B] Chemistry of f-Block elements

The f block elements are those which have partly filled f subshell of the anti-penultimate i.e. $(n-2)^{th}$ energy shell in their elementry or ionic state. These elements are also called inner transition elements & are divided into two series i.e.

1) The Lanthanide series
2) The Actinide series.

The general electronic configuration of the f-block element is

$$(n-2)f^{1-14}, (n-1)d^{0-1}, ns^2$$

① Lanthanides :-

Lanthanum (Z = 57) & the next 14 elements (Z = 58-71) are called lanthanides or lanthanones.

ⓘ Electronic configuration:-

At. NO.	Element	Electronic configuration
57	La	$[xe]\ 5d^1\ 6s^2$
58	Ce	$[xe]\ 4f^1\ 5d^1\ 6s^2$
59	Pr	$[xe]\ 4f^2\ 5d^1\ 6s^2$
60	Nd	$[xe]\ 4f^3\ 5d^1\ 6s^2$
61	Pm	$[xe]\ 4f^4\ 5d^1\ 6s^2$
62	Sm	$[xe]\ 4f^5\ 5d^1\ 6s^2$
63	Eu	$[xe]\ 4f^6\ 5d^1\ 6s^2$
64	Gd	$[xe]\ 4f^7\ 5d^1\ 6s^2$
65	Tb	$[xe]\ 4f^8\ 5d^1\ 6s^2$
66	Dy	$[xe]\ 4f^9\ 5d^1\ 6s^2$
67	Ho	$[xe]\ 4f^{10}\ 5d^1\ 6s^2$
68	Er	$[xe]\ 4f^{11}\ 5d^1\ 6s^2$
69	Tm	$[xe]\ 4f^{12}\ 5d^1\ 6s^2$
70	Yb	$[xe]\ 4f^{13}\ 5d^1\ 6s^2$
71	Lu	$[xe]\ 4f^{14}\ 5d^1\ 6s^2$

(b) Lanthanide contraction :-

The steady decrease in ionic radius g all along the series is known as Lanthanide contraction.

Total decrease = 0.22A°

Ion	Radius	Ion	Redius
La^{3+}	1.15 A°	Tb^{3+}	1.00
Ce^{3+}	1.11	Dy^{3+}	0.99
Pr^{3+}	1.09	Ho^{3+}	0.97
Nd^{3+}	1.08	Er^{3+}	0.96
Pm^{3+}	1.06	Tm^{3+}	0.95
Sm^{3+}	1.04	Yb^{3+}	0.94
Eu^{3+}	-	Lu^{3+}	0.93
Gd^{3+}	1.02		

- ~~case~~ consequences of Lanthanide contraction:-

Lanthanide contraction is an important factor in allowing the separation g Lanthanides from one another. Also, it has highly significant effect on the relative Properties g the elements which Precede & follow the lanthanides in the Periodic table.

e.g. The radius g La^{3+} is 0.21 A° larger than that g Y^{3+} ion which lies above in Periodic table.

- The ionic radius of Hf^{4+} ion should have been greater than that of Zr^{4+} ion by about 0.2Å. But the occurance of lanthanide contraction of about the same order almost exactly cancels the expected increase. This results in Hf^{4+} & Zr^{4+} ions have almost identical radii. It also shows almost identical chemical properties.
- Similarly, as a result of lanthanide contraction the atomic (covalent) radii of the elements which follow lanthanides e.g. Hf, Ta, W etc are very simillar to those of the elements of the previous row. The properties of these pairs of elements are also very simillar.

It is thus a direct consequences of lanthanide contraction, that elements of the 2nd & 3rd transition series resemble each other much more closely than do the elements of 1st & 2nd transition series.

⊙ Cause of Lanthanide contraction :-

o As we move through the lanthanide series, 4f $\bar{e}$ are being added one by one.
- The mutual shielding effect of f $\bar{e}$ is very little, being even smaller than that of d-$\bar{e}$s. This is due to shape of the f-orbitals. Due to increase in nuclear charge the inward pull experienced by the 4f $\bar{e}$ increases. This cause a reduction in the size of the entire $4f^n$ shell. The sum of the successive reduction gives the total lanthanide contraction.

⊙ Magnetic Properties of Lanthanides :-

The La^{3+}, Lu^{3+}, Ce^{4+} & Yb^{2+} ions which have $4f^0$ or $4f^{14}$ electronic configuration are dimagnetic. The rest of the trivalent lanthanide ions which contain unpaired $\bar{e}$ in the 4f orbitals are paramagnetic. The magnetic properties of the lanthanides are different from those of the transition elements.

