Lanthanides

[A] 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	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 upto 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 $2,8,18,4s^2\ p^6\ d^{10}\ f^{0,2\text{-}14}$, $5s^2\ p^6\ d^{0\text{ or }1}\ 6s^2$.

The valence shell configuration is $4f^{0,2\text{-}14}\ 5d^{0\text{ or }1}\ 6s^2$. 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 is 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} =0.96^0A and Y^{+3}=0.93 A^0).

(b) Y generally occurs in nature associated with the ores of heavier lanthanides and resembles Tb (III) and Dy (III) in its compounds. It therefore because 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 have been placed separately in the lower part of the periodic table.

- **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 ThO_2 =7.5%, Ce_2O_3 =30%, P_2O_5=29%, 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 210^0C 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.

$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4 \rightarrow 2H^+ + 2H_2PO_4^-$$

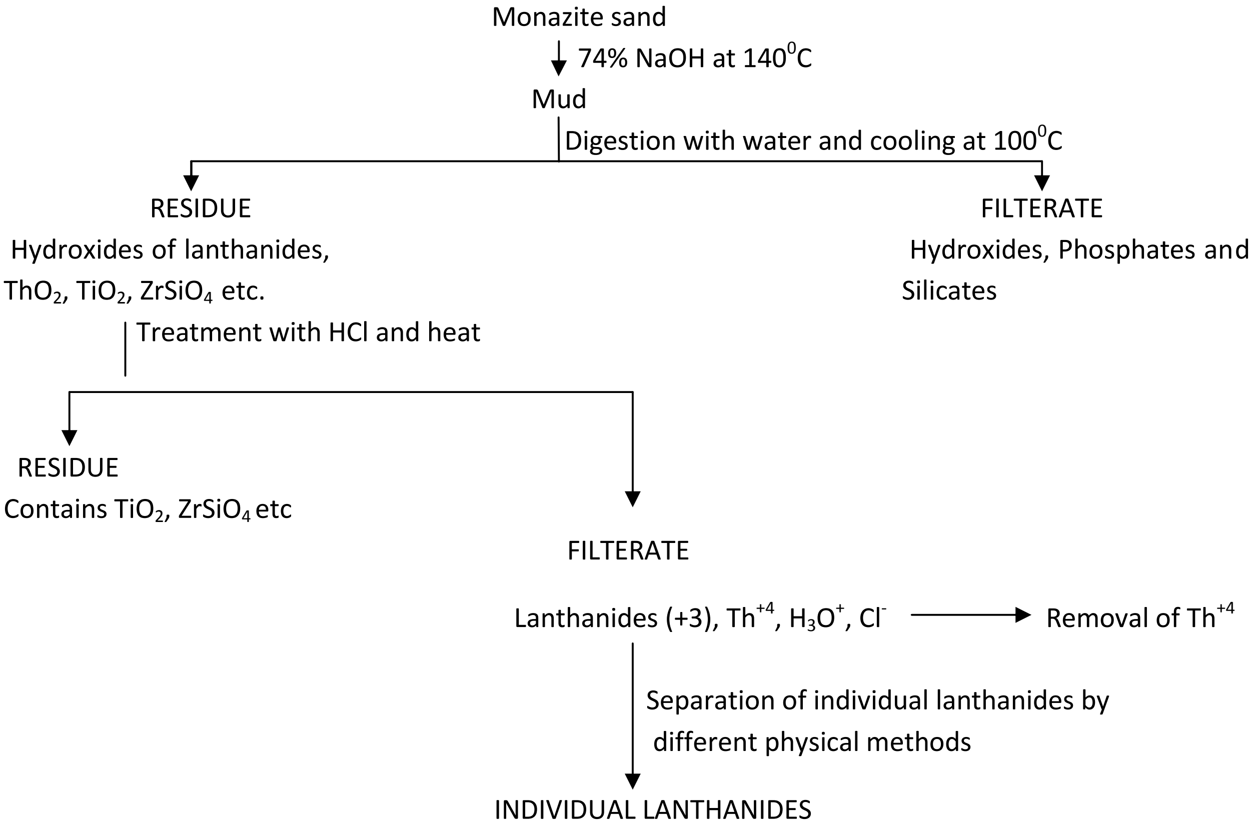
This solution is treated with sodium pyrophosphate($Na_2P_2O_7$) to precipitate thorium as $Th(P_2O_7)_2$. The remaining filtrate is treated with oxalic acid to precipitate a mixture of oxalates of lanthanides and little amount of thorium and zirconium oxalates. This mixture is then boiled with ammonium 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 ^{0}C mixture of oxides of lighter lanthanides with a rough composition of La_2O_3 = 17%, CeO_2 = 5%, Pr_2O_3 = 8% Nd_2O_3= 20%, Sm_2O_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 $Ce(NO_3)_4$ which is further converted into red basic nitrate $Ce(OH)(NO_3)_3{\cdot}3H_2O$ 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.



