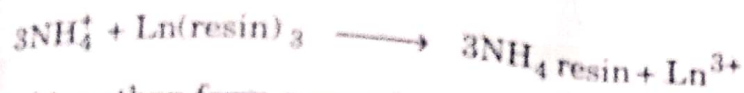
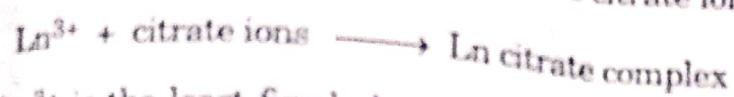


greater will be the hydration. Therefore, in case of lanthanide ions, the smallest lanthanide ion, namely Lu^{3+} will be the most heavily hydrated. Thus it will have the maximum size and therefore the least firmly bound to the resin while La^{3+} (aq) will have the minimum size and therefore will be the most firmly bound to the resin.

A solution containing several lanthanide ions is dropped slowly down a column of synthetic ion exchange resin so that the lanthanide ions are bound less firmly to the resin in the order La^{3+} to Lu^{3+} . They are then eluted from the column by using a solution containing citric acid and ammonium citrate. Firstly the ammonium ions elute the metal ions from the resin as:



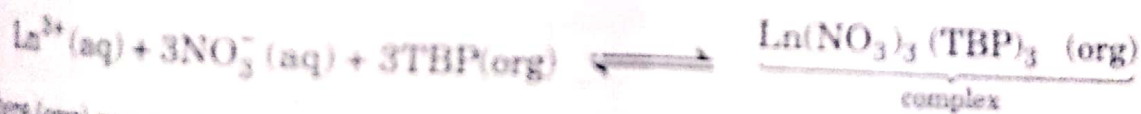
The metal ions then form a complex with the citrate ions.



Since Lu^{3+} is the least firmly bound to resin therefore on elution, Lu citrate complex is obtained first from the bottom of the column while La citrate complex emerges last of all from the bottom of the column. Complexing agents such as EDTA, aminocarboxylic acids, and hydroxycarboxylic acids have also been found to be convenient eluants or eluates or eluting agent.

In actual practice the process of elution is to be repeated several times by careful control of concentration of ammonium citrate acid solutions.

(ii) **Solvent Extraction method.** This method is based on the differences in the solubility of lanthanide salts in water and an immiscible or partially miscible organic solvent. These organic solvents are called *extracting solvents* or *extractants*. The technique consists of passing the aqueous solution of lanthanide salts counter-current to the organic solvent which extracts the lanthanides from water. The most widely used extracting solvent is tri-n-butyl phosphate (TBP) in an inert medium like kerosene or xylene to extract the lanthanides from nitric acid solutions. TBP forms complexes with Ln^{3+} (aq) ions in presence of NO_3^- ions.



where (org) represents the organic phase. The extent of extraction of lanthanide elements by organic solvents increases with increase in atomic number because increase in nuclear charge results in decrease in ionic radius which in turn increases complexation.

Solution of lanthanide nitrate in nitric acid is made to flow counter to a solution of tri-n-butyl phosphate in kerosene and thus some of the lanthanide nitrates migrate to the organic solvent layer. Thus by using a continuous counter current method, it is possible to separate lanthanides such as Gd from other lanthanides on a kilogram scale. Pure Gd (95%) has been prepared by this method.

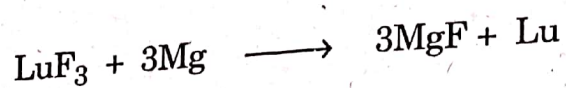
12.7 Production of Lanthanide Metals

(i) **Electrolysis of fused chlorides.** The anhydrous lanthanide (+3) chlorides are fused with Na, K or calcium chloride by external heating and the molten mass is electrolysed in an iron pot or in a refractory lined pot which serves as the anode. Graphite cathodes are used. The molten metal collects as a pool at the bottom of the pot from where it is drawn and cast into ingots.

