

B.Sc. (Semester-III)
Subject: Inorganic Chemistry (US03CCHE21)
UNIT: III Lanthanides and Actinides

By Dr. K. D. Patel

LANTHANIDES

LANTHANIDES: 4f- block elements

Definition: The f- block (inner transition) elements containing partially filled 4f-subshells are known as Lanthanides or Lanthanones because of their close similarities with element lanthanum (atomic no: 57). The fourteen elements from atomic no: 58 to 71 constitute lanthanides.

Nos	Name	Symbol and Atomic number	Electronic configuration
1	Lanthanum	La ₅₇	[Xe] 4f ⁰ 5d ¹ 6s ²
2	Cerium	Ce ₅₈	[Xe] 4f ² 5d ⁰ 6s ²
3	Praseodymium	Pr ₅₉	[Xe] 4f ³ 5d ⁰ 6s ²
4	Neodymium	Nd ₆₀	[Xe] 4f ⁴ 5d ⁰ 6s ²
5	Promethium	Pm ₆₁	[Xe]4f ⁵ 5d ⁰ 6s ²
6	Samarium	Sm ₆₂	[Xe]4f ⁶ 5d ⁰ 6s ²
7	Europium	Eu ₆₃	[Xe] 4f ⁷ 5d ⁰ 6s ²
8	Gadolinium	Gd ₆₄	[Xe] 4f ⁷ 5d ¹ 6s ²
9	Terbium	Tb ₆₅	[Xe] 4f ⁹ 5d ⁰ 6s ²
10	Dysprosium	Dy ₆₆	[Xe] 4f ¹⁰ 5d ⁰ 6s ²
11	Holmium	Ho ₆₇	[Xe] 4f ¹¹ 5d ⁰ 6s ²
12	Erbium	Er ₆₈	[Xe] 4f ¹² 5d ⁰ 6s ²
13	Thulium	Tm ₆₉	[Xe] 4f ¹³ 5d ⁰ 6s ²
14	Ytterbium	Yb ₇₀	[Xe] 4f ¹⁴ 5d ⁰ 6s ²
15	Lutetium	Lu ₇₁	[Xe] 4f ¹⁴ 5d ¹ 6s ²

From the above electronic configuration, it can be seen that at La $5d$ orbital is singly occupied but after La further filling of $5d$ orbital is discontinued.

As the nuclear charge increases by one unit from La to Ce, $4f$ orbitals were higher in energy up to Lu, fall slightly below the $5d$ level $4f$ - orbitals, therefore begin to fill and are completely filled up to Lu, before filling of $5d$ orbital is resumed.

Points may be noted from above configuration:

(i) The complete electronic configuration of lanthanides can be represented by general configuration is $2,8,18,4s^2 p^6 d^{10} f^{0,2-14}, 5s^2 p^6 d^{0 \text{ or } 1} 6s^2$.

The valence shell configuration is $4f^{0,2-14} 5d^{0 \text{ or } 1} 6s^2$. This configuration indicates that the additional electron enters the $4f$ -level without altering the electrons in the $6s$ -orbital.

(ii) The filling of $4f$ -orbitals is not regular, e.g. the additional electron in Gd does not enter $4f$ -orbital but it goes to $5d$ -level. This is because the $4f$ -& $5d$ -orbital in Gd are at about the same energy level and Gd atom has tendency to retain the configuration with half- filled $4f$ -levels which are relatively more stable.

Position of Lanthanides in the periodic table:

All the lanthanides have atomic weights between those of Barium ($Z=56$) and Hafnium ($Z=72$) and therefore must be placed between these two elements as also proved by Moseley.

Barium has exactly the same outer electronic configuration as Ca and Sr and resembles them very closely. In a similar way Hf ($Z=72$) is similar to Zr ($Z=40$).

Hence Ba must be placed below Sr and Hf below Zr, thus leaving only one place between them which lies exactly below Y ($Z=39$).

Since all the lanthanides resembles one another in many respects, they must be placed in the same group. These elements also resemble Y because of the following additional similarities:

(a) Owing to the lanthanide contraction the ionic radius of Y^{+3} ion is almost similar to that of Er^{+3} ion ($Er^{+3}=0.96 \text{ \AA}$ and $Y^{+3}=0.93 \text{ \AA}$).

(b) Y generally occurs in nature associated with the ores of heavier lanthanides and resembles Tb (III) and Dy (III) in its compounds. Hence it is necessary to accommodate all the fifteen lanthanides together at one place. This has been done by placing the first element viz. La below Y and remaining fourteen elements viz. Ce to Lu. They have been placed separately in the lower part of the periodic table.

GENERAL PROPERTIES OF LANTHANIDES:

From the electronic configuration of lanthanides, we see that these elements are characterized by progressive filling up of the well shielded $4f$ -orbitals. Hence, there occurs no appreciable change in the outer most arrangement of the electronic shells with increase in atomic number.

Oxidation states and oxidation potentials:

The observed oxidation states of lanthanides noted either in solution or in insoluble compounds are given below. From which it may be noted that whatever the electronic configurations of the lanthanides in the ground state, all of the lanthanides form the tripositive lanthanides cations.

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
			+2		+2	+2						+2	+2	
+3	+3	+3	+3	+3		+3	+3	+3	+3	+3	+3	+3	+3	+3
	+4	+4			+4			+4	+4					

This fact is not directly evident from the electronic configurations, it is actually due to the fact that the magnitude of the energy required to remove an electron from the gaseous ion in its lower oxidation state (i.e. ionization energy) and of that released when two gaseous ions combine with water to form the aquated species (i.e. hydration energy). Therefore, all the tetrapositive species (except Ce^{+4}) and all the dipositive species (except Eu^{+2}) revert to the tripositive species. Thus, this leads to the conclusion that tripositive species are more stable than the di- and tetrapositive species in aqueous solution.

In the solid state to the combination of ionization energy and the energy released when gaseous ions combine to produce crystalline solids (i.e. the lattice or crystal energy) is more negative for the tripositive species than for di- and tetrapositive species. Consequently, the tripositive lanthanides are also the most common in the solid compounds.

Stability of the various oxidation states:

It is possible to correlate the stability of various oxidation states of lanthanides with the electronic configuration of their ions. On the basis of general rule that empty, half-filled and completely filled 4f orbitals are highly stable, the formation of Ce^{+4} , $La^{+3}(4f^0)$, Th^{+4} , Eu^{+2} , $Gd^{+3}(4f^7)$ and Yb^{+2} , $Lu^{+3}(4f^{14})$ ions can be explained. It is however, difficult to explain the stability of oxidation states of the cations other than those given above. Hence it is assumed that in addition to the special stability associated with $4f^0$, $4f^7$ and $4f^{14}$ configurations, there may be other factors such as thermodynamic and kinetic in determining the stability of various oxidation states of lanthanides.

The stability order of +2 state is $Eu > Yb > Sm > Tm \sim Nd$. LnI_2 solids ($Ln = La, Ce, Pr$ and Gd) do not contain Ln^{+2} ions, but are metallic in nature. The stability order of +4 state is $Ce > Tb \sim Pr > (Nd \sim Dy)$.

The ease of formation of the various oxidation states in solution is indicated by the values of the standard electrode potential, E^0 .

From the observed values (in volts) for different couples of lanthanides such as $Ln^0 \rightarrow Ln^{+3} + 3e^-$,

$Ln^{2+} \rightarrow Ln^{+3} + e^-$ and $Ln^{3+} \rightarrow Ln^{4+} + e^-$, for 1M Perchloric acid at 25°C, we observed that:

(i) The high positive values of oxidation electrode potentials for the couple $Ln^0_{(s)} = Ln^{3+}_{(aq)} + 3e^-$ indicates that the elemental lanthanides are powerful reducing agents, i.e. oxidation of the lanthanide metals to the tripositive state occurs readily and vigorously. The gradual decrease in the values of E^0 indicates very slight decrease in chemical activity from one element to the next one.

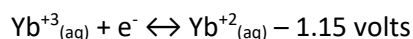
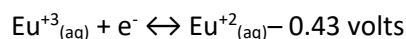
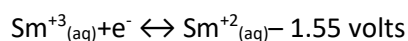
(ii) The enhanced stabilities associated with the empty, half-filled and completely filled $4f$ -orbital is also indicated by these values. Thus $Ce^{+4}(4f^0)$ is much less readily reduced to the tripositive ion, $Ce^{+3}(4f^1)$ than Pr^{+4} ion ($4f^1$). The $4f^7$ species (e.g. Eu^{+2} ion) and the $4f^{14}$ species (e.g. Yb^{+2} ion) are the weakest reducing agents of the dipositive species.

(iii) The values of E^0 for couples $Ln^0_{(s)} \rightarrow Ln^{+3}_{(aq)} + 3e^-$ decrease with the increase of atomic number.

Chemistry of +2 state:

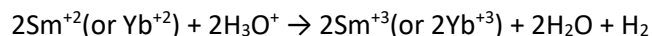
This is an anomalous oxidation state. The lanthanides showing oxidation state can be divided into +2 two categories:

(a) Sm, Eu and Yb: The dipositive ions of these lanthanides (i.e. Sm^{+2} , Eu^{+2} and Yb^{+2}) exist in solution. The standard oxidation potentials at $25^\circ C$, in acid solution, of these cations are given below:



These values indicate that Sm^{+2} , Eu^{+2} and Yb^{+2} ions are strong reducing agents and their reducing strength is in the order: $Sm^{+2} > Yb^{+2} > Eu^{+2}$

Sm^{+2} and Yb^{+2} ions are rapidly oxidized by H_3O^+ ion, while Eu^{+2} ion is fairly stable and is only slowly oxidized by H_3O^+ ion.



