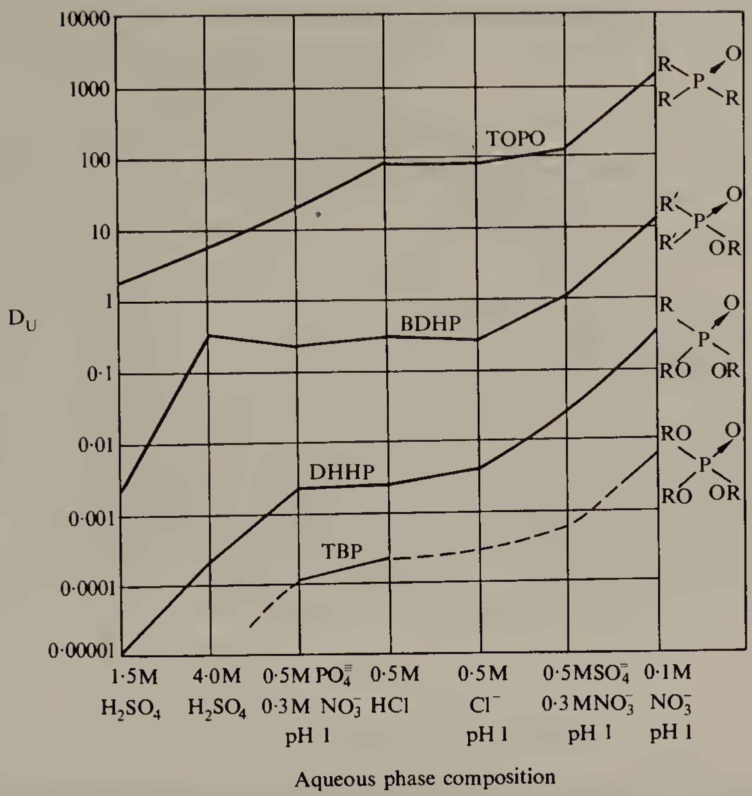

Fig. 56. Comparison of neutral organophosphorus extractants. Aqueous phase is 0·004 M in U(VI). Organic phase is 0·1 M reagent in kerosene. BDHP, butyl-dihexyl phosphinate. DHHP, dihexylhexyl phosphonate. TBP and TOPO, see text. 25°C[264].

basicity of the phosphoryl compounds as compared to the carboxo compounds causes a great regularity in the actinide extraction behavior (see Table 32). This regularity is strikingly illustrated for the extraction of U(VI) in Fig. 56. The effect of various substituents in the phosphoryl compounds has been extensively studied by Siddall, Shevchenko, Peppard and others[156,161,162,165]. The extracted complexes do not contain water, except perhaps for the M(VI) perchlorates[265].

Salting-out effects and the extraction dependence of the HNO_3 concentration are illustrated in Fig. 33, which also demonstrates the superior extractive power of TBP as compared to hexone.

The M(IV), M(V) and M(VI) actinides are efficiently extracted from HCl by TBP and TOPO (Table 31). The different extractabilities of M(III), M(IV) and M(VI) in the TBP and TOPO systems are illustrated in Figs. 57 and 58. On the introduction of H_2SO_4 or H_3PO_4 the distribution ratios decrease, and more so for the tetravalent actinides than for the hexavalent because the former form stronger sulphate and phosphate complexes[266]. This has been used by Gourisse *et al.*[267] to effect a very efficient separation of the M(VI) and

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[264] C. A. Blake, Jr., C. F. Baes, Jr., K. B. Brown, C. F. Coleman and J. C. White, *Proc. Int. Conf. Peaceful Uses of Atomic Energy*, Vol. 28, p. 289, Geneva (1958).

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[266] J. C. White and W. J. Ross, *Separations by Solvent Extraction with Tri-n-octylphosphine Oxide*, NAS-NS 3102, Natl. Acad. Sci., Washington D.C. (1961).

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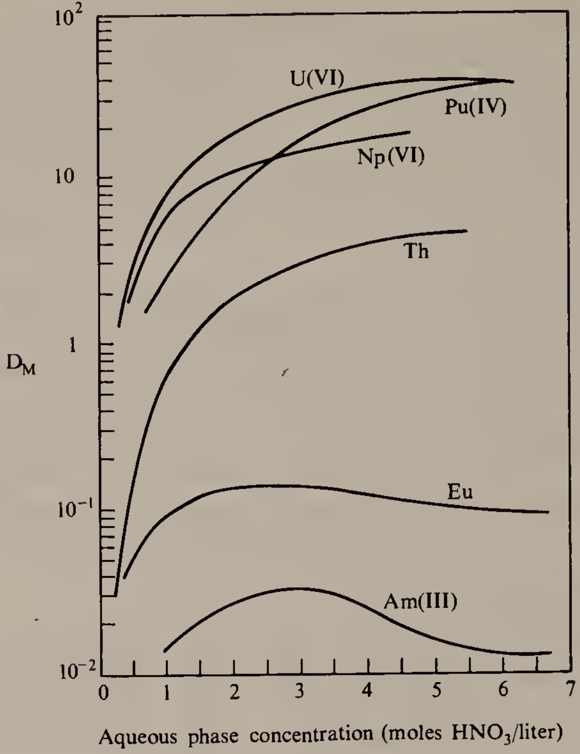

FIG. 57. Distribution of actinide species between 30 vol. % TBP in kerosene and aqueous HNO_3.[163]

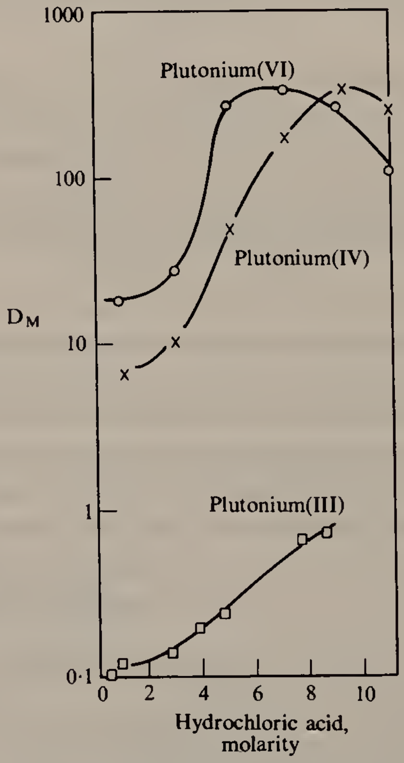

FIG. 58. Extraction of plutonium from HCl with 0·1 M TOPO in cyclohexane[266].

M(IV) actinides. Using ~18% TBP in dodecane and 0·4 M H_2SO_4 + 1 M HNO_3 a separation factor (i.e. D_{M1}/D_{M2}) of ~50 is obtained for U(VI)/Pu(IV) and ~350 for U(VI)/Np(IV).

The M(IV) and M(VI) states are also extractable by phosphoryls from $HClO_4$ solutions, as are the M(III) from thiocyanate solutions. Thus a D_{Am} value of 400 is obtained in the system 0·05 M NH_4SCN and 20% TOPO in decane; replacing TOPO by 25% TBP gives the lower value D_{Am} 0·01[265, 268–270]. The extraction of Am(III) by a number of different organophosphoric compounds is given in Table 34.

Table 31 also includes some less common extractants, representing the diphosphoryls, sulphoxides and amine oxides. These compounds extract water and acids analogously to the carboxo and phosphoryl compounds[163,271]. Very high distribution ratios are obtained for U(VI) with the diphosphoryl extractant. The similarity between the sulphoxides and phosphines oxides suggests that the former should be able to extract the tetra- and hexavalent actinides, though less effectively, because of the lower basicity of the R_2SO oxygen as compared to the R_3PO oxygen[272]. This is in fact observed, the maximum extraction from HNO_3 being D_{Th} 2·5 (2 M HNO_3) and $D_{U(VI)}$ 5 (4 M HNO_3) with 1 M diheptylsulphoxide (B) in 1,1,2-trichloroethane. The extracted species are identified as $Th(NO_3)_4B_2$ and $UO_2(NO_3)_2B_2$[273].

4.7.3. *Chelate Systems*

Which organic acids form inner-sphere and which form outer-sphere complexes with the actinide ions has been widely discussed[274], but no reliable answer is yet available. For the sake of simplicity we shall assume that all anionic organic molecules which form extractable neutral complexes with actinide cations are bound to the cation in the inner sphere. This seems probable, because water (which normally fills the inner coordination sphere) is rarely extracted with these complexes into organic diluents. The higher extractability of these complexes into inert than into polar diluents also supports the assumption that only inner-sphere complexes are formed. Under these circumstances it is also reasonable to assume that the organic acids, which in addition to the OH group also contain an adjacent basic oxygen, form 4- or higher-membered chelate rings with the metal. Thus the extraction of actinides by all organic acids can be discussed under this heading.

Some general properties of these reagents have been discussed in section 4.5.3 and will, therefore, not be repeated here. The mathematics of extraction has been treated in section 4.6.2, where it was concluded from eqn (4.22) that D_M was expected to first rise to a plateau, where $D_M = \lambda_i$, and then decrease again with increasing $[A^-]$ (see Fig. 41). The ascending part with increasing [HA] (and/or pH) is always observed, and sometimes a plateau is reached. Although many cases are known where D_M decreases after passing a maximum (see Fig. 59), experiments are usually not carried out to such high ligand activities that negatively charged chelates are formed.

A number of representative actinide extraction systems are given in Table 35. Two types

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[273] G. J. Lawrence, M. T. Chaieb and J. Talbot, ref. 121, p. 1150.

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TABLE 34. EXTRACTION OF Am(III) WITH DIFFERENT ORGANOPHOSPHORUS COMPOUNDS[a]

Aqueous phase	Organic phase (in kerosene)*	D_{Am}
8 M LiCl, pH 1	20 % TBP	<0·5
	20 % DAMP*	1
	20 % TOPO	10
0·05 M NH_4SCN	25 % TBP	0·012
	20 % DAMP	1·8
	20 % TOPO	400
1 M LiCl, 0·05 M HCl	0·2 M HDEHP	12
	0·2 M H_2MEHP*	215

* Approximately decane, DAMP = diamylmethylphosphonate. H_2MEHP = mono(2-ethylhexyl)phosphoric acid.

[a] E. S. Gureev, V. D. Dedov, S. M. Karpacheva, I. K. Shvetsov, M. N. Ryzhov and P. S. Trukchlayev, *Process Chemistry*, 4 (1970) 631.

of complexes have to be considered, MA_n and MA_nB_p, i.e. complexes with the anion only, and with the anion and an adduct molecule. Only MA_n complexes (including self-adducts, $MA_n(HA)_p$) are listed in Table 35.

The over-all extraction constant K_{DM} for reaction (15) ($p = 0$) is given for a number of systems in Table 35. Although the K_{DM} value is useful for comparing different extraction systems, it gives no information on why a particular chelating agent is more effective in extracting an actinide ion than another reagent. For that purpose it is necessary to evaluate the different independent variables in eqn (4.25): β_n, λ_i, K_a and K_d. For example, log K_{DM} is 4·4 for the extraction of Th(IV) by cupferron in $CHCl_3$, while log K_{DM} is −7·5 with oxine.

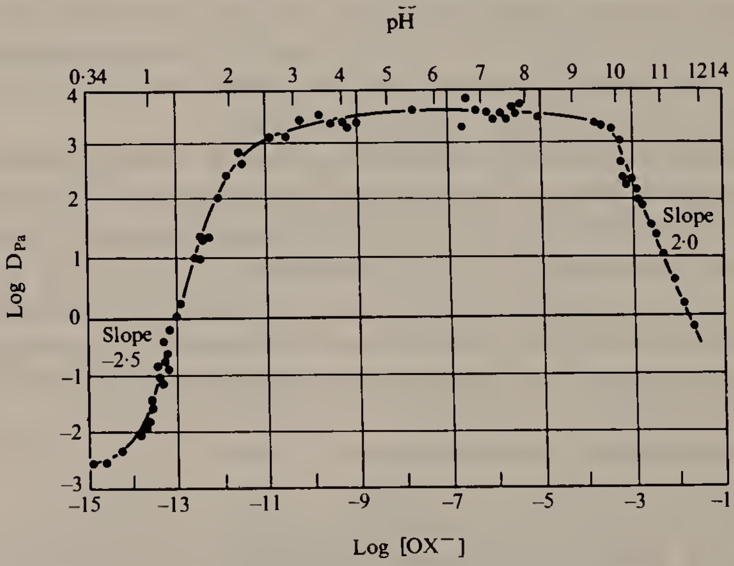

FIG. 59. The distribution of trace amounts of Pa(V), $2 \cdot 8 \times 10^{-9}$ M, between 0·1 M 8-hydroxyquinoline in chloroform and water (back extraction)[275].

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[275] C. Keller and K. Mosdzelewski, *Radiochim. Acta*, 7 (1967) 185.

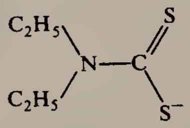
TABLE 35. ACTINIDE EXTRACTION BY CHELATING ACIDS (For each extractant, the following information is given: composition of aqueous phase / molarity or vol. % of acid extractant in organic phase; M(III) data // M(IV) data // M(V) data // M(VI) data; reference. For each actinide log D_M values are given for the specified conditions, or log K_{DM} according to footnote.)

		Reference
Salicylic acid		
0·116 A$^-$/amylacetate	−//Pu 0·91 (pH 4)//−//−	a
0·1 (Na, H)ClO$_4$/0·1, hexone	−//Th 1·26 (pH 4)//−//U 1·4 (pH 4)	b,c
Diethyldithiocarbamate (I)		
HCl, H$_2$SO$_4$/0·002, CHCl$_3$	−//−//−//U 0 ($\lesssim$ −2 for CCl$_4$), pH 5·2	d, e
Cupferron (II)		
0·1–6 HCl/amylalcohol	−//−//Pa $\gtrsim$ 1·0//−	f
0·1 (Na, H)ClO$_4$/CHCl$_3$	−//Th 4·4^1, λ_4 2·79; Pu 7·0^1//−//U < −0·35 (pH 3·5–6, 0·01 HA)	g,h,i
0·1 (Na, H)ClO$_4$/hexone	−//Th 6·0^1//−//−	g
0·1 (Na, H)ClO$_4$/diethyl ether	−//U 8·0^1//−//−	i
N-phenylbenzohydroxamic acid (III)		
0·1 (Na, H)ClO$_4$/CHCl$_3$	An(III) ~ −14^{1,2}//Th −0·68^1//−//U −3·14^1	j
Oxine (IV)		
0·1 (Na, H)ClO$_4$/CHCl$_3$	−//Th −7·12^1, λ_4 2·63; Np λ_4 2·77//Pa λ 3·6//U −2·42^{1,3}; Pu λ ~ 0	k,l,m
0·1 (Na, H)ClO$_4$/0·1, butyl alcohol	−//−//Np 0·4 (pH ~ 10, $\lesssim$ −2 for CHCl$_3$, C$_6$H$_6$)//−	n
Acetylacetone, HAA (V)		
0·1 (Na, H)ClO$_4$/CHCl$_3$	Am, Cm λ_3 −0·6//Th λ_4 2·5; U λ_4 4·0; Pu −4·06^1, λ_4 2·6//−//U λ_2 0·52, λ_2' 1·34^4	o,p,q,r,s
0·1 (Na, H)ClO$_4$/C$_6$H$_6$	−//Th λ_4 2·5; U λ_4 3·6; Pu −1·73^1, λ_4 2·5//−−//−	p,q,r
0·1 (Na, H)ClO$_4$/xylene	−//−//Pa $\gtrsim$ 2//−	t
Trifluoroacetylacetone HFTA (VI)		
0·1 (Na, H)ClO$_4$/CHCl$_3$	Am λ_3 1·2//−//−//−	o
0·5 HNO$_3$/C$_6$H$_6$	−//Pu 1·7^1//−//−	u
Benzoyltrifluoroacetone, HBTA (VII)		
0·1 (Na, H)ClO$_4$/CHCl$_3$	Am −10·3^1, λ_3 2·0//−//−//−	o
0·5 HNO$_3$/C$_6$H$_6$	−//Pu 3·95^1//−//−	u
Benzoylacetone, HBA (VIII)		
0·1 (Na, H)ClO$_4$/C$_6$H$_6$	−//Th −7·68^1; Pu ~ 1·0 (pH 4)//−//U −4·68^3	v,w,x
Dibenzoylmethane, HDBM (IX)		
0·1 (Na, H)ClO$_4$/CHCl$_3$	Am λ_3 2·1//−//−//−	o
0·1 (Na, H)ClO$_4$/C$_6$H$_6$	−//Th −6·38^1//−//U −4·12^3	v,y
Thenoyltrifluoroacetone, HTTA (X)		
0·1 (Na, H)ClO$_4$/CHCl$_3$	Am −9·13^1, λ_3 1·7//−//−//−	o
NO$_3^-$, ClO$_4^-$/C$_6$H$_6$	Am −7·90^1//Th −0·9^1, Np 5·6^1//−//U −2·26^1, Pu −1·82^1	z,A,B, C,D
1 HClO$_4$/C$_6$H$_6$	−//Pu 6·85^1//−//−	C
0·02 HNO$_3$/cyclohexane	−//−//Np ~ 1^3//−	E
1 NH$_4$ClO$_4$/methylethylketone	−//−//Np λ_1 −0·02//−	F
1-*nitroso-2-naphthol* (XI)		
0·1 (Na, H)ClO$_4$/CHCl$_3$	−//Th −1·64^1, λ_4 6·75//−//U −4·14^1	G,H
0·1 (Na, H)ClO$_4$/hexone	−//Th −4·68^1, λ_4 2·05//−//−	G,H
SO$_4^-$, NO$_3^-$/1 %, butylalcohol	−//−//Np ~ 1 (pH 9–11, ~ −1·5 for CHCl$_3$ or C$_6$H$_6$)//−	I,J

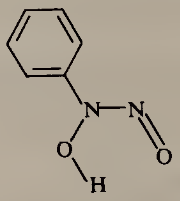
TABLE 35 (*cont.*)

		Reference
2-*nitroso*-1-*naphthol* (XII)		
0·1 (Na, H)ClO$_4$/CHCl$_3$	—//Th 0·2^1, λ_4 4·4//—//—	G
0·1 (Na, H)ClO$_4$/hexone	—//Th −2·48^1, λ_4 2·1//—//—	G
Dibutylphosphoric acid, HDBP, (RO)$_2$PO(OH)		
HNO$_3$/0·1, CHCl$_3$	Am 18^5//Th $\gtrsim$ 2 (HL 1)//—//—	K,L
2 HNO$_3$/0·1, C$_6$H$_6$	—//—//Pa $\gtrsim$ 2·7//—	M
6 (Na, H)NO$_3$/C$_6$H$_6$	—//Pu 9·3^6//—//—	N
0·1 HClO$_4$/0·1–0·5, CHCl$_3$ or C$_6$H$_6$	—//—//—//U > 2·5	O
0·1 HNO$_3$/0·3, hexane	Am > 2//—//—//—	K
Di(2-*ethylhexyl*)-*phosphoric acid, HDEHP*, (RO)$_2$PO(OH)		
HCl/1·5, toluene	Am 0 (HL ~ 0·3)//Np 4 (HL ~ 1)//Np 0 (pH 2, HA 0·7)//U 0 (HL ~ 1)	P
2 HCl/1·0, diethylbenzene	Pu −1·5//Pu 2·4//—//Pu 1·7	Q
0·05 HClO$_4$/0·003, toluene	—//—//Pa > 1·4//—	P
1·0 (Na, H)Cl/0·1, n-decanol	—//Th 0 (H$^+$ ~ 0·3)//—//U 0 (H$^+$ ~ 0·25)	S
Di(2-*hexoxyethyl*)-*phosphoric acid*, (ROC$_2$H$_5$O)$_2$PO(OH)		
1·0 (Na, H)Cl/C$_6$H$_6$	Am 0·91^7//—//—//U 4·91^8	T
1·0 (Na, H)Cl/n-decanol	Am −0·7^1//—//—//U 1·85^8	T
1·0 (Na, H)Cl/n-heptane	—//—//—//U 5·80^8	T
Di-n-octyl phosphoric acid, HDOP, (RO)$_2$PO(OH)		
1·0 (Na, H)Cl/C$_6$H$_6$	Am, Cm −1·0^9//—//—//U 3·3^8	U
1·0 (Na, H)Cl/n-heptane	Am 1·3^7//—//—//U 4·3^8	U
Di-n-octyl phosphinic acid, H[*DOP*], R$_2$PO(OH)		
1·0 (Na, H)Cl/C$_6$H$_6$	Cm −4·68^7//—//—//U 3·72^8	V
Mono-n-octyl phosphinic acid, H[*MOP*], R(H)PO(OH)		
1·0 (Na, H)Cl/C$_6$H$_6$	Cm −0·08^9//—//—//U 4·63 (X = 2·3)^{10}	V
Mono-(2-*ethylhexyl*)-*phosphinic acid, H*[*MEHP*], R(H)PO(OH)		
1·0 (Na, H)Cl/C$_6$H$_6$	Cm −1·05 (X = 2·7)^{10}//—//—//U 3·93 (X = 2·1)^{10}	V
Mono-(2-*ethylhexyl*)-*phosphoric acid, H$_2$MEHP*, ROPO(OH)$_2$		
12 HCl/0·48, toluene	Am −1·1//Th > 4//Pa > 5//U −1·8	W
0·1 HClO$_4$/0·46, toluene	Am 3·75//—//—//—	X
1·0 (Na, H)Cl/hexone	Am −1·05^{11}//—//—//U 2·85^{12}	Y
Mono-(2-*ethylhexyl*)-*phosphonic acid, H$_2$*[*MEHP*], RPO(OH)$_2$		
1·0 (Na, H)Cl/hexone	Am −2·6^{12}//—//—//U 2·55^{12}	Y