(ii) **Reduction of anhydrous chlorides with Na.** Lighter lanthanides such as La, Ce and Gd can be easily prepared by reduction of anhydrous lanthanide chlorides with Na at 1000°C.



(iii) **Reduction of anhydrous fluorides with Ca or Mg.** Heavier lanthanides such as Lu are generally prepared by the reduction of anhydride fluoride with Ca or Mg metal at 1000°C.



(iv) **Thermal decomposition of lanthanide-mercury amalgam.** Using a mercury cathode an amalgam of the lanthanides may be prepared by the electrolysis of aqueous solution. The amalgam thus formed is thermally decomposed to get the metals in a finely divided state, but complete elimination of mercury is difficult.

11.7 Applications and uses of Lanthanides and their compounds.

(A) Applications and uses of elements.

(i) Lanthanides are used in *metallothermic reactions* due to their extraordinary reducing property. *Lanthanido-thermic* processes can yield sufficiently pure Nb, Zr, Fe, Co, Ni, Mn, Y, U, B and Si. These metals are also used as de-oxidizing agents particularly in the manufacture of Cu and its alloys.

(ii) **Uses of mish-metals.** Alloys of lanthanides are known as *mish-metals*. The major constituents of mish-metals are Ce (45-50%), La (25%), Nd (5%) and small quantities of other lanthanide metals and Fe and Ca impurities.

Mish-metals are used for the production of different brands of steel like heat resistant, stainless and instrumental steels. The addition of 0.75% of mish-metal to steel raises its yield point and its workability in heated state and improves its resistance to oxidation. Mish-metal is an excellent scavenger for absorbed oxygen and sulphur in metallurgy.

Mg-alloys containing about 30% mish metal and 1% Zr are used for making parts of jet engine.

La, Ce, Pr, Nd mixed with steel are used in cigarette lighters, toys, flame throwing tanks. Cerium magnesium alloys are used in flash light powders.

(ii) Uses of the Lanthanide Compounds

The uses of the compounds of lanthanides can broadly be classified as follows.

(a) **Non-nuclear applications.** The following uses are important.

(i) **Ceramic applications.** CeO_2 , La_2O_3 , Nd_2O_3 and Pr_2O_3 are widely used for devolorizing glass.

Approximately 1% CeO_2 is used in the manufacture of protective transparent glass blocks to be used in nuclear technology because these blocks are not affected by prolonged exposure to radiations. Because lanthanide oxides can absorb ultra-violet rays, these are used as additives in glasses for special purposes, e.g., for making (i) sun glasses (by adding Nd_2O_3) (ii) goggles for glass blowing and welding work ($\text{Nd}_2\text{O}_3 + \text{Pr}_2\text{O}_3$) (iii) glasses protecting eyes from neutron radiation ($\text{Gd}_2\text{O}_3 + \text{Sm}_2\text{O}_3$) etc.

The addition of more than 1% CeO_2 to a glass gives it a brown colour. Nd_2O_3 and Pr_2O_3 give respectively red and green colours. ($\text{Nd}_2\text{O}_3 + \text{Pr}_2\text{O}_3$) gives a blue colour.

(ii) **Refractories.** CeS (m.p. = 2000°C) is used in the manufacture of a special type of crucibles which are used for melting metals in a reducing atmosphere at temperatures up to 1800°C . Borides, carbides and nitrides of lanthanides are also used as refractories.

(iii) **Abrasives.** Lanthanide oxides are used as abrasives for polishing glasses, e.g. the mixture of oxides, CeO_2 (47%), $\text{La}_2\text{O}_3 + \text{Nd}_2\text{O}_3 + \text{Pr}_2\text{O}_3$ (51%) + SiO_2 , CaO , Fe_2O_3 etc ($\approx 2\%$) which is called **Polirite** has been used for polishing glasses.