- **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-orabitals. Hence, there occurs no appreciable change in the outer most arrangement of the electronic shells with increase in atomic number.

(1) 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 from the aquated species (i.e. hydration energy) are such that 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 too 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 the 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. It may thus be 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 ~ 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 ~ Pr > (Nd ~ 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 25^0C, we observed that:

(i) The high positive values of oxidation electrode potentials for the couple $Ln^0{}_{(s)} \rightleftharpoons Ln^{3+}{}_{(aq)} + 3e^-$ 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 decries 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 25^0C, in acid solution, of these cations are given below:

$Sm^{+3}{}_{(aq)} + e^- \leftrightarrow Sm^{+2}{}_{(aq)}$ – 1.55 volts

$Eu^{+3}{}_{(aq)} + e^- \leftrightarrow Eu^{+2}{}_{(aq)}$ – 0.43 volts

$Yb^{+3}{}_{(aq)} + e^- \leftrightarrow Yb^{+2}{}_{(aq)}$ – 1.15 volts

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 oxidised by H_3O^+ ion, while Eu^{+2} ion is fairly stable and is only slowly oxidized by H_3O^+ ion.

$2Sm^{+2}(\text{or } Yb^{+2}) + 2H_3O^+ \rightarrow 2Sm^{+3}(\text{or } 2Yb^{+3}) + 2H_2O + H_2$

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.

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

$2Ln^{+2} + 2H_2O \rightarrow 2Ln^{+3} + 2OH^- + H_2 \uparrow$

Chemistry of +4 state:

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

The standard oxidation potentials at 25^0C, in acid solution, of Ce^{+4} and Pr^{+4} ions are given as under:

$Ce^{+4} + e^- \leftrightarrow Ce^{+3} + 1.74$ volts

$Pr^{+4} + e^- \leftrightarrow Pr^{+3} + 2.86$ volts

There values show that Ce(IV) and Pr(IV) are strong oxidizing agents. $Ce(SO_4)_2$ is generally used in volumetric analysis. Ce^{+4} ion is readily reduce 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 at OH^-, CO_3^{-2}, SO_4^{-2} etc. decompose on heating gives first basic salt and finally oxides.

Compounds of Ln^{+3} cation with the anions Cl^-, Br^-, I^-, NO_3^-, CH_3COO^-, BO_3^{-3} are generally soluble in H_2O, While of F^-,OH^-,O^{-2},$C_2O_4^-$ etc. are generally insoluble in H_2O.

OXIDES: The oxides Ln_2O_3 are formed by heating the metal in O_2 or by decomposition of $Ln(OH)_3$ or oxy salts like $Ln_2(CO_3)_3$ and $Ln(NO_3)_3$. Oxides are similar to alkaline earth oxides. All are insoluble in water. They absorb CO_2 and H_2O 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 by ammonia of dilute alkali to soluble salts of Ln^{+3} ion in solution.

The hydroxides are not amphoteric. They have hexagonal structure. They absorb CO_2 to give carbonate. Oxides and hydroxides are basic. The basicity decreases with increasing atomic number. La_2O_3 and $La(OH)_3$ are most basic, while Lu_2O_3 and $Lu(OH)_3$ are least basic.

Carbonates ($Ln_2(CO_3)_3$): The normal carbonates can be prepared by passing CO_2 into aq. solution of $Ln(OH)_3$. They can be prepared by adding Na_2CO_3 solution to Ln^{+3} salt solution. The CO_3^{-2} are insoluble in H_2O but dissolve in acids with liberation of CO_2 and forming Ln^{+3} salts.