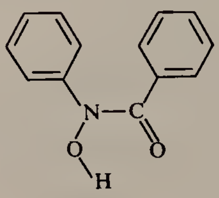
I. Diethyldithiocarbamate:



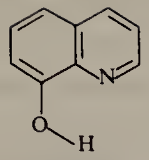
II. Cupferron:



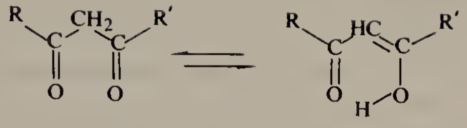
III. N-phenylbenzohydroxamic acid:



IV. Oxine:



V–X. β-diketones:



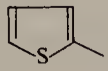
V. Acetylacetone: $R = R' = CH_3$

VI. Trifluoroacetylacetone: $R = CH_3$; $R' = CF_3$

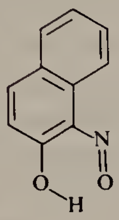
VII. Benzoyltrifluoroacetone: $R = C_6H_5$; $R' = CF_3$

VIII. Benzoylacetone: $R = C_6H_5$; $R' = CH_3$

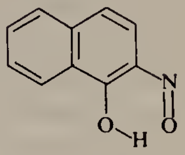
IX. Dibenzoylmethane: $R = R' = C_6H_5$

X. Thenoyltrifluoroacetone: R =  $R' = CF_3$

XI. 1-nitroso-2-naphthol:



XII. 2-nitroso-1-naphthol:



[1] $\log K_{DM}$: rel. (15) with $n = z$, $p = 0$.
[2] Deduced from value for La.
[3] $\log K_{DM}$: rel. (15) with $n = z$, $B = HA$, $p = 1$.
[4] λ_2' refers to distribution of $MO_2A_2(HA)$.
[5] $\log K_{DM}$: $M^{3+} + 3A^- + 3HA(org) \rightarrow MA_3(HA)_3(org)$.
[6] $\log K_{DM}$: $M^{4+} + 2L^- + 2(HA)_2(org) \rightarrow ML_2(HA_2)_2(org) + 2H^+$.
[7] $\log K_{DM}$: $M^{3+} + 2{\cdot}5\ (HA)_2(org) \rightarrow MA(HA_2)_2(org) + 3H^+$ (formalities).
[8] $\log K_{DM}$: $MO_2^{2+} + 2\ (HA)_2(org) \rightarrow MO_2(HA_2)_2(org) + 2H^+$ (formalities).
[9] $\log K_{DM}$: $M^{3+} + 3\ (HA)_2(org) \rightarrow M(HA_2)_3(org) + 3H^+$ (formalities).
[10] $\log K_{DM} = \log D_M + z \log [H^+] - x \log \{HA_{org,tot}\}$, where x = slope of $\log D_M$ vs. $\log [HA_{org,tot}]$.
[11] $\log K_{DM}$: $M^{3+} + 2{\cdot}5\ (H_2A)_2(org) \rightarrow M(HA)(H_3A_2)_2(org) + 3H^+$ (formalities).
[12] $\log K_{DM}$: $MO_2^{2+} + 2\ (H_2A)_2(org) \rightarrow MO_2(H_3A_2)_2(org) + 2H^+$ (formalities).
[a] B. G. Harvey *et al.*, *J. Chem. Soc.* (1947) 1010.
[b] B. Hök-Bernström, *Acta Chem. Scand.* **10** (1956) 174.
[c] B. Hök-Bernström, *Acta Chem. Scand.* **10** (1956) 163.
[d] H. Bode and F. Neumann, *Z. anal. Chem.* **172** (1959) 1.
[e] J. Stary, *The Solvent Extraction of Metal Chelates*, p. 163, Pergamon Press (1964).
[f] A. G. Maddock, G. L. Miles, *J. Chem. Soc.* (1949) 248, 253.
[g] D. Dyrssen and V. Dahlberg, *Acta Chem. Scand.* **7** (1953) 1186.
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[i] J. Stary and J. Smizanska, *Anal. Chim. Acta* **29** (1964) 545.
[j] D. Dyrssen, *Acta Chem. Scand.* **10** (1956) 353.
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[l] S. H. Eberle, Diss. KFK-281, Karlsruhe (1965).
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[n] Yu. A. Zolotov and I. P. Alimarin, *Radiokhimiya*, **4** (1962) 272.
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[p] J. Rydberg, *Arkiv Kemi*, **5** (1953) 413.
[q] J. Rydberg, *Arkiv Kemi*, **9** (1955) 81, 95.
[r] J. Rydberg, *Arkiv Kemi*, **9** (1955) 109.
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[t] J. O. Liljenzin, *Acta Chem. Scand.* **24** (1970) 1655.
[u] H. W. Crandall, J. R. Thomas and J. C. Reid, USAEC Report CN-2999 (1945).
[v] J. Stary and E. Hladky, *Analyt. Chim. Acta*, **28** (1963) 227.
[w] B. G. Harvey, H. G. Heal, A. Maddock and E. L. Rowley, *J. Chem. Soc.* (1947) 1010.
[x] J. Stary, *Coll. Czech. Chem. Comm.* **25** (1960) 890.
[y] V. Moucka and J. Stary, *Coll. Czech. Chem. Comm.* **26** (1961) 763.

However, $>99\%$ Th may be extracted with both reagents in a single step at pH 4. From the independent variables determined by Dyrssen[221] (see Table 36) it is seen that the distribution constant for the neutral thorium chelates are about the same ($10^{2.80}$ for cupferron and $10^{2.63}$ for oxine), as are the distribution constants K_d for the chelating agents themselves ($10^{2.18}$ and $10^{2.58}$, respectively). The great difference in K_{DM} values with the two reactants comes from the differences in their proton (pK_a) and metal (β_4) affinities in the aqueous phase. Using such fundamental data some general correlations between extractability (i.e. the K_{DM} value) and actinide valency state, atomic number (or radius) and structure of the chelating agent have been deduced.

Chelation of actinides occurs more easily with oxygen donor atoms than with nitrogen or sulphur atoms (cf. section 2.3). No correlation is found between ring size 4–6 and stability constants (β_n). For the same group of compounds, as for example β-diketones, the introduction of electron-attracting groups such as CF_3 or C_6H_6 decreases pK_a and thus increases K_{DM} [cf. eqn (4.25)]. However, the increase in K_a is often accompanied by a decrease in β_n. The over-all effect is often an increase in K_{DM}, probably due to the chelating effect. Thus K_{DM} increases for Pu(IV) in the sequence acetylacetone, trifluoroacetylacetone, and benzoyltrifluoroacetone (Table 35). Log β_n (and consequently $\frac{1}{i}$ log K_{DM}) usually increases with increasing charge density of the metal cation[221,276]. Accordingly, the extraction of actinides increases in the order $MO_2^+ < M^{3+} < MO_2^{2+} < M^{4+}$ (the charge density of the metal in MO_2^{2+} being higher than its formal values; cf. section 1.2). This is seen to be the case for the extraction of tetravalent actinides by acetylacetone in benzene (cf. Fig. 60). From the same figure it is also clear that the order of extraction is M(IV) > M(VI) > M(III) $(E_{Sm(III)} > E_{An(III)})^{277}$.

Introduction of hydrophilic groups into the organic structure will lower K_d. The consequence of this is an increase in K_{DM}, if λ_i is not lowered at the same time. However, λ_i and

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[276] C. Keller and S. H. Eberle, *Radiochim. Acta*, **4** (1965) 141.

[277] J. Rydberg, *Arkiv Kemi*, **9** (1955) 95.

Notes to Table 35 (*cont.*)

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[A] Ref. e, p. 76.

[B] J. C. Sullivan and J. C. Hindman, *J. Am. Chem. Soc.* 76 (1954) 5931.

[C] A. M. Poskanzer and B. M. Foreman, *J. Inorg. Nucl. Chem.* **16** (1961) 323.

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[H] M. Dyrssen, *Rec. Trav. Chim.* **75** (1956) 748.

[I] I. P. Alimarin, Yu. A. Zolotov and E. S. Palshin, *Doklady Akad. Nauk SSSR*, **124** (1959) 328.

[J] I. P. Alimarin, Yu. A. Zolotov and E. S. Palshin, *Radiokhimiya*, **2** (1960) 637.

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[L] G. Duyckaerts and P. Dreze, *Bull. Soc. Chim. Belges*, **71** (1960) 306.

[M] V. B. Shevchenko, V. A. Mikhailov and Yu. P. Zavalskii, *Zh. Analit. Khim.* **3** (1958) 1955.

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[W] D. F. Peppard, G. W. Mason and R. J. Sironen, *J. Inorg. Nucl. Chem.* **10** (1959) 117.

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TABLE 36. K_{DM} AND INDEPENDENT PARAMETERS FOR THE EXTRACTION OF Th(IV) FROM 0·1 M $NaClO_4$ BY CUPFERRON AND OXINE IN $CHCl_3$

Parameters	Cupferron	Oxine
log β_4 for ThA_4, 0·1 M $NaClO_4$	27·00	38·80
log λ_4 for ThA_4, 0·1 M $NaClO_4/CHCl_3$	2·80	2·39
pK_a of HA, 0·1 M $NaClO_4$	4·16	9·66(K_2)
log K_d of HA, 0·1 M $NaClO_4/CHCl_3$	2·18	2·28
log K_{DM} Th–HA–0·1 M $NaClO_4$–$CHCl_3$	4·44	−6·57
$pH_{\frac{1}{2}}$ 0·001 M HA in $CHCl_3$	1·9	4·6

[a] D. Dyrssen, *Svensk. kem. tidskr.* 64 (1952) 213.
[b] D. Dyrssen, *Svensk. kem. tidskr.* 68 (1956) 212.

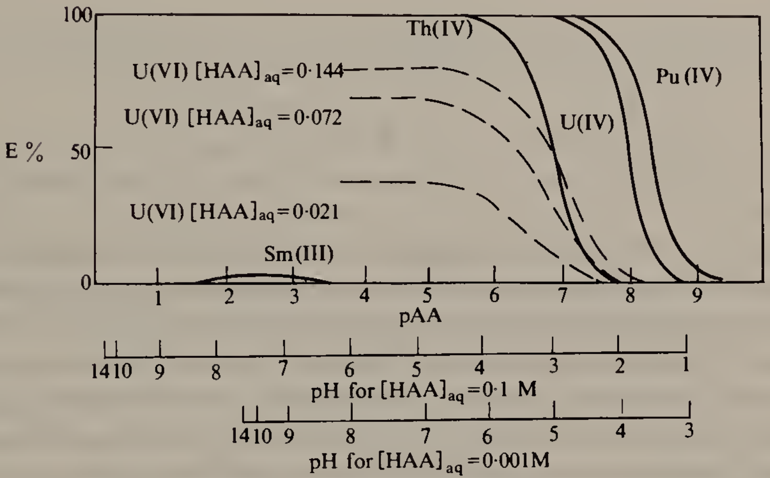


FIG. 60. The percentage extracted ($E\%$) of Th(IV), U(IV), U(VI) and Pu(IV) by acetylacetone (HAA) into benzene from 0·01 M $NaClO_4$[277].

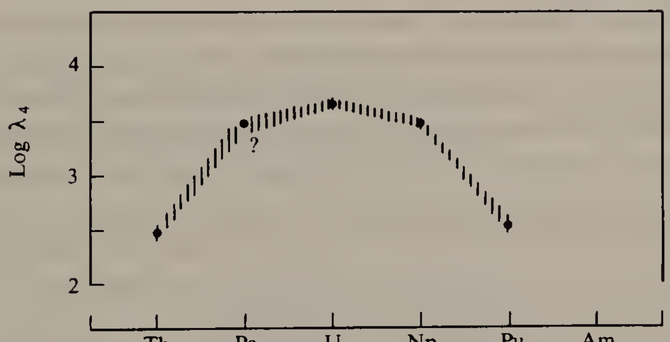
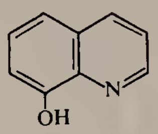


FIG. 61. The distribution constant λ_4 of MAA_4 (HAA = acetylacetone) between benzene and 0·1 M $NaClO_4$ as a function of actinide atomic number[220,222].

K_d do not vary systematically for the same metal ion with change of chelating agent. Quantitative knowledge in this area is very meager, because very few comparable λ_i values are available. Figure 61 shows how λ_4 for MAA$_4$ (HAA = acetylacetone) increases with actinide atomic number to a maximum for U(IV) and then decreases. The reason for this change in the organic phase solubility of MAA$_4$ is believed to be due to a modification in the metal chelate structure in the solution when going from Th to Pu[278]; the existence of such different structures is supported by recent crystal structure investigations[217]. For the same metal chelate, the solubility parameter concept allows a fair prediction of λ_i from K_d, and vice versa, for different inert diluents (see Fig. 39).

To illustrate the extraction with carboxo chelating agents, oxine (8-hydroxyquinoline, HOx; I) and some β-diketones will be discussed. The β-diketones are in tautomeric equilibrium between the keto(II) and enolic (III) forms. For acetylacetone (HAA), R = R′ = CH_3, and for thenoyltrifluoroacetone (HTTA), R′ = C_4SH_3 and R″ = CF_3. All are weak acids (see Table 27).



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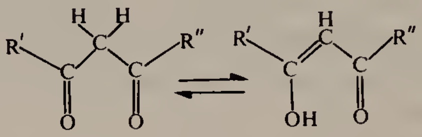

II III

Keller *et al.*[175,176,279,280] have investigated the formation and extraction of actinide oxinates. With Ac(III), Am(III) and Cm(III), basic complexes of the type M(OH)Ox$_2$ seem to form. With 0·1 M HOx in $CHCl_3$, the $pH_{\frac{1}{2}}$ values are, Cm 5·2, Am 5·4 and Ac 6·5 (see Fig. 62). Thus the M(III) actinides are preferentially extracted in this order. Pu(III) is unstable in this system in contact with air. While Np(IV) was extracted as NpOx$_4$, Pu(IV) was partly hydrolysed to Pu(OH)Ox$_3$, and, as a consequence, much less efficiently extracted than Np(IV); the $pH_{\frac{1}{2}}$ values were ~2 for Np(IV) and ~5 for Pu(IV). For Th(IV) Dyrssen[281] reports the formation of negatively charged ThOx$_n^{4-n}$ complexes at "high" Ox^- concentrations ($\gtrsim 10^{-3}$ M). The pentavalent actinides are extracted in the order Np < Pu ⋘ Pa. The slopes of the curve $\delta \log D_M/\delta \log [A^-]$ indicate that Np and Pu are present in the acidic solution as MO_2^+ ions, but Pa probably as MO^{3+}. While U(VI) is extracted as UO_2Ox_2-HOx[282], Np(VI) and Pu(VI) are reduced by oxine to the pentavalent state. The results are collected in Fig. 62.

Actinide extraction by β-diketones has been summarized by Liljenzin[283]. Although the β-diketones in addition to the normal metal coordination through the two oxygen atoms have a reactive central carbon atom with metal coordinating ability, no such complexes with actinides are known[284]. Nor have any polynuclear actinide β-diketones been reported. No complexes at all are formed if one of the hydrogen atoms at the central carbon atom is

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[278] J. O. Liljenzin and J. Rydberg, p. 255 in *Physico-chimie du protactinium*, Centre Nat. Rech. Scient. Paris (1966).

[279] C. Keller, S. H. Eberle and K. Mosdzelewski, *Radiochim. Acta*, **5** (1966) 185.

[280] C. Keller and S. H. Eberle, *Radiochim. Acta*, **8** (1967) 65.

[281] D. Dyrssen, *Svensk kem. tidskr.* **65** (1953) 43.

[282] J. Stary, *Anal. Chim. Acta*, **28** (1963) 132.

[283] J. O. Liljenzin, *Gmelin's Handbuch der Anorganischen Chemie*, 8. Auflage, Systemnr 71 (Transurane), Teil D, in press.

[284] D. W. Thompson, p. 27 in *Structure and Bonding*, Vol. 9, P. Hemmerich, C. K. Jørgensen, J. B. Neilands, R. S. Nyholm, D. Reinen and R. J. P. Williams (Eds.), Springer Verlag, Berlin (1971).

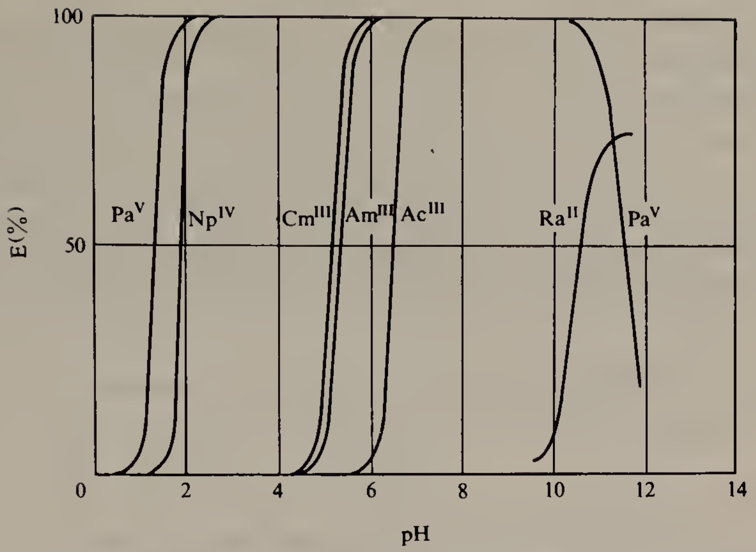

FIG. 62. The percentage ($E\%$) of tracer actinides extracted by 0·1 8-hydroxyquinoline in chloroform[275]. $pH_{1/2}$ for Th(IV) is 3·1, and for U(VI) 2·6 (not shown)[281].

substituted. Proton magnetic resonance spectra of solutions[285] and solid structure analysis[217,286] of actinide tetraacetylacetonates show that the eight oxygens are symmetrically attached to the metal atom, the structure in both liquid and solid phase being a square Archimedian antiprism (cf. Fig. 37). From the PMR data it is concluded that the metal–chelate bonding partly comes from π electrons occupying actinide *f* orbitals. With acetylacetone (HAA) the tri-, tetra-, penta- and hexavalent actinides form complexes of the types $MAA_3(HAA)_2$ for Am(III), MAA_4 for Th(IV), Np(IV), Pu(IV), $MO_2AA(HAA)_2$ for Pa(V), and $MO_2AA_2(HAA)$ for U(VI) complexes, respectively[220,287,288]. In addition, complexes with fewer self-adducts (i.e. HAA molecules) are also formed and are extracted. Similar results have been obtained with other β-diketones, for example dibenzoylmethane and thenoyltrifluoroacetone. During attempts to extract Np(VII) with dibenzoylmethane reduction to Np(IV) was observed[289]. Mixed complexes, such as $UO_2(AA)(BA)$, also form in the presence of two different β-diketones (HBA e.g. benzoylacetone); the distribution factor is slightly higher for the mixed complex than is expected from the average value of the individual $UO_2(AA)_2$ and $UO_2(BA)_2$ complexes[290].