(iv) **paints.** Lanthanide compounds are used in the manufacture of lakes, dyes and paints for porcelain, e.g; cerium molybdate gives light yellow colour, cerium tungstate gives greenish blue colour and salts of Nd give red colour.

(v) **In textiles and leather industries.** Ceric salts are used for dyeing in textile industries and as tanning agents in leather industries. $\text{Ce}(\text{NO}_3)_4$ is used as a mordant for alizarin dyes. Chlorides and acetates of lanthanides make the fabrics water-proof and acid resistant.

(vi) **In medicine and agriculture.** Dimals which are salicylates of Pr and Nd are used as germicides. Cerium salts are used for the treatment of vomiting and sea-sickness. Salts of Er and Ce increase the red-blood corpuscles and haemoglobin content of blood.

In agriculture lanthanide compounds are used as insectofungicides and as trace elements in fertilizers.

(vii) **In analytical chemistry.** $\text{Ce}(\text{SO}_4)_2$ is used as an oxidizing agent in volumetric titrations.

Radio isotopes of lanthanides (e.g., La^{140} , Ce^{142} , Er^{153} , Tb^{160} etc) are used in the study of co-precipitation, chromatographic separations etc.

(viii) **In lamps.** Salts of La, Ce, Eu and Sm are used as activators of luminophores. They are used in gas mantles, in the coatings of luminescent lamps

and for painting the screens of cathode-ray tubes.

(ix) **Catalytic applications.** Certain compounds of lanthanides are employed for the hydrogenation, dehydrogenation and oxidation of various organic compounds. Cerium phosphate is used as a catalyst in petroleum cracking.

(x) **Electronic applications.** Ferrimagnetic garnets of the type $3\text{Ln}_2\text{O}_3 \cdot 5\text{Fe}_2\text{O}_3$ are employed in microwave devices.

(xi) Neodymium oxide dissolved in selenium oxychloride is one of the most powerful liquid lasers known so far.

(xii) Cerium salts are used in analysis, dyeing cotton, lead accumulators, medicines etc.

(xiii) Gadolinium sulphate heptahydrate has been used to produce very low temperature.

Nuclear applications. Lanthanide elements and their compounds find many important nuclear uses, e.g; in nuclear fuel control, shielding and fluxing devices. Pr^{147} is used in the production of atomic battery.

ACTINIDES

12.8 Introduction

The elements in which the additional electron enters $5f$ -orbitals of $(n-2)$ th main shell are called **$5f$ -block elements, actinides or actinones.**

Thus strictly according to this definition of actinides only *thirteen* elements from ${}_{90}\text{Th}$ ($5f^0 6d^2 7s^2$) to ${}_{102}\text{No}$ ($5f^{14} 6d^0 7s^2$) should be the members of actinide series. However, all the fifteen elements from ${}_{89}\text{Ac}$ ($5f^0 6d^1 7s^2$) to ${}_{103}\text{Lw}$ ($5f^{14} 6d^1 7s^2$) are considered as the members of actinide series, since all these fifteen elements have similar physical and chemical properties. The name actinide is derived from actinium the very first member of the series. Only the first four elements of this series namely actinium, thorium, protoactinium and uranium occur in nature, the other elements are made artificially by nuclear bombardment. All the actinides are toxic to human. The actinide elements constitute the second inner transition series. Actinide elements lie in the 7th period (incomplete period with $n=7$) and IIIB group (Group 3) of the periodic table.

12.9 Position of Actinides in the Periodic Table

The existence of the lanthanide series helped the discoverers to predict that another series of elements resulting from the addition of electrons to an $(n-2)$ f - shell (i.e., $5f$ -shell) should occur somewhere in the heavy elements region. Prior to the discovery of transuranium elements, the naturally occurring heaviest known elements namely ${}_{90}\text{Th}$, ${}_{91}\text{Pa}$ and ${}_{92}\text{U}$ were placed below ${}_{72}\text{Hf}$, ${}_{73}\text{Ta}$ and ${}_{74}\text{W}$ in IVB, VB and VIB groups of the periodic table, because these elements showed +4, +5 and +6 oxidation states and resembled Hf, Ta and W respectively in many of their properties.

and 6d orbital in the atoms of actinides are partially filled while 7s orbital is completely filled ($7s^2$ configuration).