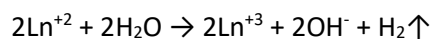
All these cations are rapidly oxidized in presence of oxygen.

e.g. $4Ln^{+2} + 4H_3O^+ + O_2 \rightarrow 4Ln^{+3} + 6H_2O$, where Ln^{+2} may be Sm^{+2} , Eu^{+2} or Yb^{+2} .

The compounds of Sm^{+2} , Eu^{+2} and Yb^{+2} which are insoluble in H_2O are not oxidized by H_2O , while hydrated water-soluble compounds of Sm^{+2} and Yb^{+2} are oxidized by their water. Hydrated water-soluble compounds of Eu^{+2} are more stable.

(b) Ce, Nd and Tm: The compounds having these elements in +2 oxidation state are known only as solid halides. These are immediately oxidized with air.

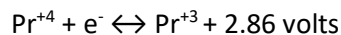
Among divalent compounds of lanthanides, Eu^{+2} ion is more stable. The compounds of Ln^{+2} ions are not stable in solution. All the Ln^{+2} compounds decompose water with evolution of H_2 .



Chemistry of +4 state:

This oxidation state is also an anomalous oxidation state. Double salts like $Ce(NO_3)_4 \cdot 2NH_4NO_3$ and $Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 2H_2O$ have also been prepared.

The standard oxidation potentials at $25^\circ C$, in acid solution, of Ce^{+4} and Pr^{+4} ions are given as under:



These values show that Ce (IV) and Pr(IV) are strong oxidizing agents. Ce(SO₄)₂ is generally used in volumetric analysis. Ce⁺⁴ ion is readily reduced to Ce⁺³ ion.

The tetravalent ions of Ce are stable in the solid state as well as in solution. Pr^{IV}, Nd^{IV}, Tb^{IV} and Dy^{IV} are stable only in solution.

Chemistry of +3 state:

All known anion form compounds with Ln⁺³ cation. These compounds are stable in solid as well as in solution state. Compounds of Ln⁺³ with anions such as OH⁻, CO₃⁻², SO₄⁻² etc. decompose on heating gives first basic salt and finally oxides.

Compounds of Ln⁺³ cation with the anions Cl⁻, Br⁻, I⁻, NO₃⁻, CH₃COO⁻, BO₃⁻³ are generally soluble in H₂O, While of F⁻, OH⁻, O⁻², C₂O₄⁻² etc. are generally insoluble in H₂O.

OXIDES [Ln₂O₃]: The oxides Ln₂O₃ are formed by heating the metal in O₂ or by decomposition of Ln(OH)₃ or oxy salts like Ln₂(CO₃)₃ and Ln(NO₃)₃. Oxides are similar to alkaline earth oxides. All are insoluble in water. They absorb CO₂ and H₂O from air to form carbonates and hydroxides respectively.

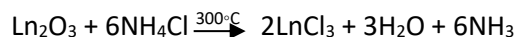
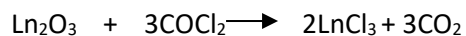
Hydroxides [Ln(OH)₃]: The hydroxides are precipitated as gelatinous precipitates from aqueous solution by the addition of ammonia or dilute alkali to soluble salts of Ln⁺³ ion in solution.

The hydroxides are not amphoteric. They have hexagonal structure. They absorb CO₂ to give carbonate. Oxides and hydroxides are basic. The basicity decreases with increasing atomic number. La₂O₃ and La(OH)₃ are most basic, while Lu₂O₃ and Lu(OH)₃ are least basic.

Carbonates [Ln₂(CO₃)₃]: The carbonates can be prepared by passing CO₂ into aq. solution of Ln(OH)₃. They can be prepared by adding Na₂CO₃ solution to Ln⁺³ salt solution. The CO₃⁻² are insoluble in H₂O but dissolve in acids with liberation of CO₂ and forming Ln⁺³ salts.

Halides [LnX₃]: Fluorides are precipitated by the addition of HF to Ln⁺³ salts solution. The fluorides of heavier lanthanides are sparingly soluble in HF due to formation of fluoro complexes.

Chlorides are obtained by direct combination of element on heating. It is obtained by heating oxides with COCl₂ or NH₄Cl.



Colour and absorption spectra of Ln⁺³ ions:

The colour of crystalline compounds of number of Ln⁺³ ions persist in aqueous and non-aqueous solutions and remain unaffected by the change of the anion present or by the addition of colourless complexing agents.

The colours of Ln^{+3} ions are:

La^{+3} – Colourless; Pm^{+3} – Pink Yellow; Er^{+3} – Reddish; Ce^{+3} – Colourless; Sm^{+3} – Pale Pink; Tm^{+3} – Green; Pr^{+3} – Green; Eu^{+3} – Pale Pink; Ho^{+3} – Pink Yellow; Nd^{+3} – Reddish; Gd^{+3} – Colourless etc...

From this the following points may be noted:

(i) Ln^{+3} ions having x electrons and $(14-x)$ electrons in $4f$ -orbital have the same colour. e.g. Pr^{+3} and Tm^{+3} ions having 2 and $(14-2) = 12$ electrons in the $4f$ -orbital respectively have the same colour green. Thus, $4f$ orbitals are source of colours of Ln^{+3} ions.

(ii) The colours of Ln^{+3} depend on the number of unpaired electrons in $4f$ -orbitals but Ln^{+2} (e.g. Sm^{+2} , Eu^{+2} , Yb^{+2} ions) and Ln^{+4} ions (e.g. Ce^{+4} ion) have same number of electrons show different colours. e.g. Sm^{+2} and Eu^{+2} having six unpaired electrons in $4f$ -orbitals but the colour are different. Eu^{+2} – colourless and Sm^{+2} – reddish.

(iii) The colours of Ln^{+3} cations can also correlate with electron configuration of Ln^{+3} ions. Thus La^{+3} ($4f^0$), Gd^{+3} ($4f^7$) and Lu^{+3} ($4f^{14}$) are colourless.

Origin of colour:

The colours are due to Laporte forbidden $f-f$ transitions. The absorption bands of Ln^{+3} ions (except Ce^{+3} and Yb^{+3} ions) are very weak but sharp when compared to those of d -block elements. Many of these bands are line – like and become even narrower as the temperature is lowered. These narrow bands appear due to $f-f$ transition and are independent of the nature of the anion present. As $4f$ -electron lie deep inside the atom, the colours of Ln^{+3} ions are not affected by changing the anion.

The coloured ions absorb in visible region. The colourless ions absorb either in ultraviolet (Ce^{+3} and Gd^{+3}) or in IR region (Yb^{+3} ions). Ln^{+2} ions strongly absorb in ultraviolet. The only Ln^{+4} ion stable in aqueous solution, the Ce^{+4} ion, absorb in the ultraviolet regions.

Laporte permitted bands due to the transitions of $4f^n \rightarrow 5d^1$ type have been observed in Ce^{+3} , Tb^{+3} , Sm^{+2} , Eu^{+2} and Yb^{+2} . These bands are strong and broader, since the transition is considerably influenced by the chemical environment. A charge transfer phenomenon is also absorbed in certain lanthanide ions. e.g. the orange red colour of Ce^{+4} is due to the electronic transition from the ligand orbital to the f -orbital of cerium. Compounds of Eu^{+3} with reducing anions are yellow due to electron transfer from the metal.

Lanthanide Contraction (or Atomic and ionic radii):

The energies of $4f$ and $5d$ -orbitals are nearly same, beginning near to atomic number 57 La. Similar behavior is also observed for $5f$ and $6d$ - orbitals at atomic number 89 Ac.

The shielding of one f - electron by another from the effect of nuclear charge is quite weak due to shape of f -orbitals and hence with increasing atomic number the effective nuclear charge experienced by each $4f e^-$ increases, because of this there is contraction of atomic or ionic - radii proceeding from La to Lu. This decrease in atomic or ionic radii is called Lanthanide Contraction. Due to Lanthanide contraction the chemical properties of Lanthanides are almost similar.

Cause of Lanthanide Contraction:

In Lanthanides the additional electrons enter $4f$ -sub-shell but not in the valence shell namely sixth shell. The shielding effect of one electron in $4f$ -sub-shell by another in the same sub-shell (i.e. mutual shielding effect of $4f$ -electrons) is being even smaller than that of d -electrons, because the shape of f -sub-shell is very much diffused. The nuclear charge (i.e. atomic number) increases by unity at each step. Thus, the nuclear charge increases at each step, while there is no comparable increase in the mutual shielding effect of $4f$ -electron. This results in that electrons in the outermost shell experience increasing nuclear attraction from the growing nucleus. Consequently, the atomic and ionic- radii go on decreasing as we move from La_{57} to Lu_{71} .

Consequences of lanthanide contraction:

Some important consequences of lanthanides contraction are as under:

(i) High density of post lanthanide elements:

Because of lanthanide contraction the atomic sizes of the post lanthanide elements become very small. The arrangement of atoms in metallic lattice is much compact that the densities are very high. The density of 2nd transition series is slightly higher than 1st transition series, while the densities of 3rd transition series is almost double than 2nd transition series.