In general, the magnetic moments arise from two types of motion of $\bar{e}$.
- Spin motion of $\bar{e}$ around its own axis produces magnetic moment called spin magnetic moment

- The orbital motiong $\bar{e}$ around the nucleus produces magnetic moment called orbital magnetic moment. The observed magnetic properties g substance are thus the result g both the spin & orbital magnetic moment.

The magnetic moment is given by

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

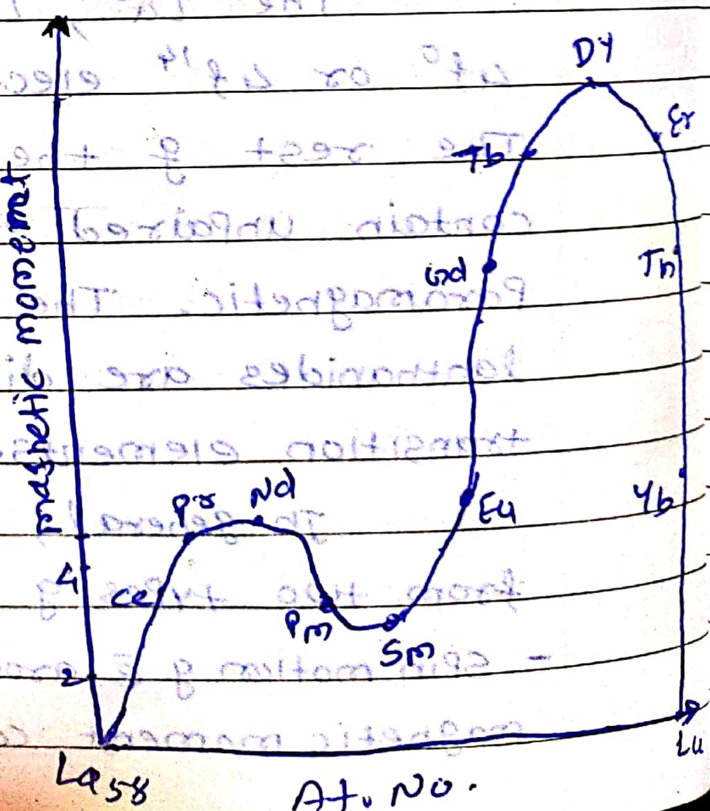
Where g =

J = total angular momentum q.N.

magnetic moments g tripositive Lanthanide ion.

Ion	Expt.	Theor
La^{3+}	0	0
Ce^{3+}	2.3-2.5	2.54
Pr^{3+}	3.4-3.6	3.58
Nd^{3+}	3.5-3.6	3.62
Pm^{3+}	—	2.62
Sm^{3+}	1.4-1.7	0.84
Eu^{3+}	3.3-3.5	0
Gd^{3+}	7.9-8.0	7.94
Tb^{3+}	9.5-9.8	9.72
Dy^{3+}	10.4-10.6	10.65
Ho^{3+}	10.4-10.7	10.60

Graph



① Variation in Properties of Lanthanides

1) oxidation state :

The common oxid^{h} state of all the lanthanide is +3.

2) Basic Character :-

All the lanthanide forms trivalent ionic compounds their hydroxide $M(OH)_3$ are ionic & basic in character.

- They are stronger bases than $Al(OH)_3$ but weaker than $Ca(OH)_2$
- since ionic size decreases from La^{3+} to Lu^{3+}, the basicity of hydroxides decreases.
- Thus $La(OH)_3$ is strongest & $Lu(OH)_3$ is weakest base.

3) oxidation Potential :-

The standard oxid^{h} Potential of Lanthanide for half reach

$$M_{(s)} \longrightarrow M^{3+}_{(aq.)} + 3e^-$$

Lanthanides have oxid^{h} Potential value quite high & in accordance with their electro+ve character.

- There is however a trend towards slight decrease in oxid^{h} potential due to lanthanide contraction.

4) colour :-

- The colour of the lanthanide ion is depends upon the number of f-electrons.
- The colour g the $x f \bar{e}$ is about the same as those with $(14-x) f \bar{e}$.
- The absorption band in the visible region arises because g the absorption g light in the visible range results in the transition of the $\bar{e}$ g lower f orbitals to higher f-orbitals.
- Thus it appears in the colour which is complementary to the colour light absorbed.
- This type g transition is known as f-f transition

e.g.