Table 12.3 Properties of actinides.

Element	Symbol	Atomic Number	Electronic Configuration	Oxidation states	Ionic radii (pm) M^{3+} M^{4+}	
Actinium	Ac	89	[Rn] $5f^0 6d^1 7s^2$	3, -	111	-
Thorium	Th	90	[Rn] $5f^0 6d^2 7s^2$	4	108	99
Protactinium	Pa	91	[Rn] $5f^2 6d^1 7s^2$	3,4,5	105	96
Uranium	U	92	[Rn] $5f^3 6d^1 7s^2$	3,4,5,6	103	93
Neptunium	Np	93	[Rn] $5f^5 6d^0 7s^2$	3,4,5,6,7	101	92
Plutonium	Pu	94	[Rn] $5f^6 6d^0 7s^2$	3,4,5,6,7	100	90
Americium	Am	95	[Rn] $5f^7 6d^0 7s^2$	3,4,5,6	99	89
Curium	Cm	96	[Rn] $5f^7 6d^1 7s^2$	3,4	98	88
Berkelium	Bk	97	[Rn] $5f^9 6d^0 7s^2$	3,4	96	-
Californium	Cf	98	[Rn] $5f^{10} 6d^0 7s^2$	2,3	95	-
Einsteinium	Es	99	[Rn] $5f^{11} 6d^0 7s^2$	2,3	-	-
Fermium	Fm	100	[Rn] $5f^{12} 6d^0 7s^2$	2,3	-	-
Mendelevium	Md	101	[Rn] $5f^{13} 6d^0 7s^2$	2,3	-	-
Nobelium	No	102	[Rn] $5f^{14} 6d^0 7s^2$	2,3	-	-
Lawrencium	Lr	103	[Rn] $5f^{14} 6d^1 7s^2$	3	-	-

2. Oxidation states. Most of the actinides exhibit +3 oxidation state. +3 oxidation state becomes more and more stable as the atomic number increases in the actinide series. Since in the first half of the actinide series (i.e. lower actinides), the energy required for the conversion $5f \rightarrow 6d$ is small, they show more higher oxidation states such as +4, +5, and +7. Correspondingly, since in the second half of the actinide series (i.e., higher actinides), the energy required for the conversion $5f \rightarrow 6d$ is somewhat high, the higher actinides show lower oxidation states such as +2.

It is found that most stable oxidation states of the elements upto uranium is the one involving all the valency electrons. Neptunium forms +7 oxidation state using all the valency electrons but this is oxidizing and the most stable state is +5. Plutonium also shows oxidation state upto +7 and americium upto +6 but the most stable state drop to Pu(+4) and Am (+3) and latter elements tend to be stable in +3 oxidation state. Berkelium in +4 state is strongly oxidizing but is more stable than curium and americium in +4 state to f^7 configuration. Similarly nobelium is markedly stable in +2 state due to its f^{14} configuration. Oxidation states of actinides are given in the above table.

3. There is no regular trend in the *melting and boiling points* of actinides.

4. Reducing power. All the actinides have relatively high E° values (about 2 volts). Therefore, they are strong reducing agents.

5. Ionic radii. Crystal structure data have provided the basis for ionic radii of the actinide elements. There is a regular decrease in ionic radii of the tripositive and tetrapositive actinide ions (i.e. An^{3+} and An^{4+}) with increase in atomic number from actinium to lawrencium. This steady decrease in the size of Ln^{3+} and Ln^{4+} cations in the actinide series is called **actinide contraction** which is analogous to lanthanide contraction found in lanthanides.