In addition to $PaO_2AA(HAA)_2$ ($\lambda > 100$), Liljenzin[287] found both PaO_2AA (λ 1·05) and $PaOAA_3$ (λ 0·87), indicating the existence of both PaO^{3+} and PaO_2^+ in the aqueous phase. These complexes should be compared with the species $PaO_2(TTA)$, $PaO_2TTA(HTTA)_2$, $PaO(OH)(TTA)_2(HTTA)_2$ and $PaO(OH)(TTA)_2(TBP)_2$ reported by Guillaumont[291], and $PaO(TTA)_3(HTTA)$ reported by Kolarik *et al.*[292] Although all these species may form, the lack of uniformity between the results is disturbing. The experimental difficulties associated with the investigation of protactinium[278] may be responsible for the reporting of some of these complexes. In this connection it is interesting to note the improved

[285] C. Wiedenheft, *Inorg. Chem.* **8** (1969) 1174.
[286] H. Titze and B. Allard, *Acta Chem. Scand.* **24** (1970) 715.
[287] J. O. Liljenzin, *Acta Chem. Scand.* **24** (1970) 1655.
[288] S. K. Patil and H. D. Sharma, *Can. J. Chem.* **47** (1969) 3851.
[289] Yu. P. Novikov, B. F. Myasoedov and S. A. Ivaneva, *Radiochem. Radioanal. Letters*, **9** (1972) 85.
[290] L. Newman and P. Klotz, ref. 128, p. 128.
[291] R. Guillaumont, *Bull. Soc. Chim.* **1965**, 132, 135.
[292] R. T. Kolarik, V. A. Ryan and R. P. Schuman, *J. Inorg. Nucl. Chem.* **29** (1967) 783.

extraction of the Np(V)–HTTA complexes by polar diluents (see Fig. 63) indicating the unsaturated nature of the neutral NpO_2TTA complex[293].

The hexavalent actinides form chelates of type $MO_2A_2(HA)_x(H_2O)_y$, where $x = 0$ or 1, and $x + y \lesssim 2$ (see Fig. 42 for experimental data). The lower extractability of $UO_2AA_2(H_2O)_y$ (λ 3·3) as compared to $UO_2AA_2(HAA)(H_2O)_y$ (λ 22) indicates that the first complex may be hydrated in the organic phase (i.e. $y \lesssim 2$). This is supported by the fact that uranyl(VI) acetylacetonate is more easily extracted by the polar solvent hexone (pH$_{\frac{1}{2}}$ 2·3) than by less-polar benzene or chloroform (pH$_{\frac{1}{2}}$ 2·9; both cases 1 M HAA in the diluent)[220]. This should be compared with the lower extraction of the saturated complex $ThAA_4$ from hexone (pH$_{\frac{1}{2}}$ 3·9) as compared to benzene (pH$_{\frac{1}{2}}$ 2·8) or chloroform (pH$_{\frac{1}{2}}$ 3·4). The coordination number of 6 for the UO_2 group can be satisfied by (a) two bidentate AA^- and one bidentate (ketonic) HAA, (b) two bidentate AA^- and one monodentate HAA plus one water, or (c) through one bidentate AA^- and a tetradentate hydrogen bridged di-acetylacetonate $H(AA)_2^-$ complex (or a bidentate $H(AA)_2^-$ plus two water). The last type of complex has been suggested to occur in the extraction of UO_2A_2HA, where HA is tropolone or oxine[294]. Both alternatives (a) and (c) satisfy the uranyl 6-coordination without water of solvation. Although the evidence is not conclusive, it seems reasonable to assume that the two complexes are of the type $MO_2A_2(H_2O)_2$ and MO_2A_2HA.

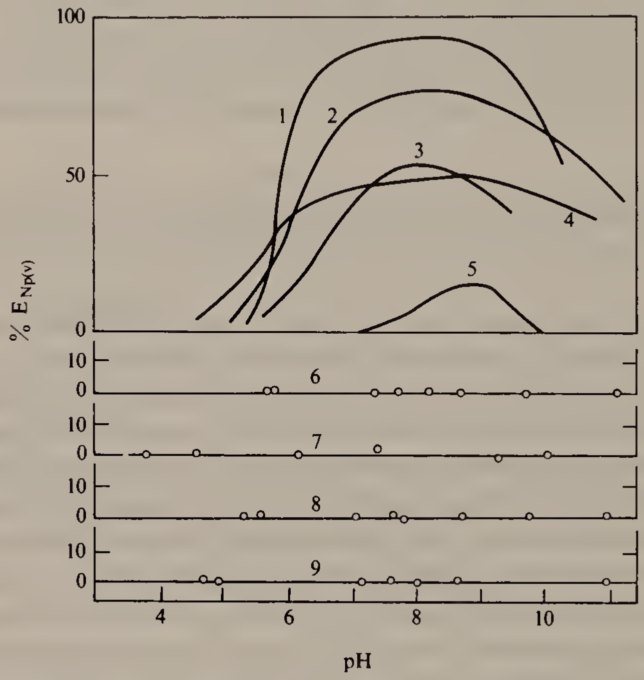

FIG. 63. Dependency of the percentage of extraction of tracer Np(V) by thenoyltrifluoroacetone on the nature of the solvent. (1) isobutanol, (2) cyclohexanone, (3) ethyl acetate, (4) methyl ethyl ketone, (5) amyl acetate, (6) benzene, (7) chloroform, (8) carbon tetrachloride, (9) diethyl ether[293].

Many authors have found that at very high ligand concentrations D_M decreases as shown in Fig. 41, and they assume the formation of negatively charged complexes, such as

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[293] Yu. A. Zolotov and I. P. Alimarin, *J. Inorg. Nucl. Chem.* **25** (1963) 691.
[294] D. Dyrssen, *Trans. Royal Inst. Techn.* No. 188, Stockholm (1962).

$UO_2A_3^-$[295] or ThA_6^{2-} (HA being tropolone[296] or salicylic acid[297]). These complexes seem to form only at high pH where pH > pK_a, and consequently where competition from hydrolysis increases faster than the complex formation with A^-. Thus it is reasonable to assume that the decrease in D_M at pH > pK_a is partly or wholly due to hydrolysis and not necessarily due to the formation of negatively charged actinide chelates.

The use of HTTA has been suggested for the isolation of macro amounts of Pu(IV), because of the very high D value for this valency state. However, the organic phase solubility of the metal complexes is rather low, and the kinetics of extraction are slow, particularly in the stripping procedure. The keto-enol equilibrium is also slow, and radiolysis of HTTA gives products which hamper the extraction. The use of HTTA will therefore probably be confined to the laboratory, where it has an important position as a very versatile extracting reagent. It has been shown to be particularly useful in connection with aqueous complex chemistry studies (sections 2.1.3 and 4.6.2).

A very large number of differently substituted organophosphoric acids have been investigated as extractants for actinides or lanthanides[156,167]. A few representative examples are given in Table 35. Two groups may be distinguished, the mono- and the diacidic acids containing phosphorus bound alkyl or alkoxy groups. The monoacidic comprise the phosphoric acids, (RO)(R′O)PO(OH), the phosphonic acids, (RO)R′PO(OH), and the phosphinic acids, RR′PO(OH). The diacidic are the monoalkylphosphoric acids, $(RO)PO(OH)_2$, and the less well-known monoalkyl phosphonic acids, $RPO(OH)_2$.

The monoacidic extractants are all monomeric in dilute solutions of highly polar solvents such as higher alcohols, and dimeric in low polar "inert" solvents, e.g. dodecane. Figure 40 shows the array of species formed in the two-phase kerosene–HNO_3(aq) system with dibutyl phosphoric acid, HDBP[257]. The extraction of the various actinide oxidation states has been summarized by Peppard and Mason[298,299]:

in monomerizing solvents:

$$M^{3+} + 3HA(org) \rightleftharpoons MA_3(org) + 3H^+ \tag{16a}$$

$$M^{4+} + 4HA(org) \rightleftharpoons MA_4(org) + 4H^+ \tag{17a}$$

$$MO_2{}^{2+} + 2HA(org) \rightleftharpoons MO_2A_2(org) + 2H^+ \tag{18a}$$

in dimerizing solvents:

$$M^{3+} + 3H_2A_2(org) \rightleftharpoons M(HA_2)_3(org) + 3H^+ \tag{16b}$$

$$M^{4+} + 3H_2A_2(org) \rightleftharpoons MA_2(HA_2)_2(org) + 4H^+ \tag{17b}$$

$$MO_2{}^{2+} + 2H_2A_2(org) \rightleftharpoons MO_2(HA_2)_2(org) + 2H^+ \tag{18b}$$

Figure 64 shows how the U(VI) extraction increases with the concentration of di(2-ethylhexyl)phosphoric acid (HDEHP) concentration in n-amyl alcohol. $\delta \log D_M/\delta \log [HA]$ changes from a slope of 2 (according to reaction 18a) to a slope of 4 (according to reaction 18b) at high HDEHP concentration. Similar results are obtained for the extraction of Am(III) (slope changes from 3 to 6, reactions 16) and Th(IV) (slope changes from 4 to 6, reactions 17). No evidence was found for the formation of mixed complexes of the kind $ML_nA_p^{z-n-p}$.

[295] V. Moucka and J. Stary, *Coll. Czech. Chem. Commun.* **26** (1961) 763.
[296] D. Dyrssen, *Acta Chem. Scand.* **9** (1955) 1567.
[297] B. Hök-Bernström, *Acta Chem. Scand.* **10** (1956) 174.
[298] D. F. Peppard and G. W. Mason, *Nucl. Sci. Eng.* **16** (1963) 382.
[299] G. W. Mason, S. Lewey and D. F. Peppard, *J. Inorg. Nucl. Chem.* **26** (1964) 2271.

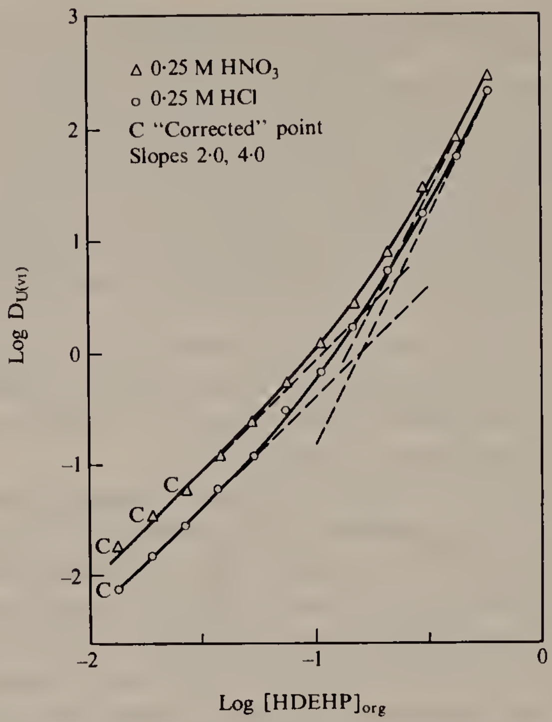


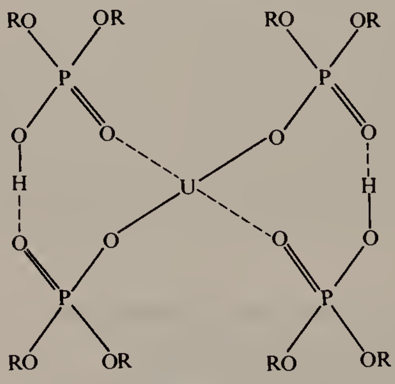
FIG. 64. Dependence of U(VI) extraction from HNO_3 and HCl solutions on di(2-ethylhexyl)-phosphoric acid (HDEHP) concentration in n-amyl alcohol diluent[299].

Dreze and Duyckaerts[300] investigated the extraction of Pu(IV) from nitric acid solutions by HDBP in benzene. The results can be summarized partly by Fig. 65. The $\delta \log D_M / \delta \log X$ slopes are -2 for $X = [H^+]$, -1 for $X = [NO_3^-]$, and $+2$ for $X = [H_2A_2]$. From this it was concluded that extraction occurred according to the reaction

$$Pu(NO_3)_3{}^+ + 2H_2A_2(org) \rightleftharpoons Pu(NO_3)_2(HA_2)_2(org) + 2H^+ + NO_3{}^- \qquad (19)$$

Thus mixed complexes also are formed to a large extent in these systems. This is further illustrated in Fig. 66, where, however, also a monomeric self-adduct is assumed to be formed.

Obviously $UO_2(HA_2)_2$ and $UO_2A_2(HA)_2$ are isomeric. With HDEHP as HA the structure at the plane perpendicular to the O–U–O-axis may in the former case be[298]



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[300] Ph. Dreze and G. Duyckaerts, EUR 436 f, Euratom (University of Liege), Bruxelles (1963).

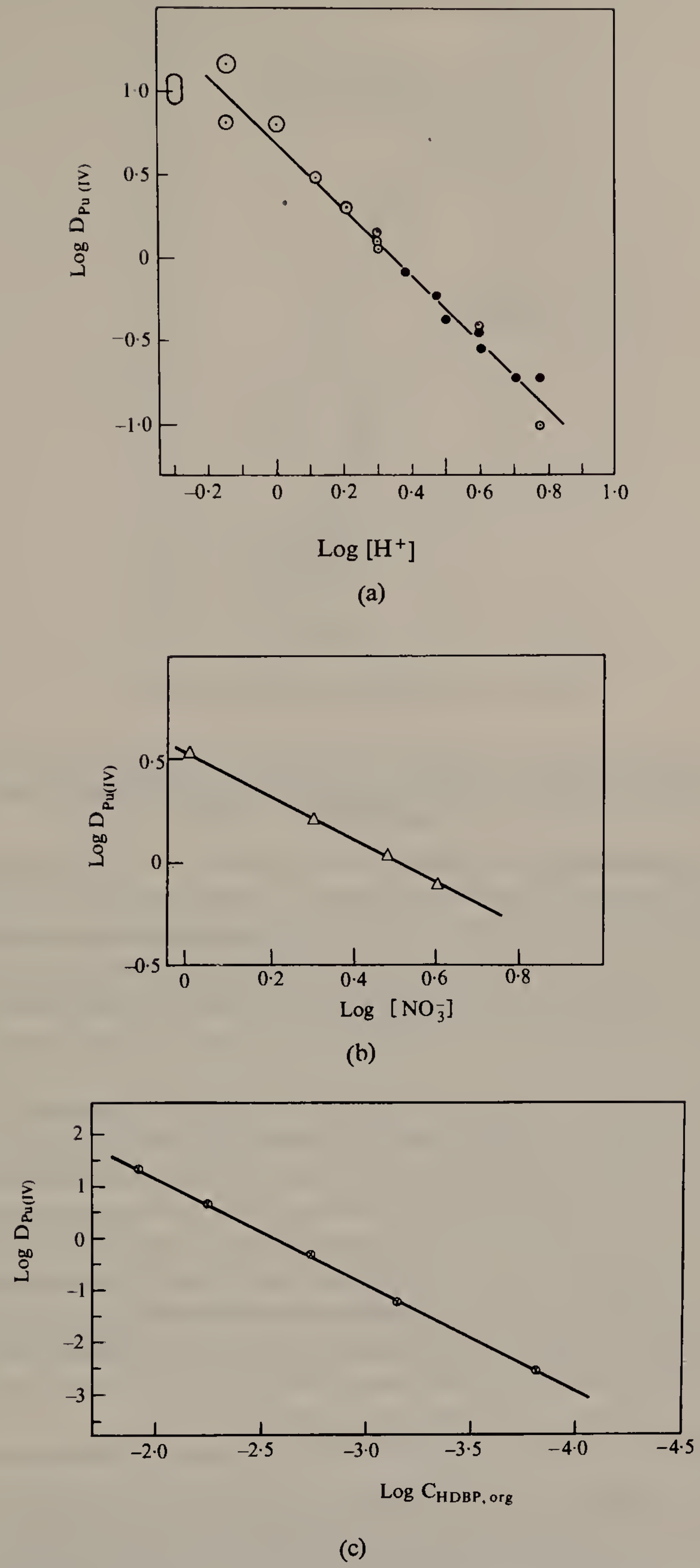

FIG. 65. The extraction of Pu(IV) from nitric acid solutions by dibutylphosphoric acid, HDBP, in benzene. (a) hydrogen ion dependency in 6 M [NO_3^-]; (b) nitrate ion dependency in 4 M HNO_3 + $HClO_4$; (c) [HDBP] dependency with 6 M HNO_3; 25°C[300].

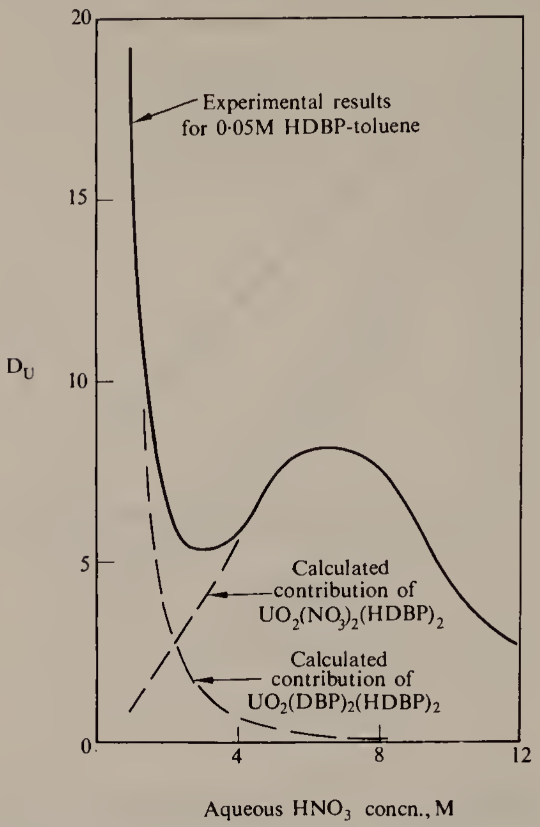

FIG. 66. Variation of D_U with HNO_3 concentration in the HNO_3–dibutylphosphoric acid (HDBP)–toluene system[257].

This, however, does not satisfy 6-coordination of the UO_2 group, a requirement which is better met by the alternative formula $UO_2A_2(HA)_2$. It should be realized that the "monomerizing" polar solvents (B) in reactions (16a), (17a) and (18a) probably solvate the complexes indicated to the right in the reactions. Thus, for example, $UO_2A_2B_2$ may be formed in reaction (18a), and correspondingly $UO_2A_2(HA)_2$ in reaction (18b) (see also section 4.7.4). At very high U(VI) concentration a gel-like polymeric solid of the overall composition UO_2A_2 is obtained.

The extraction of trivalent actinides by HDEHP, HEHϕP (2-ethylhexyl phenyl phosphonic acid) and HMeHϕP (1-methyl-heptyl phenyl phosphonic acid) in dodecane is illustrated in Fig. 67. The D_M values for the trivalent actinides vary with the atomic number Z in a non-regular manner similar to the D_M values for the lanthanides. This illustrates the so-called tetrad effect, in which the lanthanides seem to fall into four groups of four elements each.[303a,b] The break at $_{96}$Cm indicates a half-filled 7*f* shell and another break at $_{99}$Es approximately 3/4-filled shell. An explanation of this effect is given by Jørgensen[304].

HDEHP was used in the first solvent extraction process for the recovery of uranium from ore in the United States (the Dapex process)[305a,b].

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[301] B. Weaver and R. R. Shoun, *J. Inorg. Nucl. Chem.* **33** (1971) 1909.

[302] D. F. Peppard, C. A. A. Bloomquist, E. P. Norwitz, S. Lewey and G. W. Mason, *J. Inorg. Nucl. Chem.* **32** (1970) 339.

[303a] I. Fidelis and S. Siekierski, *J. Inorg. Nucl. Chem.* **33** (1971) 3191.

[303b] D. F. Peppard, G. W. Mason and S. Lewey, *J. Inorg. Nucl. Chem.* **31** (1969) 2271.

[304] C. K. Jørgensen, *J. Inorg. Nucl. Chem.* **32** (1970) 3128.

[305a] K. B. Brown, C. F. Coleman, D. J. Crouse, C. A. Blake and A. D. Ryon, *Proc. Int. Conf. Peaceful Uses of Atomic Energy*, Vol. 3, p. 472, Geneva (1958).

[305b] W. C. Hazen, *Mining Eng.* **9** (1957) 994.

