INORGANIC CHEMISTRY

CHEMISTRY OF ACTINOIDS

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Introduction

Elements from atomic no. 90 (thorium) to atomic no.103 (lawrencium) are called the actinoids (earlier called actinides). Actinium (named after the Greek word ***aktis*** means ray) is regarded as prototype for these fourteen elements. Thorium, protactinium and uranium occur naturally but elements above atomic number 92 are man-made (i.e., synthetic) by nuclear transmutations and are called as transuranium elements. Twenty transuranium elements have been discovered, and eleven of these transuranium elements i.e. up to atomic number 103 are called actinoids (Table 1).while elements above atomic number 103 are known as transactinoids The transuranium elements are named after the planets, places and famous scientists, for example neptunium and plutonium are named after the planets, Neptune and Pluto. Americium, californium and berkelium are named after places, America, Berkeley and California. Einsteinium, fermium, mendelevium, nobelium and lawrencium are named after the famous scientists, viz., Albert Einstein, Enrico Fermi, Mendeleev, Alfred Nobel and Ernest Lawrence, respectively. Actinoids are heavy metals, and are radioactive and toxic to humans. They are characterized by filling up of electrons in the 5*f* subshell. Nuclear stability of actinoids decreases with increasing atomic number and thus the isotopes of elements with high atomic numbers have short half lives and undergo rapid radioactive decay. Therefore, study of actinoids is dominated by nuclear chemistry. Actinoids have a large number of practical applications, e.g., uranium and plutonium, because of their property of undergoing nuclear fission on interaction with thermal neutrons, are used not only as nuclear fuels in nuclear reactors for generating electricity but also in nuclear weapons (uranium enriched bomb, code named "Little Boy" dropped over Hiroshima and plutonium bomb code named "Fat Man" dropped over Nagasaki). The particle emitting nuclides such as ^{238}Pu ($t_{½}$=87.7 years), ^{244}Cm ($t_{½}$=18.1 years) and ^{245}Cm ($t_{½}$=8500 years) are used in radionuclide power sources to power remote sensing instruments packages and in SNAP

(Space Nuclear Auxiliary Power) to power satellites. (Radionuclide power source is one in which decay energy of radionuclide is converted to heat which in turn is converted to electricity using a thermoelectric device). Radionuclide power sources are light weight, rugged and portable. ^{241}Am is used in household and industrial smoke detectors; for diagnosis of thyroid disorders and for measuring and controlling the thickness of industrial materials. ^{252}Cf is used in neutron radiography, in neutron moisture gauges which are used to find water and oil bearing layers in oil wells, and in airport neutron activation detectors to inspect airline luggage for hidden explosives as well as for irradiation of tumors.

Table 1 - Actinoids and Electronic configuration

Atomic number	Element	Symbol	Outer electronic configuration
90	Thorium	Th	$6d^2\,7s^2$
91	Protactinium	Pa	$5f^2\,6d^1 7s^2$
92	Uranium	U	$5f^3 6d^1 7s^2$
93	Neptunium	Np	$5f^4 6d^1$7s2
94	Plutonium	Pu	$5f^6 7s^2$
95	Americium	Am	$5f^7 7s^2$
96	Curium	Cm	$5f^7 6d^1 7s^2$
97	Berkelium	Bk	$5f^9 7s^2$
98	Californium	Cf	$5f^{10} 7s^2$
99	Einsteinium	Es	$5f^{11} 7s^2$
100	Fermium	Fm	$5f^{12} 7s^2$
101	Mendelevium	Md	$5f^{13} 7s^2$
102	Nobelium	No	$5f^{14}$7s^2
103	Lawrerncium	Lr	$5f^{14} 7s^2$

Neptunium, americium and curium and higher actinoids are produced by nuclear transmutation in the nuclear reactors. Hence, spent fuel from a reactor contains not only unused uranium but also plutonium, americium curium and higher actinoids. With increasing use of nuclear reactors for production of electricity there is large scale production of actinoids in nuclear reactors which has led to increasing concern about release of these elements in the environment and possible radiological hazards to mankind. Another cause for concern amongst the environmentalists is the plutonium released in the atmosphere due to testing of nuclear weapons and reentry of artificial satellites equipped with ^{238}Pu power sources. Plutonium is reported to be one of the most toxic substances and has carcinogenic properties. Americium, placed next to plutonium in terms radiological hazards of actinoids, is released in the environment by discarded smoke detectors

Position of actinoids in the periodic table

Before the discovery of transuranium elements, Th, Pa and U were placed at the corresponding position just below the sixth period transition elements, hafnium, tantalum and tungsten, respectively because of their resemblance to these elements in various properties. In the year 1940, plutonium and neptunium were discovered and it was found that chemical properties of

these elements resemble uranium and not those of transition elements such as Re and Os. This led G. T. Seaborg to suggest that elements having atomic numbers greater than that of Ac (at. no. 89) must be placed in a second series of inner transition elements, similar to the lanthanoid series. During 1940-1960 (considered as the golden age of synthesis of elements), all transuranium elements were discovered by bombardment techniques G. T. Seaborg and E.M McMillan of the University of California, Berkeley, CA, USA were awarded the 1951 Nobel Prize for chemistry for their discoveries in the chemistry of the transuranium elements. Element with atomic number 106 has been named seaborgium after Seaborg, the co-discoverer of plutonium and nine other transuranium elements. Subsequent to the discovery of transuranium elements (atomic number 93 to 103) and studies of their properties, it was established that they were *f* block elements and should occupy the position in periodic table as suggested by Seaborg (Table 2).

Table 2 - **Position of Actinoids**

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

Lanthanoids	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinoids	Th	Pa	U	Np	Pu	Am	Cm	Bk	cf	Es	Fm	Md	No	Lr

Preparation of actinoids

Actinoids above atomic number 92 can be prepared either (i) by capture of neutron by heavy nuclei followed by β emission, or (ii) by capture of nuclei of light elements ranging from helium to neon by heavy nuclei, which increases atomic number by several units in one step. Neutron capture by nucleus increases its neutron-to-proton ratio which makes the nucleus unstable and it decays by converting a neutron into a proton and β particle (electron). Thus, the *n/p* ratio is reduced and atomic number increases by one, giving rise to a new element, one place to the right in the periodic table. For example,

$$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{236}_{92}U + ^{1}_{0}n \rightarrow ^{237}_{92}U \xrightarrow{\beta} ^{237}_{93}Np$$

Heavier actinoids can be prepared by successive neutron capture but two difficulties arise; firstly the yield of heavier nucleus falls sharply as the number of neutron addition steps from the starting material increases. Secondly, there is decrease in nuclear stability with increasing atomic mass. To overcome these difficulties two methods can be used. The first method involves subjecting the target nucleus to very high flux or density of neutrons, without allowing time for intermediate products to decay. Einsteinium and fermium were detected as by-products of thermonuclear explosion as a result of multiple neutron capture. But this method is not convenient and practical. The second method is to bombard the heavy nucleus with accelerated small ions having sufficient energy to overcome columbic repulsion between the ion and heavy

nucleus. The simplest ion is α- particle, i.e., helium nucleus, which increases the mass number by four and atomic number by two.

$^{239}_{94}Pu + {}^{4}_{2}He \rightarrow {}^{241}_{96}Cm + 2\,({}^{1}_{0}n)$

Ions other than the α- particle, B^{5+}, C^{6+}, N^{7+} and O^{8+} are also used for production of heavier elements e.g.,

$^{238}_{92}U + {}^{14}_{7}N \rightarrow {}^{249}_{99}Es + 3({}^{1}_{0}n)$

$^{238}_{92}U + {}^{16}_{8}O \rightarrow {}^{250}_{100}Fm + 4({}^{1}_{0}n)$

$^{246}_{96}Cm + {}^{12}_{6}C \rightarrow {}^{254}_{102}No + 4({}^{1}_{0}n)$

$^{252}_{98}Cf + {}^{11}_{5}B \rightarrow {}^{257}_{103}Lr + 6({}^{1}_{0}n)$

Synthesis of actinoids is listed in Table 3.

Table3 - Preparation of Actinoids

Atomic number	Element	Isotope	Half life	Synthesis reaction
93	Neptunium	^{237}Np	2.2×10^{6} years	$^{235}_{92}U \xrightarrow{(n,\gamma)} {}^{236}_{92}U \xrightarrow{(n,\gamma)} {}^{237}_{92}U \xrightarrow[6.75\,days]{\beta} {}^{237}_{93}Np$
94	Plutonium	$^{244}_{94}Pu$	8.28×10^{7} years	$^{239}_{94}Pu \xrightarrow{five\,(n,\gamma)} {}^{244}_{94}Pu$
95	Americi-um	^{243}Am	7650 years	$^{239}_{94}Pu \xrightarrow{four\,(n,\gamma)} {}^{243}_{94}Pu \xrightarrow{\beta} {}^{243}_{95}Am$
96	Curium	^{244}Cm	17.6 years	$^{239}_{94}Pu \xrightarrow{four\,(n,\gamma)} {}^{243}_{94}Pu \xrightarrow[5.0\,h]{\beta} {}^{243}_{95}Am \xrightarrow{(n,\gamma)} {}^{244}_{95}Am \xrightarrow[26min]{\beta} {}^{244}_{96}Cm$
97	Berkeliu m	^{243}Bk	4.5 hours	$^{241}_{95}Am \xrightarrow{(\alpha,\,n)} {}^{243}_{97}Bk$
98	Californiu m	^{245}Cf	44 minute	$^{242}_{96}Cm \xrightarrow{(\alpha,n)} {}^{245}_{98}Cf$
99	Einsteiniu m	^{253}Es	20 days	Mike thermonuclear explosion (leading to ^{253}ES)
100	Fermium	^{255}Fm	20 hours	Mike thermonuclear explosion (leading to ^{255}Fm)
101	Mendelev -ium	^{256}Md	76 minute	$^{253}_{99}Es \xrightarrow{(\alpha,\,n)} {}^{256}_{101}Md$
102	Nobelium	^{252}No	2.3 second	$^{244}_{96}Cm + {}^{12}_{6}C \rightarrow {}^{252}_{102}No + 4({}^{1}_{0}n)$
103	Lawrenci-um	^{258}Lr	4.3 second	$^{252}_{98}Cf + {}^{11}_{5}B \rightarrow {}^{258}_{103}Lr + 5({}^{1}_{0}n)$

Electronic configuration and oxidation states

Atomic number of actinium is 89 and its electronic configuration is [Rn] $6d^{1}7s^{2}$. Contrary to the lanthanoids, where the 4*f* orbitals are lower in energy than the 5*d* orbitals, the energies of 5*f* and

6*d* orbitals of actinoids are comparable and electrons can occupy either 5*f* or 6*d* orbitals or both. In the later actinoids, from plutonium onwards, energy of 5*f* subshell is lower than 6*d*, hence 5*f* sub-shell is filled regularly and these elements closely resemble the lanthanoids. Electronic configuration of various actinoids is listed in Table 1. In contrast to lanthanoids, the actinoids show greater multiplicity of oxidation states, that is, besides the 3+ state, actinoids also show 2+, 4+, 5+, 6+ and 7+ oxidation states. Metals in higher oxidation states exist as oxo cations, MO_2^+ and MO_2^{2+}, whereas lower oxidation states exist as simple cations**.** Similar to lanthanoids, all actinoids show 3+ oxidation state, but 3+ oxidation state is most stable only for later actinoids, i.e., americium (at no.95) to lawrencium (at no 103) excluding nobelium. For a given set of solution conditions each actinide exhibits a different set of oxidation states. Higher oxidation states are more stable in basic solution whereas lower oxidation states are stable in acid solution. Up to uranium, most stable oxidation state is the one involving all valence electrons, e.g., in the case of uranium the most stable state is 6+ since outer electronic configuration is $5f^3 6d^1 7s^2$. Oxidation states of actinoids are given in Table 4. Electropositive character of metals increases with increasing atomic number and hence the stability of higher oxidation state decreases.