Causes of actinide contraction. As we move from one element to the next one in the actinide series, the nuclear charge (i.e. atomic number) and the number of $5f$ electrons increase by one unit at each step. It is also known that the shielding of one electron in $5f$ -orbital by the other one residing in the same orbital is very poor. Due to the negligible amount of mutual shielding effect between the electrons residing in $5f$, the increase in nuclear charge by +1 at each next element in the actinide series brings the valence shell nearer to the nucleus and hence the size of An^{3+} and An^{4+} cations goes on decreasing as we move from one element to the next one in the series.

However, in actinide contraction there are bigger jumps in contraction between the consecutive elements as compared to lanthanides. The greater contraction is due to the lesser shielding of $5f$ -electrons which are therefore, pulled more strongly by the nucleus. The actinide contraction, as usual, leads to a decrease in the basicity of the elements with increasing atomic number.

6. Colour and absorption spectra of actinide ions. Most of the tripositive and tetrapositive cations (An^{3+} and An^{4+} cations) are coloured and the colour depends upon the number of $5f$ electrons. The colour exhibited by actinide cations is due to $f-f$ transitions. Electrons change their positions from one f orbital to another f orbital. It should be noted that An^{3+} and An^{4+} cations having $5f^0$, $5f^1$ and $5f^7$ configuration are colourless while those having $5f^2$, $5f^3$, $5f^4$, $5f^5$ and $5f^6$ configuration are coloured.

It can be seen, by comparing the colours of Ln^{3+} and An^{3+} cations, that the pairs of ions which have the same number of f -electrons ($4f$ and $5f$ electrons) have roughly comparable colours. The pairs e.g. (i) Nd^{3+} ($4f^3$ -reddish) and U^{3+} ($5f^3$ -red) and (ii) Gd^{3+} ($4f^7$ - colourless) and Cm^{3+} ($5f^7$ - colourless) illustrate this point. Ce^{3+} ($4f^1$) and Pa^{4+} ($5f^1$) ions are colourless.

The absorption spectra of actinide ions, in aqueous solution and in crystals, contain narrow bands in the visible, near-ultraviolet and near-infrared regions of the spectrum.

The bands seen in case of actinide ions arise from electronic transitions between energy states within the $5f$ -electron subshell. It has been found, in general, that the absorption bands seen in case of actinide ions are about ten times sharper than those seen in case of lanthanide ions.

Charge-transfer phenomena occur more frequently and the bands are more

intense in the actinides because of lower energy involved in transitions. Moreover the overlap of $5f$ -orbitals with the ligand orbitals increases the intensity of absorption bands.

7. Magnetic Properties. Tripositive (e.g. U^{3+} , Np^{3+} etc) and tetrapositive (e.g. Pa^{4+} , U^{4+} etc) actinide cations are paramagnetic like the tripositive lanthanide cations like Co^{3+} , Pr^{3+} , Nd^{3+} etc. Pu^{3+} and Am^{3+} actinide cations show the analogous behaviour as noted for Sm^{3+} and Eu^{3+} cations in lanthanide series.

The magnetic moments of actinide ions are smaller than the theoretical predicted values. This is due to the fact that $5f$ electrons of actinides are less effectively shielded (screened) from the crystal field which results in quenching of orbital contribution.

8. Complex formation. Actinides have a greater tendency to form complexes because of higher nuclear charge and small size of their atoms. Complexes formed by actinides are described below.