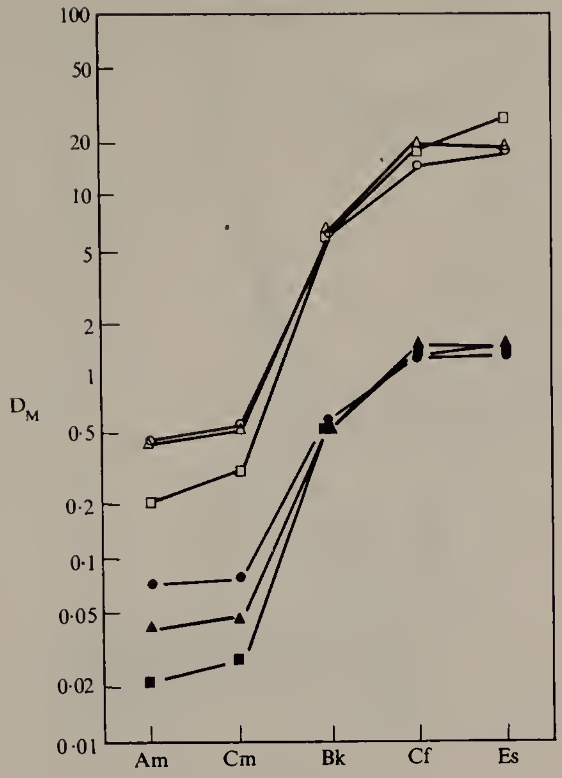

FIG. 67. Distribution coefficients of actinides between dodecane solutions of extractants and HNO_3 solutions. ○, ● 0·8 M HDEHP vs. 0·5 M and 1·0 M HNO_3; △, ▲ 0·1 M HEHϕP vs. 0·5 M and 1·0 M HNO_3; □, ■ 0·2 M HMeHϕP vs. 0·5 M and 1·0 M HNO_3[301].

A thorough investigation of metal ion extraction by dialkyl phosphoric acids, and synergistic effects with non-acidic complexing agents, has recently been given by Liem[305c].

The diacidic organophosphorus extractants have been less investigated than the monoacidic ones, because they are more soluble in water, and have a tendency to form emulsions, factors which reduce their practical value.* The extractants polymerize in inert diluents; mono-(2-ethyl hexyl) phosphoric acid (H_2MEHP) is monomeric in methyl alcohol, 4·5-meric in chloroform, and 14·5-meric in n-hexane[306]. The extraction of various actinide species by this reagent in toluene is given in Fig. 68. The superior extracting power of H_2MEHP over HDEHP (and compared with the neutral phosphoryl adducts) for Am(III) is illustrated in Table 34. Extraction data for other reagents of this type are given in Table 35.

Many organopyrophosphoric acids are very efficient extractants in so far as extremely high D_M values are obtained at normal aqueous acidities. Some of these acids are very difficult to purify, e.g. the dialkylpyrophosphoric acids. They have other drawbacks: the high D_M values make it difficult to strip the metal from the organic phase, and the acids are unstable. The instability may, however, be used for stripping: digestion of the organic phase at 90°C for 1 hr with 1 M HCl results in hydrolysis of the pyrophosphates to orthophosphates[184].

The best investigated extractant of this class is di-octyl) pyrophosphoric acid.†

* This is also true of monoacidic esteracids with moderately long straight alkyls, such as di-n-octylphosphoric acid. The alkyl branching of HDEHP is essential to its good performance.

† Common abbreviation is OPPA, suggested abbreviation is H_2DOPP.

[305c] D. H. Liem, *Diss. Royal Inst. Techn.*, Stockholm 1971.

[306] J. R. Ferraro and D. F. Peppard, *Nucl. Sci. Eng.* **16** (1963) 389.

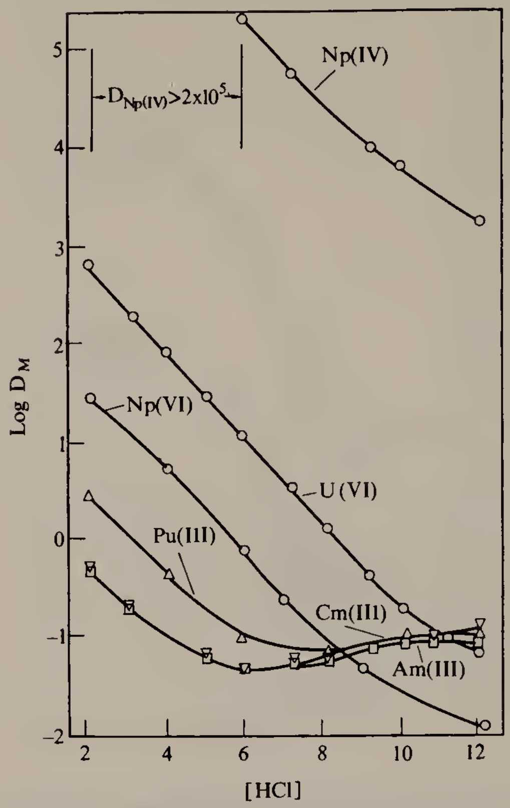

FIG. 68. Extraction of some actinide ions by mono-2-ethylhexyl phosphoric acid, H_2MEHP, in toluene[308].

H_2DOPP was primarily investigated for the extraction of uranium from phosphate ore leach solutions. $D_U \gtrsim 20$ was obtained from high concentrated sulphuric/phosphoric acid solutions with 2% H_2DOPP in hexane[307a,b]. The extraction of trivalent actinides is shown in Fig. 69. D_M is never less than 100, making extremely high enrichment possible in one step. H_2DOPP has therefore been suggested for recovering transuranium elements from rock debris from underground nuclear explosions[184]. The extraction of tetravalent actinides is also about 100% in one step, even in the presence of appreciable quantities of F^- or SO_4^{2-}.

4.7.4. *Synergistic Extraction Systems*

Synergistic (i.e. mutually enhanced) extraction can occur for complexes which can accommodate two different organic ligands. The most common case is that of the MA_nB_p type complexes, where A is a chelating anion and B a Lewis base adduct. Synergism is a common feature of all metal extractions[127], and has been observed in all systems where the neutral metal complex is coordinatively unsaturated. The first account of synergistic extraction was given in 1957[126], but the phenomenon as such was known much earlier. The classical example is that illustrated in Fig. 38, and discussed in section 4.5.3. In the same section, synergistic extraction of the Am(III)–HTTA complex by TBP and TOPO is described. Section 4.6.2 gives the pertinent equations for the extraction of MA_nB_p complexes. It has also been

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[307a] A. S. Long, D. A. Ellis and R. H. Bailes, *Proc. Int. Conf. Peaceful Uses of Atomic Energy* **8** (1956) 77.

[307b] F. Habashi, *J. Inorg. Nucl. Chem.* **13** (1960) 125.

[308] D. F. Peppard, G. W. Mason and R. J. Sironen, *J. Inorg. Nucl. Chem.* **10** (1959) 117.

FIG. 69. Extraction of trivalent actinides by 8 vol.% bis 2-ethylhexyl pyrophosphoric acid in kerosene[184].

pointed out earlier that the formation of a self-adduct is not different in principle from synergism with two different reagents.

All actinide valency states produce coordinatively unsaturated neutral complexes, except perhaps the tetravalent state. Consequently synergism has been observed for all actinide oxidation states with anionic (chelating) and neutral (adduct-forming) ligands. It has also been observed for the combination of chelating agent and amine extractant, but no information is available for the combination of an amine extractant with a neutral adduct former. Although an enormous number of combinations are possible—even for the actinides alone—the number of systems studied are as yet rather limited[127,167].

The classical system U(VI)–NO_3^-/HA + B in kerosene, where HA is HDEHP and B is a neutral phosphoryl adduct, is discussed by Baes[309]; the equilibrium constants for the following reactions are given in Table 37.

$$K_2 \quad M(HA_2)_2(org) + B(org) \rightleftharpoons M(HA_2)_2B(org) \tag{20}$$

$$K_3 \quad H_2A_2(org) + B(org) \rightleftharpoons H_2A_2B(org) \tag{21}$$

$$K_4 \quad \tfrac{1}{2}H_2A_2(org) + B(org) \rightleftharpoons HAB(org) \tag{22}$$

The formation of the H_2A_2B and HAB complexes leads to a decrease in the free concentration of HA at high B concentration, thus decreasing D_U according to the curves in Fig. 38.

[309] C. F. Baes, Jr., *Nucl. Sci. Eng.* **16** (1963) 405.

TABLE 37. EQUILIBRIUM CONSTANTS IN THE SYNERGISTIC EXTRACTION OF U(VI) BY HDEHP AND NEUTRAL PHOSPHORYL ADDUCTS[a]

Adduct	Solvent	$K_2 \times 10^{-2}$	K_3	K_4
TBPO	Kerosene	190	33	(8·3)
BDBP	Kerosene	60	18	(4·5)
DBBP	Kerosene	6	6	(1·5)
TBP	Kerosene	1·5	4	(1·0)
TBP	Hexane	0·7	2·5	(0·6)
TBP	Benzene	0·16	1	(0·25)
TBP	Benzene	1000*	—	—

BDBP, butyl dibutyl phosphinate; DBBP, dibutyl butyl phosphonate.
* Acidic reagent is HTTA, not HDEHP.
[a] C. F. Baes, Jr., *Nucl. Sci. Eng.* **16** (1963) 405.

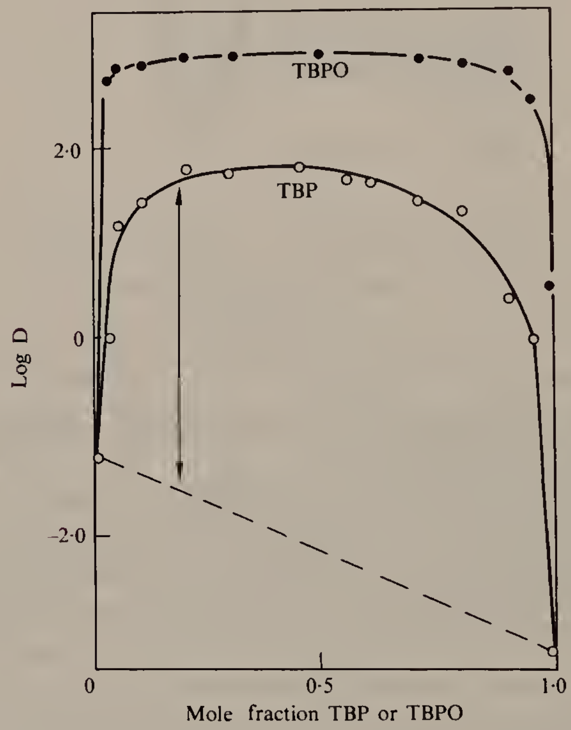

FIG. 70. Distribution of U(VI) between 0·01 M HNO_3 and mixtures of HTTA and TBP (or TBPO) of constant total molarity 0·02 M in cyclohexane[310].

Table 37 also shows the much higher synergistic effect with TTA. $UO_2(TTA)_2B_x$ ($x = 0$–3), $Th(TTA)_4B_x$ ($x = 0$–1) and $Am(TTA)_3B_x$ ($x = 1$–3) have all been identified, B being a neutral phosphoryl adduct. The Th(IV) 8-coordination is believed to be maintained through three bidentate TTA^- and one monodentate TTA^- and B[309]. The synergistic extraction of U(VI) by HTTA and TBP (or TBPO) is illustrated in Fig. 70.

Synergistic extraction with amines has also been observed, e.g. for U(VI) + HDBP +

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[310] H. Irving and D. N. Edgington, *Proc. Chem. Soc.* **1959**, 360; see also ref. 127.

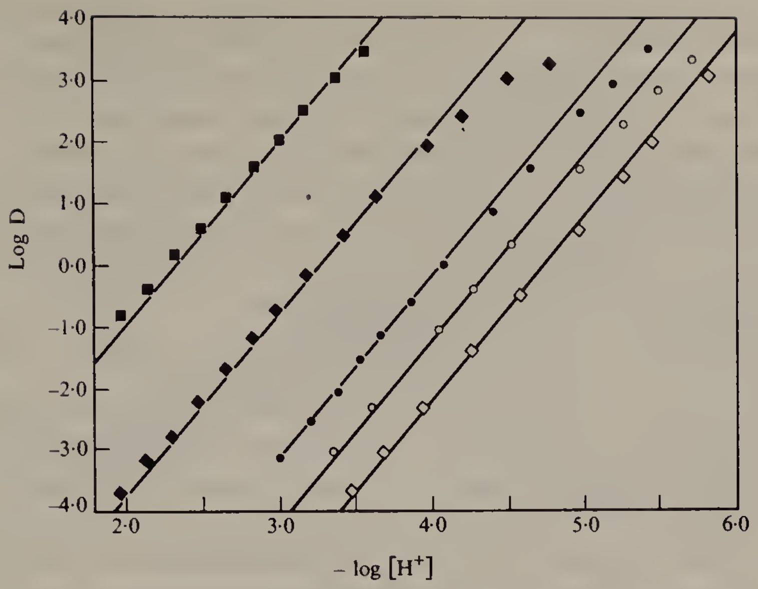

FIG. 71. Synergistic extraction of Am(III) by HTTA and TOA. Organic phase 0·02 M in HTTA and aqueous phase 2 M in chloride: ◇ no amine, ○ 10^{-4} M amine, ● 10^{-3} M amine. Organic phase 0·2 M in HTTA and aqueous phase 0·01 M in chloride: ◆ no amine, ■ 10^{-2} M amine[314].

TOA[311], U(VI) + H_2MBP + TOA[312], Th(IV) + HTTA + TOA[313], and Am(III) + HTTA + TOA[314]. For the U(VI) systems complexes of the type $(R_3NH^+)(UO_2SO_4HA_2^-)$[311] are suggested; polynuclear species are also believed to be formed. The effect is rather small (antagonistic reactions also occurring) and the explanation of its cause is inconclusive. Similar complicated complexes are suggested for the Am(III) and Th(IV) systems, e.g. the formation of $(R_3NH^+)(AmCl(TTA)_3^-)$. The formation constant for the latter complex from $Am(TTA)_3$ and $R_4NH^+Cl^-$ in benzene is calculated to be $10^{5\cdot 0}$. The effect on Am(III) is therefore quite substantial, as is seen in Fig. 71.

4.8. Separation processes

The more than academic interest in the actinide elements stems from their use as fuel in nuclear power plants. An efficient recovery of uranium from its ores, and the transformation of ^{238}U to ^{239}Pu in reactors as well as their recovery from the used fuel elements, are chemical processes of utmost importance for satisfying the energy need of our future technical society. In these processes solvent extraction is the main purification step. The flowsheets commonly adopted for these processes—the recovery of uranium from its ores (usually very low grade) and the isolation of plutonium from used fuel elements—are briefly described below, together with the Tramex process for transuranium element separation.

A *solvent extraction cycle* consists of three steps, the *extraction*, the *scrubbing* and the *stripping*. In the extraction, the aqueous feed, containing the solute of interest, is mixed in the contactor (separatory funnel, stirred vessel, etc.) with the extractant. After phase separation (in the gravitational or centrifugal field) an organic phase is obtained containing

[311] C. Deptula and S. Minc, *J. Inorg. Nucl. Chem.* **29** (1967) 159.
[312] C. Deptula, *J. Inorg. Nucl. Chem.* **32** (1970) 277.
[313] L. Newman and P. Klotz, *J. Phys. Chem.* **67** (1963) 205.
[314] L. Newman and P. Klotz, *Inorg. Chem.* **5** (1966) 461.

most of the solute (the extract), and an aqueous phase depleted in solute (the raffinate). The extract is sometimes referred to as the *loaded* (or *pregnant*) organic phase.

If impurities occur in the extract, they may be removed by scrubbing the organic phase with an aqueous *wash* (or *scrub*), producing an aqueous *waste solution.*

In the final step, the desired solute is stripped out of the extract with an aqueous phase, called *strip* (or sometimes *back-wash*) solution. After phase separation one obtains an aqueous *product* phase (or stream) and a depleted (or relieved) organic phase. The organic phase, which commonly is referred to as "solvent out", may be identical to the extractant and can be used again, thus closing the extraction cycle.

The extractions are with very few exceptions carried out counter-currently in multiple-stage mixer-settler batteries or pulse columns (cf. section 4.6.3).

A general flowsheet for the extraction of uranium from ores with a tertiary amine is shown in Fig. 72. Mainly using 2·5–3% Alamine 336 (~trioctylamine) in kerosene as extractant for sulphuric leach solutions (U content in ore $\lesssim 1\%$) about 25,000 tons of U_3O_8 were produced in 1971. In the extraction stages (three mixer-settlers) the aqueous acidic (pH ~ 1–2) feed ("pregnant") liquor meets the alkylamine sulphate (made up in the amine acidification step; cf. reaction 2a) leading to the extraction of >99·9% of uranium

$$(R_3NH)_2SO_4(org) + UO_2(SO_4)_2{}^{2-} \rightleftharpoons (R_3NH)_2UO_2(SO_4)_2(org) + SO_4{}^{2-} \qquad (23)$$

In the scrubbing stage some co-extracted impurities are washed out. Stripping is done with soda,

$$\begin{aligned}&(R_3NH)_2UO_2(SO_4)_2(org)+3CO_3{}^{2-} \rightleftharpoons\\ &\qquad \rightleftharpoons UO_2(CO_3)_3{}^{4-} + 2R_3N(org) + 2SO_4{}^{2-} + CO_2(g) + H_2O \qquad (24)\end{aligned}$$

producing a soluble uranyl tricarbonate complex and the free amine. Because of the very high and very low D_U values in the extraction and stripping stages, respectively, very low and very high flow ratios (θ) organic:aqueous may be applied. An example is $\theta = 0{\cdot}1$ in the extraction and $\theta = 10$ in the stripping stages, thus leading to a high increase in uranium concentration in the aqueous strip solution as compared to the feed. High purity uranium is produced in a second purification cycle, commonly with TBP as extractant on uranyl nitrate solutions. The purity of the end product is >99·98%.

TBP is the main extractant used in processes for the isolation of plutonium from used reactor fuel elements, although amines have lately come into some use. Several comprehensive monographs deal with plutonium chemistry and technology[156,163,315,316], in addition to numerous papers in the *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy* and other publications. Only a very brief description will be given here. It is based on the flowsheet in Fig. 73.

After the radioactivity of the fuel elements has decayed for a certain time (usually $\gtrsim$ 6 months), the cladding is removed (usually mechanically, although chemical dissolution is also used) and the fuel material containing unused uranium (and some new uranium isotopes) and produced plutonium and fission products (neglecting minor amounts of other actinides) is dissolved in hot concentrated HNO_3. By suitable redox reactions the U(VI) and Pu(IV) valency states are adjusted (Table 18), and the aqueous solution (properly diluted) is fed centrally into the solvent extraction battery (cf. Fig. 45). Uranium and plutonium are extracted by ~20% TBP dissolved in kerosene. Under these conditions the

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[315] S. O. Andersson, A. Ashbrook, D. S. Flett, G. M. Ritcey and D. R. Spink, *Solvent Extraction in Process Metallurgy*, Univ. of Waterloo, Waterloo, Ont. (1971).

[316] J. M. Cleveland, *The Chemistry of Plutonium*, Gordon & Breach, New York (1970).

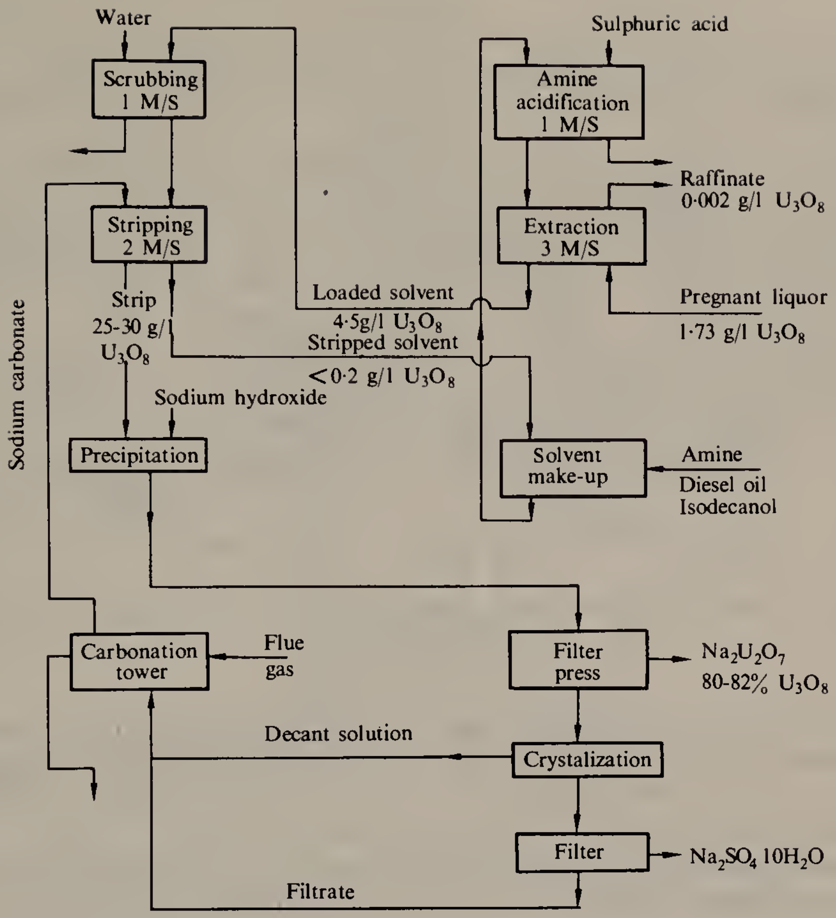

FIG. 72. General flow-sheet for the extraction of uranium with tertiary amine. 3 M/S means three mixer-settler stages[315].

main fraction of the fission products is left in the aqueous raffinate. In the extraction battery II a reducing agent is added (ferrosulphamate, U(IV), etc.), converting Pu(IV) to non-extractable Pu(III) (see Table 31 and Fig. 57, Pu(III) and Am(III) extract about equally poorly). Thus uranium and plutonium are separated, U(VI) (and some possible U(IV)) staying in the organic phase, and Pu(III) leaving with the aqueous strip solution. Plutonium is further purified through re-oxidation to Pu(IV) and extraction in battery VI, and then stripped through reduction to Pu(III) in battery VII. The uranium stream is also further purified by stripping with pure water ($D_U \ll 1$ at the low acidities obtained) in battery III, and passing through another extraction-stripping cycle. Further removal of fission products is achieved through silica-gel adsorption, solid or liquid ion exchange, etc. The final plutonium and uranium products are extremely pure, the fission product concentration being lowered by a factor of 10^8. The yield is often better than 99·8%.