(ii) Basic character of oxides, Ln_2O_3 and hydroxides, $\text{Ln}(\text{OH})_3$:

There is decrease in basic strength of oxides and hydroxides of lanthanides with increase in atomic number. The basicity decreases as ionic radii decreases. The basicity of Ln^{+3} ions may be expected to decrease in the order, $\text{La}^{+3} > \text{Ce}^{+3} > \text{Pr}^{+3} \dots > \text{Lu}^{+3}$. These differences in basicity are reflected in (a) thermal decomposition of oxy-salts. i.e. more basic oxy- salts decompose less easily (b) hydrolysis of ions- more basic ions hydrolyze less readily (c) solubilities of salts (d) formation of complexes and (e) decreasing ease of oxidation of the metals with increasing atomic number – oxidation potential for the couple $\text{Ln} \rightarrow \text{Ln}^{+3} + 3\text{e}^-$ regularly goes on decreasing.

Due to lanthanide contraction the decrease in size of Ln^{+3} ions from La^{+3} to Lu^{+3} increases the covalent character (i.e. decreases the ionic character) between Ln^{+3} and OH^- ions in $\text{Ln}(\text{III})$ hydroxides. Thus $\text{La}(\text{OH})_3$ is the most basic while $\text{Lu}(\text{OH})_3$ is the best basic.

Similarly, there is a decrease in the basic strength of the oxides, Ln_2O_3 with the increase of atomic number of Ln-atom.

(iii) Small variation in the properties on account of Lanthanide contraction allows the separation of Lanthanides by the methods based on fractional crystallization and basicity differences.

(iv) The pair of elements i.e. Zr-Hf, Nb-Ta, have almost similar size and they are much closer to one another in properties than the pairs of elements of 1st and 2nd transition series, e.g. solubilities of their salts are very much similar to one another.

(v) Occurrence of Y with heavy Lanthanides:

The crystal radii of Y^{+3} and Er^{+3} are equal ($Y^{+3}=0.93 \text{ \AA}$ and $Er^{+3} =0.96 \text{ \AA}$). This similarities in atomic size of these two cations coupled with the equality in ionic charge (= +3 in both the ions) accounts for the invariable occurrence of Y with heavier Lanthanides.

Magnetic Properties:

The paramagnetic properties of an ion or an atom are due to presence of unpaired electrons in it. Since in La^{+3} and Lu^{+3} ions have no unpaired electrons, so they are not paramagnetic but are diamagnetic. All other Ln^{+3} ions shows paramagnetic property.

Since for most of the Ln^{+3} ions, the energy difference between the two successive J values of a multiplet, there is a strong L-S coupling. In these ions the unpaired electrons in (n-2)f orbitals are quite deeply seated and hence are well shielded by 5s- and 5p- electrons from the effects of other atoms in their compounds. These effective magnetic moments of Ln^{+3} ions, except Sm^{+3} and Eu^{+3} are given by following equation:

$$\mu_{\text{eff}} = \mu_J = g\sqrt{J(J+1)}\text{B.M.} \quad \dots\dots\dots (1)$$

where g is the Lande splitting factor and is given by:

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

Where, S= resultant spin quantum number

L= resultant orbital quantum number

J = resultant inner quantum number

The value of μ_{eff} for sulphates of Ln^{+3} ions calculated by using equation (1) are given as follows:

Ln^{+3} ions : La^{+3} Ce^{+3} Pr^{+3} Nd^{+3} Pm^{+3} Sm^{+3} Eu^{+3} Gd^{+3} Tb^{+3}

μ_{eff} in B.M. : 0.00 2.54 3.58 3.62 2.70 0.80 0.00 7.94 9.70

Ln^{+3} ions: Dy^{+3} Ho^{+3} Er^{+3} Tm^{+3} Yb^{+3} Lu^{+3}

μ_{eff} in B.M. : 10.60 10.60 9.60 7.60 4.50 0.00

From these values the following points to be noted:

(i) In most of Ln^{+3} ions, there is almost good agreement between the calculated and experimental values except Sm^{+3} and Eu^{+3} ions.

(ii) We know that for Ln^{+3} ions like $La^{+3}(4f^0)$, $Gd^{+3}(4f^7)$ and $Lu^{+3}(4f^{14})$ which have "S" term symbol, so L=0, i.e. no orbit effect. For these ions when L=0, J=S and hence g=2.

Thus equation (i) reduced to

$$\mu_{\text{eff}} = \mu_S = 2 \sqrt{S(S+1)} \quad \text{B.M.}$$

$$\text{or } \mu_{\text{eff}} = \mu_{\text{spin only}} = 2 \sqrt{\frac{n}{2}(\frac{n}{2} + 1)} = \sqrt{n(n+2)} \quad \text{B.M.}$$

By using this equation, the μ_s and μ_l values for La^{+3} , Gd^{+3} and Lu^{+3} ions are same.

Extraction of lanthanides from monazite mineral:

Monazite is the chief mineral from which lanthanides are extracted. While extracting thorium from monazite, the lanthanides are obtained as byproducts.

Following operations are carried out in the extraction:

1) Concentration of mineral: The concentration of monazite is started with gravity separation using Wilfley tables. The monazite sand being heavier gets caught up on the riffles while the remaining lighter material gets washed off. This heavier portion is then subjected to magnetic separator whereby the monazite being less magnetic gets separated from other magnetic material. At the end of this operation, a refined monazite with a rough composition of $\text{ThO}_2 = 7.5\%$, $\text{Ce}_2\text{O}_3 = 30\%$, $\text{P}_2\text{O}_5 = 29\%$, $\text{SiO}_2 = 1.5\%$ and 32% of other rare earths is obtained.

2) Cracking/ processing or opening up of the mineral:

This chemical treatment may be applied by either (a) Acidic method using H_2SO_4 or (b) Alkaline method using NaOH .

(a) Acidic method using H_2SO_4 :

First of all, the refined monazite obtained from the concentration process is heated with 93% H_2SO_4 at 210°C in cast iron vessels having mechanical stirrers. After about four hours, a viscous paste is obtained. This paste contains sulfates of lanthanides and thorium. This paste is leached with water for about 15 hours when all these sulfates go into solution. Only insoluble SiO_2 , unreacted mineral and traces of TiO_2 and ZrSiO_4 are left behind. This residue is then crushed and returned for recycle. The leached solution is acidic because of formation of phosphoric acid.



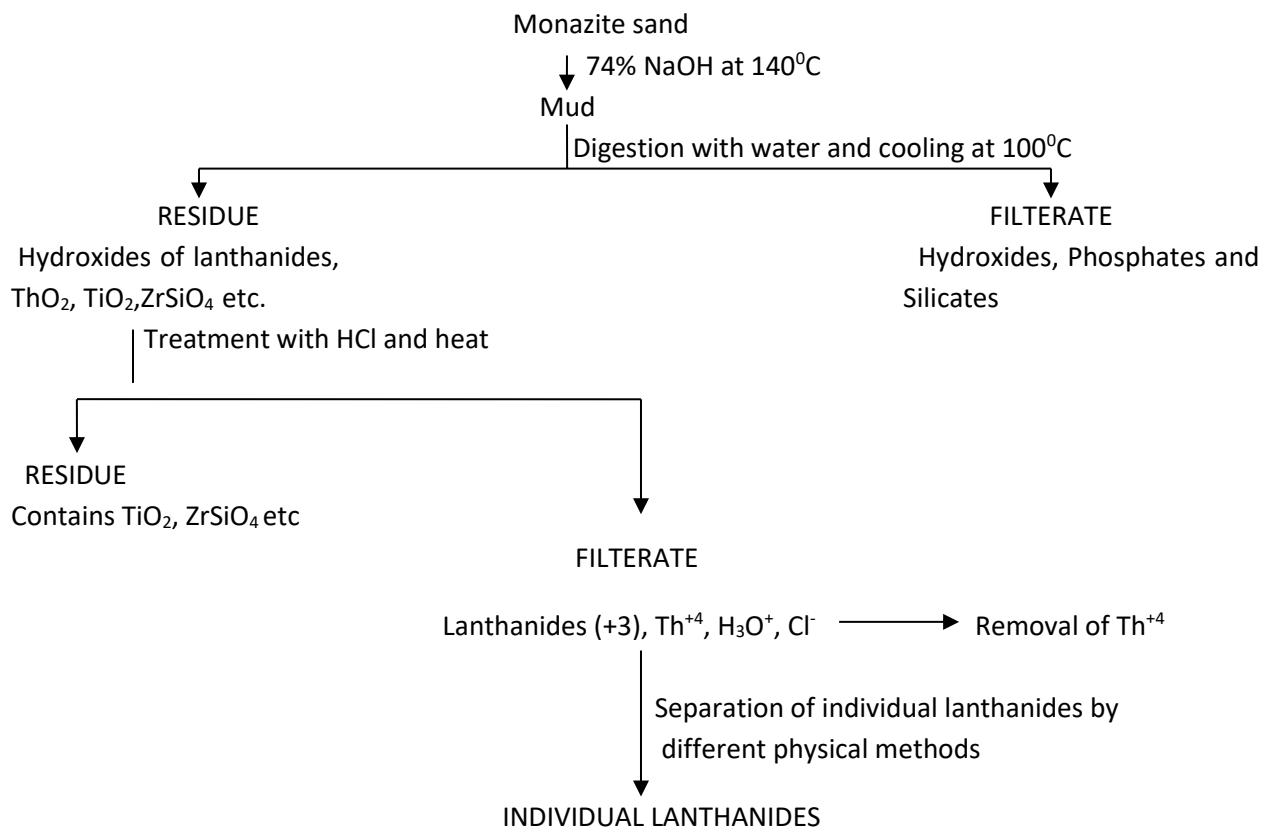
This solution is treated with sodium pyrophosphate ($\text{Na}_2\text{P}_2\text{O}_7$) to precipitate thorium as $\text{Th}(\text{P}_2\text{O}_7)_2$. The remaining filtrate is treated with oxalic acid to precipitate a mixture of oxalates of lanthanides and little amount of thorium and zirconium oxalates. This mixture is then boiled with ammonium oxalates to dissolve the thorium and zirconium oxalate. The residue is then ignited carefully with concentrated sulfuric acid. Sodium sulfate is added to the clear solution of sulfates of lanthanides so that the lighter lanthanides (La 57 to Eu 63) precipitate as double sulfates while the heavier ones remain in the solution as single sulfates. The addition of hot sodium hydroxide to the precipitates yields a mixture of hydrated oxides. Upon drying this mixture in air at 100°C mixture of oxides of lighter lanthanides with a rough composition of $\text{La}_2\text{O}_3 = 17\%$, $\text{CeO}_2 = 5\%$, $\text{Pr}_2\text{O}_3 = 8\%$, $\text{Nd}_2\text{O}_3 = 20\%$, $\text{Sm}_2\text{O}_3 = 5\%$ and little Eu_2O_3 is obtained.