Halides (LnX_3): Fluorides are pptd. by the addition of HF to Ln^{+3} salt solution. The fluorides of heavier lanthanides are sparingly soluble in HF to Ln^{+3} salt solutions. 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 $COCl_2$ or NH_4Cl.

$$Ln_2O_3 + 3COCl_2 \longrightarrow 2LnCl_3 + 3CO_2$$

$$Ln_2O_3 + 6NH_4Cl \xrightarrow{300\ C} 2LnCl_3 + 3H_2O + 6NH_3$$

Color and absorption spectra of Ln^{+3} ions:

The colour of crystalline compounds of number of Ln^{+3} ions persists 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 correlated 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 bonds 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 considerable influenced by the chemical environment. A charge transfer phenomena 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 4 fe^- 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.

Case of Lanthanide Contraction:

In Lanthanides the additional electrons enters 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, $Ln(OH)_3$:

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 decreases in the order, $La^{+3} > Ce^{+3} > Pr^{+3} .... > Lu^{+3}$. 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 hydrolyse 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 $Ln \rightarrow Ln^{+3} + 3e^-$ 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 Ln(III) hydroxides. Thus $La(OH)_3$ is the most basic while $Lu(OH)_3$ 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 A^0 and Er^{+3} =0.96 A^0). 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 show 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:

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

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

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

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

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

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

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

Methods used for the separation of Lanthanides:

The methods of separation of lanthanides are broadly classified into two classes:

(a) old classical methods:

(i) Fractional crystallization (ii) Fractional precipitation method (iii) Fractional thermal decomposition of oxy- salts (iv) Change of oxidation states by selective oxidation or reduction procedures.

(b) 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

- **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 $–SO_3H$ or –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 $–SO_3H$ or –COOH group of the resin and get fixed on the resin.

$$Ln^{+3}{}_{(aq)} + 3HR_{\ (solid)} \leftrightarrow LnR_{3(solid)} + 3H^+{}_{(aq)}$$

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

$$LnR_3 + NH_4^+ \rightarrow NH_4R + Ln^{+3}$$

$$Ln^{+3} + \text{citrate ion} \rightarrow \text{Ln-citrate complex}$$

We have seen that since $La^{+3}{}_{(\ aq)}$ is attached to resin with maximum and $Lu^{+3}{}_{(\ aq)}$ 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 pass 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 $Ln^{+3}_{(aq)}$ ions in presence of NO_3^- ions.

$$Ln^{+3}_{(aq)} + 3\,NO^-_{3\,(aq)} + 3TBP_{(org)} \leftrightarrow \underset{\text{Complex}}{Ln(NO_3)_3(TBP)_{3(org)}}$$

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

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

$$= \frac{C_{Ln}(NO3)_3\ (TBP)_3(org)}{C_{Ln}{}^{+3}\ \ (aq)} \qquad \text{..........(1)}$$

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

$$\alpha = \frac{\lambda'}{\lambda} = \frac{C_{Ln}(NO3)_3\ (TBP)_3(org) \cdot C_{Ln}{}^{+3}\ \ (aq)}{C_{Ln}(NO3)_3\ (TBP)_3(org) \cdot C_{Ln}{}'^{+3}\ \ (aq)} \qquad \text{...........} \quad (2)$$

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:

$$K = \frac{C_{Ln}(NO3)_3\ (TBP)_3(org) \cdot C_{Ln}{}^{+3}\ \ (aq)}{C^{+3}_{Ln\ (aq)} \cdot C^3_{NO3-} \cdot C^3_{TBP(org)}} \qquad \text{.............} \quad (3)$$

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

$$K = \frac{\lambda}{C^3_{NO3-} \cdot C^3_{TBP(org)}} \qquad \text{OR} \quad \lambda = K \cdot C^3{}_{NO3^-} \cdot C^3{}_{TBP(org)}$$

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.

- **Uses of lanthanides and there compounds:**

(A) Uses of elements:

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

(ii) Uses of mish- methods: Alloys of lanthanides are known as mish- methods. The major constituents of mish –methods 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. Mg- alloys containing about 30% mish metal and 1% Zr are useful in making parts of jet engine.

(B) Uses of lanthanide 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. = 2000^0C) is used in the manufacture of a special type of crucible which are used for melting metals in a reducing atmosphere at temperatures upto 1800^0C. 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 dying 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 $3Ln_2O_3 \cdot 5Fe_2O_3$ 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.