The Tramex process has been developed as part of the comprehensive U.S. program for the production of large amounts of heavy actinides centered at the Oak Ridge National Laboratory. Plutonium (mainly ^{242}Pu) is irradiated in the high-flux isotope reactor, leading to the production of fission products and isotopes of Cm, Bk and Cf. After dissolution of the target, plutonium and some fission products are removed by extraction with HDEHP. The

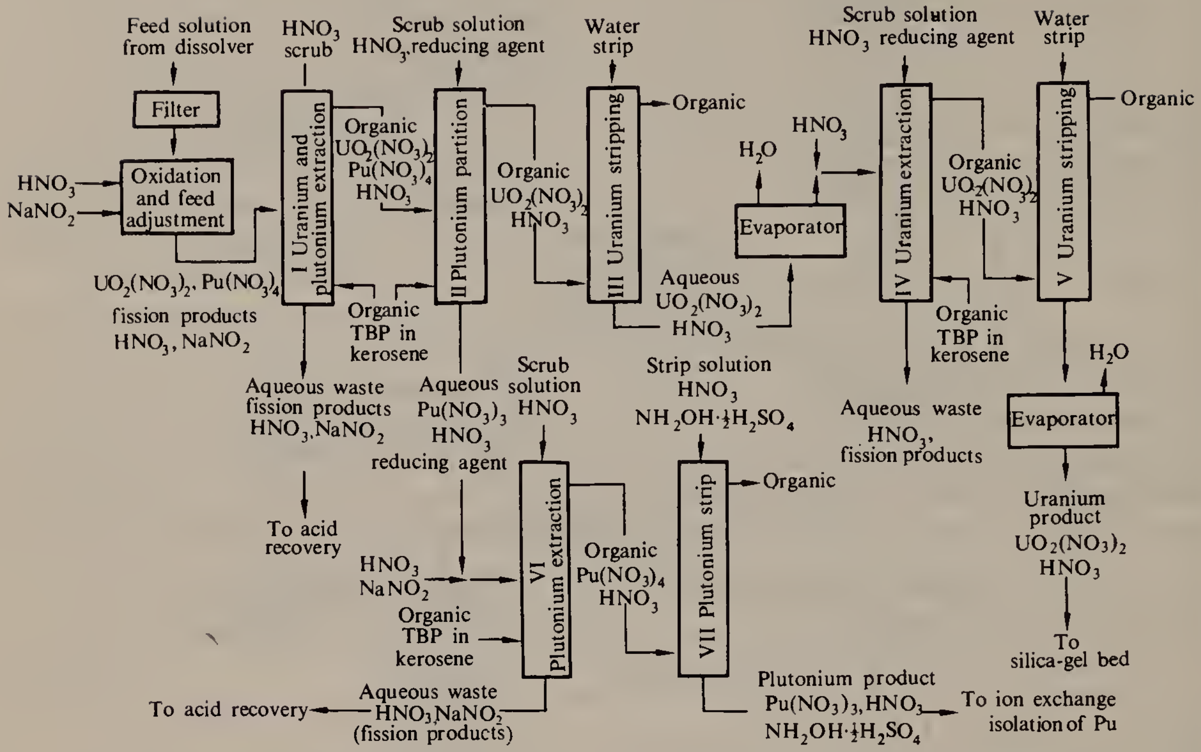

FIG. 73. General flow-sheet of the Purex process for separation of uranium, plutonium and fission products by extraction with tributyl phosphate (TBP) in kerosene[317].

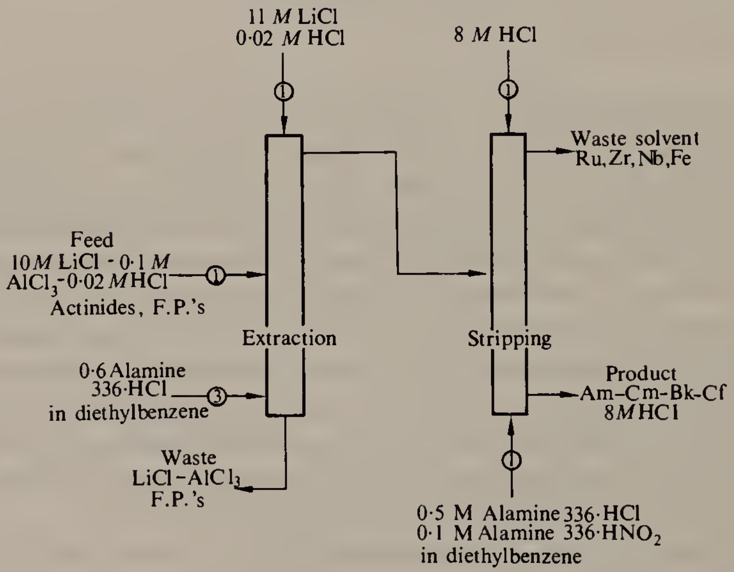

FIG. 74. The Tramex flow-sheet for the isolation of heavy actinides through amine extraction from LiCl–HCl solutions[232].

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[317] M. Benedict and T. H. Pigford, *Nuclear Chemical Engineering*, McGraw-Hill, New York (1957).

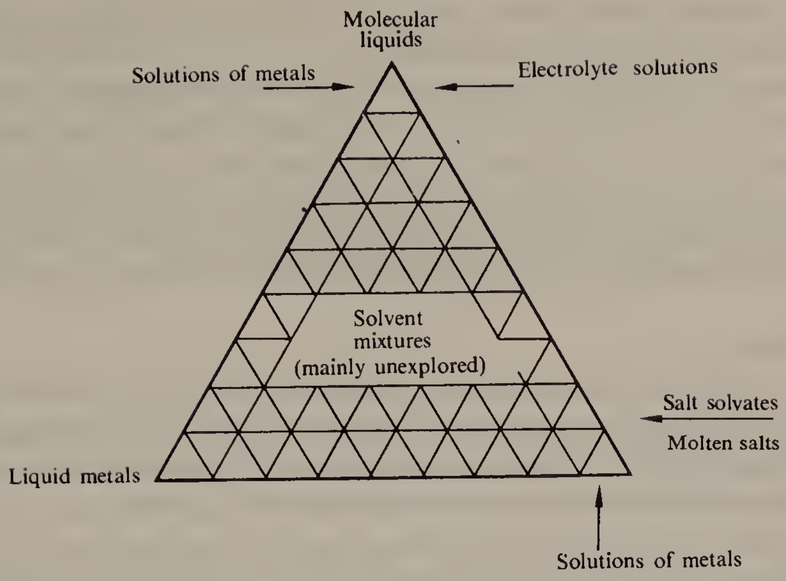

FIG. 75. Solvent classes. The arrows indicate the approximate position of some well-known solution types.

next step is illustrated in Fig. 74. The task is to separate the trivalent actinides from trivalent lanthanide fission products. This is accomplished by extraction with a tertiary amine from 11 M LiCi + dilute HCl, a possibility which is obvious from Fig. 47. In the stripping column, Am, Cm, Bk and Cf are removed from most of the fission products extracted in the first column. Final individual separation of the actinides is achieved through cation-exchange. The Tramex process has been used in the isolation of >0·1 g of the important neutron-emitting nuclide ^{252}Cf (ref. 184).

5. NON-AQUEOUS SOLVENTS

Non-aqueous solvents are liquid media other than water which dissolve a reasonable number of compounds and allow the occurrence of chemical reactions[318]. They can be classified according to their type of bonding (see Fig. 75) as molecular liquids, ionic melts and liquid metals. Because the molecular liquids include water, many properties described here are paralleled in water solutions.

Most experimental work has centered around the corners of Fig. 75, leaving a vast field of solvents and solvent mixtures unexplored. Liquid metal solvents will only be discussed in this section when they act as a second phase in two-phase distribution equilibria. They have been studied and used as solvents for the fuel in certain types of nuclear reactors[319] and as extractants in the reprocessing of spent molten salt fuels[320].

The knowledge of solubilities and properties of actinide compounds and ions in non-aqueous solvents is relatively limited, most information pertaining to thorium and uranium. Protactinium, neptunium, plutonium and americium have been studied to only a small extent and the heavier actinides hardly at all. This situation, an enormous range of solvents

[318] V. Gutmann, *Coordination Chemistry in Non-Aqueous Solutions*, Springer-Verlag, Wien (1968).

[319] M. Blander (Ed.), *Molten Salt Chemistry*, Interscience, New York (1964).

[320] L. E. McNeese, J. S. Watson, B. A. Hannaford, C. W. Kee and M. E. Whatley, p. 129 in *Proc. ICSEC* 71, Vol. I, Society of Chemical Industry, London (1971).

and only a few actinides investigated in very few of the solvents, makes general statements difficult to formulate and inherently uncertain.

The properties of non-aqueous systems which have been studied are usually the ultraviolet, visible and near infrared spectra at a single solute concentration, the molar conductance at various solute concentrations and the height and form of polarographic waves. Most of these investigations give only qualitative results, e.g. evidence for the formation of a specific ion pair or oxidation to a certain valence state. The chemistry of actinide element complexes in molten salts has very recently been reviewed in detail by Kertes[321].

5.1. Solvent systems

Anhydrous solvents are often difficult to handle as they may require low temperatures, e.g. liquid NH_3, or high temperatures, e.g. molten salts, or they may be corrosive, poisonous, inflammable, hygroscopic, etc. However, such drawbacks may be offset by other favorable factors. Some reasons for the importance of non-aqueous solvents are:

1. The solute reacts with water to yield unwanted compounds, e.g. $PaBr_5$ reacts with water to form oxygenated species with strong Pa–O bonds, but it can be dissolved in acetonitrile (AN) as a solvate, probably as $PaBr_5$, 3AN[322].
2. The solute forms strong complexes with the solvent with an associated change in the redox potentials in favor of one oxidation state, e.g. UO_2^+ is apparently more stable in dimethylsulphoxide (DMSO) solution than in water[323,324].
3. The decomposition of the solvent occurs at a higher or lower potential relative to the $E°$ of a certain actinide redox couple than for the corresponding aqueous system. Thus evidence has been obtained for the reduction of Am(III) to Am(II) in a $PuCl_3$ containing (K, Na)Cl melt in contact with liquid Pu metal at 698–775°C[325].
4. The solvent may still be liquid at low temperatures, e.g. NH_3, or stable at high temperatures, e.g. salt melts.
5. The solvent dissolves the reactants but the desired product is insoluble. This simplifies preparative work to a great extent. In many cases metathetical reactions can be used. As an example UCl_5, TCAC (TCAC = trichloroacryloylchloride) and 8-hydroxyquinoline (Hox) are soluble in benzene, whereas the product $UCl_5 \cdot 4Hox$ is insoluble in benzene and precipitates when solutions of the reactants in benzene are mixed[326].
6. The solvent does not react or mix with a molten metal phase, but can dissolve metal ions. Thus molten BeF_2–LiF–ThF_4 does not react with molten Bi–Li, but other actinides are partly reduced and distribute between the two melts depending on the Li content of the metal phase[327].
7. The solvent dissolves a large amount of solute. This is especially so in the case of some molten salt mixtures where the solute may constitute a considerable part of the liquid, e.g. Th(IV) as ThF_4 is considerably "soluble" in a BeF_2–LiF–ThF_4 melt[328].

[321] A. S. Kertes, *Act. Rev.* **1** (1971) 371.

[322] D. Brown and P. J. Jones, *J. Chem. Soc.* (A) **1966**, 262.

[323] G. Gritzner and J. Selbin, *J. Inorg. Nucl. Chem.* **30** (1968) 1799.

[324] J. Selbin, J. D. Ortego and G. Gritzner, p. 550 in *Progress in Coordination Chemistry, Proc. XIth ICCC.* M. Cais (Ed.) Elsevier, N.Y. (1968).

[325] L. J. Mullins, A. J. Beaumont and J. A. Leary, *J. Inorg. Nucl. Chem.* **30** (1968) 147.

[326] J. Selbin, N. Ahmad and M. J. Pribble, *J. Inorg. Nucl. Chem.* **32** (1970) 3249.

[327] L. M. Ferris, J. C. Mailen, J. J. Lawrence, F. J. Smith and E. D. Nogueira, *J. Inorg. Nucl. Chem.* **32** (1970) 2019.

[328] W. R. Grimes, F. F. Blankenship, G. W. Keilholz, H. F. Poppendiek and M. T. Robinson, *Proc. 2nd Geneva Conf.* Vol. 28, p. 99 (1958).

8. The solvent increases association and ion-pair formation. This may be used to obtain high distribution ratios for actinide salts between the solution and an anion exchanger. For example, $ThCl_4$ is only weakly adsorbed from aqueous solution on anion exchangers, but very strongly adsorbed from a solution in ethanol[329].

To facilitate the choice of a suitable solvent for an actinide compound some solubility data are given in Table 38. Even though much of this information is of a qualitative nature it gives a general picture of the solubilities in non-aqueous solvents (see also ref. 330).

5.2 Species in solution

The large variation in solvent properties among the non-aqueous solvents results in a correspondingly large variation in solute species ranging from the partly ordered arrangement of naked ions occurring in ionic melts to the strongly associated and often polymeric species occurring in solutions of actinide alkoxides in non-polar organic solvents. To facilitate the description of the species in solution the molecular solvents will be divided into polar and non-polar liquids.

5.2.1. *Species in Ionic Melts*

Nitrate melts, typically the $(K,Li)NO_3$ eutectic, possess comparatively weak complexing properties. However, their oxidizing action rapidly converts the lower oxidation states of dissolved actinide ions to the higher ones, limiting the stability in nitrate melts to species such as UO_2^{2+}, NpO_2^{+}, and PuO_2^{2+} [331]. Th(IV) forms insoluble oxynitrate compounds[332]. Americium is the first actinide to exist as the M^{3+} ion in these solvents[332]. Spectral studies indicate that the actinide ions are solvated by coordination of the nitrate oxygens in a somewhat similar way to water coordination in aqueous solutions. For this reason nitrate melts have been used as solvents in studies of chloride and fluoride complexes by spectrophotometry, solvent extraction and ion-exchange. Addition of chloride or fluoride to a nitrate melt is accompanied by the stepwise formation of the corresponding actinide–halide complexes in a way similar to that in water[331,333,334,335].

Chloride melts, typically the (K,Li)Cl eutectic, have strong complexing properties and almost all oxidation states known for the actinide elements are stable in chloride melts.

The divalent state has not been certainly proven for any actinide in these solvents but some evidence has been obtained for the formation of Am(II) in a KCl–LiCl–$PuCl_3$ melt in contact with metallic Pu.[325]

The trivalent state has been investigated for uranium, neptunium, plutonium and americium. The M^{3+} ions form chloride complexes of the same type as those occurring in about 12 M hydrochloric acid[331,332]. This similarity is seen in Fig. 76. The actual composition of such chloride complexes cannot be obtained from measurements in pure chloride melts.

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[329] J. Korkisch and F. Tera, *J. Inorg. Nucl. Chem.* **15** (1960) 177.

[330] W. F. Linke and A. Seidell, *Solubilities of Inorganic and Metal Organic Compounds*, American Chemical Society, Washington D.C. (1965).

[331] D. M. S. Gruen, S. Fried, P. Graf and R. L. McBeth, *Proc. 2nd Geneva Conf.* Vol. 28, p. 112 (1958).

[332] D. M. Gruen, R. L. McBeth, J. Kooi and W. T. Carnall, *Ann. N.Y. Acad. Sci.* **79** (1960) 941.

[333] D. M. Gruen and R. L. McBeth, *J. Org. Nucl. Chem.* **9** (1959) 290.

[334] N. M. Isaac, P. R. Fields and D. M. Gruen, *J. Inorg. Nucl. Chem.* **21** (1961) 152.

[335] H. Wirries, Thesis, Braunschweig (1964).

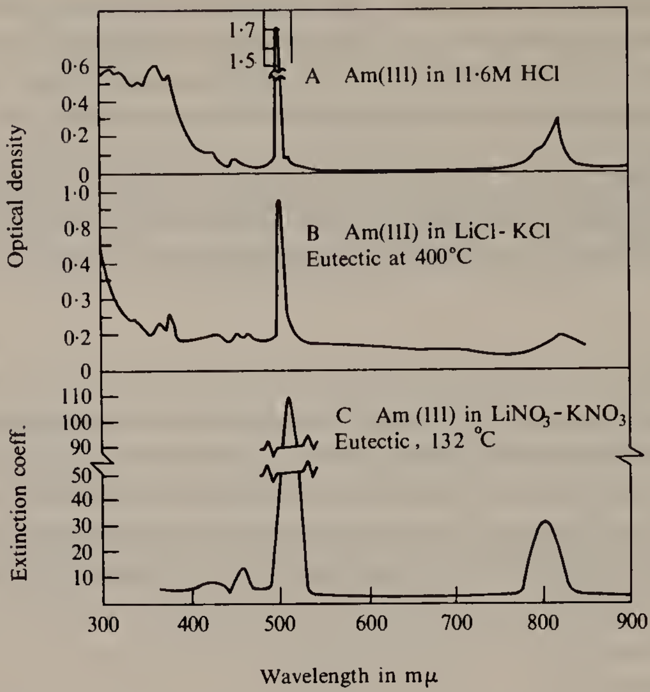

FIG. 76. Optical spectra of americium in three solvents. The similarity of 11·6 M HCl and (K,Li)Cl melt indicates that the same types of chloro-complexes are formed in these two solvents. The spectrum of Am(III) in (K,Li)NO$_3$ melt is believed to be similar to that in aqueous nitric acid solution.

The complexes must, however, be weaker than the MCl_6^{2-} complex ions formed by the tetravalent actinide ions as the measured M(IV)/M(III) redox potential differs by 0·36 V from the calculated thermodynamic value[332].

The tetravalent state is stabilized by strong chloride complexing. In general, anions of the type MCl_6^{2-} dominate. The six chloride ions are arranged in an octahedral configuration. Thus the spectra of these solutions are very similar to those of solid compounds of the types $[(CH_3)_4N]_2MCl_6$ and Cs_2MCl_6[331,336]. The stabilities of the MCl_6^{2-} ions in general may be expected to vary with the solvent in much the same way as for UCl_6^{2-}, namely CsCl–$CsAlCl_4 \approx KCl–KAlCl_4 > CsCl > KCl > NaCl > ZnCl_2$[336]. The interdiffusion coefficient for U(IV) in (Li,K)Cl eutectic at 400°C has been found to be $4{\cdot}9 \times 10^2$ m^2/sec. The diffusion has a heat of activation of 32 kJ/mole[337].

The pentavalent oxidation state exists as -yl ions of type MO_2^+ and no evidence of M^{5+} species has been obtained. Only uranium and neptunium have, however, been studied in the pentavalent state. Attempts to prepare PuO_2^+ have failed[331,332]. UO_2^+ is believed to be formed at 650°C by the reaction $Cl^- + UO_2^{2+} = \frac{1}{2}Cl_2 + UO_2^+$ [342,398]. The MO_2^+ ion probably forms a weak chloride complex.

Uranium(VI) exists as the -yl ion MO_2^{2+} in chloride melts and there is no evidence of other ion types[319]. Np(VI) and Pu(VI) have not yet been observed in these solvents. The uranyl ion is most probably present as chloride complexes, a conclusion which is supported by the formation of comparatively strong uranyl chloride complexes in chloride containing nitrate melts[334].

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[336] J. R. Morrey, *Inorg. Chem.* **2** (1963) 163.

[337] C. E. Thalmayer, S. Bruckenstein and D. M. Gruen, *J. Inorg. Nucl. Chem.* **26** (1964) 347.