T**able 4 – Oxidation States of Actinoids**

Elements			Oxidation	States		
	2+	3+	4+	5+	6+	7+
Thorium						
Protactinium						
Uranium						
Neptunium						
Plutonium						
Americium						
Curium						
Berkelium						
Californium						
Einsteinium						
Fermium						
Mendelvium						
Nobelium						
Lawrencium						

Most important oxidation state (i.e., in general the most abundant and stable)

Oxidation states other than the most stable state.

Unstable oxidation states

Oxidation states, which do not exist.

Oxidation state 2+

- Americium and heavier elements exhibit oxidation state 2+. Am^{2+} does not exist in aqueous medium, although Cf^{2+}, Es^{2+} and Fm^{2+} do exist. Nobelium has electronic configuration [Rn] $5f^{14}7s^2$ and 2+ state is the most stable oxidation state as it will lead to fully filled *f* sub shell. No^{2+} is more stable than the corresponding lanthanoid, Yb^{2+}.

Oxidation state 3+

- This is the most common oxidation state for actinoids. For the first four elements(Th→Np), the 3+ state is not the most stable oxidation state but for later actinoids, Am to Lr (except No for which 2+ oxidation state is most stable), this is the most stable oxidation state and the properties are similar to those of lanthanoids.

Oxidation state 4+

- Actinoids from thorium to berkelium exhibit oxidation state 4+. For thorium it is the most stable oxidation state, M^{4+} ions (M=Pa, U, Np, Pu, and Bk) are known in solution, but for Am and Cm in solution, only complex fluoro anions exist. Bk^{4+} is strongly oxidizing but more stable than Cm^{4+} and Am^{4+}. Actinoids in 4+ oxidation state closely resemble lanthanoids in 4+ state. A large number of compounds are formed by actinoids in 4+ state, for example, dioxides MO_2 (ThO_2, PaO_2 and CfO_2), tetrahalides MX_4(X=F, Cl, Br, I) and oxohalides MOX_2(M= Th, Np).

Oxidation state 5+

- Actinoids from protactinium to americium show oxidation state 5+ and it is the most stable oxidation state for protactinium. Pa^{5+} resembles Nb^{5+} and Ta^{5+}. Actinoids in 5+ oxidation state form solid compounds and do not occur in solution although pentahalides such as UF_5 and PaF_5 are known. Oxo cations such as MO_2^+ (M= U, Np, Pu and Am) also exist. Stability of oxo cations are determined by the ease of disproportionation.

Oxidation state 6+

- U, Np and Pu and Am show 6+ oxidation state in fluorides, and oxo cations MO_2^{2+}(M=U, Np, Pu, Am). Besides fluorides, uranium also forms UCl_6, $U(OR)_6$ and oxohalide UOF_4. Dioxo ions are stable in aqueous solution and the order of stability is $UO_2^{2+} > NpO_2^{2+} > PuO_2^{2+}$.

Oxidation state 7+

- Only Np and Pu show 7+ oxidation state and very few, marginally stable, Np^{7+} and Pu^{7+} compounds are known.

General properties of actinoids

Actinoids are radioactive and a health hazard to the experimenter. Hence, special experimental techniques are required for studying these elements. Also, only very small amounts of the heavier elements are available (due to their instability). Np and Am are available in kilogram and 100 gram quantities. Cm ,Bk, Cf, and Es are produced in mg scale and Fm in μg scale. Isotopes of mendelevium, nobelium and lawrencium have short half lives and are available in small amounts, e.g., in the case of mendelevium, 1 to 3 atoms are produced per experiment. Thus, the concept of bulk properties is not applicable to some of the actinoids. For elements which are available in macroscopic amounts such as Np and Pu (available in kilogram quantities), the major problem is constant build up of decay products and heat generated due to radioactive decay which affects the measured properties. The magnitude of energy generated in radioactive decay is much larger than a chemical bond. Studying aqueous chemistry of short lived isotopes of actinoids poses problems because the heat produced as a result of radioactive

decay is sufficient to decompose water into H and OH radicals and produce H_2O_2. These radicals can reduce higher oxidation states of plutonium and americium. Hence, ultra micro chemical techniques are used in chemical studies of actinoids.

Crystal structure

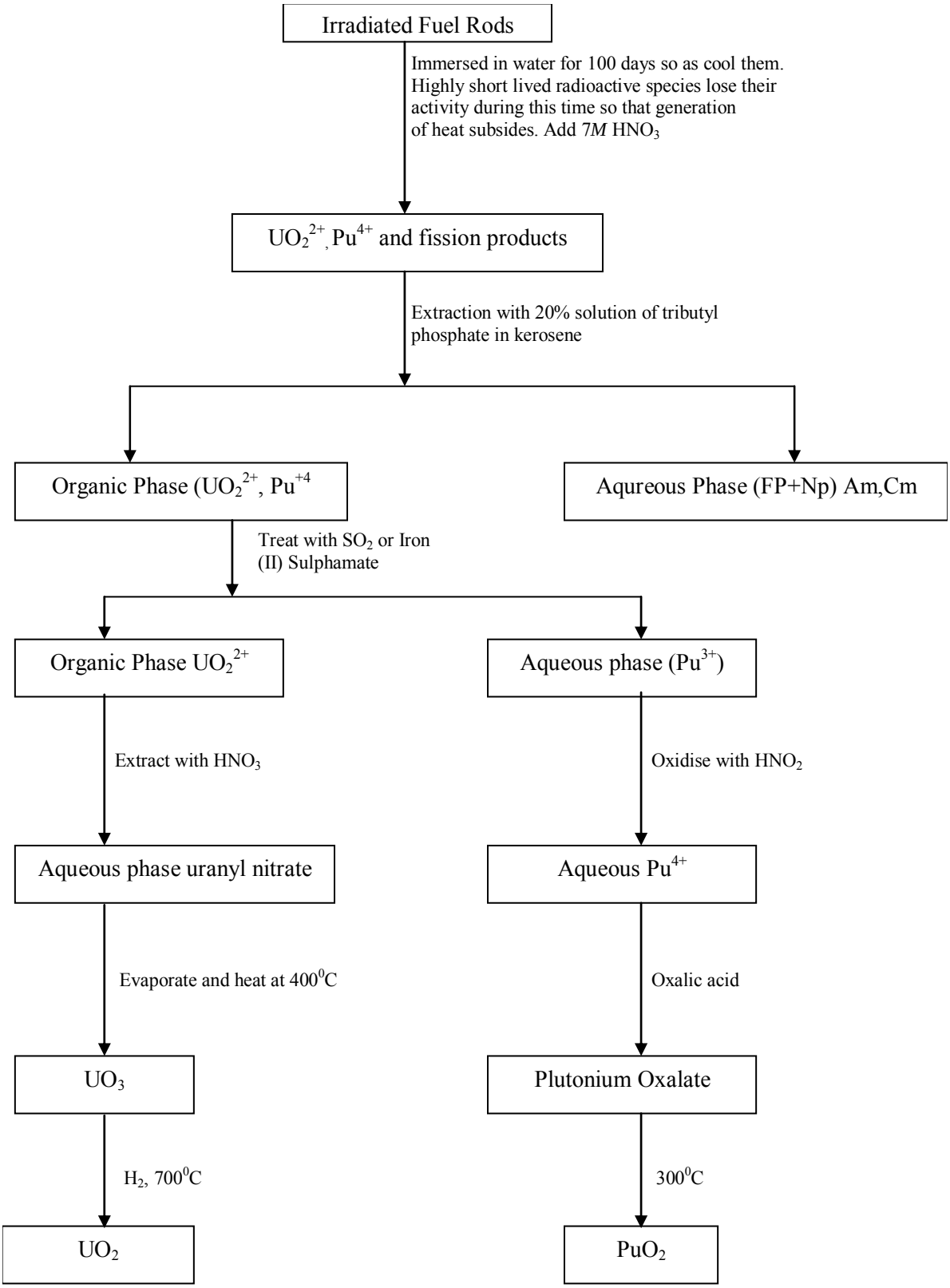
All actinoids are silvery in appearance. Actinoids (except californium) exist in more than one form, for example, uranium exists in three different forms: (i) *the low temperature (alpha) form,* is stable up to 660°C and has a orthorhombic lattice, (ii) *the medium temperature (beta) form* is stable between 660-770°C and has a tetragonal lattice, and, (iii) *the high temperature (gamma) form is* stable above 770°C and has body centered cubic structure. Neptunium also occurs in different crystal forms: *Orthorhombic* alpha form is stable from room temperature to 278±5°C. *Tetragonal* form is stable from 278 to ~ 550°C while the *body centered cubic* form is stable above 550°C. Similarly, plutonium exists in six different forms.

Density and melting point

The actinoids are highly dense; densities of uranium and neptunium are 19.05 and 20.45 g/cc, respectively. Melting points of actinoids are also high. There is no regular trend for density and melting points from thorium to lawrencium. Melting points and densities of actinoids are listed in Table 5.