Extraction of Ce: Upon treatment of this mixture with dilute nitric acid, all the lanthanide oxides except that of Ce gets dissolved. The residual CeO_2 is dissolved in 85% nitric acid to make crude $\text{Ce}(\text{NO}_3)_4$ which is further converted into red basic nitrate $\text{Ce}(\text{OH})(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ by reacting with dilute sulfuric acid.

The solution containing nitrates of the remaining lanthanides is then subjected to different methods for further separation. The solution containing heavier lanthanides is also similarly subjected to different methods for separation of individual lanthanides.

(b) Alkaline method using NaOH:

Alternatively, the cracking of monazite sand to obtain lanthanides can also be carried out by an alkaline method using sodium hydroxide. This process is described as shown in the following flow sheet.



Methods used for the separation of Lanthanides:

Following are the modern methods which are now used for the separation of lanthanides:

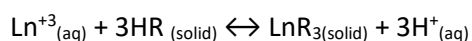
Modern methods:

1. Ion – exchange method
2. Solvent (liquid-liquid) extraction method
3. Paper chromatography
4. Gas chromatography
5. Thin layer chromatography
6. Complex formation

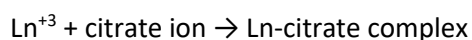
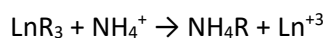
Q: Discuss in detail the Ion-exchange method for the separation of lanthanides:

(1) Ion – exchange method:

This is the most modern method for the separation of lanthanide elements. In this method synthetic cation resins are used. These resins contain $-\text{SO}_3\text{H}$ or $-\text{COOH}$ groups, the hydrogen of which are replaced by cations. The aqueous solution containing a mixture of trivalent positive Lanthanide ions, Ln^{+3} is allowed to pass down a column filled with cation – exchange resin. The Ln^{+3} ions replaced H^+ ions of $-\text{SO}_3\text{H}$ or $-\text{COOH}$ group of the resin and get fixed on the resin.



In order to remove Ln^{+3} ions fixed as $\text{LnR}_3(\text{solid})$ on the resin, the column is leached with a complexing agent in aqueous solution like buffer solution of Ammonium citrate- citric acid ($\text{pH} = 4$ to 7). Such complexing agents called eluants or eluates or eluting agents. During eluation process NH_4^+ ions of the eluating agent replace Ln^{+3} ions from $\text{LnR}_3(\text{solid})$ to give Ln^{+3} ions which reacts with citrate ion to form the Ln-citrate complex.



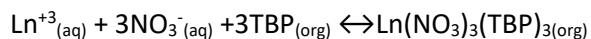
We have seen that since $\text{La}^{+3}_{(\text{aq})}$ is attached to resin with maximum and $\text{Lu}^{+3}_{(\text{aq})}$ with minimum firmness, Lu-citrate complex comes out of the column first and La-citrate complex comes out last.

In actual practice the process of elution is to be repeated several times by careful control of concentration of Ammonium Citrate- Citric Acid solutions.

By using this method 99.99% pure rare-earth elements can be isolated.

(2) Solvents (liquid-liquid) extraction method:

This method was first reported by Fischer. The method is based on the difference in the solubility of Lanthanides salts in water and immiscible organic solvents. These organic solvents are called extracting solvent. This method is used on both tracer and micro scales. In this process the aqueous solution of lanthanide salts passes through the organic solution, in which lanthanide extract 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 $\text{Ln}^{+3}_{(\text{aq})}$ ions in presence of NO_3^- ions.



Complex

Where (org) represents the organic phase. The distribution between these two phases (i.e. solvents) is described by distribution ratio λ , given by

$$\lambda = \frac{\text{Total concentration of solute in one solvent}}{\text{Total concentration of solute in other solvent}}$$

$$\lambda = \frac{C_{Ln}(\text{NO}_3)_3(\text{TBP})_3(\text{org})}{C_{Ln}^{+3}(\text{aq})} \dots\dots\dots (1)$$

For two tripositive lanthanide ions, Ln^{+3} and Ln'^{+3} , the separation factor, α is given as

$$\alpha = \frac{\lambda'}{\lambda} = \frac{C_{Ln}(\text{NO}_3)_3(\text{TBP})_3(\text{org}) \cdot C_{Ln}^{+3}(\text{aq})}{C_{Ln}(\text{NO}_3)_3(\text{TBP})_3(\text{org}) \cdot C_{Ln}'^{+3}(\text{aq})} \dots\dots\dots (2)$$

Peppard has reported that an average separation factors for adjacent lanthanides for 15.8 M nitric acid – 100% TBP system is about 1.5.

Equilibrium constant K, is given by:

$$K = \frac{C_{Ln}(\text{NO}_3)_3(\text{TBP})_3(\text{org}) \cdot C_{Ln}^{+3}(\text{aq})}{C_{Ln}^{+3}(\text{aq}) \cdot C_{\text{NO}_3^-}^3 \cdot C_{\text{TBP}(\text{org})}^3} \dots\dots\dots (3)$$

Combination of equation (3) with equation (1) gives following equation:

$$K = \frac{\lambda}{C_{\text{NO}_3^-}^3 \cdot C_{\text{TBP}(\text{org})}^3} \quad \text{OR} \quad \lambda = K \cdot C_{\text{NO}_3^-}^3 \cdot C_{\text{TBP}(\text{org})}^3$$

Kilogram quantities of 95% pure lanthanides have been prepared by solvent extraction technique. Another organic solvent which is a better extractant than TBP is Di-(2-ethyl hexyl) phosphoric acid.

The major uses of solvent extraction process for separation of Ln^{+3} from Ln^{+4} , ions such as Ce^{+4} and Th^{+4} and in the purification of Ce, Th, and La.

Complex formation:

The lanthanides are moderate in their complex forming ability which increases to the right in the periodic table. The 4f-electrons of lanthanides are too well shielded to interact. Consequently, each lanthanide ion is effectively an inert gas-type ion, like those of the alkaline earth metals, that attracts ligands only by overall electrostatic forces. On this basis, we observe a general decrease in case of complex ion formation with a specific ligand in the series $\text{Ln}^{+4} > \text{Ln}^{+3} > \text{Ln}^{+2}$.

The tendency of the anhydrous Ln^{+3} ions to form complexes increases from La^{+3} to Lu^{+3} , whereas that of the hydrated Ln^{+3} ions, $\text{Ln}^{+3}(\text{aq})$, decreases in the same order. The difference in complexation tendencies of the anhydrous and hydrated ions is due to the fact that while the size of the Ln^{+3} ions decreases, that of the $\text{Ln}^{+3}(\text{aq})$ increases with the increasing atomic number.

Lanthanides due to the unavailability of orbitals for bonding, high basicity and larger size of their cation Ln^{+3} form few complexes which are mostly formed with oxygen or oxygen plus nitrogen containing chelating ligands such as β -diketones, hydroxo acids, amino acids, EDTA and oxine.

Since lanthanides are highly electropositive, they have little or no tendency to form complexes with π -bonding ligands. A complete study of $\text{Ln}(\text{C}_6\text{H}_5)_3$ shows that these compounds are salts rather than complex compounds. Eu and Yb also form the cyclopentadienides of the type $(\text{C}_6\text{H}_5)_2\text{Ln}$ where $\text{Ln} = \text{Eu}$ or Yb . Most

complexes are octahedral. But some 8, 9, and 10 coordinated complexes have been prepared. Bonding between lanthanide ions and coordinating ligands depends on the electronegativity of the bonding atom in the ligand. Bond formation follows the order F^- , OH^- , H_2O , NO_3^- , Cl^- etc., for monodentate ligands. Complex formation with bidentate ligands in the presence of water is usually successful only with ligands that form chelate rings through oxygen atoms.