TABLE 38. SOLUBILITY OF ACTINIDE COMPOUNDS IN NON-AQUEOUS SOLVENTS (Qualitative data are reported as very soluble, *vs*; soluble, *s*; slightly soluble, *ss*; insoluble, *i*; and decomposes, *d*. Measured solubilities are given in g/kg of solvent and the actual temperature is given as index on the *s*. The symbol > is used to indicate that solutions of this concentration have been reported, but the solubility may be much larger. The abbreviations used in the table are explained at the end of the table.)

Compound	Solubility
Thorium	
$Th(Ac)_4$	METAM[330] $s_{30} = 708\cdot1$; EN[330] $s_{30} = 43$; EG[330] $s_{30} = 4\cdot1$
$Th(ClO_4)_4$	AN[a] *s*
$Th(IO_3)_4$	NH_3(1)[330] $s_{25} = 0\cdot8$
$Th(NO_2)_4$	DMF, MeOH[b] s_{23}
$Th(NO_3)_4$	EtOH[c] *vs*; DEE[c] $s = 369$ g/l; DMSO[d] $s > 1\cdot4$ g/l; Acet[c], DMF[e] *s*
$Th(NO_3)_4$, 2·5DMF	DMF[e] $s > 1$ g/l
$Th(NO_3)_4$, 4DMSO	DMSO[e] $s > 2\cdot1$ g/l
$Th(NO_3)_4$, $4H_2O$	TBP[330] $s_{25} = 957$; MeOH[330] $s_{25} = 756$; Acet[330] $s_{25} = 682$; EGME[330] $s_{25} = 681$; MEK[330] $s_{25} = 641$; EtOH[330] $s_{25} = 639$; MeAc[330] $s_{25} = 575$; PrOH[330] $s_{25} = 541$; BuOH[330] $s_{25} = 513$; EG[330] $s_{25} = 511$; i-PrOH[330] $s_{25} = 506$; EtAc[330] $s_{25} = 499$; Dioxane[330] $s_{25} = 493$; DEE[330] $s_{25} = 492$; MIBK[330] $s_{25} = 485$; i-BuOH[330] $s_{25} = 459$; i-AmOH[330] $s_{25} = 435$; ACPH[330] $s_{25} = 426$; MeAmK[330] $s_{25} = 422$; CHexol[330] $s_{25} = 413$; Hexol[330] $s_{25} = 384$; MeHexK[330] $s_{25} = 357$; CHexon[330] $s_{25} = 328$; BzOH[330] $s_{25} = 240$; DIPK[330] $s_{25} = 239$; PrPH[330] $s_{25} = 217$; DBE[330] $s_{25} = 30\cdot9$; DIAmE[330] $s_{25} = 12\cdot9$; *m*-Cresol[330] $s_{25} = 1\cdot2$; *o*-Toluidine[330] $s_{25} = 1\cdot0$; DIMeAn[330] $s_{25} = 0\cdot8$; CCl_4, ETDC[330] $s_{25} = 0\cdot6$; CBz, PeE[330] $s_{25} = 0\cdot3$; EtBr, NB, TCM, Toluene[330] $s_{25} = 0\cdot2$; Aniline, $CHCl_3$, $MeCCl_3$, Piperidine[330] $s_{25} = 0\cdot1$
$Th(Ox)_2$, $2H_2O$	NH_3(1)[330] $s_{25} = 5\cdot1$
$Th(SCN)_4$	Acet, DMSO[f] *s*; MeOH[f,g] s_{25}
$Th(Trop)_4$	EtOH[i] *s*
$Th(TTA)_4$	Bz, EtOH[j] *s*
$ThBr_4$	Acet[340] $s > 400$ g/l
$ThBr_4$, 2HMPA	AN, DCM, NM[340] *ss*; Acet, Bz, DEE, EtAc, 2-Mebu[340] *i*
$ThBr_4$, 3HMPA	Acet, An, DCM, EtOH[340] *vs*; Bz, NM[340] *s*
$ThBr_4$, 4AN	Acet[340] $s > 100$ g/l
$ThBr_4$, 6DMSO	AN[340] *s*; Acet, DMSO, EtOH, NM[340] *ss*; Bz, CCl_4, DCM, DEE, EtAc, 2-MeBu[340] *i*
$ThCl_3(OH)$, 2TPPO, H_2O	AN, NM[k] *i*
$ThCl_4$	Acet[340] $s > 200$ g/l; EN[330] $s_{30} = 111$ g/l; (K, Li)Cl[332] $s_{500} > 100$; DMSO[e] $s > 0\cdot7$ g/l; AmOH, BuOH, i-BuOH, EtOH, MeOH, PrOH, i-PrOH[329c,e] $s > 0\cdot2$ g/l; DMF[e] *s*; DEE[c] *ss*; (K,Li)NO_3[331] i_{160}
$ThCl_4$, 1·5HMGA	Acet[m] *i*
$ThCl_4$, 1·5HMMA	Acet[m] *s*; 2-MeBu[m] *i*
$ThCl_4$, 1·5TMGA	Acet[m] *i*
$ThCl_4$, 2HMPA	AN, DCM, NM[340] *s*; Acet[340] *ss*; Bz, DEE, EtAC, EtOH, 2-MeBu[340] *i*
$ThCl_4$, 2TMMA	Acet[m] *i*
$ThCl_4$, 4AN	Acet[340] $s > 100$ g/l
$ThCl_4$, 5DMSO	AN[340] *s*; NM[340,n] *s*; Acet, DMSO, EtOH[340] *ss*; Bz, CCL_4, DCM, DEE, EtAc, 2-MeBu[340] *i*
$ThCl_5(OH)$, 2 TPP, H_2O	AN, NM[k] *s*
ThF_4	BeF_2–LiF–ThF_4[320,327] vs_{600}
Protactinium	
PaF_4	BeF_2–LiF–ThF_4[320,327] s_{600}
$(Et_4N)PaBr_6$	An[o,p], NM[o] *s*
$(H_4N)PaCl_6$	$SOCl_2+ICl$[o] *i*
$(Me_4N)_3PaCl_8$	AN, NM[o] *s*; CS_2[o] *i*
$(Me_4N)Pa(NO_3)_6$	AN[p] *s*
$(Me_4N)PaBr_6$	AN[o,p], NM[o] *s*
$(Me_4N)PaCl_6$	AN[o] *s*; $SOCl_2+ICl$[p] *i*
$(Ph_4As)PaCl_6$	CS_2[o] *i*

TABLE 38 (*cont.*)

Compound	Solubility
Cs_2PaF_7	Acet^{o} *i*
$CsPaCl_6$	$SOCl_2+ICl^{o}$ *i*
K_2PaF_7	Acet^{o} *i*
$KPaCl_6$	$SOCl_2+ICl^{o}$ *i*
Li_2PaF_7	Acet^{o} *ss*
Na_2PaF_8	Acet^{o} *i*
$Pa(OH)_5$	$SOCl_2{}^{p}$ *s*
$Pa_2O(NO_3)_8$, 2AN	AN^{p} *ss*
$PaBr_5$	AN^{321,o,p,q} *vs*; Acet, NM^{q} *s*; Bz, DCM, i-Pent^{322} *i*
$PaBr_5$, 3AN	AN^{322} *s*
$PaCl_5$	MeOH^{r} $s > 10$ mg/l; $CCl_4{}^{r}$ $s = 7$ mg/l; AN^{s,t}, NM^{s,u}, $SOCl_2{}^{o}$ *s*
$PaCl_5$, $(C_8H_{17})_3PO$	Organic solvents^{p} *s*
$PaCl_5$, $(PhCH_2)_3PO$	Organic solvents^{p} *s*
$PaCl_5$, BDPPO	DCM^{s} *vs*; Acet, AN^{s} *s*; i-Pent^{o,s} *i*
$PaCl_5$, TPPO	DCM^{s} *vs*; Acet, AN^{s}, Organic solvents^{p} *s*; i-Pent^{o,s} *i*
PaO_2Br	AN, Bz, DCM, i-Pent^{322} *i*
$PaOBr_3$	$AN+R_4NBr^{p}$ *s*; AN, Bz, DCM, i-Pent^{322} *i*
Rb_2PaF_7	Acet^{o} *i*
$SO(PaCl_6)_2$	$SOCl_2{}^{o,p,u}$ $s = 234$ g/l
Uranium	
UCl_3	$AlCl_3$–KCl^{v,w} s_{727}; DIP+DBP, DIP+TBP, DIP+TOA^{354} s_{180}; (K,Li)Cl^{333} s_{400}; HAc^{x} *ss*
UF_3	BeF_2–LiF–$ThF_4{}^{320,327}$ s_{600}
UI_3	HAc^{x} *s*
$(Et_4N)_2UBr_6$	AN^{343} $s > 21$ g/l; Acet^{343} *ss*
$(Et_4N)_2UCl_6$	AN^{343} $s > 22$ g/l
$(Bu_4N)_2UI_6$	$AN+Bu_3PrNI^{343}$ $s > 83$ g/l
$(UCl_4)_2$, $C_{26}H_{24}P_2$	Acet, DEE, Dioxane, THF^{y} *i*
Cs_2UCl_6	NM^{340} $s > 66$ g/l; AN^{340} *s*
$FeU(Ac)_6$	HAc, PeE^{z} *i*
$LiU(Trop)_5$	DMSO^{i} *s*
$MgU(Ac)_6$	HAc, PeE^{z} *i*
$U(Ac)_4$	$HAc+HClO_4{}^{x}$ *vs*; HAc^{x,z} *i*
$U(CKA)_4$	Bz, DMF, DMSO, NM^{y} *vs*; CCL_4, $CHCl_3{}^{y}$ *ss*; AN, DEE^{y} *i*
$U(Ensal)_2$	Bz, DMF, DMSO, EtOH, NB, NM, THF^{y} *s*
$U(KojA)_4$	DMF, DMSO^{y} *s*; EtOH^{y} *ss*; AN, $CHCl_3$, DEE, NM^{y} *i*
$U(SCN)_4$	MeOH^{aa} *s*
$U(Trop)_4$	DMSO, EtOH^{i} *s*
$U(TTA)_4$	Bz^{j} *s*; EtOH^{j} *ss*
UBr_4	Acet^{340} $s > 200$ g/l; AN, NM^{bb} *s*
UBr_4, 2HMPA	DCM, EtOH, NM^{340} *s*; Acet, AN^{340} *ss*; Bz, DEE, EtAc, 2-MeBu^{340} *i*
UBr_4, 4AN	Acet^{340} $s > 100$ g/l
UBr_4, 6DMSO	Acet, AN, DMSO, EtOH, NM^{340} *ss*; Bz, CCl_4, DCM, DEE, EtAc, 2-MeBu^{340} *i*
$UCl_3(CN)$, $4HN_3$	DMA, NM^{cc} *d*; Acet, AN, DCM, EtAc, NH_3, THF^{cc} *i*
UCl_4	Acet^{340} $s > 200$ g/l; NaCl^{dd} $s_{1000} > 69$ g/l; CsCl^{dd} $s > 67$ g/l; KCl^{dd} $s_{825} > 66$ g/l; $AlCl_3$–KCl^{dd} $s_{400} > 0{\cdot}1$ mol %; $ZnCl_2{}^{dd}$ $s > 26$ g/l; HAc^{x}, MeOH^{341} *vs*; AN^{bb,ee} *s*; DIP+TBP, DIP+TOA^{354} s_{180}; DMF, DMSO^{ff} *s*; (K,Li)Cl^{331,333,337} s_{400}; MeOH+TAP, MeOH+TBP^{341}, NM^{bb} *s*; PyCl^{333} s_{160}; TAP, TBP^{341}, THF^{y} *s*; $(K,Li)NO_3{}^{331,333}$ s_{160}, oxidizes
$UCl_4(DiPy)Cl$	NM^{326} *s*; Bz^{326} *i*
UCl_4, 1·5HMGA	Acet^{m} *i*
UCl_4, 1·5TMGA	Acet^{m} *i*
UCl_4, 1·5TMMA	Acet^{m} *i*
UCl_4, $2C_{26}H_{24}As_2O_2$	THF^{y} *i*
UCl_4, 2HMPA	DCM, NM^{340} *s*; Acet, AN, NM+EtAc^{340} *ss*; Bz, DEE, EtAc, EtOH, 2-MeBu^{340} *i*

Compound	Solubility
UCl_4, 2NB	DMF, DMSO, EtOH[y] *s*; AN[y] *ss*; Bz, $CHCl_3$, DEE, THF[y] *i*
UCl_4, 2TBP	TBP[ee] *s*
UCl_4, 3DMSO	Acet, DMSO, NM[340] *ss*; Bz, CCl_4, DCM, DEE, EtAc, EtOH, 2-MeBu[340] *i*
UCl_4, 4AN	Acet[340] $s > 100$ g/l
UCl_4, HMMA	Acet[m] *i*
UF_4	BeF_2–LiF–ThF_4[328] s_{600}; BrF_3[gg], Hydrazine[hh] *s*; (K, Li)Cl[331] s_{400}; (K,Li, Na)F, (Li,Na,Rb) F, (K,Li)F[328] $s_{500} < 150$
UI_4	HAc[x] *vs*
$(Me_4N)_3UCl_8$	CS_2[o] *i*
$(Me_4N)UCl_6$	$SOCl_2$[342] *s*
$(Ph_4As)UCl_6$	CS_2[o] *i*
$(Pr_4N)UCl_6$	$SOCl_2$[342] *s*
$(SO)_3(UCl_8)_2$	$SOCl_2$[oo] *s*
$CsUCl_6$	AN, NM, $POCl_3$[342] *s*
$RbUCl_6$	$SOCl_2$[342] *s*
$SO(UCl_6)_2$	$SOCl_2$[oo] *s*
$SOUCl_7$	$SOCl_2$[oo] *s*
$U(OAm)_5$	Bz[qq] s_{80}
$U(OBu)_4(OEt)$	Bz[pp] s_{80}
$U(OBu)_5$	Bz[qq] s_{80}
$U(OBu)_5$, BuOH	Bz[pp] s_{80}
$U(OEt)_2(OBu)_3$	Bz[pp] s_{80}
$U(OEt)_5$	Bz[qq], CCl_4[342] *s*
$U(OMe)_5$	Bz[qq] s_{80}; MeOH[qq] *ss*
$U(OPr)_5$	Bz[qq] s_{80}
$U(OSiEt_3)_5$	Bz, EtOH[kk] *s*; HMDS[kk] *ss*
$U(OSiMe_2Et)_5$	Bz, EtOH[kk] *s*
$U(OSiMe_3)_5$	Bz, EtOH[kk] *s*
$U(OSiMeEt_2)_5$	Bz, EtOH[kk] *s*
UCl_5	CCl_4, $SiCl_4$[324,342], $SOCl_2$[oo] *s*
UCl_5, 2Ensal	$CHCl_3$[326] *s*; AN, NM[326] *ss*; Bz[326] *i*; DCM[326] *d*
UCl_5, 2MCPy	AN, Bz, NM[326] *i*
UCl_5, 2OPhen	AN, Bz, NM[326] *i*
UCl_5, 2Paz	AN, NM[326] *s*; Bz, $CHCl_3$, DCM[326] *i*
UCl_5, 2Py	Bz[326] *i*; AN, NM[326] *d*
UCl_5, 2Pyaz	AN, NM[326] *s*; Bz[326] *i*
UCl_5, 4HOxine	Bz[326] *i*; NM[326] *d*
UCl_5, EBDPP	NM[326] *ss*; Bz[326] *i*
UCl_5, PhSeSePh	AN, $CHCl_3$[326] *s*; Bz, DCM[326] *i*; NM[326] *d*
UCl_5, PhTeTePh	AN, $CHCl_3$, DCM, NM[326] *s*; Bz[326] *i*
UCl_5, $SOCl_2$	CCl_4[342], $SOCl_2$[342,o] *s*; EtOH[349] *d*
UCl_5, TCAC	Bz[324,326] $s > 35$ g/l; Toluene[326] $s > 23$ g/l; CCl_4[324], CS_2[342] *s*;
UCl_5, TPP	NM[326] *ss*; Bz[326] *i*
$UO_2(NO_3)$	DMSO[323,324] *s*, oxidizes
UO_2Cl	(K,Li)Cl[342,rr] s_{650}
$UOCl_3$, EtOH	EtOH[349] *s*; Bz[349] *i*
$(Bu_3NH)UO_2(NO_3)_3$	MIBK[ii] *s*
$(Bu_4N)UO_2(NO_3)_3$	Acet, MIBK[ii] *s*
$(Et_4N)UO_2(Ac)_3$	Et_4NAc[jj] $s > 14$ g/l; Acan, Acet, NM, Sucn[jj] *s*; EtOH[jj] *ss*
$(Et_4N)UO_2(NO_3)_3$	CHexon[ii] *s*
$(PyH)UO_2(NO_3)_3$	MIBK[ii] *s*
$CsUO_2(Ac)_3$	AN+Sucn[jj] *s*
$U(OSiEt_3)_6$	Bz, EtOH[kk] s_{80}
$U(OSiMe_2Et)_6$	Bz, EtOH[kk] s_{80}
$U(OSiMe_3)_6$	Bz, EtOH[kk] s_{80}
$U(OSiMeEt_2)_6$	Bz, EtOH[kk] s_{80}
$U_3O_5F_8$	DMSO, MeOH[ii] *d*
$UCl_4(OH)_2$, 2TPP	EtOH, NB[mm] *s*; AN[mm] *ss*
UF_6	HF[nn] $s < 10$ mol %

TABLE 38 (*cont.*)