Table 5 - Properties of Actinoids

Element	Melting point	Boiling point	Density (g/cc)	Radius M^{3+}(A^o)	Radius M^{4+} (A^o)
Thorium	1750	4850	11.78		0.94
Protactinium	1572	4227	15.37	1.04	0.90
Uranium	1132	3818	19..05	1.02	0.89
Neptuniuim	639	5235	20.45	1.01	0.87
Plutonium	640	3232	19.86^{Alpha}	1.00	0.86
Americium	1173	2607	13.67	0.97	0.85
Curium	1350		13.51	0.97	0.85
Berkelium	986		14.78	0.96	0.83
Californium				0.95	0.82
Einsteinium					
Fermium					
Mendelevium					
Nobeliium					
Lawrencium					



PUREX PROCESS

Scheme-1

Ionic /crystal radii

Filling of electrons in 5*f* orbitals in actinoids is accompanied by significant decrease in atomic and ionic radii. This effect is called actinoid contraction similar to lanthanoid contraction. This is attributed to the addition of electrons in inner 5*f* subshell so that the increment they produce in atomic volume is less than reduction due to greater nuclear charge(Relativistic effects also contribute to actinoid contraction by expanding *f* orbitals which results in less effective shielding from nuclear charge. Relativistic effects result in (i) splitting of energy levels due to spin orbital coupling i.e. degenerate three *p*, five *d* and seven *f* orbitals split into one $p_{½}$, two $p_{3/2}$, two $d_{3/2}$ and three $d_{5/2}$, three $f_{5/2}$ and four $f_{7/2}$ and (ii) contraction and stablisation of *p* orbitals and expansion of *d* and *f* orbitals). Ionic radii of M^{3+} and M^{4+} ions are listed in Table 5.

Nuclear properties

Binding energy per nucleon is lower for very heavy nuclei and hence the heavy nuclei are unstable. Actinoids can undergo decay by emitting alpha particles, beta particles and gamma rays. They can also undergo fission. Actinoids such as uranium, plutonium and curium undergo α decay (for example $^{238}_{92}U$ undergoes α- decay to form $^{234}_{90}Th$, which has a binding energy higher than uranium. $^{235}_{92}U$ when irradiated with slow neutrons undergoes nuclear fission to form fission products depending upon how the nucleus splits e.g.,

$$^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{138}_{53}I + {}^{95}_{39}Y + 3\,{}^{1}_{0}n$$

Magnetic properties

The spin as well as the orbital angular momentum of the unpaired electron gives rise to magnetic field. The magnetic moment in Bohr magneton is calculated as follows:

$$\mu = g\sqrt{J(J+1)} \qquad \ldots (1)$$

$$g = 1½ + \frac{S(S+1)-L(L+1)}{2J(J+1)}$$

where L = resultant orbital momentum quantum number, and, S = resultant spin quantum number.

Coupling between the spin contribution and orbital contribution (spin orbit coupling or Russell Saunders Coupling) gives quantum number J. J can take the values J =L+S, L+S-1…….L-S(or S-L if S>L) with each value corresponding to a different energy level. The ground state of the ion is J=L-S, if the f sub shell is less than half-full, and J=L+S if the f sub shell is more than half-full. Strength of spin orbit coupling indicates the magnitude of separation between adjacent states of a term.

Crystal field splittings in the case of actinoids are of much greater magnitude than lanthanoids due to larger size of 5*f* orbitals in comparison with that of 4*f* orbitals (larger orbitals are more affected by ligands). Spin orbital coupling parameters for actinoids are twice that of the 4*f* series. Hence, for actinoids, spin orbit coupling is no longer a small perturbation and intermediate coupling system, i.e., coupling intermediate to Russell –Saunders and j-j coupling should be considered. Therefore, Russell Saunders coupling which is applicable in the case of lanthanoids is not applicable to actinoids. (Magnetic moments of actinoids are lower than the values calculated from Russell Saunders coupling. However, for lanthanoids, the experimental values are in close agreement with calculated values).

Spectral properties

Absorption spectrophotometry is a useful tool for studying actinoid chemistry to obtain information regarding symmetry, coordination number, the nature and strength of bonding and to identify complexes. In the case of actinoids, spectra obtained depends on: (i) relative energies of 5*f* and 6*d* electrons, (ii) magnitude of crystal field splitting, and, (iii) spin orbit coupling. In contrast to lanthanoids, absorption spectra in the case of actinoids, vary from one compound to another for the same ion due to change in magnitude of crystal field splitting. Various types of transitions which give rise to absorption spectra in the case of actinoid compounds are as follows:

a) transitions between electronic states involving 5*f* orbitals, i.e., *f-f* transitions. Due to these transitions broad absorption bands with weak intensity are obtained in visible and ultra violet region. (Absorption bands in the case of actinoids are broader and more intense than in the case of lanthanoids because 5*f* orbitals are more capable of interacting with ligands than the 4f orbitals). Although *f-f* transition are Laporte forbidden (transitions which involve a change in the subsidiary quantum number are Laporte allowed, while transitions for which change in l=0, are Laporte forbidden), selection rule is partially relaxed because of crystal field distorting the symmetry of metal ion. These transitions are responsible for the colour of actinoid compounds, e.g., aqueous solutions of M^{4+} (M= U, Np, Pu, Am, Cm) are yellow, green, brown, pink and pale yellow, respectively.
b) transitions involving transfer of electron from 5*f* to 6*d* orbitals, i.e., Laporte allowed 5*f*-6*d* transitions. These occur in ultraviolet region and do not affect the colour of ions. Since Laporte forbidden transitions are weaker than the Laporte allowed transition, these transitions are more intense than *f-f* transitions and occur at lower energies than 4*f*-5*d* transitions in lanthanoids.
c) transitions involving transfer of electron from ligand orbital to a metal orbital or vice versa i.e., charge transfer. These allowed transitions produce broad and intense absorptions mostly in the U.V. region but sometimes in the visible region these impart intense yellow, red, brown or black colour of many actinoid compounds.

Tendency to form complexes

In contrast to lanthanoids, actinoids have a much greater tendency to form complexes since the 5*f* orbitals extend spatially farther than the 4*f* orbitals. Actinoids form complexes with oxo anions, halide ions and other chelating agents. Tendency to form complexes depends upon ionic size and charge and shows an order: $M^{4+} > MO_2^{2+} > M^{3+}$. Unlike transition elements, higher coordination numbers are very common for actinoid ions because of their relatively large size coupled with high electrostatic charge (due to formal charge 3+ to 6+) and large number of valence shell orbitals available for bonding.

Nature of bonding

The energies of the 5*f*, 6*d*, 7*s* and 7*p* are comparable and bond energy is greater than promotion energy required for promotion of an electron from 5*f* to 6*d*. Hence, levels occupied by the electrons may change depending on nature of ligands and also whether the ion is in the solid state or in solution . Thus, it is difficult to know which orbitals are used and whether bonding is covalent or ionic.

Chemical properties

Actinoids tarnish in air forming oxide coating which is protective in the case of thorium but less so in other elements. They react with boiling water or dilute acids and release hydrogen. Thorium, uranium and plutonium are rendered passive by the action of conc. nitric acid. Actinoids do not react with alkalies but combine with most non metals such as oxygen, hydrogen, halogens, nitrogen, carbon etc especially if heated. All actinoids are pyrophoric(if finely divided) and highly electropositive. The electropositive character increases with increasing atomic number. Metals can be prepared by electrolysis of molten salts or reduction of halides with electropositive metal. Cations of U, Np, Pu, and Am have complex chemistry because free energy of various oxidation states differs little, for example in the case of plutonium all the four oxidation states(3+, 4+, 5+, and 6+) can co exist.

Separation of actinoids

Actinoids produced as a result of nuclear reactions can be isolated from target material and irradiated nuclear fuels by following methods:

Precipitation Method

This method is based on precipitation reactions. Actinoids in tri- and tetra- positive oxidation states can be precipitated from acid solutions as fluorides or phosphates, whereas actinoids in higher oxidation states are either not precipitated or can be prevented from being precipitated by complex formation. Thus, in order to separate actinoids by precipitation method, metal ions in solution are brought in different oxidation states by suitable choice of oxidizing or reducing agents. For example, on addition of potassium bromate to a solution containing neptunium, plutonium and americium, neptunium and plutonium are oxidized to NpO_2^{2+} and PuO_2^{2+} while americium will remain as Am^{3+}. Hence, addition of HF results in precipitation of americium only. In case quantity of actinoid ion is insufficient, coprecipitation with carrier such as LaF_3 is adopted.

Separation of neptunium and plutonium from uranium and fission products:

Target material is dissolved in nitric acid and diluted to a concentration less than O.5*M* uranium. The lanthanum carrier (0.1 to 0.5 mg/cc) is added and SO_2 is passed through the solution for a few minutes. HF is added and precipitate formed is centrifuged and washed (uranium remains in solution while fission products, neptunium and plutonium are precipitated). Precipitate is dissolved in concentrated nitric acid and HF is added to reprecipitate fission products, neptunium and plutonium. Precipitate is converted to hydroxide by the action of concentrated solution of KOH and the hydroxide is then dissolved in HNO_3. Neptunium and plutonium present in solution are oxidised by addition of $KBrO_3$ and then HF is added again to precipitate LaF_3. (Neptunium and plutonium remain in solution whereas other fission products are precipitated).

Separation of americium and curium from uranium and fission products:

1. Target material is dissolved in hot concentrated sulphuric acid and evaporated to dryness and then dissolved in dilute nitric acid. Nitric acid and hydrofluoric acid mixture can also be used for dissolving the target material.
2. Plutonium and neptunium present in solution are oxidised using suitable oxidising agent such as $KBrO_3$.
3. HF is added to the solution obtained in step 2. Neptunium and plutonium remain in solution while rare earths, americium and curium and a few other impurities are precipitated as fluoride.
4. Precipitate is dissolved in nitric acid solution saturated with boric acid and then KOH is added to precipitate lanthanum hydroxide.

5. Lanthanum hydroxide is dissolved in nitric acid and steps 2, 3 and 4 are repeated so as to eliminate neptunium and plutonium.
6. Lanthanum hydroxide precipitate is dissolved in O.5*M* $HClO_4$ and solution is equilibrated with a small amount of Dowex 50 resin.
7. Resin is transferred to a column of Dowex 50 colloidal aggregates and elution is carried out with 13M HCl that is conc. hydrochloric acid saturated with hydrogen chloride gas. Americium and curium are eluted first, slightly separated from each other while rare earths are eluted later.
8. In order to separate americium and curium from each other, hydrochloric acid solution is evaporated and then diluted to 0.5N HCl and finally adsorbed on a small quantity of resin .Resin is transferred to 20cm × 2mm column of spherical fines (Dowex50) and elution is carried out with ammonium citrate solution.
9. To extract neptunium and plutonium, solution obtained in step 2 is saturated with ammonium nitrate (acidified with nitric acid) and mixed with ethyl ether or methyl isobutyl ketone.