- (i) Small and highly charged An^{4+} ions exhibit greatest tendency towards complex formation e.g., Pu^{4+} forms very strong anion complexes.
- (ii) Most actinide halides form adducts with alkali metal halides. For example $ThCl_4$ forms the complexes $MThCl_5$, M_2ThCl_6 and M_2ThCl_7 where M is the alkali metal.
- (iii) With pyridine, $ThCl_4$ as well as $ThBr_4$ form monopyridine complexes.
- (iv) They form complexes with acetylacetonate, oxine, EDTA, such as tetrakis(acetyl acetonate) thorium, $Th(acac)_4$ and $UO_2(C_9H_6NO)_2 \cdot C_9H_7ON$.
- (v) UO_2^{2+} forms rather unstable complexes with EDTA as compared to lanthanides.
- (vi) The degree of complex formation in case of actinides decreases in the order
 $An^{4+} > AnO_2^{2+} > An^{3+} > AnO_2^+$

The complexing power of different singly charged and double charged anions follows the order:

Singly-charged anions: $F^- > NO_3^- > Cl^-$

Doubly-charged anions: $CO_3^{2-} > C_2O_4^{2-} > SO_4^{2-}$

9. Reactivity. Actinide metals are very reactive. When actinides combine with oxygen, oxides are formed, ThO_2 , UO_2 , PaO_2 , NpO_2 , AmO_2 , CmO_2 etc. When H_2 acts on actinides, hydrides are formed, e.g. ThH_4 , PaH_3 , UH_3 , PuH_2 , AmH_2 etc. Chlorides, bromides and iodides are formed when the actinide metal is acted on by Cl_2 , Br_2 and I_2 respectively. Actinides are attacked by acids with the liberation of H_2 .

The *f*-BLOCK

12.11 Comparison between Lanthanides and Actinides: Similarities. Since *f* shell is being filled in lanthanides (4*f* shell) and actinides (5*f* shell), the elements of these two series have close relationship in properties with one another.

- (i) In both the series, the extra electron enters (n-2)*f* orbitals.
- (ii) The elements of both the series show +3 oxidation state.
- (iii) Just like lanthanide contraction we have actinide contraction.
- (iv) The nitrates, perchlorates and sulphates of trivalent actinides as well as lanthanides are soluble while the hydroxides, fluorides and carbonates are insoluble in water.
- (v) In the absorption spectra of the elements of both the series sharp line-like bands appear due to *f-f* transition.

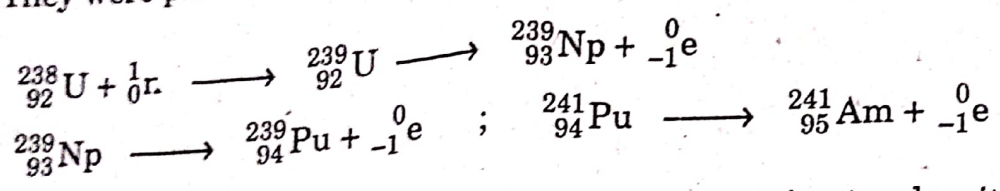
Dissimilarities. Although important similarities exist between the elements of the two series, very important differences also occur. These differences are due mainly to the relatively lower binding energies and less effective shielding of the 5*f*-electrons (in actinides) than close of 4*f*-electron (in lanthanides).

Lanthanides	Actinides
1. Binding energy of 4 <i>f</i> are higher.	1. Binding energy of 5 <i>f</i> are lower
2. 4 <i>f</i> electrons have greater shielding effect.	2. 5 <i>f</i> electrons have poor shielding effect.
3. Maximum oxidation state exhibited by lanthanides is +4 e.g., Ce ⁴⁺ .	3. Due to lower binding energies they show higher oxidation states such as +4, +5 and +6.
4. The additional electron enters 4 <i>f</i> orbitals.	4. The additional electron enters 5 <i>f</i> orbitals.
5. They do not form oxocations.	5. They form oxocations such as UO ₂ ²⁺ , UO ₂ ⁺ , NpO ₂ ⁺ , PuO ₂ ⁺
6. Except Pm, all the remaining lanthanides are radioactive.	6. All the actinides are radioactive
7. They do not form complexes easily. Their complexes with π-bonding ligands are not known.	7. They form complexes with π-bonding ligands such as alkyl phosphines, thioethers etc.
8. They are paramagnetic but magnetic properties can be easily explained.	8. They are also paramagnetic but it is difficult to explain magnetic properties.