Uses of lanthanides compounds:

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

(1) Ceramic applications: CeO_2 , La_2O_3 , Nd_2O_3 and Pr_2O_3 are widely used for decolorizing glass. Lanthanide oxides can absorb ultra-violet rays; thus, 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 ($Nd_2O_3 + Pr_2O_3$) (iii) glass protecting eyes from neutron radiation ($Gd_2O_3 + Sm_2O_3$). 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. ($Nd_2O_3 + Pr_2O_3$) gives a blue colour.

(2) Refractories: CeS (m.p. = $2000^\circ C$) is used in the manufacture of a special type of crucible which are used for melting metals in a reducing atmosphere at temperatures upto $1800^\circ C$. Borides, carbides and nitrides of lanthanides are also used as refractories.

(3) Abrasives: lanthanide oxides are used as abrasives for polishing glasses. e.g. the mixture of oxides, CeO (47%); $La_2O_3 + Nd_2O_3 + Pr_2O_3$ (51%) + SiO_2 , CaO , Fe_2O_3 etc. (=2%) which is called polirite has been used for polishing glasses.

(4) 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.

(5) In textiles and leather industries: Ceric salts are used for dyeing in textile industries and as tanning agents in leather industries. $Ce(NO_3)_4$ is used as a mordant for alizarin dyes. Chlorides and acetates of lanthanides make the fabric water proof and acid resistant.

(6) 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 insecto-fungicides and as trace elements in fertilizers.

(7) In lamps: salts of La, Ce, Eu and Sm are used as activators of luminophores. They are used in the manufacture of gas mantles, in coatings of luminescent lamps and for painting the screens of cathode-ray tubes.

(8) In analytical chemistry: $Ce(SO_4)_2$ is used as an oxidizing agent in volumetric titrations. Radio-isotopes of lanthanides are used in the study of co-precipitation, chromatographic separations etc.

(9) 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.

(10) 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.

(11) Nuclear applications: Certain elements and compounds of lanthanides used in nuclear fuel control and shielding and fluxing devices. Pr^{147} is used in the production of atomic battery.

Actinides

Actinides: (5f- Block elements)

Definition: The elements in which the extra electron enters 5f- orbitals of (n-2)th main shall are known as 5f-block elements, actinides or actinones. Thus, according to the definition of actinides only thirteen elements from $\text{Th}_{90}(5f^0 6d^2 7s^2)$ to $\text{No}_{102}(5f^{14} 6d^0 7s^2)$ should be the members of actinide series. However, all the fifteen elements from $\text{Ac}_{89}(5f^0 6d^1 7s^2)$ to $\text{Lw}_{103}(5f^{14} 6d^1 7s^2)$ are considered as the members of actinide series, since all these fifteen elements have same physical and chemical properties. In fact, actinium is prototype of actinides as lanthanum is the prototype of lanthanides.

The complete electronic configuration of actinides can be represented by general configuration is $2, 8, 18, 32, 5s^2, p^6 d^{10} f^{0-14}, 6s^2 p^6 d^{0-2}, 7s^2$

The valence shell configuration is $5f^{0,2-14} 6d^{0,1,2} 7s^2$. This configuration indicates that the additional electron enters the 5f-level without altering the electrons in the 7s-orbital.

Electronic configuration of actinides:

Nos.	Name	At. No. and symbol	Electronic configuration
1	Actinium	Ac_{89}	$[\text{Rn}] 5f^0 6d^1 7s^2$
2	Thorium	Th_{90}	$[\text{Rn}] 5f^0 6d^2 7s^2$
3	Protactinium	Pa_{91}	$[\text{Rn}] 5f^2 6d^1 7s^2$
4	Uranium	U_{92}	$[\text{Rn}] 5f^3 6d^1 7s^2$
5	Neptunium	Np_{93}	$[\text{Rn}] 5f^4 6d^1 7s^2$
6	Plutonium	Pu_{94}	$[\text{Rn}] 5f^6 6d^0 7s^2$
7	Americium	Am_{95}	$[\text{Rn}] 5f^7 6d^0 7s^2$
8	Curium	Cm_{96}	$[\text{Rn}] 5f^7 6d^1 7s^2$
9	Berkelium	Bk_{97}	$[\text{Rn}] 5f^9 6d^0 7s^2$
10	Californium	Cf_{98}	$[\text{Rn}] 5f^{10} 6d^0 7s^2$
11	Einsteinium	Es_{99}	$[\text{Rn}] 5f^{11} 6d^0 7s^2$
12	Fermium	Fm_{100}	$[\text{Rn}] 5f^{12} 6d^0 7s^2$
13	Mendelevium	Md_{101}	$[\text{Rn}] 5f^{13} 6d^0 7s^2$
14	Nobelium	No_{102}	$[\text{Rn}] 5f^{14} 6d^0 7s^2$
15	Lawrencium	Lw_{103}	$[\text{Rn}] 5f^{14} 6d^1 7s^2$

Oxidation states of actinide elements:

Comparison of the oxidation states of lanthanides with those of actinides indicates that +3 oxidation state is most common for both the series of elements. The oxidation state of actinide element is given below:

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw
						+2								
+3	-	-	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3
	+4	+4	+4	+4	+4	+4	+4	+4						
		+5	+5	+5	+5	+5								
			+6	+6	+6	+6								
				+7	+7									

This oxidation state becomes increasingly more stable as the atomic number increases in the actinide series. The increasing stability of +3 oxidation state is illustrated by the increasing difficulty of oxidation above +3 oxidation state. Actinides show a greater multiplicity of oxidation states. Since in the first half of the actinide series (i.e. lower actinides) the energy required for the conversion $5f \rightarrow 6d$ is less than that required for the conversion $4f \rightarrow 5d$, the lower actinides should show higher oxidation state such as +4, +5, +6 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 more than that required for the conversion $4f \rightarrow 5d$, and the higher actinides should show more lower oxidation states such as +2.

The tripositive oxidation state occurs widely in each series. The two groups of elements are not entirely comparable in this respect. The +3-state characteristic of lanthanides does not appear in aqueous solution of Th and Pa and this oxidation state become the predominantly stable oxidation state in aqueous solution of the actinides only when we reach Am.

For Th & Pa the +4 & +5 oxidation states are important respectively. From Uranium onward there is very closely related groups U, Np, Pu & Am in which the stability of higher oxidation state takes place.

The different oxidation states are explained as under:

+2 oxidation state: Only Am (Americium) is known to form a stable +2 state. This state is stable in CaF_2 only and has been studied by optical and electron spin resonance spectra.

+3 oxidation state: +3 state is a general oxidation state for most of the actinides. For Th and Pa +4 and +5 state respectively are important. An^{+4} ions resemble Ln^{+4} ions in their properties. A large number of isomorphous salts are given by the elements of both the series. Trichlorides and trifluorides of Ac, U, Np, Pu and Am are isomorphous. On hydrolysis all the halides give oxyhalides Ac, Pu, and heavier elements give the oxides of An_2O_3 type. Nitrate, perchlorates and sulphates are soluble while hydroxides, fluorides and carbonates are insoluble.

+4 oxidation state: This is the principle oxidation state for Th and is a stable oxidation state up to Am. Am^{+4} and Cm^{+4} exist only as complexes in concentrated fluorides solution of low acidity.

General chemistry of An^{+4} ions is similar to that of Ln^{+4} ions. The hydrated fluorides and phosphates of both An^{+4} and Ln^{+4} ions are insoluble ThO_2 , PaO_2 , UO_2 , NpO_2 , AmO_2 , CmO_2 and BkO_2 have fluorite structure. The tetrachlorides and tetrabromides of Th, Pa, U and Np are only known, while tetraiodides of Th, U and Np can be prepared by heating AnX_4 with Sb_2O_3 . An^{+4} ions form complexes mostly with anionic ligands like HSO_4^- , NO_3^- , Cl^- etc.

+5 oxidation state: This state is very important for Pa. Pa⁺⁵ resemble very much Na⁺⁵ and Ta⁺⁵. U, Np, Pu and Am also exist in +5 oxidation states, but these are less characterized. The only known pentahalides are those of Pa⁺⁵ and U⁺⁵. Fluoro anions of Pa, U, Np and Pu of the types AnF₆⁻, AnF₇⁻² and AnF₈⁻³ are known to exist in the solid state; AnO₂⁺ is the most important ion which contains An⁺⁵ cation. It has linear structure both in solid and solution.

+6 oxidation state: U, Np, Pu and Am show +6 oxidation state in divalent dioxo cation AnO₂⁺². This cation is linear both in solid and solution. The simple molecular halide, UO₂F₂ has the linear O-U-O group with fluorine bridges. The O-U bond distance is 1.75 Å to 2.00 Å. The overall structure is flattened octahedron. Although AnO₂⁺² cation is linear in shape, it forms complexes with exceptional geometries, e.g. four, five and six co-ordinated complexes are given by this cation.

+7 oxidation state: +7 oxidation state is shown only by Np and Pu. Electrolysis or ozone oxidation of Np⁺⁵ or Np⁺⁶ in NaOH gives a green solution of NpO₅⁻³ which is slowly reduced to Np⁺⁶ at 25°C.

Atomic and ionic radii - Actinide Contraction: The shielding of one *f*-electron by another from the effect of nuclear charge is quite weak on account of the shape of the *f*-orbital, hence with increasing atomic number, the effective nuclear charge experienced by each 5*f*-electron increases. This causes shrinkage in the radius of atoms or ions as one proceeds from Ac to Lw. This accumulation of successive shrinkage is called actinide contraction.