Solvent extraction method

In this technique, aqueous solution of actinoids is brought into contact with a solvent which is essentially immiscible with water and the *p*H is adjusted, since extraction of actinoids varies with *p*H. For example, extraction coefficient of actinoids in 6*M* HNO_3 is lower for M^{3+} but higher for M^{4+} and the reverse is true with 12*M* HNO_3. Solvents such as methyl isobutyl ketone, ethyl ether and tributyl phosphate (solution in kerosene) are used. This method is used to recover uranium and plutonium from spent nuclear fuels by a process known as PUREX process. (Plutonium Uranium Reduction and Extraction, Scheme 1). Fuel rods are immersed in large cooling ponds of water for 100 days, so that short lived radioactive species lose their activity and generation of heat subsides. Irradiated fuel rods are then dissolved in 7*M* HNO_3 when uranium and plutonium go into solution as UO_2^{2+} and Pu^{4+} respectively along with other fission products. Solution obtained is extracted with tributyl phosphate (20% solution in kerosene) and the fission products along with Np, Am, Cm remain in aqueous phase, while uranium and plutonium are extracted in organic phase. In order to separate uranium and plutonium, organic layer is treated with aqueous iron (II) sulfamate. Uranium remains in tributyl phosphate solution, while Pu^{4+} is reduced to Pu^{3+} and it goes into aqueous solution. Uranium is then extracted as uranyl nitrate from organic layer with O.2*M* HNO_3. The solution containing uranyl nitrate is evaporated and heated to 400°C. By this process, uranyl nitrate is converted to UO_3, which on treatment with hydrogen at 700°C yields UO_2. HNO_2 is added to aqueous phase containing Pu^{3+} followed by addition of oxalic acid to precipitate plutonium as oxalate, $Pu(C_2O_4)_2.6H_2O$. Plutonium oxalate is heated to 300°C and PuO_2 is obtained.

Ion exchange method

This involves adsorption of actinoid ions on a cation or anion exchange resin followed by elution with a suitable reagent. This method is not suitable for separation of macro quantities of the elements due to their intense radioactivity which causes damage to resin. However, it can be used for small amounts. It is a two-step process which involves, firstly separation of actinoids from lanthanoids(obtained as fission products in bombardments which produce actinoids), and secondly, separation of actinoids from each other. The former process is affected by adsorption of ions using a cation exchange resin and carrying out elution with concentrated HCl as eluting agent. Actinoids ions form chloro complexes and hence desorped first from the resin. The latter process is affected by re-adsorption on the resin and elution with ammonium citrate.

INDIVIDUAL ELEMENTS

Thorium

Thorium is the 39th most abundant element on the earth's crust. It is as abundant as boron and three times more abundant than uranium. The most important commercial source of thorium is monazite which is a rare earth phosphate containing up to 12% of thorium oxide. Deposits of monazite sand are found in India, Brazil, and South Africa. India has one of the world's largest reserves of thorium, which can fuel nuclear reactors for more than 2000 years. Thorium also occurs in the form of uranothorite (mixed silicate of Th and U). Large number of radioisotopes of thorium have been characterized, the most abundant and most stable being Th-232 with half life of 14.05 billion years. Although ^{232}Th is not fissile but when bombarded with slow neutrons, it produces ^{233}U, which is fissile (similar to the process by which fast neutrons breed fissile ^{239}Pu from non-fissile ^{238}U). Due to this thorium is important as a potential fuel source in nuclear reactors. In order to utilize thorium reserves (since it is more abundant than uranium, and all of the mined thorium can be used in the reactors whereas in the case uranium only 0.7% is usable in the reactors), scientists are studying thorium-uranium fuel cycle as alternative to uranium-plutonium fuel cycle. Fresh thorium metal is silver white in colour but tarnishes to dark gray on continued exposure to air. The structure of the metal is cubic close packed. It readily forms alloys with iron, cobalt, nickel, copper, gold etc. Metal is obtained by reducing ThO_2 with Ca, or $ThCl_4$ with Ca or Mg. Dilute nitric acid and sulphuric acid attack thorium slowly with evolution of hydrogen, but it is not attacked by alkalis. It reacts with non metals such as hydrogen, nitrogen, carbon and phosphorus to give binary compounds. Most stable oxidation state for thorium is 4+ which is known both in solid state and solution. It forms large number of compounds such as halides, sulphates , sulphides, carbides, oxalates and oxides (discussed in detail later).

Uses

1. Thorium is used in Welsbach mantles(device for generating bright light when heated by flame) used as portable gas lights. These devices contain ThO_2 with 1% cerium and other ingredients.
2. It is used as a nuclear fuel. Naturally occurring ^{232}Th isotope is not fissionable but on irradiation it gives ^{233}U which is fissionable.
3.ThO_2 is added to glass to impart it high refractive index and low dispersion, which is used in scientific instruments and high quality camera lenses.
4. ThO_2 is used for high temperature laboratory crucibles.

Protactinium

Protactinium is one of the rarest of all the naturally occurring elements. It is found in minute quantities, in the range of 0.1ppm in uranium ore pitchblende. It is silvery metal and resistant to attack by air. The metal is prepared by thermal decomposition of pentahalides usually iodide or by reduction of tetrafluoride with barium at 1500ºC. It shows 4+ and 5+ oxidation states but 5+ is most stable oxidation state. In aqueous solution, 4+ oxidation state can be obtained by reduction of Pa^{5+} with Cr^{2+} or Zn / Hg but Pa^{4+} is rapidly reoxidised by air. Compounds of Pa in 5+ oxidation state such as oxides and halides are known. Study of the chemistry of protactinium poses problems because its compounds hydrolyze in solution to give polymeric species and colloids which are adsorbed on vessels and precipitates

URANIUM

Uranium, the most important actinoid, was discovered in 1789 by Martin Heinrich Klaproth from mineral pitchblende and is named after the planet Uranus discovered by William Herschel (William Herschel was a German born British astronomer and composer of various musical works, including 24 symphonies and church music. His interest in music led him to mathematics and hence to astronomy. He is also credited with discovery of infra red radiation and two satellites of Saturn). After Klaproth's discovery, for a century and a half the main application of uranium compounds was for colouring glass and ceramics. Much of the interest in uranium developed after the discovery of uranium fission by Otto Hahn in 1938 and use of U and UO_2 as nuclear fuel by E. Fermi for carrying out the first man-made nuclear chain reaction in 1942. Fermi's work led to the development of Manhattan Project (It was developed by United States in collaboration with UK and Canada and other European countries during World War II to make atom bomb) and subsequent discovery of transuranium elements. Manhattan project was successful in development of uranium enriched bomb code named Little boy (dropped over Hiroshima) and plutonium bomb code named as Fat man(dropped over Nagasaki).

Uranium is the forty-eighth most abundant element in the earth's crust. It is more abundant than silver, mercury and cadmium. Sources of uranium are carnotite ($K_2(UO_2)_2(VO_4)_2.3H_2O$), uraninite and pitchblende. Carnotite mineral is vandate of potassium and uranium with small amounts of radium. Pitchblende contains 55-57% UO_2, up to 30% of UO_3 and a small amount of water.

It is found in nature in the form of three isotopes ^{238}U(99.28%), ^{235}U(0.71%) and ^{234}U(0.006%). ^{235}U undergoes nuclear fission on interaction with neutrons, hence used as fuel in nuclear reactors. Chemically $^{235}U$and ^{238}U are identical but differ in physical properties such as atomic mass and nuclear properties i. e., ^{235}U is fissile and ^{238}U is non fissile. Because of difference in mass, isotopes can be separated and it is possible to increase i.e. enrich the percentage of ^{235}U. Most of the nuclear reactors use enriched uranium that is proportion of ^{235}U is increased from 0.7% to 3% or up to 5%. However, uranium used for nuclear weapons is enriched in special plants to produce 90% ^{235}U.

S*eparation of isotopes (enrichment*)

Following methods are used.

1.Thermal diffusion
2.Gaseous diffusion
3.Centrifugation
4.Electromagnetic isotope separation.
5. Laser enrichment.

Thermal diffusion method

Mixture (gaseous or liquid) containing the isotopes to be separated is placed in a vertical tube with an electrically heated central wire. Due to thermal diffusion and thermal convection, heavier isotopes collect at the bottom of the tube and lighter at the top, whereby both fractions may be withdrawn

Gaseous diffusion method

It is based on the principle of difference in the rate of diffusion of gases that differ in densities. In order to separate isotopes by this process, metallic uranium is converted to gaseous compound UF_6. Molar mass of $^{235}UF_6$ and $^{238}UF_6$ are 349 and 352, respectively, so the rate of diffusion of $^{235}UF_6$ is marginally higher than that of $^{238}UF_6$(since rate of diffusion is inversely proportional to

the square root of its density). In this process, gas is pumped through thousands of filter barriers and the operation is repeated thousand of times. After each stage, lighter fraction moves forward while heavier fraction moves backwards.

Centrifugation method
It is based on the principle of centripetal effect. Current of mixed gases $^{235}UF_6$ and $^{238}UF_6$ is passed through a cylinder rotating at a high speed. Lighter$^{235}UF_6$ concentrates in the centre and $^{238}UF_6$ on the walls of the cylindrical centrifuge. It is more economical and can be used for separation on a small scale.

Electromagnetic method
It was developed in 1940 under the Manhattan Project to make enriched uranium used in Hiroshima bomb. It is based on the principle that charged particles are deflected in magnetic field and amount of deflection depends upon particle mass. For this process, ions must be produced by bombarding samples with electrons at low pressure. Stream of charged particles is passed through a system of electric and magnetic fields. Deflection produced will depend on their masses and thus providing a means for their separation.

Laser enrichment method
In this process known as AVLIS (Atomic vapor laser isotope separation), laser is tuned to a wavelength which excites only one isotope of the material and ionizes those atoms preferentially. The ionized atoms can be removed from the samples by applying electric field. Lasers are used to produce charge on ^{235}U atom while ^{238}U is left uncharged. Charged ^{235}U is drawn towards negatively charged plates while uncharged ^{238}U passes unaffected. This process is economical in comparison to other processes due to low cost and low energy input.

Properties
Uranium is silvery white, toxic, highly reactive radioactive metal. It is malleable, ductile and poor conductor of electricity. Powdered uranium is pyrophoric. It is teratogenic. In air, its surface is rapidly converted into non-protective film. Uranium reacts with all the non metals and also forms numerous intermetallic compounds. It reacts slowly with HF, H_2SO_4, H_3PO_4 but rapidly with HCl.

Uses
1. It is used as a fuel in nuclear power plants.
2. It is used in nuclear weapons.
3.^{238}U is used for production of plutonium, which is used in breeder rectors as well as in nuclear weapons.
4. Because of high density it is used for radiation shielding.