Compound	Solubility
$UO_2(Ac)_2$	Acet^{330,jj} $s_{15} = 23\cdot7$ MeOH^{330} $s_{15} = 7\cdot4$, $s_{66} = 8\cdot3$; HAc^{x} $s = 0\cdot76$ g/l; HAc+HClO$_4^{x}$ *vs*
$UO_2(Ac)_2$, $2H_2O$	HAc^{z} *i*
$UO_2(C_{11}H_{15}O_3)_2$	Bz^{330} $s_7 = 791$ g/l; CHCl$_3^{330}$ $s_7 = 610$ g/l; EtAc^{330} $s_7 = 526$ g/l; DEE^{330} $s_7 = 224$ g/l; Acet^{330} $s_7 = 135$ g/l
$UO_2(ClO_4)_2$	Bz^{ss} *ss*
$UO_2(ClO_4)_2$, $2\cdot5$DMF	DMF^{ff} $s > 0\cdot65$ g/l
$UO_2(ClO_4)_2$, $4\cdot6$DMSO	DMSO^{ff} $s > 2\cdot7$ g/l
$UO_2(NO_3)_2$	(K,Li)NO$_3^{331,333,334}$ $s_{160} > 3\cdot94$ g/l; Acet^{ll,tt,uu} BuOH^{vv}, EtOH^{ww,xx} HAc^{yy,zz}, Heptan-2-one, MEK^{tt}, MeOH^{ww,xx}, MIBK^{tt}, PrOH^{ww} *s*; PP+TBP^{334} s_{150}
$UO_2(NO_3)_2$, $2\cdot5$DMF	DMF^{ff} $s > 0\cdot58$ g/l
$UO_2(NO_3)_2$, 2DEE	DEE^{330} $s_{15} = 137$
$UO_2(NO_3)_2$, +DEE, $2H_2O$	DEE^{330} $s_{15} = 3390$
$UO_2(NO_3)_2$, $2H_2O$	DEE^{330} $s_{20} = 1270$
$UO_2(NO_3)_2$, $2Ph_3AsO$	EGME^{346} *ss*; Bz, EtOH, MeOH, NPO^{346} *i*
$UO_2(NO_3)_2$, 2TBP	CHCl$_3^{A}$ *ss*
$UO_2(NO_3)_2$, 2TPPO	NB^{346} $s > 1\cdot0$ g/l
$UO_2(NO_3)_2$, 2Urea	EtOH^{A} *ss*
$UO_2(NO_3)_2$, 5DMSO	DMSO^{323,324,ff} $s > 2\cdot5$ g/l
$UO_2(NO_3)_2$, $6H_2O$	MeOH^{330,341} $s_{20} = 2080$; Acet^{330,341,ll} $s_{12} = 15$, $s_{20} = 1610$; EtOH^{330,341} $s_{20} = 1595$; i-PrOH^{330} $s_{20} = 1220$; MEK^{330,341} $s_{20} = 1210$; PrOH^{330} $s_{20} = 1120$; CHexon^{330,ii} $s_{20} = 1050$ g/l; DECell^{330} $s_{20} = 1020$ g/l; DEE^{330} $s_{20} = 967$; MPK^{330} $s_{20} = 939$; DMCell^{330} $s_{20} = 920$ g/l; sec-BuOH^{330} $s_{20} = 892$; THF^{330} $s_{20} = 866$; EtAC^{330} $s_{20} = 863$; BuOH^{330,346} $s_{20} = 844$; BuAc^{330} $s_{20} = 800$; i-BuOH^{330} $s_{20} = 789$; TBP^{330,341} $s_{20} = 770$; DEK^{330} $s_{20} = 760$ g/l; MIBK^{330,341,ll} $s_{20} = 752$; MBK^{330} $s_{20} = 740$; EHCell^{330} $s_{20} = 680$ g/l; CHexol^{330,346} $s_{20} = 675$; i-AmOH^{330} $s_{20} = 652$; i-PrAc^{330} $s_{20} = 640$ g/l; AmOH^{330} $s_{20} = 631$; MeHexK^{330} $s_{20} = 629$; MeAmK^{330} $s_{20} = 618$; sec-BuAc^{330} $s_{20} = 610$ g/l; i-AmAc^{330} $s_{20} = 550$ g/l; AmAc^{330} $s_{20} = 528$; Hexol^{330} $s_{20} = 517$; MIBC^{330} $s_{20} = 515$; i-BuAc^{330} $s_{20} = 500$ g/l; DBCell^{330} $s_{20} = 490$ g/l; Heptanol^{330} $s_{20} = 450$; Dioxane^{330,341} $s_{20} = 410$; DIPK^{330} $s_{20} = 410$ g/l; Octanol^{330} $s_{20} = 389$; 2-Octanol^{330} $s_{20} = 372$; DIPrE^{330} $s_{20} = 177$; NM^{330} $s_{20} = 163$; DBE^{330} $s_{20} = 160$ g/l; DAmE^{330} $s_{20} = 110$ g/l; DHE^{330} $s_{20} = 90$ g/l; NE^{330} $s_{20} = 53\cdot7$; NB^{330} $s_{20} = 15$ g/l; NP^{330} $s_{20} = 11\cdot1$; Acet+SnCl$_2^{341}$ $s_{20} > 5\cdot0$ g/l; Acac, AN, Formamide^{341} *s*
$UO_2(NO_3)_2$, DAP	EtOH^{341} $s > 19$ g/l
$UO_2(NO_3)_2$, DBP	EtOH^{341} *s*
$UO_2(NO_3)_2$, DEE, $2H_2O$	DEE^{330} $s_{15} = 1900$
$UO_2(NO_3)_2$, MAP	EtOH^{341} $s > 15$ g/l
$UO_2(NO_3)_2$, MBP	EtOH^{341} *s*
$UO_2(NO_3)_2$, OPhen	EtOH^{A} *i*
$UO_2(NO_3)_2$, TAP	EtOH^{341} *s*
$UO_2(NO_3)_2$, TBP	EtOH^{341} *s*
$UO_2(SCN)_2$	EtOH^{346}, MeOH^{B} *s*
$UO_2(SCN)_2$, $2Ph_3AsO$	EGME^{346} *ss*; Bz, EtOH, MeOH, NPO^{346} *i*
$UO_2(SCN)_2$, 2TPPO	NB^{346} $s > 1\cdot0$ g/l; EGME^{346} *ss*; Bz, EtOH, MeOH, NPO^{346} *i*
$UO_2(Trop)_2$	DMF, DMSO^{C} *s*; Bz, Organic solvents^{C} *ss*; MeOH^{C} *i*
$UO_2(Trop)_2$, HTrop	DMF, DMSO^{C} *s*; Bz, Organic solvents^{C} *ss*; MeOH^{C} *i*
$UO_2(TTA)_2$	Bz, CCl$_4^{C}$, EtOH^{j,D}, MeOH^{D} *s*
$UO_2(TTA)_2$, 3MeOH	MeOH^{D} *ss*
$UO_2(TTA)_2$, EtOH	EtOH^{D} *ss*
UO_2Br_2	Bz^{E} *s*
UO_2Br_2, $4\cdot5$DMSO	DMSO^{F} $s > 1\cdot7$ g/l; AN^{F} $s > 1\cdot3$ g/l; EtOH^{F} $s > 1\cdot2$ g/l; DMF^{F} $s > 0\cdot9$ g/l; Acac, Acet^{F} *s*
UO_2Br_4, 2TPP	AN, NM^{k} *s*

Compound	Solubility
UO_2Cl_2	CHexol[mm] $s > 34$ g/l; Acet[G] s; DIP+TBP[354] s_{180}; (K,Li)Cl[331,333,rr] s_{400}; PyCl[333] s_{160}
UO_2Cl_2, 1·5TMGA	Acet[m] i
UO_2Cl_2, 1·5TMMA	Acet[m] i
UO_2Cl_2, $2Ph_3AsO$	EGME[346] ss; Bz, EtOH, MeOH, NPO[346] i
UO_2Cl_2, 2TPPO	NB[346] $s > 1{\cdot}0$ g/l; EtOH[346] ss; Bz[346] i
UO_2Cl_2, 3DMSO	DMF[F] $s > 8{\cdot}7$ g/l; MeOH[F] $s > 1{\cdot}1$ g/l; AN, DMSO[F] $s > 1{\cdot}0$ g/l; EtOH[F] $s > 0{\cdot}8$ g/l; Acac, Acet[F] s
UO_2Cl_2, $3H_2O$	BuOH, CHexol, EtAc[346] s
UO_2Cl_2, HMGA	Acet[m] ss
UO_2Cl_2, HMMA	Acet[m] ss
UO_2Cl_4, 2TPP, $C_6H_{12}O$	AN, NM[k] s
UO_2F_2	DMSO, MeOH[ll] s, (K,Na)Cl[H] s_{700}
Neptunium	
$NpCl_3$	(K,Li)Cl[331] s_{600}
NpF_3	BeF_2–LiF–ThF_4[327] s_{600}
$(Et_4N)_2NpBr_6$	AN[343] $s > 0{\cdot}05$ g/l
$(Et_4N)_2NpCl_6$	AN[343] $s > 0{\cdot}05$ g/l
$Np(OEt)_4$	CCl_4[I] vs; EtOH[I] ss; DEE, THF[I] i
$Np(OEt)_4$, 4EtOH	CCl_4[I] $s > 36$ g/l
$Np(OMe)_4$	Bz, CCl_4, MeOH, THF[I] i
$NpCl_4$	(K,Li)Cl[331] s_{600}; MeOH[I] s; PyCl[331] s_{160}; (K, Li)NO_3[331] s, oxidizes
$NpBr(OEt)_4$	THF[I] s; EtOH[I] ss; CCl_4, DEE, Dioxane[I] i
NpO_2Cl	DIP+TBP[354] s_{180}; (K,Li)Cl[331] s_{400}
NpO_2NO_3	PP+TBP[334] s_{150}
$NpO_2(NO_3)_2$	(K,Li)NO_3[331,334] $s_{150} > 0{\cdot}8$ g/l; Acet[J] s; PP+TBP[334] s_{150}
NpO_2Cl_2	DIP+TBP[354] s_{180}
Plutonium	
PuF_3	BeF_2–LiF–ThF_4[327] $s_T = 3–2{\cdot}4/T(\mathrm{K})$ mol %
$Pu(ClO_4)_3$	AN[350] $s > 1{\cdot}1$ g/l
$PuCl_3$	HAc[x] vs; AN, AN+Sucn[347] s; DIP+TOA[354] s_{180}; (K, Li)Cl[332] s_{400}; (K,Li)NO_3[331] d
PuF_3	BeF_2–LiF–ThF_4[327] s_{600}; (K,Li)Cl[332] s_{400}
$(Et_4N)_2PuBr_6$	An[343] $s > 13$ g/l
$(Et_4N)_2PuCl_6$	AN[343] $s > 19$ g/l
Cs_2PuCl_6	CsCl[331] s; (K, Li)Cl[332] s_{400}
$Pu(Ac)_4$	HAc+$HClO_4$[x] s; HAc[x] i
$Pu(NO_3)_4$	DBCell[L] s
$Pu(TTA)_4$	Bz[j] s; EtOH[j] ss
$PuCl_4$	DIP+DBP[354] s_{180}
$PuCl_4$, 2TBP	TBP[ee] s
PuF_4	(K,Li)Cl[332] s_{400}
$CsPuO_2$	AN+Sucn[jj] $s > 0{\cdot}02$ g/l
$PuO_2(ClO_4)_2$, $6H_2O$	DMF, DMSO, EtOH[M] s
$PuO_2(NO_3)_2$	Acet[N], BuCHOH[O] s; (K,Li)NO_3[331] s_{160}
$PuO_2(NO_3)_2$, $6H_2O$	DMF, DMSO, EtOH[M] s
PuO_2Cl_2	HAc, HAc+$HClO_4$[x] s
Americium	
$Am(ClO_4)_2$	AN[350] $s > 0{\cdot}5$ g/l
$Am(NO_3)_3$	(K,Li)NO_3[B], PP+TBP[334P], PP+TPPO[P] s_{150}
$AmCl_3$	AN+Et_4NCl[Q] s; DIP+TBP, DIP+TOA[354] s_{180}; (K,Li)NO_3[331] s_{160}
AmF_3	BeF_2–LiF–ThF_4[327] s_{600}
Curium	
$Cm(NO_3)_3$	DIP+TBP[354] s_{180}; (K, Li)NO_3[334,P], PP+TBP[334,P], PP+TPPO[P] s_{150}
CmF_3	BeF_2–LiF–ThF_4[327] s_{600}

TABLE 38 *(cont.)*

Compound	Solubility
Berkelium	
$BkCl_3$	AN+Et_4NCl^Q $s > 20$ mg/l
$Bk(NO_3)_4$	(K,Li)NO_3^P s_{150}; PP+TBP, PP+$TPPO^P$ i_{150}?
$BkCl_4$	AN+Et_4NCl^Q $s > 20$ mg/l
Californium	
$Cf(NO_3)_3$	(K,Li)NO_3, PP+TBP, PP+$TPPO^P$ s_{150}
CfF_3	BeF_2–LiF–ThF_4^{327} s_{600}

The following abbreviations are used in Table 38. Ac, acetate; Acan, acetic acid anhydride; Acet, acetone; ACPH, acetophenone; AmAc, amyl acetate; AmOH, amyl alcohol; AN, acetonitrile; BN, benzonitrile; BuAc, butyl acetate; BuOH, butanol; Bz, benzene; BzOH, benzyl alcohol; $C_{11}H_{15}O_3$, campho carbonate; CBz, chlorobenzene; CHexol, cyclohexanol; CHexon, cyclohexanone; CKA, chlorokojic acid; DAmE, diamyl ether; DAP, diamyl phosphoric acid; DBCell, dibutyl cellosolve; DBE, dibutyl ether; DBP, dibutyl phosphoric acid; DMC, dichloro methane; DEC, dichloroethylene carbonate; DECell, diethyl cellosolve; DEE, diethyl ether; DEF, diethyl formamide; DEK, diethyl ketone; DHE, dihexyl ether; DIAmE, di-isoamyl ether; DIMeAn, dimethyl aniline; DIP, diphenyl; DIPrE, di-isopropyl ether; DIPK, di-isopropyl ketone; DIPy, dipyridyl; DMA, dimethyl acetamide; DMCell, dimethyl cellosolve; DMF, dimethyl formamide; DMSO, dimethyl sulphoxide; EBDPP, ethylenebis(diphenylphosphine); EG, ethyleneglycole; EGME, ethyleneglycole monomethyl ether; EHCell, ethyl hexyl cellosolve; EN, ethylenediamine; Ensal, ethylenediamine salicylic acid; ES, ethylene sulphite; EtAc, ethyl acetate; EtBr, ethyl bromide; ETDC, ethylene dichloride; EtOH, ethanol; HAc, acetic acid; Hexol, hexanol; HMDS, hexamethyl disiloxane; HMPA, hexamethylphosphoric amide; KojA, kojic acid; MAP, monoamyl phosphoric acid; MBK, methyl butyl ketone; MBP, monobutyl phosphoric acid; MCPy, 2-mercaptopyridine; MeAc, methyl acetate; MeAmK, methyl amyl ketone; 2-MeBu, 2-methyl butane; $MeCCl_3$, methyl chloroform; MeHexK, methyl hexyl ketone; MEK, methyl ethyl ketone; MeOH, methanol; METAM, monoethanol amine; MIBC, methyl isobutyl carbinol; MIBK, methyl isobutyl ketone; MPK, methyl propyl ketone; NB, nitrobenzene; NE, nitroethane; NM, nitromethane; NP, 1-nitropropane; NPO, non-polar organic solvents; OPhen, *o*-phenanthroline; Ox, oxalate; Oxine, 8-hydroxyquinoline; Paz, phtal azine; PDC, propanediol-1,2-carbonate; PeE, petroleum ether; i-Pent, isopentane; PhSeSePh, diphenyl diselenide; PhTeTePh, diphenyl ditelluride; PP, polyphenyle; PrAc, propyl acetate; PrOH, propanol; PRPH, propiophenone; Py, pyridine; Pyaz, pyrazine; Sucn, succinonitrile; TAP, triamyl phosphate; TBP tributyl phosphate; TCAC, trichloro acrylyl chloride; TCM, trichlorometylene; THF, tetrahydrofuran; TMP, trimethyl phosphate; TOA, trioctyl amine; TPP, triphenyl phosphine; Trop, tropolone.

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No evidence has been obtained for the formation of higher oxidation states in chloride melts.

Fluoride melts, typically BeF_2–LiF–ThF_4 mixtures, have mainly been investigated as potential solvents for nuclear reactor fuel. There is much evidence for the formation of strong fluoride complexes although their formation and stability has not been studied to the same extent as the chloride complexes[335,338].

No evidence has been reported for the formation of divalent actinide species in fluoride

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melts. The trivalent oxidation state is known to exist in these solvents for U, Np, Pu, Am, Cm and Cf[327]. The tetravalent state exists for Th, Pa, U and probably also for Np and Pu. Very little is known regarding the penta- and hexavalent oxidation states, but by analogy with the chloride melts oxygenated forms are expected.

5.2.2. *Species in Polar Molecular Liquids*

For the purpose of this discussion the polar molecular liquids may be considered as intermediate between the ionic melts and non-polar molecular liquids. They are comparatively good ionizing solvents for inorganic compounds and also comparatively good solvents for metal–organic compounds such as alcoholates (see Table 38).

Many of the solid compounds obtained from these solvents contain coordinated solvent molecules indicating that they also are solvated in solution. The coordinated solvent molecules may be replaced by other solvent molecules when these form stronger bonds. The tendency for solvents to form such bonds makes it possible to classify them into two groups: acceptor solvents, which solvate electron pair donors, mainly anions, and donor solvents, which solvate electron pair acceptors, mainly metal ions[318]. Most actinide compounds are soluble in donor solvents. At the present no quantitative prediction can be made from the donor–acceptor theory, although the *donor number* (*DN*) concept gives some usable semi-quantitative results.[339] For example, $ThBr_4$,4AN can be obtained from a $ThBr_4$ solution in acetonitrile ($DN_{SbCl_5} = 14$). When dimethylsulphoxide ($DN_{SbCl_5} = 30$) is added to a solution of $ThBr_4$,4AN in acetone ($DN_{SbCl_5} = 17$) a precipitate of $ThBr_4$,6DMSO is obtained in accordance with the expectation that DMSO, having the higher donor number, should replace solvent around Th. This product is soluble in acetonitrile and can be recrystallized unchanged from this solvent, observations which are also expected from the considerable difference in donor numbers[340].

The donor number concept is also useful as a framework for discussion of autocomplex formation (see below) and monomer–polymer equilibria in organic solvents. The ionization of a solute is dependent on the dielectric constant of the solvent (cf. section 4.5.1). The dissociation of a solute, on the other hand, is dependent on the donor strength of the solvent, because the dissociation involves an exchange of ligand for solvent molecules. When the dielectric constant and donor strength are both small, the solute will easily polymerize and this can be regarded as a coordination of the solute molecules to each other. This situation will often occur in non-polar solvents (see 5.2.3 below). When the dielectric constant increases, this primarily leads to increased ionization which releases ligands into the solution. These may then form anionic complexes if they have stronger donor properties than the solvent, i.e. autocomplex formation. An example of this is the formation of $UO_2(NO_3)_3^-$ ions when $UO_2(NO_3)_2$ is dissolved in acetone[341]. On the other hand, a solvent with high donor properties will displace the anions (e.g. in $UO_2(NO_3)_2$) thus causing a formation of ions or ion aggregates (e.g. $UO_2S_x^{2+}$) depending again on the dielectric constant of the solvent. Thus a solution of $UO_2(NO_3)_2$ in acetylacetone shows no sign in its spectrum of uranyl ions coordinated by nitrate. At the same time the conductivity of the solution is remarkably high in comparison with a corresponding acetone solution.[341].

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[341] B. Jezowska-Trzebiatowska, A. Bartecki, M. Chmielowska, H. Przywarska, T. Mikulski, K. Bukietynska and W. Kakotowicz, *Proc. 2nd Geneva Conf.*, Vol. 28, p. 253 (1958).

5.2.3. *Species in Non-polar Molecular Liquids*

The solubility of inorganic actinide compounds is small in these solvents, mainly as a consequence of the low dielectric constant. This leads to a large degree of "self-coordination" which implies dimers or larger polymeric aggregates and hence to small solubility. UCl_5 is thus slightly soluble in carbon tetrachloride as the dimer $(UCl_5)_2$[324,342].

Metal–organic actinide compounds and organic chelates are usually fairly soluble in all organic solvents. Even for such compounds, however, the solubility usually decreases with increasing hydrocarbon nature of the solvent. Thus $Th(TTA)_4$, $U(TTA)_4$, $Pu(TTA)_4$ and $UO_2(TTA)_2$ are soluble in benzene, less soluble in ethanol and sparingly soluble in n-hexane. This property has often been used for preparative purposes. A solution of the compound in benzene is mixed with an aliphatic hydrocarbon yielding a precipitate of the desired compound (see also section 4).

5.3. Equilibria in solution

Despite the different structures of ionic melts and molecular liquids and the differences existing both in dielectric constant and temperature the species encountered are astonishingly similar. Thus complex formation leading to such ions as UCl_6^{2-}, $NpCl_6^{2-}$ or $PuCl_6^{2-}$ occur in a KCl–LiCi melt at 400°C as well as in acetonitrile containing dissolved tetramethylammonium chloride at 20°C[331,332,333,336,343]. However, despite such similarities these two classes of solvents will be treated separately, mainly because the knowledge of actinide chemistry covers different areas for these solvent classes.

5.3.1. *Equilibria in Ionic Melts*

Many investigations of actinides in molten salts have been of a purely qualitative nature. The formation of UO_2^{2+} and NpO_2^+ chloro-complexes in $(K,Li)NO_3$ eut at 160°C and the formation of UO_2^{2+} fluoride complexes in (K,Na)Cl at 700°C are the only cases for which stability constants have been published. These are given in Table 39 together with values for Am^{3+} and Cm^{3+} chloro-complexes which have been estimated from the data given in ref. 334. The chloro-complexes are obviously formed to about the same extent as in aqueous

TABLE 39. THE STABILITY OF ACTINIDE HALOGENIDE COMPLEXES IN IONIC MELTS

Actinide ion	Halogenide	Melt	Temp. °C	$K_1(M^{-1})$	$K_2(M^{-2})$	log β_4†	Ref.
UO_2^{2+}	Cl^-	$(K,Li)NO_3$	160	4·37	0·72	—	a
UO_2^{2+}	F^-	(K,Na)Cl	690–830	—	—	$-3·93–4380T^{-1}$	b
NpO_2^+	Cl^-	$(K,Li)NO_3$	160	0·83	—	—	a
Am^{3+}	Cl^-	$(K,Li)NO_3$	160	~1·5	~0·3	—	*
Cm^{3+}	Cl^-	$(K,Li)NO_3$	160	~1·6	—	—	*

* Estimated from data in ref. 334.
† Mole fractions.
[a] H. Wirries, Thesis, Braunschweig (1964).
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solutions. However, as the temperature in the melt is some 140°C higher this indicates that the heat of formation is higher in the melt than in water. One reason for this may be that the nitrate groups in the melt are more weakly coordinated to the actinide ions than water molecules, a possibility which is also quite reasonable on steric grounds.

5.3.2. *Equilibria in Molecular Liquids*

Water and organic solvents are both molecular liquids that have been extensively used and therefore are discussed in detail in sections 1–4 above. A more general approach is given here.

The common molecular liquids have often dielectric constants smaller than that of water. This generally decreases the solubility of ionic and polar compounds. Thus the general solubility equilibrium

$$ML_n\cdot S_p(s) + qS(l) \rightleftharpoons ML_n(S)_{N-n}(l) + (p+q-N+n)S(l) \tag{1}$$

governs the amount in solution[344]. Reaction (1) illustrates how a solid solvate $ML_n\cdot S_p$ is brought into solution in a solvent S. N is the coordination number of M.