Comparison of Actinide and Lanthanide elements:

Lanthanides	Actinides
1. In lanthanide the newly added electron enters in 4 <i>f</i> - orbitals.	1. In actinide the newly added electron enters in 5 <i>f</i> - orbitals.
2. The name lanthanide is given because the first element is lanthanum and all the other elements have similar property to that of lanthanum element.	2. The name actinide is given because the first element is actinium and all the other elements have similar property to that of actinium element.
3. They have less binding energy, hence less shielding effect in 4 <i>f</i> - orbital.	3. They have more binding energy, hence more shielding effect in 5 <i>f</i> - orbital.
4. They have low tendency to form complex. They form complex with ligand having oxygen or oxygen plus nitrogen like glycine, oxalate etc.	4. They have greater tendency to form complex with π-accepter ligand and anions.
5. Their colour absorptive spectra are less intense than actinides.	5. Their colour absorptive spectra are more intense than lanthanides.
6. They have lower ionic radii than actinides.	6. They have greater ionic radii than lanthanides.
7. They have more magnetic moment than the actinides.	7. They have less magnetic moment than the lanthanides.

Position of Actinides in the Periodic table:

The position of actinides can be explained in two ways:

(i) Prior to the discovery of the trans-uranium elements:

Before 1940, the existence of the lanthanide series helped that another series of elements resulting from the addition of the electrons to an $(n-2)f$ -shell (i.e. $5f$ -shell) should occur somewhere in the heavy elements region. Prior to the discovery of trans-uranium elements, the naturally occurring heaviest known elements namely Th_{90} , Pa_{91} , and U_{92} were placed below Hf_{72} , Ta_{73} , W_{74} in IV B, V B and VI B 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. The undiscovered trans-uranium elements with atomic numbers 93 to 100 were thus expected to occupy the position in the periodic table below Re_{75} , Os_{76} , Ir_{77} , Pt_{78} , Au_{79} , Hg_{80} , Tl_{81} and Pb_{82} respectively as shown below:

																		III A	VII A																	
																		boron 5 10.811 B	carbon 6 12.0107 C																	
																		aluminum 13 26.981538 Al	silicon 14 28.0855 Si																	
III B	IV B	VB	VIB	VII B	VIII								IB	II B	III A	IV A	V A	VI A	VII A	VIII A	IX A	X A														
Sc 21 44.95591 sca ndium	Ti 22 47.867 tita nium	V 23 50.9415 van adium	Cr 24 51.9961 chro mium	Mn 25 54.93805 mang nese	Fe 26 55.845 iron	Co 27 58.9332 cob alt	Ni 28 58.6934 nick el	Cu 29 63.546 cop per	Zn 30 65.409 zinc	Ga 31 69.723 gall ium	Ge 32 72.64 ger man ium																									
Y 39 88.90585 ytha nium	Zr 40 91.224 zirc onium	Nb 41 92.90638 niba rium	Mo 42 95.94 moly bden um	Tc 43 [98] techn etium	Ru 44 101.07 ruth enium	Rh 45 102.9055 rho dium	Pd 46 106.42 pall adium	Ag 47 107.8682 sil ver	Cd 48 112.411 cad mium	In 49 114.818 ind ium	Sn 50 118.710 sta nnum																									
La 57 138.9055 latha nium	Hf 72 178.49 hafa nium	Ta 73 180.9479 tanta lum	W 74 183.84 wola fram ium	Re 75 186.207 rhen ium	Os 76 190.23 osmi um	Ir 77 192.2217 iridi um	Pt 78 195.078 plat inum	Au 79 196.96655 gola dium	Hg 80 200.59 mer cury	Tl 81 204.3833 thall ium	Pb 82 207.2 lead																									
actinium 89 [227] Ac	thorium 90 [232] Th	protactinium 91 [231] Pa	uranium 92 [238] U	93	94	95	96	97	98	99	100																									
<table border="1" style="width: 100%; border-collapse: collapse; text-align: center;"> <tr> <td>cerium 58 140.116 Ce</td> <td>praseodymium 59 140.90785 Pr</td> <td>neodymium 60 144.24 Nd</td> <td>promethium 61 [145] Pm</td> <td>samarium 62 150.36 Sm</td> <td>europium 63 151.964 Eu</td> <td>gadolinium 64 157.25 Gd</td> <td>terbium 65 158.9253 Tb</td> <td>dysprosium 66 162.50 Dy</td> <td>holmium 67 164.930 Ho</td> <td>erbium 68 167.259 Er</td> <td>thulium 69 168.934 Tm</td> <td>ytterbium 70 173.04 Yb</td> <td>lutetium 71 174.967 Lu</td> </tr> </table>																						cerium 58 140.116 Ce	praseodymium 59 140.90785 Pr	neodymium 60 144.24 Nd	promethium 61 [145] Pm	samarium 62 150.36 Sm	europium 63 151.964 Eu	gadolinium 64 157.25 Gd	terbium 65 158.9253 Tb	dysprosium 66 162.50 Dy	holmium 67 164.930 Ho	erbium 68 167.259 Er	thulium 69 168.934 Tm	ytterbium 70 173.04 Yb	lutetium 71 174.967 Lu	
cerium 58 140.116 Ce	praseodymium 59 140.90785 Pr	neodymium 60 144.24 Nd	promethium 61 [145] Pm	samarium 62 150.36 Sm	europium 63 151.964 Eu	gadolinium 64 157.25 Gd	terbium 65 158.9253 Tb	dysprosium 66 162.50 Dy	holmium 67 164.930 Ho	erbium 68 167.259 Er	thulium 69 168.934 Tm	ytterbium 70 173.04 Yb	lutetium 71 174.967 Lu																							

(ii) Following the discovery of the trans-uranium elements:

The discovery of the element neptunium (Np_{93}) came in 1940 and this discovery was followed shortly by the discovery of plutonium (Pu_{94}) in 1941. The tracer chemical experiment with Np_{93} and Pu_{94} showed that the chemical properties of these of Re_{75} and Os_{76} . On this basis in 1944, the position of U_{92} , Np_{93} and Pu_{94} was shown in the periodic table as shown below:

caesium 55 132.90545 Cs	barium 56 137.327 Ba	lanthanum 57 174.967 La	hafnium 72 178.49 Hf	tantalum 73 180.9479 Ta	tungsten 74 183.84 W	rhenium 75 186.207 Re	osmium 76 190.23 Os	iridium 77 192.217 Ir	platinum 78 195.078 Pt														
francium 87 [223] Fr	radium 88 [226] Ra	actinium 89 [227] Ac	thorium 90 [232] Th	protactinium 91 [231] Pa	uranium 92 [238] U																		
<table border="1" style="width: 100%; border-collapse: collapse; text-align: center;"> <tr> <td>uranium 92 [238] U</td> <td>neptunium 93 [237] Np</td> <td>plutonium 94 [244] Pu</td> <td>95</td> <td>96</td> </tr> </table>										uranium 92 [238] U	neptunium 93 [237] Np	plutonium 94 [244] Pu	95	96									
uranium 92 [238] U	neptunium 93 [237] Np	plutonium 94 [244] Pu	95	96																			
<table border="1" style="width: 100%; border-collapse: collapse; text-align: center;"> <tr> <td>cerium 58 140.116 Ce</td> <td>praseodymium 59 140.90785 Pr</td> <td>neodymium 60 144.24 Nd</td> <td>promethium 61 [145] Pm</td> <td>samarium 62 150.36 Sm</td> <td>europium 63 151.964 Eu</td> <td>gadolinium 64 157.25 Gd</td> <td>terbium 65 158.9253 Tb</td> <td>dysprosium 66 162.50 Dy</td> <td>holmium 67 164.930 Ho</td> <td>erbium 68 167.259 Er</td> <td>thulium 69 168.934 Tm</td> <td>ytterbium 70 173.04 Yb</td> <td>lutetium 71 174.967 Lu</td> </tr> </table>										cerium 58 140.116 Ce	praseodymium 59 140.90785 Pr	neodymium 60 144.24 Nd	promethium 61 [145] Pm	samarium 62 150.36 Sm	europium 63 151.964 Eu	gadolinium 64 157.25 Gd	terbium 65 158.9253 Tb	dysprosium 66 162.50 Dy	holmium 67 164.930 Ho	erbium 68 167.259 Er	thulium 69 168.934 Tm	ytterbium 70 173.04 Yb	lutetium 71 174.967 Lu
cerium 58 140.116 Ce	praseodymium 59 140.90785 Pr	neodymium 60 144.24 Nd	promethium 61 [145] Pm	samarium 62 150.36 Sm	europium 63 151.964 Eu	gadolinium 64 157.25 Gd	terbium 65 158.9253 Tb	dysprosium 66 162.50 Dy	holmium 67 164.930 Ho	erbium 68 167.259 Er	thulium 69 168.934 Tm	ytterbium 70 173.04 Yb	lutetium 71 174.967 Lu										

It was thought that the undiscovered elements with atomic numbers 95 and 96 should be very much like U_{92} , Np_{93} and Pu_{94} in their chemical properties. This assumption, however, proved to be wrong, since the experiments directed towards the discovery of elements with atomic numbers 95 and 96 on the pattern of discovery of Np_{93} and Pu_{94} failed. Later on, in the same year (1944) Seaborg thought that all the known elements heavier than Ac_{89} were wrongly placed in the periodic table as shown in above figure.