Nuclear reactors
Nuclear reactor is a device in which nuclear chain reaction is carried out in controlled manner. Nuclear reactors can be based on nuclear fission or nuclear fusion. Most of the nuclear reactors are nuclear fission based and have a large number of applications. One of the major applications is for generation of electricity (heat produced in the nuclear reaction is used to boil water to produce steam and drive a steam turbine which is used for generation of electricity). Nearly 20% of the world's electricity is derived from nuclear power. Energy released in nuclear fusion can also be used for production of electricity. The International Thermonuclear Energy Reactor

(ITER), a multi-million dollar international project that seeks to make use of fusion energy for electricity production, is to be built in Cadarache, France. Seven international partners in the ITER include India, China, Europe, Japan, South Korea, Russia and the USA. Nuclear reactors can be classified as thermal or fast breeder depending on the energy of the neutrons used for inducing nuclear fission. Thermal reactor is one in which neutrons are in thermal equilibrium with the reactor's materials whereas fast breeders are marked by absence of moderator.

Construction of nuclear reactor

A typical nuclear reactor consists of a reactor core in which the nuclear reaction takes place. Components of a reactor core are (i) fuel rods, (ii)control rods, (iii)moderators, (iv)coolant and (v)shield. Outside the core are turbines, the heat exchanger, and cooling system. Fissionable material in the reactor is called as fuel. Fuel is made in the form of rods. In order to control fission process, rods made of cadmium or boron are suspended between fuel rods. When control rods are lowered fission does not occur because they absorb neutrons. Moderator is used to slow down the speed of neutrons so that they are easily captured by fuel and fission process can occur efficiently. Graphite and water are used as moderators. Coolant is used to absorb heat produced in fission. In most reactors coolant and moderator is the same, i.e., water.

Types of reactors

Various types of nuclear reactors along with fuel, coolant and moderator are given in Fig. 1.

Thermal reactors

In thermal reactors a moderator e.g. graphite is used to slow down the neutrons. Besides graphite,light water or heavy water can also be used. Thermal reactor can be gas cooled or water cooled.

Gas cooled reactors are of the following types.

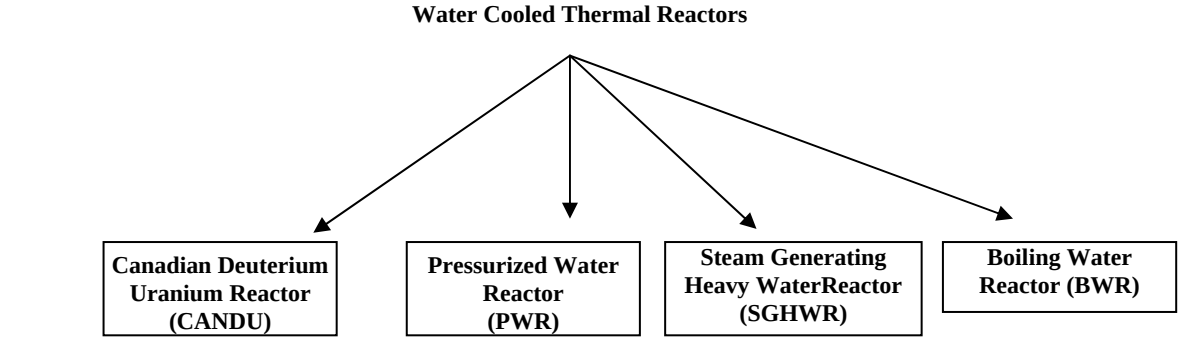
(a) Magnox
(b) Advanced gas-cooled reactor(AGR)
(c)High temperature reactor(HTR)

Water cooled reactor reactors are of following types:

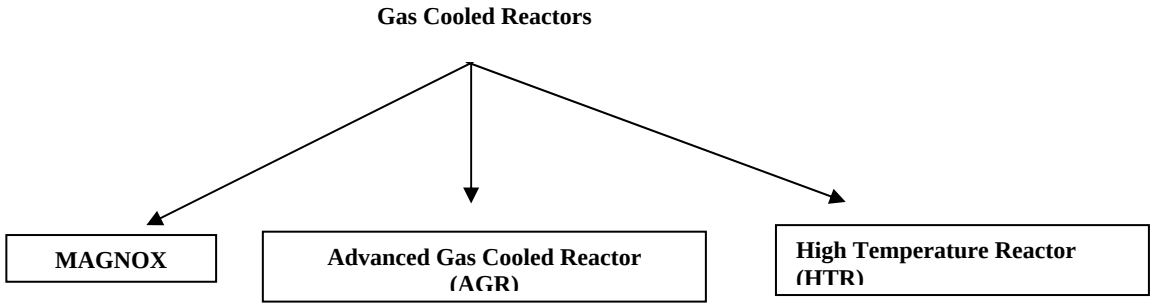
(a)Pressurized water reactor (PWR)
(b)Boling water reactor (BWR)
(c)Steam generating heavy water reactor (SGHWR)
(d)Canadian deuterium uranium reactor (CANDU)

Fast Breeder Reactors

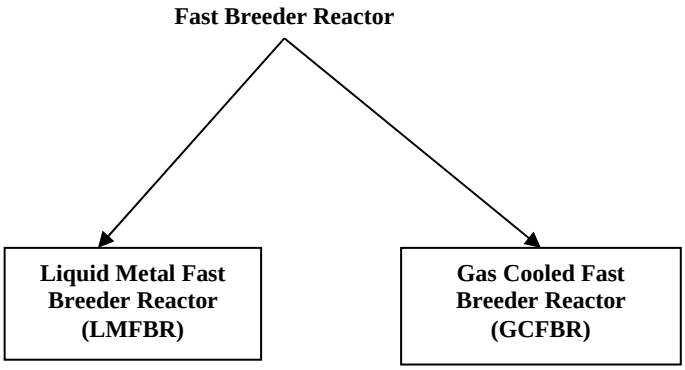
These are termed breeder reactors because fissile material produced is more than that used in the process. Since no moderator is used the neutrons are fast neutrons.Enrichment is also not required as all isotopes of plutonium are fissile. Coolant is either liquid sodium metal (LMFBR) or helium gas (GCFBR). In these breeder reactors, PuO_2 is used as fuel. In case, the depleted UO_2 is used as fuel, then the non fissile ^{238}U is converted in to fissile ^{239}Pu.



Fuel:	UO_2	UO_2	UO_2	UO_2
Enrichment:	natural	3%	2.3%	2.2%
Moderator:	D_2O	H_2O	D_2O	H_2O
Coolant:	D_2O	H_2O	H_2O	H_2O



Fuel:	Uranium Metal	UO_2 Pellets	UC_2
Enrichment:	Natural	2%	90%
Moderator:	Graphite	Graphite	Graphite
Coolant:	CO_2	CO_2	He



Fuel:	PuO_2	PuO_2
Coolant:	Liquid sodium	Helium

Fig. 1 – Different types of nuclear reactors.

Neptunium

Neptunium the first synthetic transuranium element, was discovered by Mc Millan and Abelson by bombardment of uranium with neutrons. Isotopes of neptunium with mass number 231-241 are known. ^{237}Np is most stable isotope with half life of 2.25×10^6. ^{237}Np is available in large quantities scale from spent uranium fuel rods of reactors. Neptunium is a reactive metal and has a low melting point (640ºC). It shows oxidation states 3+, 4+, 5+ and 6+ and 5+ is the most stable oxidation state. Neptunium ions in aqueous solution show characteristic colours(Np^{3+} pale violet, Np^{4+} pale green , Np^{5+} green blue and NpO_2^{2+} purple). Np^{6+} which exists as NpO_2^{2+} varies from colourless to pink or yellow green depending on the acid present. NpO_2^{2+} is stable to disproportionation but in acid solution it disproportionates.

Plutonium

It was the second transuranium elements to be discovered and is named after the planet Pluto.^{238} Pu was produced by G.T. Seaborg et al. by deutron bombardment of uranium. Large numbers of isotopes of plutonium are known and all isotopes are radioactive. The most stable isotope is ^{244}Pu ($t_{½}= 7.6\times10^7$ years) But most important isotope of plutonium is ^{239}Pu ($t_{½} = 2.4\ 9\times10^4$ years) because of its property of being fissionable and hence its usage in nuclear weapons. Plutonium is silvery white in appearance and tarnishes to yellow when oxidized. It exhibits six allotropic modifications (which differ in crystal structure and densities). A large piece of plutonium is warm to touch because of heat produced as a result of α- decay. This heat is sufficient to boil water. Plutonium forms numerous alloys. It combines with oxygen, sulphur, halogens, carbon and other non-metals to form compounds. It reacts slowly with water and dissolves in concentrated hydrochloric, hydroiodic or perchloric acids and is rendered passive in dilute or conc. HNO_3. In aqueous solution, it shows 3+, 4+, 5+ and 6+ oxidation states having characteristic colors(e.g., Pu^{3+} blue lavender and Pu^{4+} brown). Each state is separated from the adjacent state by oxidation potential of one volt. If Pu^{4+} is introduced in water, there will be simultaneous formation of 3+, 5+, 6+ oxidation states (i.e. all four oxidation states coexist).

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

$$Pu^{3+} + 2H_2O \rightarrow PuO_2^+ + 4H^+ + e^-$$

PuO_2^{2+} disproportionates to give Pu^{4+} and PuO_2^{2+}. Plutonium in oxidation state 5+ resembles uranium. Large numbers of compounds of plutonium are similar in properties to corresponding compounds of uranium and neptunium.

Uses

Plutonium is used in the manufacture of nuclear weapons. It is also used in nuclear reactors for generation of electricity and in radionuclide power sources.

Americium

It was synthesized by G. T. Seaborg et al. by subjecting ^{239}Pu to successive neutron capture in a nuclear reactor. It is a silvery white metal and more silvery than plutonium or neptunium as well as more malleable than Np or U. Americium is obtained by reduction of AmF_3 with barium vapour. It forms compounds in oxidation states 2+ to 6+ but Am^{3+} is the most stable oxidation state. Am^{2+} has f^7 configuration and closely resembles Eu^{2+}. Americium does not form 2+ state in aqueous medium. Am^{+4} exists only in solid compounds. AmO_2^{2+} disproportionates to Am^{3+} and AmO_2^{2+}. Americium closely resembles lanthanoids and it is analogous to europium. It forms halides and oxides similar to lanthanoids. Americium also forms the hydride MH_2.

Uses

^{241}Am (produced and recovered from nuclear reactors) is used in smoke detectors. Alpha particles, associated with decay of americium, ionize air between the electrodes causing small current to flow. When smoke particles enter the space between electrodes, the ions get attached to smoke particles, thus causing a decrease in detector current, due to which the alarm sounds. Americium is also used as a source of gamma rays in neutron radiography.