Ion	unpair $\bar{e}$				
La^{3+}	0	colourless	Tb^{3+}	06	Pale Pink
Ce^{3+}	1	colourless	Dy^{3+}	05	Yellow
Pr^{3+}	2	Green	Ho^{3+}	04	Pale yellow
Nd^{3+}	3	Lilac	Er^{3+}	03	Pink
Pm^{3+}	4	Pink	Tm^{3+}	02	Pale green
Sm^{3+}	5	yellow	Yb^{3+}	01	colourless
Eu^{3+}	6	Pale Pink	Lu^{3+}	0	colourless
Gd^{3+}	7	colourless			

5) Chemical reactivity :-

- Lanthanides are highly reactive
- Lanthanides are differ only in number of $4f \bar{e}$

that is why they show very little difference in their Chemical reactivity.

- They react with oxygen to give sesquioxide (M_2O_3)
- Lanthanide combines with hydrogen to form hydrides MH_2 & MH_3
- It also reacts with non-metals like X, S, P, N C, Si gives corresponding compounds.

6) complex formation :-

- Lanthanide ions inspite of the high Charge (+3) have low Charge density because of their large size.
- Therefore they have weak tendancy to form complexes.
- Their complexes with unidentate ligands are very few.
- They donot Form complexes with π bonding ligands.
- The tendancy to form complexes & their stability increases with increase in atomic number.

① Separation of Lanthanide by ion exchange Chromatography :-

This is most useful & rapid method for the separation of Lanthanides

The reacn that takes place is

$$M^{3+} + 3H\text{-}Resin \rightleftharpoons M(Resin)_3 + 3H^+$$

"The technique which is used for the separation of lanthanide ions with the help of cation exchanger is known as cation exchange chromatography."

- In this technique, the soln containing a mixture of lanthanides ions is passed through a column packed with particles of a suitable cation exchange resin.
- The cations in soln undergo exchange with the H^+ or any other cation that may be present in the ion exchanger.
- The cation which has the maximum capacity to undergo exchange process is held near the top & the other cations are held further down the column in the order of their decreasing capacities to undergo the exchange reaction.
- Another soln containing a stronger exchanger such as H^+ ions, is then used as an eluent.

- The function of the eluent is to release the lanthanides ions held on the resin.
- dil. HCl is good eluent in many cases. It allow to Percolate slowly through the column H^+ ion displace the other cation held on the resin.

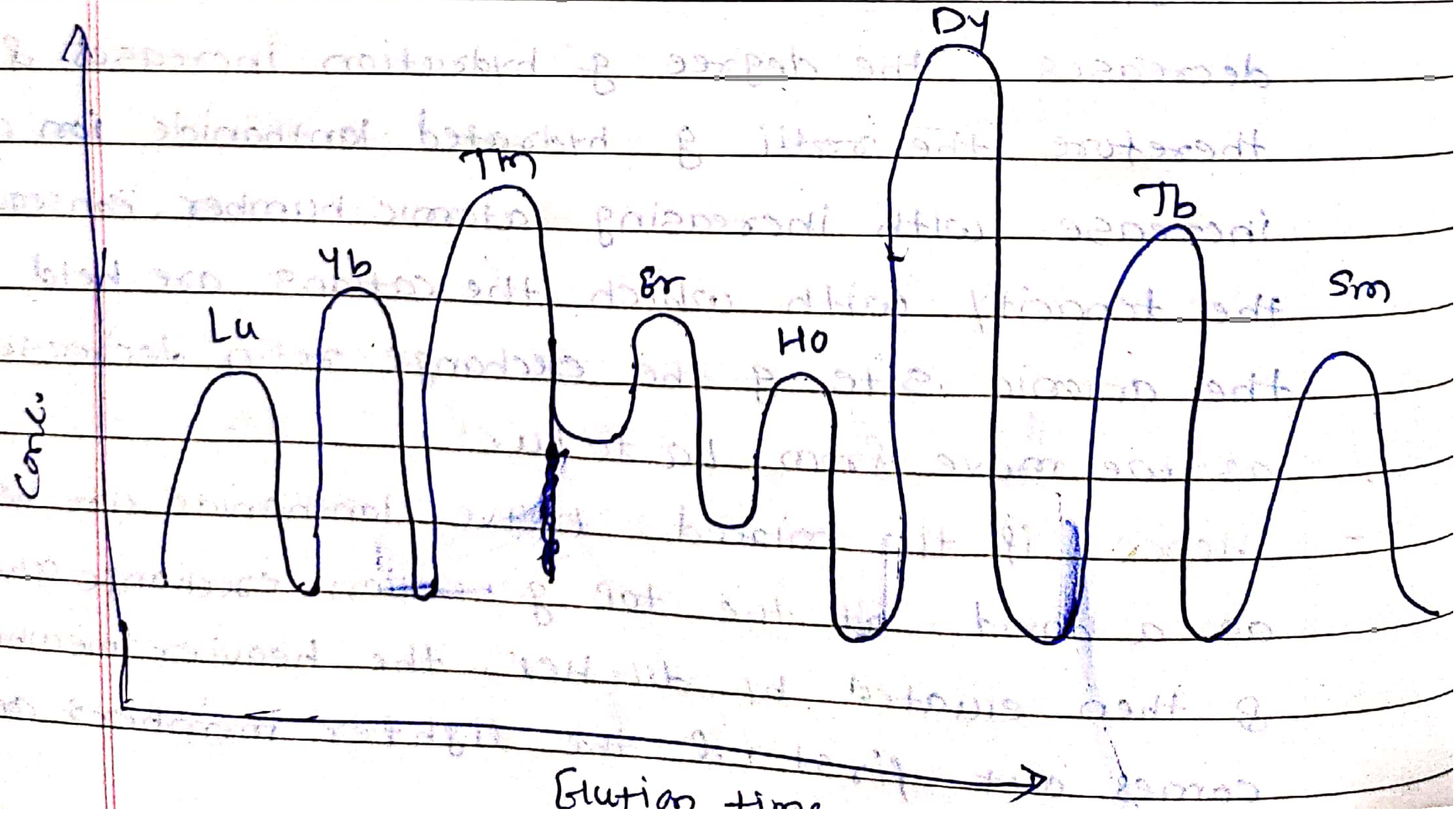
$$M(Resin)_3 + 3H^+ \longrightarrow 3H-Resin + M^{3+}$$