He advanced the idea that the elements having atomic numbers greater than that of Ac_{89} might constitute a second series of inner transition elements similar to the lanthanide series. These elements are called

actinide elements. The new position of the actinides was further confirmed by the fact that all the predicted elements up to 130 were discovered by 1961. As shown in figure below:

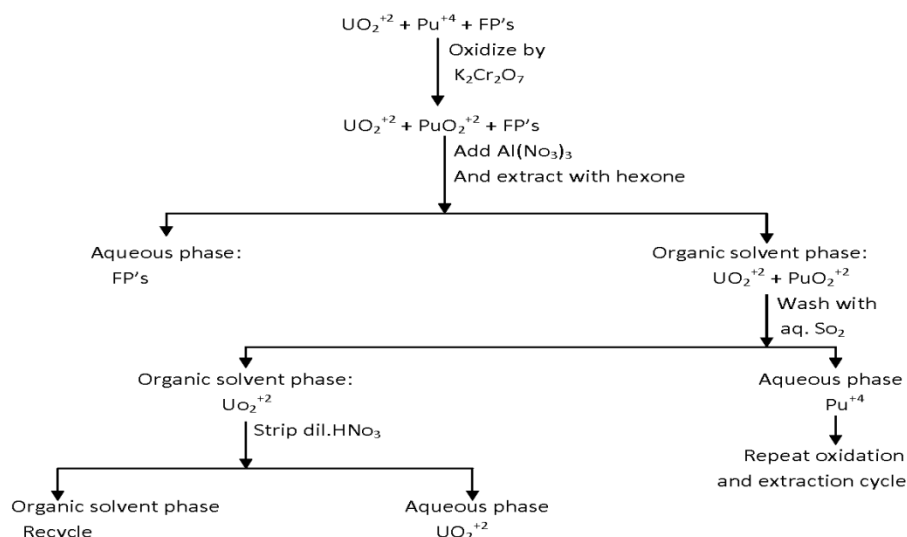
Lanthanides														
lanthanum 57 La 138.9055	cerium 58 Ce 140.116	praseodymium 59 Pr 140.90765	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.964	gadolinium 64 Gd 157.25	terbium 65 Tb 158.9253	dysprosium 66 Dy 162.50	holmium 67 Ho 164.930	erbium 68 Er 167.259	thulium 69 Tm 168.934	ytterbium 70 Yb 173.04	lutetium 71 Lu 174.967
Actinides														
actinium 89 Ac [227]	thorium 90 Th 232.038	protactinium 91 Pa 231.0369	uranium 92 U 238.0289	neptunium 93 Np [237]	plutonium 94 Pu [244]	95	96	97	98	99	100	101	102	103

Separation of Actinide elements:

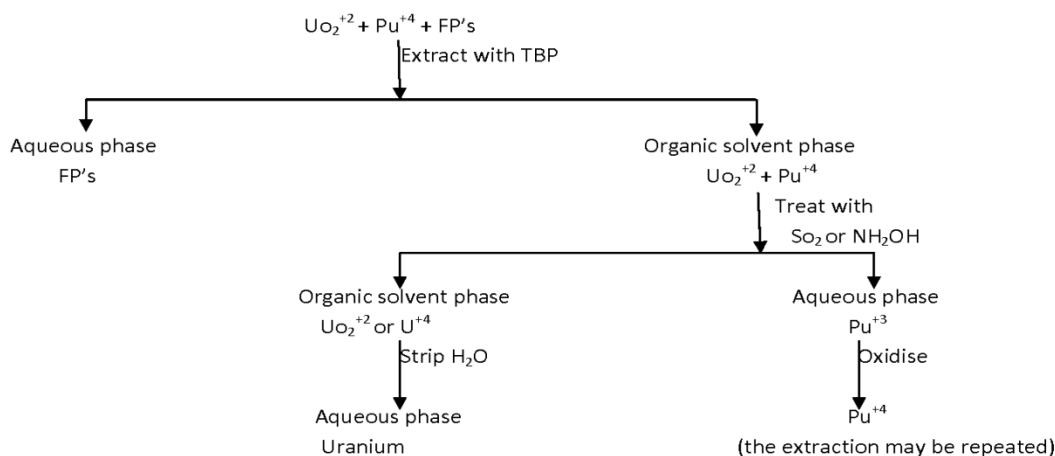
(1) Solvent extraction method:

This method depends on the extractability of the various oxidation state of actinide elements. This technique finds extensive application in the recovery of U and Pu from used – up nuclear fuels. This 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 solvent which are used as extractants. Because of the high velocity and density, TBP is used as 20% solution in kerosene. The method is preferentially applied to nitrate system, because other ions like sulphate, perchlorate, fluoride etc. are strongly complexing and tend to retain the method in aqueous solution. Hexane and diethyl ether require a high concentration of NO_3^- ions in the aqueous phase and it is achieved by adding $Al(NO_3)_3$ 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 below:

(i) Separation of Pu and U from fission products (FP's) by solvent extraction with hexone (Redox process).



(ii) Separation of Pu and U from fission products (FP's) by solvent extraction with tributyl phosphate TBP (Purex process):



(2) Ion – exchange method:

This is the best technique to separate the actinide ions. This method involves the following two steps:

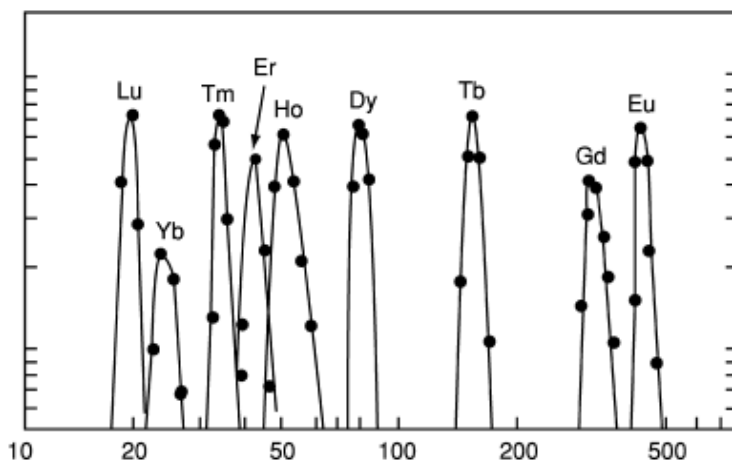
(i) Lanthanide – actinide separation:

The actinide as a group are separated from lanthanides by cation – exchange resin. Strong HCl is used as the eluting agent. The actinide ions from chloride complexes more easily and hence are eluted first.

Separation of actinides from Lanthanides is now done on an anion – exchange resin with 10ml LiCl as eluent at elevated temperature up to $90^\circ C$ with the exceptions of Gd, Ho and of Cm, Es the elution sequences proceed in the order of increasing atomic number. Thus, La is absorbed least strongly.

(ii) Separation of individual actinide elements:

The actinide ions can be separated from each other by removing from the cation exchange resin by elution with ammonium citrate, lactate, α -hydrogen isobutyrate and ethylene diamine tetraacetate. If the activity is plotted against the number of drops of eluent, elution curves will be obtained as shown below:



Lw (at. no. $Z = 103$) is predicted to leave the column first to be followed by No ($Z = 102$) and so on down the scale of atomic numbers. Elution position for Md ($Z = 101$), Fm ($Z = 100$) and down to Am ($z = 95$) are shown in the typical elution curves for lanthanides are also shown in figure as under.

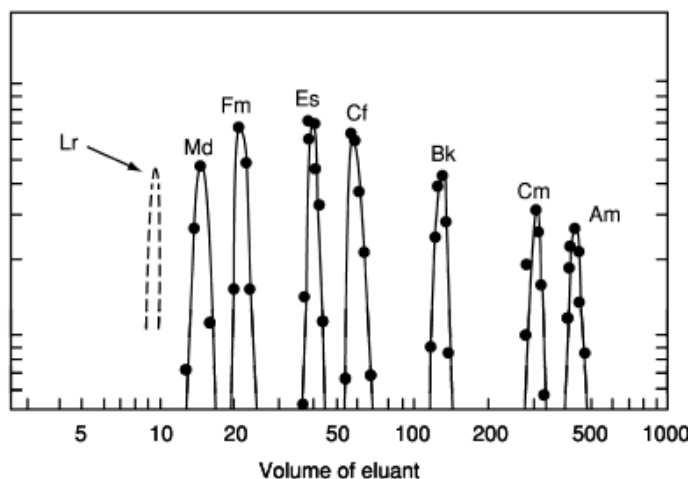


Figure: Elution curves showing the elution positions of Ln^{3+} and An^{3+} ions eluted from Dowex-50 ion-exchange resin with ammonia alpha-hydroxy-isobutyrate. The dotted elution curve indicates the predicted position of the undiscovered elements with atomic number 102.

It may be noted that a very striking similarity occurs in the spacing of the corresponding elements in the two series (e.g. Am and Eu, Cm and Gd, Bk and Tb etc.). It is similarity that made possible for scientists to predict the elution positions of the elements from Bk_{97} to Md_{101} before their discovery and which also makes possible today to predict the elution position of elements with No ($z = 102$) and Lw ($z = 103$).

There is a distinct breakdown between Gd and Tb (Lanthanide series) and between Cm and Bk (actinide series), which can be attributed to the small change in ionic radii made by the half-filling of $4f$ and $5f$ shells respectively. The elution order is not always regular as shown in above figure.