Curium

It was identified by G. T. Seaborg and coworkers. Isotopes with mass numbers 247 ($t_{½}$ = 1.64×10^7years), 245 ($t_{½}$ = 9320 years), 246 ($t_{½}$=5480 years) and 248 ($t_{½}$ = 4.7×10^5 years) are known. It is a silvery white reactive metal obtained by the reduction of its fluoride with barium at 1200-1400ºC. Curium is lanthanoid like and resembles gadolinium. However, it differs from gadolinium in forming compounds in 4+ oxidation state. Concentration of curium must be kept low in experiments due to formation of reducing medium by the action of ^{242}Cm α particles on water. Studies of compounds of curium by X-ray also pose problems, because of fogging of film due to radioactivity and destruction of lattice by emitted particles. It shows 3+ and 4+ oxidation states. Cm^{3+} has f^7 configuration and hence is more stable than Cm^{4+}. Cm^{4+} is stabilized in aqueous solution by fluoride ion. Reactions of Cm^{3+} in solution resemble lanthanoids and actinoid ions in 3+ oxidation states. Solid curium compounds CmF_3, CmF_4, Cm_2O_3 and CmO_2 are known.

Uses

Curium is used in radionuclide power sources in satellites and crewless space probes. On lunar missions , ^{242}Cm has been used to bombard moon's soil with α particles to determine the soil composition.

Berkelium

It was synthesized by Seaborg et al. by bombardment of ^{241}Am with helium ions and named after the site of its discovery, Berkeley. It exists in two crystalline modifications and exhibits 3+ and 4+ oxidation states both in aqueous solution and solid state. Bk^{4+} is stable due to half filled *f* sub shell. In solution, Bk^{3+} is oxidized by bromate to yellow or orange coloured Bk^{4+}. Berkelium metal is obtained by reduction of BkF_3 with Li. Compounds of berkelium such as Bk_2O_3, BkX_3 (X= F, Cl, Br, I), BkOX (X = Cl, Br, I) are known. It also forms cubic hydride, BkH_{2+X}, and hexagonal, BkH_3. It closely resembles terbium, the corresponding lanthanoid. BkO_2 and $Cs_2[BkCl_6]$, cesium have also been isolated.

Californium

It was produced by Seaborg et al. by bombardment of microgram quantities of ^{242}Cm with helium ions. Isotopes of californium with mass number), 244($t_{½}$ = 470 years), 245($t_{½}$=55 minute), 250($t_{½}$ = 10 years), 251($t_{½}$ = 700 years), and 252($t_{½}$ = 2.2 years) are known. Californium was studied using tracer techniques and shows properties similar to lanthanoids. It shows 2+, 3+ and 4+ oxidation states. Cf^{3+} state exists both in solution and solid compounds while Cf^{4+} is relatively unstable and compounds are obtained only as solids. Compounds of californium in 4+ oxidation state CfF_4, CfO_4 ,3+ state Cf_2O_3, 2+ state $CfBr_2$, and CfI_2 are known(compounds of californium in +2 state are less stable).

Uses

Californium is used as an efficient source of neutrons (one microgram of californium -252 produces 170 million neutrons per minute). ^{252}Cf is used in neutron radiography, in neutron

moisture gauges which are used to find water and oil bearing layers in oil wells and for irradiation of tumors (when gamma ray treatment is ineffective).

Einsteinium and Fermium

Both einsteinium and fermium were detected in the debris of thermonuclear explosion that occurred in South pacific in 1952. All isotopes of both fermium and einsteinium are radioactive. Isotopes of fermium with mass no. 248-256 are known and obtained by bombardment of uranium and plutonium isotopes with heavy ions or by bombardment of α particles on californium isotopes. Isotopes of einsteinium with mass no. 245-246, 248-252, and 253 and 255 are known. The most stable isotope with mass no.254 has half life of 270 days. Isotopes of einsteinium decay either by α- particle emission, e. g., isotopes with mass no. 245, 252, 254 or by electron capture, e.g., isotope with mass no.250. Both fermium and einsteinium show 3+ oxidation state. Einsteinium does not form 4+ state, but shows 2+ state in dihalides. Es^{3+} is stable in solution and in solids. Fm^{2+} state is more stable.

Mendelevium

It was the first element to be discovered on atom at a time basis. ^{256}Md was produced by bombardment of ^{253}Es with accelerated α particles. Ion exchange treatment of the dissolved gold foil gave only one to three atoms of ^{256}Md ($t_{½}$ = 1.3 hr). ^{256}Md decays by K- electron capture to ^{256}Fm. Isotope of mendelevium with mass no 255 ($t_{½}$ =30m) is produced by bombardment of ^{253}Es with α- particle. Md^{2+} is stable in aqueous solution and mildly reducing conditions while Md^{3+} state is stable both in solution and in solids.

Nobelium

It is named after Alfred Nobel. Ghiorso et al. prepared ^{254}No by bombardment of ^{256}Cm with accelerating ^{12}C ions. Isotopes of nobelium with mass no), 252 ($t_{½}$= 2.3 second), 254 ($t_{½}$ =55 second), 255 ($t_{½}$ = 3 minute) 257 ($t_{½}$=23 second), are known. It shows 2+ and 3+ oxidation states. No^{2+} has f^{14} configuration and is more stable than No^{3+}.

Lawrencium

Ghiorso et al. identified lawrencium in 1961. Mixture of californium isotopes was bombarded with accelerated boron ions, and atoms of lawrencium (mass no. 257) recoiled from the target into an atmosphere of helium where these were electrostatically collected on copper conveyor tape. Another isotope of lawrencium with mass number.256 ($t_{½}$ = 45 second) was produced by bombardment of oxygen ions on ^{243}Am. Electronic configuration of lawrencium is [Rn] $5f^{14}\ 6d^{1}\ 7s^{2}$ It exists in 3+ oxidation state and resists both oxidation and reduction (due to extra stability of fully filled *f* sub shell).

Compounds of Actinoids

Halides

Actinoids form extensive series of halides in 2+, 3+, 4+, 5+and 6+ oxidation states. Number of halides formed in 2+ state are much less as compared to other oxidation states. Largest number of halides are formed in 3+ oxidation state (except Th and Pa which form halides in 4+ and 5+ oxidation states). Halides of actinoids in various oxidation states are listed in Table 6.

Table 6 - Halides of Actinoids

Oxidation state	Fluorides	Chlorides	Bromides	Iodides
2+		$AmCl_2$,Black	$AmBr_2$, Black	AmI_2 , Black
		$EsCl_2$	$EsBr_2$	EsI_2
3+				ThI_3, Black
				PaI_3, black
	UF_3 , Black	UCl_3, Green	UBr_3, Red	UI_3, Black
	NpF_3, Purple	$NpCl_3$, Green	$NpBr_3$, Green	NpI_3,.Purple
	PuF_3, Violet	$PuCl_3$, Green	$PuBr_3$,	PuI_3, Green
	AmF_3, Pink	$AmCl_3$, Pink	$AmBr_3$, White	AmI_3, Yellow
	CmF_3, White	$CmCl_3$, White	$CmBr_3$, White	CmI_3, White
	BkF_3, Yellow	$BkCl_3$, Green	$BkBr_3$, Yellow	BkI_3, Yellow
	CfF_3, light green	$CfCl_3$, Green	$CfBr_3$,.Pale green	CfI_3, Yellow
	EsF_3	$EsCl_3$	$EsBr_3$	EsI_3
4+	ThF_4, White	$ThCl_4$, White	$ThBr_4$, White	ThI_4, White
	PaF_4, Brown	$PaCl_4$, Green	$PaBr_4$, Brown	PaI_4, Green
	UF_4, Green	UCl_4, Green	UBr_4, Brown	UI_4, Black
	NpF_4, Green	$NpCl_4$, Red	$NpBr_4$, Dark red	
	PuF_4, Red brown			
	AmF_4, Tan			
	CmF_4, Brown			
	BkF_4,			
	CfF_4, Green			
5+	PaF_5, White	$PaCl_5$, Yellow	$PaBr_5$, Dark red	PaI_5, Black
	UF_5, Pale blue	UCl_5, Brown	UBr_5, Brown	
6+	UF_6, White	UCl_6, Dark green		
	NpF_6, Orange			
	PuF_6, Brown			

Dihalides

Dihalides of americium, thorium and einsteinium are known.

Method of preparation

Halides of americium such as $AmCl_2$, $AmBr_2$, and AmI_2 are prepared as follows:

$$Am + HgX_2 \xrightarrow{400-500°C} AmX_2 + Hg \text{ (X=Cl, Br, I)}$$

Thorium di-iodide is prepared by heating thorium tetra- iodide and thorium at 700-800°C in a tantalum container.

$$ThI_4 + Th \xrightarrow{700\text{-}850°C} 2ThI_2$$

Structure and properties

- Halides of americium are structurally similar to europium halides. ThI_2 is golden colored and an electrical conductor. ThI_2 is regarded as Th^{4+}, $2I^-$ and 2 electrons in conduction band.

Trihalides

- Fluoride MF_3 (M=U→Es)
- Chloride MCl_3(M=U →Es)
- Bromide MBr_3 (M=U→Es)
- Iodide MI_3 (M = Th→Cf)

Method of preparation

Method of preparation depends on the nature of actinoids involved but in general heavier actinoid (Am→Cf) halides are prepared by heating sesquioxide or dioxide in HX, while lighter actinoids require reducing conditions (for example, for the preparation of neptunium and plutonium trifluorides, H_2/HF mixture is used, since 3+ state is of reducing nature).

$$MO_2 + 4HF \rightarrow MF_3 + \tfrac{1}{2}F_2 + 2H_2O$$

Neptunium fluoride is prepared as follows.

$$2NpO_2 + 6\,HF + H_2 \xrightarrow{\Delta} 2\,NpF_3 + 4\,H_2O$$

Fluorides can also be prepared by heating or reduction of tetrafluorides e.g.

$$UF_4 \xrightarrow[900°C]{Al} UF_3$$

$$PuF_4 \xrightarrow{\Delta} PuF_3$$

Chlorides of plutonium, einsteinium and uranium are prepared as follows:

$$Pu \xrightarrow{Cl_2,450°C} PuCl_3$$

$$Es_2O_3 \xrightarrow{HCl,500°C} EsCl_3$$

$$UH_3 \xrightarrow{HCl,300°C} UCl_3$$

Bromides of californium, plutonium and uranium are prepared as follows:

$$Cf_2O_3 \xrightarrow{HBr,800°C} CfBr_3.$$

$$PuBr_3.6H_2O \xrightarrow[vacuum]{70-100°C} PuBr_3$$

$$U \xrightarrow{Br_2,500°C} UBr_3$$

Iodides of neptunium, americium and uranium are prepared as follows.

$$NpO_2 \xrightarrow{AlI_3,500°C} NpI_3$$

$$AmCl_3 \xrightarrow{NH_4I/H_2,400°C} AmI_3$$

$$2U + 3I_2 \xrightarrow{500°C} 2UI_3$$

Thorium tri-iodide is prepared by heating tetra-iodide with thorium at 600-700°C in tantalum container.

$$3ThI_4 + Th \xrightarrow{600\text{-}700°C} 4ThI_3$$

Stucture of trihalides

- All trifluorides (except CfF_3) have structure similar to LaF_3 with irregular arrangement of nine fluoride ions around each metal with fluorine bridging to metal ions. CfF_3 has eight coordinated structure.
- All chlorides are isostructural with each chloride ion bridging a metal ion to two other metal ions. The metal ions are arranged in six membered rings stacked vertically one above the other. UBr_3 and α-$NpBr_3$ have same structure as chloride while β-$NpBr_3$, $PuBr_3$, $AmBr_3$, $CmBr_3$, $BkBr_3$ have different structures.
- Structure of tri-iodides resemble those of lanthanoid iodides. PaI_3, UI_3, NpI_3 and PuI_3 have eight coordinated $PuBr_3$ structure whereas AmI_3, CmI_3, BkI_3, CfI_3 have six coordinated $FeCl_3$ structure.