In the solution the solute may be involved in a number of reversible equilibria. These may be grouped into two separate classes: reactions leaving the inner sphere coordination configuration around M unchanged and reactions changing the coordination around M.

The first class may also be designated as substitution equilibria. These are of different types. Firstly two solvent molecules S and S′ may compete for the available coordination sites (reaction 2) (see also section 4)

$$ML_nS_{N-n} + pS' \rightleftharpoons ML_nS_{N-n-p}S_p' + pS \tag{2}$$

e.g. acetonitrile in UCl_4,4AN will be displaced by DMSO in acetone solution[345]. When the solvent S has sufficiently good donor properties it may even displace some of the anions from the inner sphere.

$$ML_nS_{N-n} + S \rightleftharpoons [ML_{n-1}S_{N-n+1}]^+\cdot L^- \tag{3}$$

This occurs, for example, when $UO_2(NO_3)_2$ is dissolved in an alcohol[341].

A second anion, A^-, may be present in the solution as a salt M′A and give rise to an exchange of L^-.

$$ML_nS_{N-n} + pM'A \rightleftharpoons ML_{n-p}AS_{N-n} + pM'L \tag{4}$$

Thus perchlorate may be exchanged for nitrate, etc. An example is the preparation of $UO_2(SCN)_2$ by addition of KSCN to a solution of $UO_2(NO_3)_2$ in ethanol. The KNO_3 formed precipitates and can be removed by filtration. $UO_2(SCN)_2$,2-ethanol can then be obtained by evaporation of the solution[346].

When the added anion is identical to L^- this may lead to displacement of solvent and the formation of an ion pair in the solution.

$$ML_nS_{N-n} + pM'L \rightleftharpoons M'^+[ML_{n+p}S_{N-n-p}]^- + pS \tag{5}$$

In reactions (1) to (5) the coordination number N has been assumed to be constant; for example the addition of tetraethylammonium chloride to a solution of $PuCl_3$ in succinonitrile–acetonitrile mixture (85%–15%) results in the formation of $PuCl_6^{3-}$ ions[347].

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In the second class a change of N to N' is induced by the reactions. Solvents with a dielectric constant $\lesssim 30$ may induce loss of solvent,

$$\mathrm{ML}_n\mathrm{S}_{N-n} \rightleftharpoons \mathrm{ML}_n\mathrm{S}_{N'-n} + (N - N')\mathrm{S} \tag{6}$$

When the dielectric constant is higher reaction (6) may be accompanied by a formation of ion pairs which results in the following reaction

$$2\mathrm{ML}_n\mathrm{S}_{N-n} \rightleftharpoons [\mathrm{ML}_{n-1}\mathrm{S}_{N-n+1}]^+[\mathrm{ML}_{n+1}\mathrm{S}_{N'-n-1}]^- + (N - N')\mathrm{S} \tag{7}$$

Typical examples are uranyl salts dissolved in methanol[341].

Finally, a powerful donor solvent may induce a change in the coordination number, for example the formation of "adducts" with TBP and its homologs.

$$\mathrm{ML}_n\mathrm{S}_{N-n} + (N'-n)\mathrm{S}' \rightleftharpoons \mathrm{ML}_n\mathrm{S}'_{N'-n} + (N'-n)\mathrm{S} \tag{8}$$

A very typical example of this reaction is also the change in coordination occurring when $ThBr_4$,4AN (AN = acetonitrile) is dissolved in acetone, HMPA (hexamylphosphoricamide) added and the sparingly soluble $ThBr_4$,3HMPA produced[340].

5.4. Redox reactions

The region of stability towards oxidation and reduction for many non-aqueous solvents exceeds that of water. They have thus been used for the preparation and study of actinide oxidation states and ionic forms which are unstable in water. The region of stability for a (K,Li)Cl eutectic melt is about 3·5 V and for a CsCl–$MgCl_2$ eutecticum 2·6 V at 700°C[331]. The corresponding range for water is about 1·2 V for evolution of oxygen and hydrogen, if all overvoltages are excluded.

U(III) species are stable in chloride melts up to several hundred degrees. The same is true for both Np(III) and Pu(III). The trivalent ions of these elements can be obtained by reduction with many metals, e.g. Li, Al, Pu[325,331,332]. Evidence has even been obtained for the reduction of Am to the divalent state by Pu metal in contact with molten $PuCl_3$–NaCl–KCl mixture[325]. A U(V) species, probably UO_2^+, has been observed in (K,Li)Cl melts at 650°C[348].

Electrolytic reduction in molten salts can be used to prepare metallic actinides from their salts.

Pentavalent uranium is very unstable in aqueous solution. In non-aqueous solvents three different forms of U(V) are known. Compounds of the type UX_5, where X is a halogen or alcohol group, are undissociated and covalent in character. A few cases are known where the entity MO^{3+} exists, e.g. in $UOCl_3$ and $PaOBr_3$[322,349]. These compounds are usually slightly soluble in organic solvents. The fully oxygenated cation of U(V), UO_2^+, is also known to form on the electrolytic reduction of UO_2^{2+} in dimethyl sulphoxide solution (this is the most suitable solvent for the preparation of UO_2^+). Even in this solvent UO_2^+ slowly oxidizes to UO_2^{2+} with a half-time of about 1 hr.

The polarographic reduction of Am(III) to Am(II) in acetonitrile has been reported[350]. Redox reactions have also been used to transfer actinides to and from a melt and into a molten metal phase. The similarity to usual two-phase extraction processes is great and this will therefore be treated in section 5.6.

Some measured and calculated potentials are listed in Table 40.

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[348] D. A. Wenz, M. D. Adams and R. K. Steunenberg, *Inorg. Chem.* **3** (1964) 989.

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TABLE 40. REDOX POTENTIALS FOR ACTINIDE IONS IN NON-AQUEOUS SOLUTIONS

Element	Oxidation states	Solvent	Temperature (°C)	$E°$(V)	Ref.
Uranium	IV–III	(K,Li)Cl	450	−0·56*	a
	III–0	(K,Li)Cl	450	−1·61*	a
Neptunium	III–0	(K,Li)Cl	450	−1·7‡	a
Plutonium	III–0	KCl	450	−1·72†	a
Americium	III–II	Acetonitrile	25	−1·4*	b
	III–0	(K,Li)Cl	450	−1·9†	a

* Measured value.

† Extrapolated from a measurement.

‡ Predicted value.

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[b] B. F. Myasoedov and K. Myuzikas, *Radiokhimiya*, **12** (1970) 856.

5.5. Ion-exchange

Conventional ion-exchange in solvents of low water content and adsorption of ions on active surfaces from water-free systems will be treated together. The differences between these materials, such as specificity for a special ion class (anion-exchangers or cation-exchangers), tend to disappear when the water content diminishes. Thus Th^{4+} is not normally taken up by an anion-exchanger in the nitrate form, but it is strongly adsorbed from an alcohol solution[329,351]. The reason for this behavior is twofold. Firstly the formation of ion pairs in the bulk of the solution increases and these may enter the ion-exchanger phase where the negative part is attached to the functional groups of the resin. Secondly the resin phase will retain a certain amount of water and thus offer better solvating properties

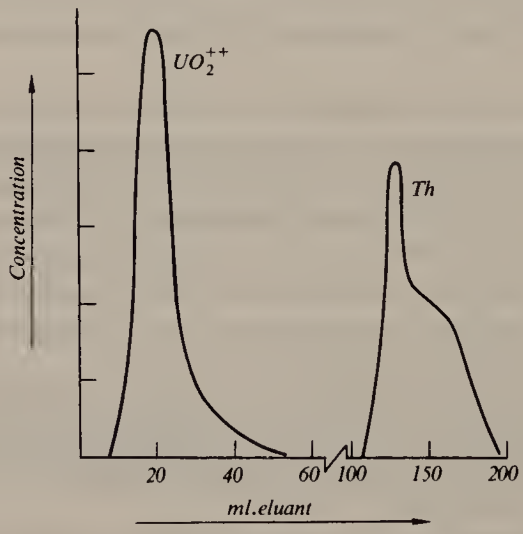

FIG. 77. UO_2^{2+}–Th^{4+} separation on KU-2 resin bed using a solvent mixture consisting of >90% acetone, 5% HCl and water[351].

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[351] S. Ionescu, O. Constantinescu, D. Topor and E. Gärd, *Proc. 2nd Geneva Conf.*, Vol. 28, p. 58 (1958).

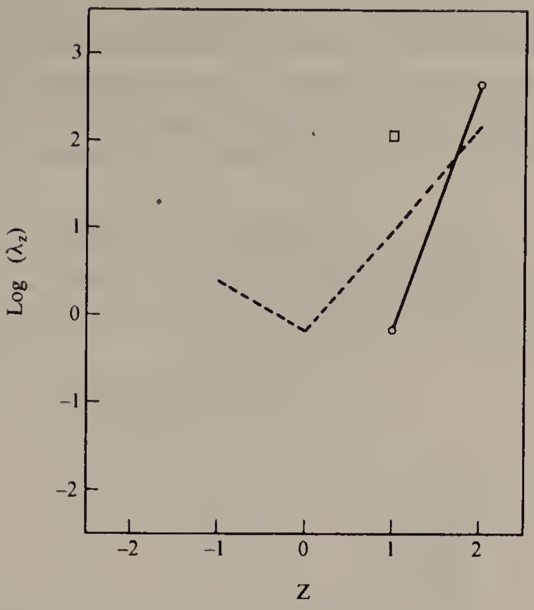

FIG. 78. The variation of the distribution constants λ_z between γ-Al_2O_3 and (K,Li)NO_3 melt for ions and chloride complexes of various formal charge, z. ○ = UO_2^{2+}, □ = NpO_2^+ and ● = Co^{2+} [335].

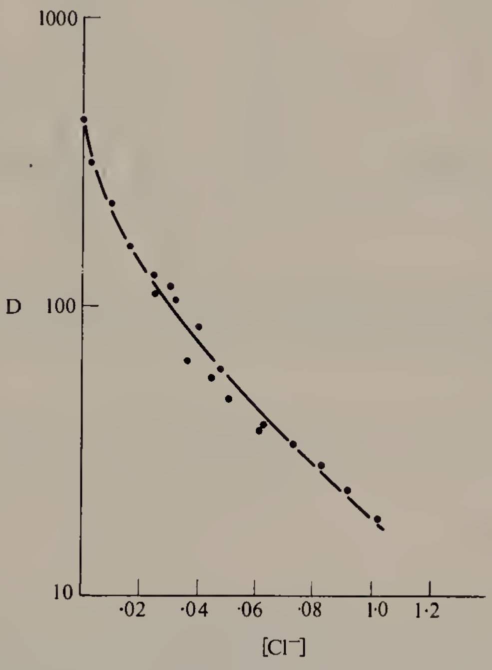

FIG. 79. The influence of chloride ions on the distribution of U(VI) between γ-Al_2O_3 and (K,Li)NO_3 melt at 160°C[335].

for the Th^{4+} ions than the external solution[352]. The different behavior of UO_2^{2+} and Th^{4+} in ethanol solution is used for the separation of U from Th on an anion-exchanger[351] (see Fig. 77). When the resin phase becomes dry in anhydrous solvents, the rates of adsorption and desorption are very small, making it impractical to use organic ion-exchangers.

[352] O. Samuelsson, *Ion Exchange Separations in Analytical Chemistry*, p. 145. Almqvist & Wiksell, Stockholm (1963).

A major part of the quantitative knowledge about actinide chloride complexes in nitrate melts has been obtained using γ-Al_2O_3 as an inorganic ion-exchanger (see Fig. 79). The character of an amphoteric ion-exchanger is seen from Fig. 78. The adsorption isotherms are generally slightly curved and the capacity is low, but the temperature stability allows it to be used even at 680°C[335]. The distribution coefficients for Np and U are given in

TABLE 41. DISTRIBUTION CONSTANTS FOR VARIOUS IONS BETWEEN γ-Al_2O_3 AND A $(K,Li)NO_3$ MELT AT 160°C (from ref. 335)

Ion	Distribution constant (molal units)
UO_2^{2+}	434·0
UO_2Cl^+	0·66
UO_2Cl_2	0
NpO_2^+	107·5
NpO_2Cl	0

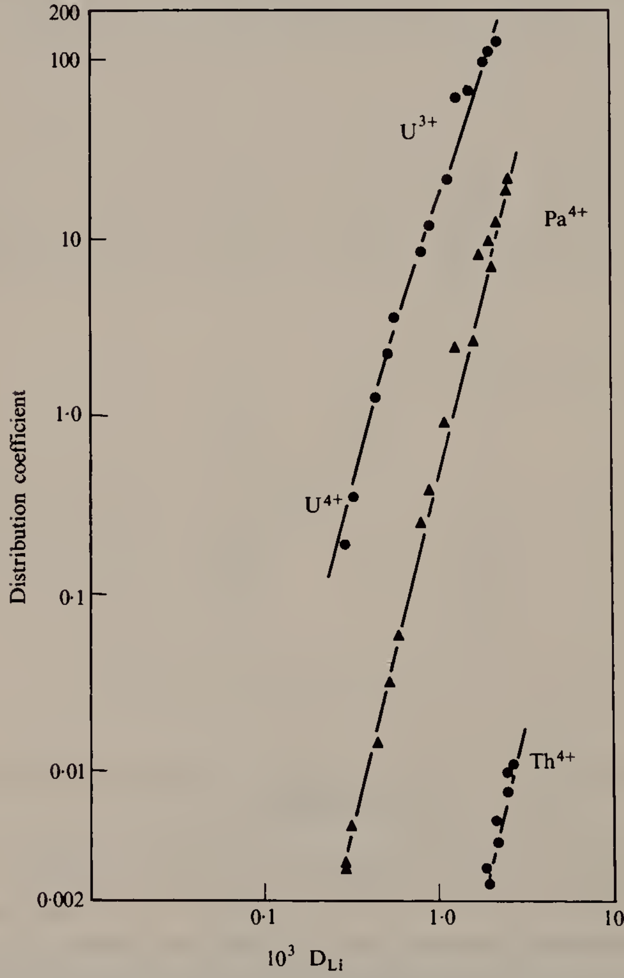

FIG. 80. Distribution of U, Pa and Th between (LiF–ThF_4) melt and (Li,Be) metal at 650°C for various amounts of Li[327].

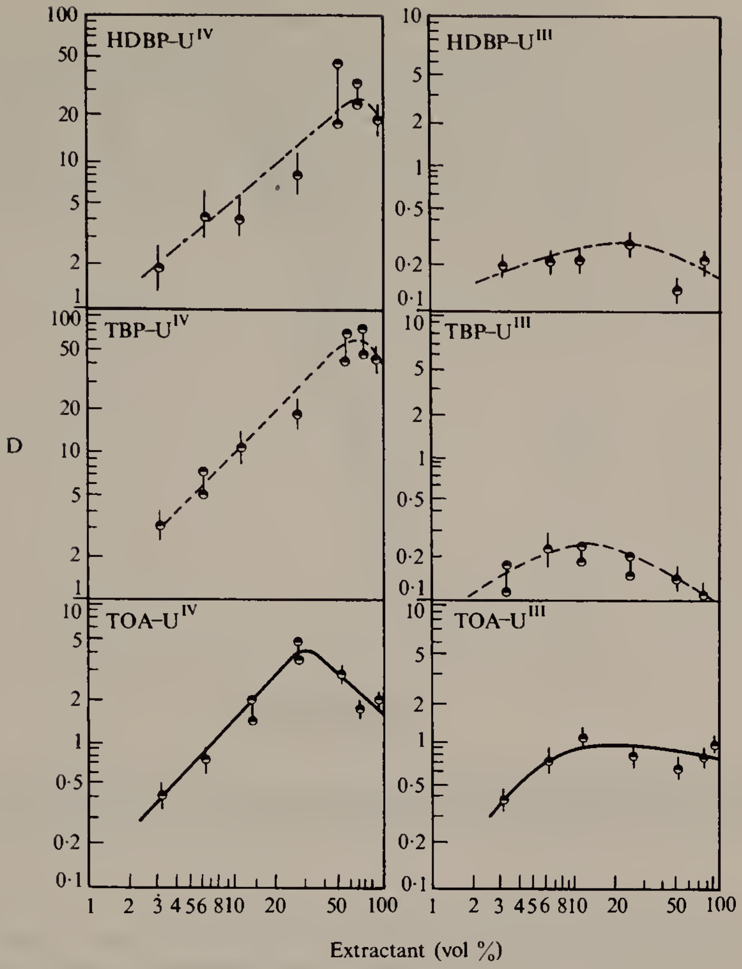

FIG. 81. Distribution of U(III) and U(IV) between molten diphenyls containing various extractants and a (K,Cu)Cl melt for various concentrations of the extractant[354].

Table 41. γ-Al_2O_3 has also been used in nitrate and chloride melts as an ion-exchanger for elution chromatography[331,335].

5.6. Solvent extraction

Two anhydrous extraction systems have been used. In one system, consisting of molten metal–molten salt[325,327,353], the phase transfer is accompanied by a redox reaction. Usually the molten metal phase contains a reducing metal, e.g. Li or Mg. By changing the concentration of the reductant, the redox potential can be changed. The slopes of the distribution curves reflect the oxidation state in the salt phase (see Fig. 80). Evidence for Am(II) has been obtained in these systems as the slope for Am is one unit lower than for Pu(III) in a diagram similar to Fig. 80[325]. The other actinides are usually present in their lowest oxidation state, i.e. Pa(IV), Th(IV), U(III), Np(III) and Pu(III).

[353] W. Knoch, *Ein neues Hochtemperatur-Verfaren zur Aufbereitung von Brutreaktorbrennstoffen*, Habilitationsshrift, Braunschweig (1967).

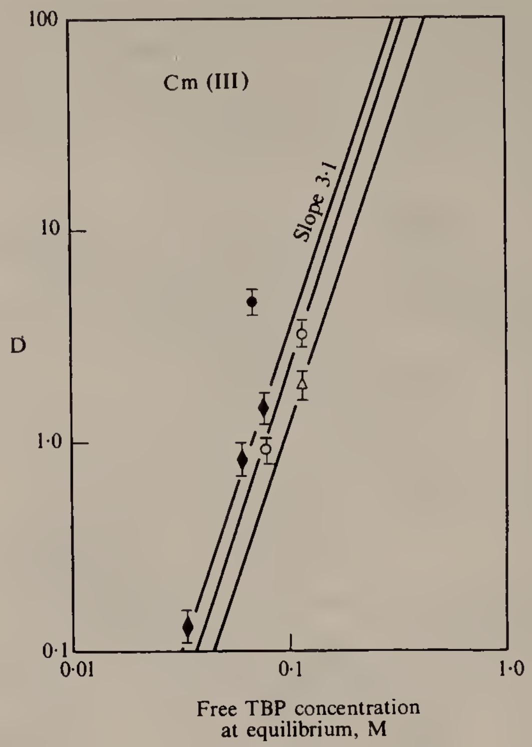

FIG. 82. The distribution of Cm(III) between a molten polyphenyl–TBP mixture and a (K,Li)NO_3 melt. ◆ = pure nitrate melt, ○ = 0·24 m chloride, △ = 0·43 M chloride[334].

Intermediate between the metal–salt systems and the salt–salt or salt–organic systems are systems with a metal salt of a low valence state present in a large amount, e.g. a salt system containing Cu(I) mixed with KCl[354]. Here the phase transfer depends on the amount of Cu(I) present in the system and on the redox potential for the solute in question. By choosing a suitable combination of extractant and Cu(I) concentration a specific actinide can be extracted to the organic phase (trioctylamine, tridecylamine, tributylphosphate or di-2-ethylhexylphosphoric acid in molten diphenyls) or stripped into the salt. The picture is complicated by the distribution of Cu(I) itself between the phases. Figure 81 shows the distribution of U(III) and U(IV) for various concentrations of extractant.

A redox process would also offer the possibility of controlling the distribution of actinides in molten salt–molten salt two-phase system. These have, however, not yet been investigated.

The second extraction system consists of molten salt–organic liquid, which is very similar to the corresponding aqueous systems. It can be regarded as an extreme case of salted aqueous extraction system where no water is left. The degree of freedom is very limited as more dramatic changes in the composition of the salt phase usually increases the solidification temperature to a level the organic cannot stand. As a consequence most work has been done by varying the extractant concentration in the organic phase. Figure 82 shows how the extraction of Cm(III) changes when the TBP concentration of the organic phase is varied. Similar aqueous systems are described in section 4 above.

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[354] Z. Borkowska, M. Mielcarsky and M. Taube, *J. Inorg. Nucl. Chem.* 26 (1964) 359.

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MASTER INDEX

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