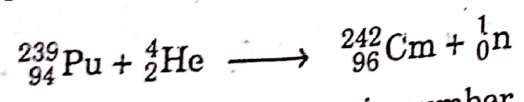
12.12 Identification and Nuclear Synthesis of Trans-uranium elements

Of all naturally occurring elements, uranium has the highest atomic number

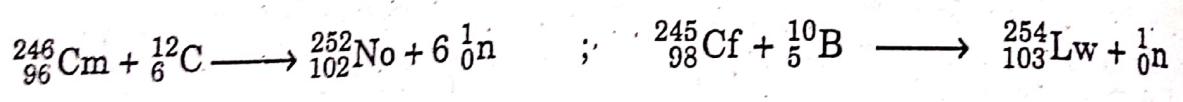
equal to 92. Since 1940 eleven elements namely ${}_{93}\text{Np}$, ${}_{94}\text{Pu}$, ${}_{95}\text{Am}$, ${}_{96}\text{Cm}$, ${}_{97}\text{Bk}$, ${}_{98}\text{Cf}$, ${}_{99}\text{Es}$, ${}_{100}\text{Fm}$, ${}_{101}\text{Md}$, ${}_{102}\text{No}$ and ${}_{103}\text{Lr}$ have been identified and synthesized by the transformation of naturally occurring elements by nuclear reactions. The elements with atomic numbers greater than that of uranium ($Z=92$) are called **transuranium elements** because they occur immediately following uranium in the periodic table. Elements 93 (neptunium) and 94 (plutonium) were first discovered in 1940. They were produced by bombarding uranium-238 with neutrons:



Curium-242 is formed when a plutonium-239 target is struck with accelerated alpha particles:



The atoms of highest atomic number have been prepared by bombardment using comparatively massive particles such as ${}_{5}^{10}\text{B}$, ${}_{6}^{12}\text{C}$ and ${}_{7}^{14}\text{N}$:

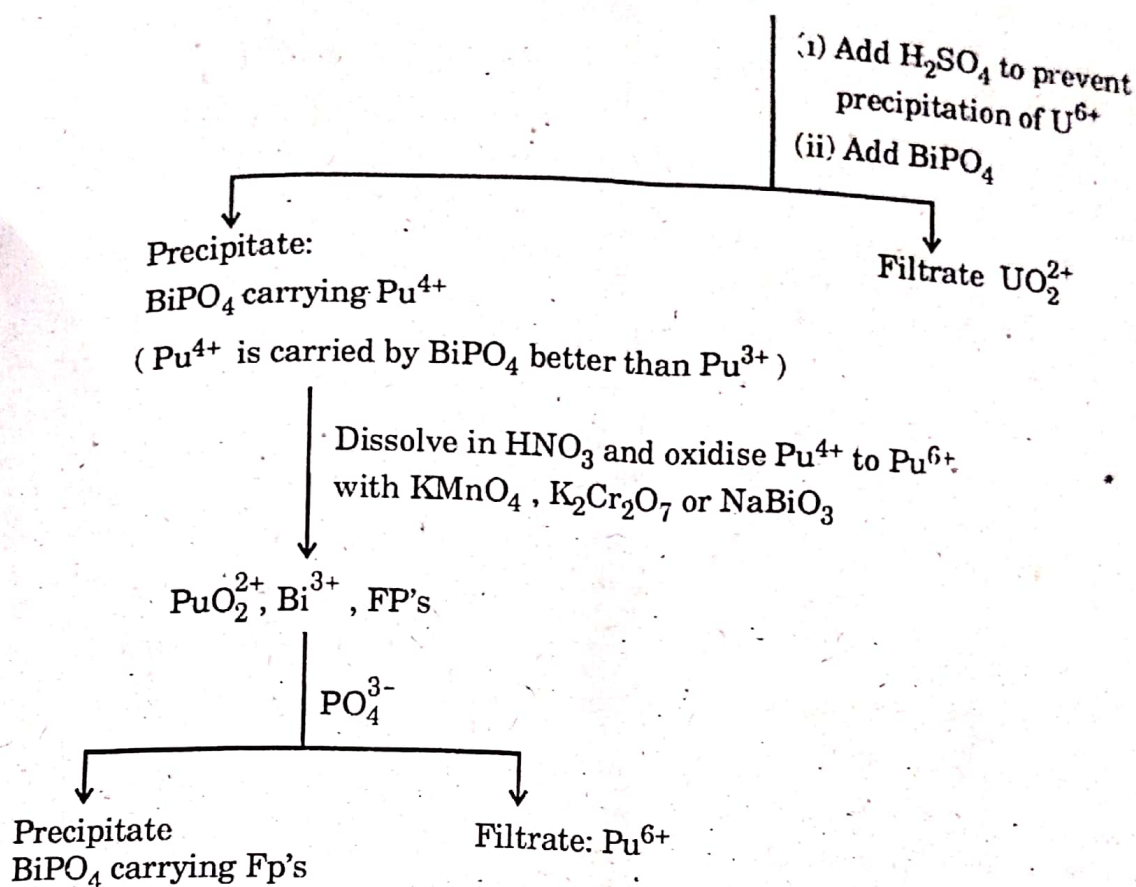
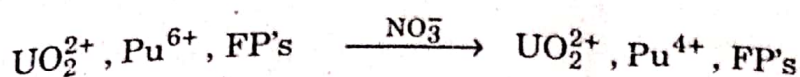


12.13 Separation of Actinide Elements

Transuranium elements, produced as a result of nuclear reactions, are isolated from the target materials and irradiated nuclear fuels by the following methods.

1. Precipitation method. Tri- and tetrapositive actinides can be precipitated as fluorides or phosphates from acidic solution. Actinides in higher oxidation states do not give a precipitate or form complexes. This method is particularly useful for the separation of actinide elements of U-Am group. When the quantity of the actinide ion is insufficient to precipitate by itself, coprecipitation with a *carrier* like LiF_3 or BiPO_4 is adopted. The LiF_3 coprecipitation method has been used for the separation of Np and Pu (obtained by neutron irradiation of uranium) from uranium and other fission products. The BiPO_4 -coprecipitation method has been discovered by Thomson and Seaborg and is used for the large scale production of Pu from uranium and fission production (FP's).

Flow sheet 1: LiPO_4 coprecipitation method for the separation of Pu from U and fission products (FP's)



2. Solvent Extraction Method. This method depends on the extractability of the various oxidation states of actinide elements. This technique finds extensive application in the recovery of U and Pu from used-up nuclear fuels. The process is based on the distribution of a metal between the aqueous solution and an organic solvent. Thus with *methyl isobutyl ketone* (hexone) Np^{4+} , Np^{5+} , Pu^{6+} and U^{6+} are extracted while Pu^{3+} is not extracted. *Diethyl ether* and tri-n-butyl phosphate (TBP) are other solvents which are used as extractants. Because of the high viscosity and density, TBP is used as 20% solution in kerosene. The method is preferentially applied to nitrate systems, because other ions like SO_4^{2-} , ClO_4^- , F^- etc. are strongly complexing and tend to retain the metal in aqueous solution. Hexone and diethyl ether require a high concentration of NO_3^- ions in the aqueous phase and it is achieved by adding $\text{Al}(\text{NO}_3)_3$ which has a high salt-out action. TBP is resistant to nitric acid oxidation and acts by itself as a salt agent. Solvent extraction of Pu and U by hexone and TBP is shown in flow sheets 2 and 3 respectively.