Properties of trihalides

- Large number of tri halides are coloured as shown in Table 6.Trihalides of actinoids show properties similar to lanthanoid trihalides. Trifluorides are ionic, high melting and insoluble in water whereas other trihalides are hygroscopic, and water soluble e.g. UCl_3 and UBr_3 are hygroscopic and UCl_3 dissolves in water to give purple solution which gives off H_2 to form green solution of U^{4+}. UCl_3 reacts with air to give UO_2Cl_2. Halides of Np, Pu and Am are similar to uranium halides in structure and properties. ThI_3 is different from other trihalides (since Th^{4+} is more stable). ThI_3 reacts with water and liberates hydrogen. It is readily oxidized by air. ThI_3 is regarded as Th^{4+}, $3I^-$and an electron in conduction band.

<u>Dihalides</u>

Dihalides of americium, thorium and einsteinium are known.

Method of preparation

Halides of americium such as $AmCl_2$, $AmBr_2$, and AmI_2 are prepared as follows:

$$Am + HgX_2 \xrightarrow{400-500°C} AmX_2 + Hg \ (X=Cl, Br, I)$$

Thorium di-iodide is prepared by heating thorium tetra- iodide and thorium at 700-800°C in a tantalum container.

$$ThI_4 + Th \xrightarrow{700\text{-}850°C} 2ThI_2$$

Structure and properties

- Halides of americium are structurally similar to europium halides. ThI_2 is golden colored and an electrical conductor. ThI_2 is regarded as Th^{4+}, $2I^-$and 2 electrons in conduction band.

<u>Tetrahalides</u>

- Fluoride MF_4(M=Th→Cf)
- Chloride MCl_4(M= Th→Np)
- Bromide MBr_4(M=Th→Np)
- Iodide MI_4(M=Th→U)

Method of preparation

In general, tetrafluorides MF_4 (M=Th→Pu) are prepared by heating dioxides in HF but in the presence of H_2 for PaF_4 (to prevent oxidation) and in the presence of O_2 for NpF_4 and PuF_4 (to prevent reduction). AmF_4, CmF_4, CfF_4 are prepared by heating trifluoride with fluorine.

$NpO_2 + 4HF \xrightarrow{\Delta} NpF_4 + 2H_2O$

$Pa_2O_5 + H_2(excess) + 8HF \xrightarrow{600°C} 2PaF_4 + 5H_2O$

Tetrachlorides are prepared by heating dioxides in CCl_4 or chlorinated hydrocarbons while tetrabromides and tetraiodides are prepared from the elements e.g.

$ThO_2 \xrightarrow{CCl_2F_2, 400°C} ThF_4$

$Th \xrightarrow{Br_2, 700°C} ThBr_4$

$Th \xrightarrow{I_2, 400°C} ThI_4$

$PaBr_4$ and PaI_4 are obtained by reduction of $PaBr_5$ and PaI_5 by aluminium.

$PaBr_5 \xrightarrow{Al\ at\ 400°C} PaBr_4$

Structure and properties

- In case of fluorides metal is eight coordinated, surrounded by slightly distorted square anti prismatic array of F^- ions. Tetrafluorides are insoluble in water. ThF_4, UF_4 and PuF_4 are precipitated as hydrates.$MF_4.2½\ H_2O$. Tetrachlorides, bromides and iodides are hygroscopic and dissolve readily in water and polar solvents. Throrium tetrahalides are white in colour(due to absence of d or f electrons), high meting and hydrolyse in moist air giving oxo halides, $ThOX_2$. On strong heating, ThI_4 decomposes to the elements. Hence thorium is purified by heating ThI_4 (Van Arkel Method).

<u>Pentahalides</u>

Pentahalides are not formed by actinoids beyond neptunium. Only protactinium forms all the pentahalides, i.e. fluoride, chloride, bromide and iodide, since 5+ is most stable oxidation state for Pa. Uranium also forms pentahalides UX_5 (X=F,Cl,Br). NpF_5 is also known.

Method of preparation

$PaBr_5$ and UF_5 are prepared as follows:

$Pa_2O_5 \xrightarrow{C + Br_2,\ 700°C} PaBr_5$

$UF_6 + Me_3SiCl \rightarrow Me_3SiF + \frac{1}{2}Cl_2 + UF_5$

Uranium pentafluoride can also be prepared by reduction of uranium hexafluoride.

$UF_6 + HBr \xrightarrow{65°C} UF_5 + HF + \frac{1}{2}Br_2$

Uranium petachloride is prepared from uranium oxide UO_3.

$UO_3 \xrightarrow{SiCl_4, 450°C} UCl_5$

Structure and properties

- $PaCl_5$ has polymeric structure consisting of infinite chains of irregular pentagonal bipyramidal $PaCl_7$ units sharing edges. $PaCl_5$ sublimes at 160°C, is soluble in THF and readily hydrolyses to oxochlorides such as Pa_2OCl_8. UCl_5 has dimeric structure, in which two UCl_6 octahedra share an edge in both solid as well as in solution. Except PaF_5 other pentahalides are colored as listed in Table 6. Pentahalides of uranium are unstable and undergo either decomposition or disproportionation e.g., UCl_5 disproprortionates to UCl_4 and UCl_6.

$2UCl_5 \xrightarrow{Room\ temperature} UCl_4 + UCl_6$

$2UCl_5 \xrightarrow{vacuum} 2UCl_4 + Cl_2$

Hexahalides

- MF_6(M=U, Np, Pu) and UCl_6 are known.

Method of preparation

Uranium hexafluoride is prepared on a large scale since it is used for separation of uranium isotopes (by gas diffusion method). It is prepared by following methods:

$$UF_4 + F_2 \xrightarrow{220°C} UF_6$$

$$UO_2F_2 + 2F_2 \xrightarrow{270°C} UF_6 + O_2$$

$$2UF_4 + O_2 \xrightarrow{800°C} UF_6 + UO_2F_2$$

Plutonium hexafluoride is prepared by direct combination of elements or by the reaction of plutonium tetrafluoride with oxygen at high temperature whereas NpF_6 is prepared from NpF_4

$$2PuF_4 + O_2 \xrightarrow{\text{high temperature}} PuF_6 + PuO_2F_2$$

$$NpF_4 + F_2 \xrightarrow{\Delta} NpF_6$$

Structure and properties

- Uranium hexafluoride and hexachloride are octahedral and dissolve in strong acids to give UO_2^{2+} ions. Halides are sensitive to moisture. UF_6 is colourless, melting point of 64ºC. It is powerful fluorinating agent and gets rapidly hydrolyzed by water.

Oxides

Uranium forms a large number of oxides such as U_3O_8(most stable),UO_2, UO_3, and U_2O_5. UO_2 is used as a nuclear fuel. Thorium forms only one oxide i.e. ThO_2. Protactinium forms Pa_2O_5, PaO_2. Neptunium forms Np_2O_5, NpO_2 and NpO. The oxides MO, MO_2, and M_2O_3(M= Am, Cm, Bk, Cf) are formed in 2+, 3+, and 4+ oxidation states (Table 7).

Table 7 - Oxides of Actinoids

Element		Oxidation state			
	2+	3+	4+	5+	6+
Thorium			ThO_2		
Protactinium	PaO		PaO_2	Pa_2O_5	
Uranium	UO		UO_2	U_2O_5	UO_3
Neptunium	NpO		NpO_2	Np_2O_5	
Plutonium	PuO	Pu_2O_3	PuO_2		
Americium	AmO	Am_2O_3	AmO_2		
Curium	CmO	Cm_2O_3	CmO_2		
Berkelium	BkO	Bk_2O_3	BkO_2		
Californium	CfO	Cf_2O_3	CfO_2		
Einsteinium		Es_2O_3			

Compounds in magenta are the most stable oxides for the element.

Method of Preparation

UO_3 is prepared by heating uranyl nitrate, while U_3O_8 and UO_2 are prepared from UO_3 as follows:

$$UO_2(NO_3)_2.2H_2O \xrightarrow{350°C} UO_3$$

$$3UO_3 \xrightarrow{700°C} U_3O_8 + \tfrac{1}{2}O_2$$

$$UO_3 + CO \xrightarrow{350ºC} UO_2 + CO_2$$

Thorium oxide is formed by heating nitrate or the metal in air. Pa_2O_5 is obtained by heating protactinium hydroxide in air. Np_2O_5 is prepared by reaction of neptunium hydroxide (4+ oxidation state) with ozone and heating the resulting $Np_2O_3.H_2O$ at 300ºC under vacuum. Dioxides of Np, Pu and Am are prepared by heating nitrates or hydroxides in air.