Colour and absorption spectra of actinide ions:

Colours and the wavelengths of the more prominent light absorption bands of actinide ions like An^{3+} , An^{4+} , AnO_2^+ and AnO_2^{+2} are given in table as under.

Table: Colour and Wave lengths (in Å) of more prominent light absorption bands of actinide ions.

Elements	An^{3+} ions	An^{4+} ions	AnO_2^+ ions	AnO_2^{2+} ions
Ac	Colourless($5f^0$)	–	–	–
Th	–	Colourless($5f^0$)	–	–
Pa	–	Colourless($5f^1$) (2240, 2550, 2700)	Colourless	–
U	Red ($5f^3$) (5200, 8800, 9000)	Green ($5f^2$) (5500, 6500)	–	Yellow (4000, 4110, 4250)
Np	Blue or Purple ($5f^4$) (5520, 6610, 7875)	Yellow-Green ($5f^3$) (5040, 7430, 8250)	Green	Pink to Red (4760, 5570)
Pu	Blue or Violet ($5f^5$) (5600, 6000, 6030)	Tan to orange brown ($5f^4$) (4700, 6550, 8150)	Reddish- Purple	Yellow to pink orange (8330, 9530, 9830)
Am	Pink ($5f^6$) (5027, 8200)	Rose ($5f^2$)	Yellow (5131, 7151)	Run-coloured (6660, 9950)
Cm	Colourless($5f^7$) (2368, 2680, 2774)	–	–	–

If may be seen that by comparing the colours of Ln^{+3} and An^{+3} ions the pairs of ions which have the same number of f - electrons ($4f$ and $5f$ electron) have roughly comparable colour. The pairs viz. (i) Nd^{+3} ($4f^3$ - reddish) and U^{+3} ($5f^3$ - reddish) 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 sub- shell. It has been found that the absorption bands seen in case of actinide ions are about ten times sharper than those seen in case of lanthanide ions. The absorption spectra of lanthanide ions are observed due to electronic transitions between energy states within the $4f$ -electron sub-shell.

Light absorption spectra of lanthanides are much more affected by environment. 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 absorptions bands.

Magnetic properties of Actinide elements:

In the $5f$ -series, Pu^{+3} and Am^{+3} ions show analogous behavior as noted for Sm^{+3} and Eu^{+3} ions in $4f$ -series. The magnetic properties of the actinide's ions are considerably more difficult to explain than those of the lanthanide ions. The values of magnetic moments found experimentally are usually lower than those calculated using Russell-Saunders coupling scheme. This is due perhaps to the inadequacy of the Russell-Saunders coupling scheme for $5f^n$ ions and also to more soluble ligand field effects which involve $5f$ - orbitals to a greater extent than the $4f$ -orbitals are involved in bonding in the lanthanide complexes.

An equation used for the calculation of molar susceptibility χ_M is given by,

$$\chi_M = \frac{Ng^2\beta^2J(J+1)}{3kT} + N\alpha$$

Where N = Avogadro's number, g = lande splitting factor

Which is given by:

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

$$\beta = \text{Bohr magneton} = \frac{eh}{2\pi mc}$$

$$= 9.27 \times 10^{-21} \text{ erg/gauss}$$

J = Total angular momentums of atom = | L+S |

k = Boltzmann constant, T = absolute temperature and α = small temperature independent term due to second order Zeeman effect.

Strictly speaking the above equation can be applied only to gaseous ions in which the multiplet intervals are larger compound to kT and value of J to be used in it is taken from the ground state symbols of ions.

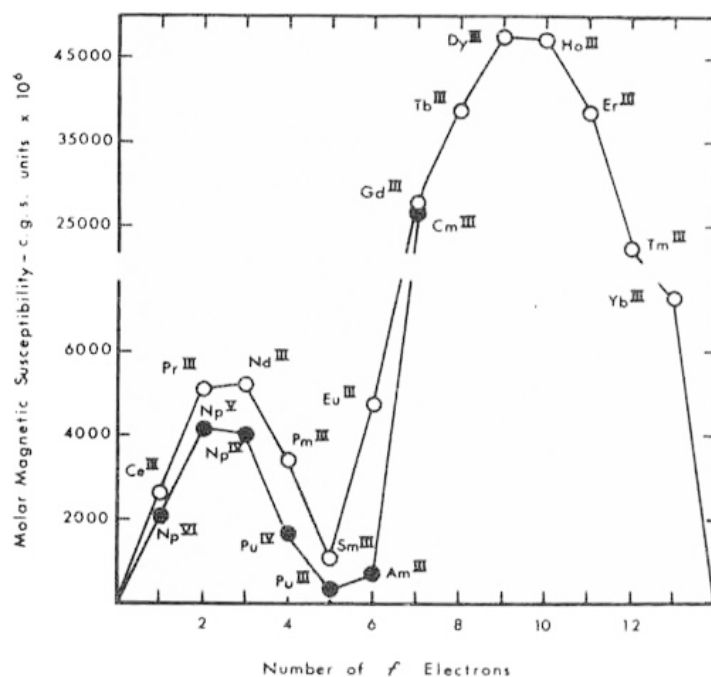


Figure: Comparison of magnetic susceptibility of Lanthanides and Actinides

A comparison of the plots of molar magnetic susceptibilities of tripositive lanthanide and actinide ions against the number of 4f- or 5f- electrons (as shown in above figure) reveals that there are remarkable similarities between the two plots. The plot of lanthanide ions has two humps while that of actinide ions has only one. In both the cases the first hump is at the identical place. The moments of the lanthanide ions agree closely with theoretical predictions but those of the transuranic ions are somewhat lower than expected as shown in figure below. This is because the 5f-electrons of the transuranic ions are less effectively screened from the crystal field and then are the 4f-electrons of the lanthanide ions.

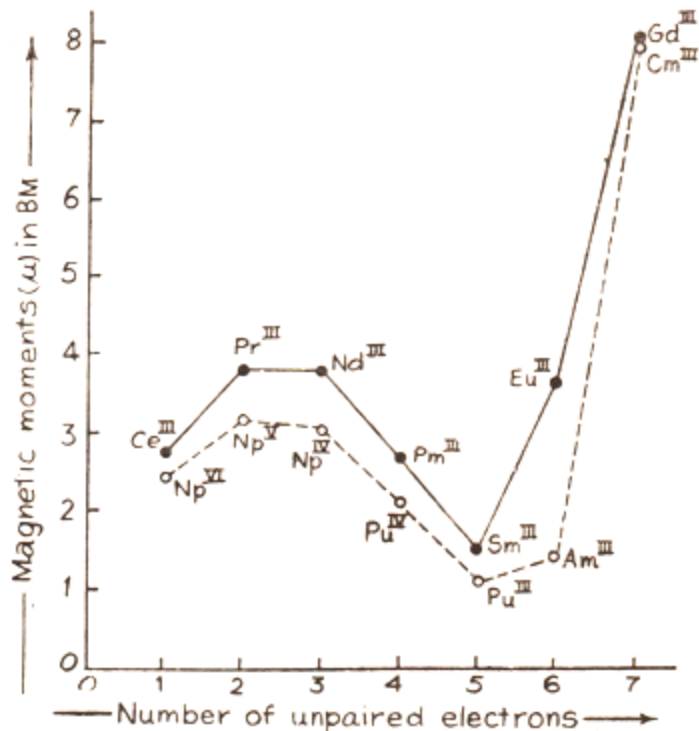
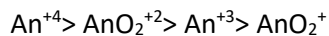


Figure: Comparison of magnetic moments of Lanthanides and Actinides.

Complex formation of Actinide elements

The degree of complex formations decreases in the order:



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

Singly charged anions: $\text{F}^- > \text{NO}_3^- > \text{Cl}^-$

Doubly charged anions: $\text{CO}_3^{2-} > \text{Ox}^{2-} > \text{SO}_4^{2-}$

Actinides also form complexes with a large number of organic substances.

LONG FORM OF THE PERIODIC TABLE

PERIODS ↓	Representative Elements		Transition Elements										Representative Elements						Noble gases	
	←s-Block→	→d-Block←	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16		17
GROUPS →	(IA)	(IIA)	(IIIB)	(IVB)	(VA)	(VIB)	(VIIB)	(VIII)	(VIII)	(VIII)	(VIII)	(IB)	(IIB)	(IIIA)	(IVA)	(VA)	(VIA)	(VIIA)	(VIIA)	(0)
1 (1s)	1 H																			2 He
2 (2s 2p)	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne	
3 (3s 3p)	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
4 (4s 3d 4p)	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr		
5 (5s 4d 5p)	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe		
6 (6s 4f 5d 6p)	55 Cs	56 Ba	57 La*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn		
7 (7s 5f 6d 7p)	88 Fr	88 Ra	89 Ac**	104 Ku/Rt	105 Ha	106 Unh	107 Ns	108 Hs	109 Mt	110 Uhm										

Inner Transition Elements or f-Block Elements
 $[(n-2) f^{1-14} (n-1) d^{0-1} ns^2]$

LANTHANIDES* (4f ¹⁻¹⁴ 5d ⁰⁻¹ 6s ²)	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
ACTINIDES** (5f ¹⁻¹⁴ 6d ⁰⁻¹ 7s ²)	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Table 2.1 : Long form of the periodic table