Structure and properties

- Monoxides have fcc rock salt structure while dioxides, have fcc fluorite structure (in which metal atom has coordination number eight) and contain electrons in delocalized conduction bands. Most of the oxides are colored except ThO_2, Pa_2O_5, and Cm_2O_3 which are white in colour. Actinoid oxides are good refractory materials. Thorium oxide has the highest melting point (3390ºC). Uranium oxides (UO_3, U_3O_8 and UO_2) are basic and dissolve in HNO_3 forming uranyl ion UO_2^{2+}. Crystallizing the solution gives uranyl nitrate $UO_2(NO_3)_2(H_2O)_n$, n= 2,3 or 6 depending upon whether crystallised from fuming ,concentrated or dilute HNO_3

Hydrides

Hydrides of the type MH_2 (M=Th, Np, Pu, Am, Cm, Bk) and MH_3 (Pa→Bk) have been obtained e.g. Uranium reacts with hydrogen at 250 to 300ºC to give UH_3 as black pyrophoric powder.

$$U + \tfrac{3}{2}H_2 \xrightarrow{\Delta} UH_3$$

Most of the actinoid hydrides are black in colour and have cubic or tetragonal structure. Hydrides are thermally unstable and reactive towards air and moisture.

$$2UH_3 + 4H_2O \rightarrow 2UO_2 + 7H_2$$

Uranium hydride reacts with Cl_2, H_2S, HF, HCl and NH_3 to give UCl_4, US_2, UF_4, UCl_3 and UN.

$$UH_3 \xrightarrow{Cl_2,\,200°C} UCl_4$$

$$UH_3 \xrightarrow{H_2S,\,450°C} US_2$$

$$UH_3 \xrightarrow{HCl,\,250\text{-}300°C} UCl_3$$

$$UH_3 \xrightarrow{HF,\,400°C} UF_4$$

Thorium reacts with hydrogen to form hydrides ThH_2 and $ThH_{3.75}$. Thorium hydride is completely decomposed to the elements by heating at 900°C in vacuum. It reacts readily with oxygen to form ThO_2. Plutonium reacts with hydrogen to give PuH_2 (black ,cubic) and PuH_3(black hexagonal).

Complexes of actinoids

Complexes of actinoids in oxidation states 3+ to 6+ are known. Complexes formed in oxidation state 4+ outnumber the complexes in other oxidation states because these metals have the highest effective charge in this oxidation state A few complexes of actinoids along with their geometries are listed in Table 8. For a given oxidation state, a range of coordination numbers is allowed. Coordination numbers between six and twelve are reported for $M^{3+}$and M^{4+}ions and between two and eight for actinyl ions. Aqua ions of actinoids exhibit coordination number that varies with oxidation state e.g.,4 to 5 for $MO_2^{+,}$ 5 to 6 for MO_2^{2+}, 8 to 10 for M^{3+} and 9 to 12 for M^{4+} ions. Stability of actinide complexes for a given oxidation state increases with atomic number.

Actinoids also form complexes with oxo anions (e.g., NO_3^-, SO_4^{2-}, CO_3^{2-}, $C_2O_4^{2-}$), halide ions and other chelating agents.

Table 8 – Complexes of Actinoids

Oxidation state	Coordination number	Geometry	Examples
3+	6	Octahedral	$[M(acac)_3]$, $[M(H_2O)_6]^{3+}$, $[MCl6]^{3-}$ (M=Np, Am, Bk)
	8	Bicapped trigonal prism	$[AmCl_2(H_2O)_6]^+$
4+	6	Octahedral	$[MX_6]^{2-}$ (M=U, NP, Pu; X=Cl, Br)
	8	Cubic	$[M(NCS)_8]^{4-}$ (M=Th→Pu)
	8	Dodecahedral	$[Th(ox)_4]^{4-}$
	8	Square antiprismatic	$[M(acac)_4]$ (M= Th, U, Np, Pu)
	12	Icosahedral	$[Th(NO_3)_6]^{2-}$
5+	8	Cubic	$Na_3[MF_8]$(M= Pa, U, Np)
	9	Tricapped trigonal prism	$M_2[PaF_7]$ (M= NH_4, K, Rb, Cs)
6+	8	Hexagonal bipyramidal	$[UO_2(NO_3)_2\ (H_2O)_2]$

Halide complexes

Actinoids form a large number of complexes with halide ions in different oxidation states. Metals in 4+ oxidation state form fluoro complexes of the type $[MF_5]^-$, $[MF_6]^{2-}$, $[MF_8]^{4-}$ and $[M_6F_{31}]^{7-}$ (M = U, Np, Pu and Am). Chloro complexes such as Cs_2MCl_6 and $(NEt_4)_2MCl_6$ (M = U, Np, Pu and Am) are also known. Thorium forms fluoro complexes such as K_5ThF_9, Na_4ThF_8, and Na_3ThF_7. Besides fluoro complexes, thorium also forms chloro, bromo and iodo complexes such as Rb_2ThCl_6, $(C_5H_5NH)_2ThBr_6$. Uranium in 4+ oxidation state, forms UF_6^{2-}, UF_7^{3-}, UF_8^{4-}, UCl_6^{2-}, and UBr_6^{2-}. Complexes Cs_2UCl_6 and $(NH_4)_4UF_8$ and $(NH_4)_2UF_6$ are prepared as follows:

$$2CsCl + UCl_4 \xrightarrow{\text{aqueous HCl}} Cs_2UCl_6$$

$$4NH_4F + UF_4 \xrightarrow{100°C,\ \text{sealed tube}} (NH_4)_4UF_8 \xrightarrow{\text{heat}} (NH_4)_2UF_6$$

Metals in 5+ oxidation state also form fluoro complexes such as $[MF_6]^-$(M=Pa, U), $[MF_7]^{2-}$ (M=U, Np, Pu), and $[MF_8]^{3-}$(M=U, Np). Protactinium in 5+ oxidation state forms complexes such as PaF_8^{3-}, PaF_7^{2-}, PaF_6^- $PaCl_8^{3-}$, $PaCl_6^-$, $PaBr_6^-$ and PaI_6^-. Complex K_2PaF_7 is prepared by reaction of KF with PaF_5.

$$2KF + PaF_5 \xrightarrow[\text{acetone}]{17M\,HF} K_2PaF_7$$

Coordination number of protactinium is eight in $RbPaF_6$ and Na_3PaF_8 but 9 in K_2PaF_7. Chloro, bromo and iodo complexes are not formed in aqueous solution due to hydrolysis. Na_3NpF_8 is prepared by the action of the sodium fluoride on neptunium hexafluoride.

$$NpF_6 + 3NaF \xrightarrow{200°C} Na_3NpF_8 + \tfrac{1}{2}F_2$$

Fluoro complex of plutonium $Cs[PuF_6]$ is prepared by the action of CsF on PuF_6

$$PuF_6 + 2CsF \xrightarrow{300°C} F_2 + Cs_2PuF_6 \xrightarrow{F_2,\ 300°C} CsPuF_6$$

Complexes $Na_3[MF_8]$ (M=Pa, U, Np) have cubic structure and coordination number is eight. Complexes $Cs[MF_6]$ (M=U, Np, Pu) have octahedral structure with coordination number six.

Complexes with O- donor ligands

Complexes of actinoids with O-donor ligands are more stable than complexes with S- donor ligands. Acetylacetone complexes $M(acac)_4$ of uranium, neptunium and plutonium are known. Carbonato complexes $[M(CO_3)_5]^{6-}$,(M=Th,U, Pa) and nitrato complexes $[M(NO_3)_6]^{2-}$(M=Th, U, Np, Pu) have been reported.

Organometallic compounds

Actinoids form organometallic compounds similar to those formed by *d* block elements. Organometallic compounds such as cyclopentadienyls, cycloctatetraenyls, annulene and cycloheptatrienyls are known. Due to involvement of 5*f* orbitals in bonding in organoactinoids, these compounds are more covalent than organolanthanoids. Organoactinoid compounds, in general, are thermally stable but sensitive to air and water.

Cyclopentadienyls

The trivalent actinoids form cyclopentadienyls such as $[M(C_5H_5)_3]$ (M= U → Cf);whereas tetravalent actinoids form $[M(\eta^5\text{-}C_5H_5)_4]$(M=Th→Np) and $[M(\eta^5\text{-}C_5H_5)_3X]$, (M= Th, U, Np) where X = halide, alkyl or alkoxy group.

Method of preparation

Triscyclopentadienyls M $(C_5H_5)_3$ (M= Pu, Am, Cm, Bk, Cf) are prepared from trichlorides and beryllium cyclopentadienyl.

$$2MCl_3 + 3Be(C_5H_5)_2 \xrightarrow{65°C} 2M(C_5H_5)_3 + 3BeCl_2$$

$U(C_5H_5)_3$ is prepared from UCl_3 and potassium cyclopentadienyl.

$$UCl_3 + KC_5H_5 \xrightarrow{\text{Benzene}} U(C_5H_5)_3 + 3KCl$$

$[M^{IV}(C_5H_5)_4]$ (M= Th,U, and Np) are prepared from MCl_4 and potassium cyclopentadienyl.

$$MCl_4 + 4KC_5H_5 \xrightarrow{\text{Benzene}} [M(C_5H_5)_4] + 4KCl$$

$Pa(C_5H_5)_4$ is prepared from $PaCl_4$ and $Be(C_5H_5)_2$. Halides derivatives such as $[M^{IV}(C_5H_5)_3X]$ (M= Th andU) are prepared as follows:

$$MCl_4 + KC_5H_5 \xrightarrow{\text{Benzene}} [M(C_5H_5)_3X] + 3KCl$$

Properties

These compounds are thermally stable but sensitive to air and water, e.g., $M(C_5H_5)_3$ compounds are hydrolyzed by water as follows:

$$M(C_5H_5)_3 + 3H_2O \rightarrow M(OH)_3 + 3C_5H_6$$

However $U(C_5H_5)_3Cl$ gives a stable $[U(C_5H_5)_3]^+$ species in water, suggesting that bonding of cyclopantadienyl group in U(IV) compounds is different from U(III) compounds.

Triscyclopentadienyls $M(C_5H_5)_3$ are similar to lanthanoid compounds and form adducts. In $[U(C_5H_5)_3Cl]$ and $[Th(C_5H_5)_3Cl]$, Cl can be replaced by groups such as F, Br, OR, BH_4 etc .$[U(C_5H_5)_3R]$ (R= Me, Bu, Ph etc.) can be prepared by action of lithium alkyls or phenyl on $U(C_6H_5)_3Cl$

Annulene and cycloheptatrienyl

[M (η^8–$C_8H_8)_2$] (M=Th→Pu) are known. Uranocene or bis(cyclo-octatetraenyl)uranium(IV) is prepared as follows:

$$UCl_4 + 2K_2C_8H_8 \xrightarrow{THF} [U(C_8H_8)_2] + 4KCl$$

Uranocene is green coloured, pyrophoric compound stable to water and acetic acid. It has sandwich structure with planar ring and D_{8h} symmetry. $M(C_8H_8)_2$(M= Th, Np, and Pu) have similar structure but get decomposed by water. The cycloheptatrienyls are prepared by interaction of UCl_4 and C_7H_8 in THF.

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