The eluate contains the 1st component (cation) which was least firmly held on the resin. It is followed by other component (cations) in order of increasing strength with which they are held by resin. Thus the eluate coming out last from the bottom of the column is that which was most firmly held by the resin.

- In lanthanides from La to Lu the ion size decreases, the degree of hydration increases & therefore the radii of hydrated lanthanide ion (III) increase with increasing atomic number. consequently the tenacity with which the cations are held by the anionic site of the exchange resin decreases as we move from La to Lu.
- Hence if the mixed tri +ve lanthanide are held as a band at the top of cation exchange column & then eluated by dil. HCl. the heavier members comes out first & the lighter members comes

out last. But in lanthanide size do not vary much, the separation by this technique is only partial. so that citrate sol^n is used (Instead of HCl)

- As we move La^{3+} to Lu^{3+} stability of complex increases. due to citrate ion lanthanide ions no longer remain hydrated & their radii decreases with increase in atomic number.
- Hence during elution with citrate buffer sol^n Lu^{3+}- citrate complex ion have max. stability & hence maximum preference for the aq. mobile phase (eluent) comes out first while the La^{3+} citrate complex having minimum stability & minimum preference for aq. phase comes out last



① uses of Landhanides / Applications :

- Steel mixed with La, Ce, Pr & Nd is used in the manufacturing of flame throwing tanks.
- Ce - mg alloys are used for the mft. of flash light powders.
- Ce absorbs both heat & U.V. light ∴ Ce glass is used in glare-reducing spectacles
- oxides of Ce are used in gas mantles.
- Ce salts are used in qualitative analysis as well as for dyeing cotton. They are also used as catalyst.
- Ln salts have been used in Lasers.

Actinides

⊙ Electronic Configuration :-

At. NO.	Element	Electronic configuration
89	Ac	$[Rn]\ 6d^1 7S^2$
90	Th	$[Rn]\ 5f^1 6d^1 7S^2$
91	Pa	$[Rn]\ 5f^2 6d^1 7S^2$
92	U	$[Rn]\ 5f^3 6d^1 7S^2$
93	Np	$[Rn]\ 5f^4 6d^1 7S^2$
94	Pu	$[Rn]\ 5f^5 6d^1 7S^2$
95	Am	$[Rn]\ 5f^7 6d^0 7S^2$
96	Cm	$[Rn]\ 5f^7 6d^1 7S^2$
97	Bk	$[Rn]\ 5f^8 6d^1 7S^2$
98	CF	$[Rn]\ 5f^{10} 6d^0 7S^2$
99	Es	$[Rn]\ 5f^{11} 6d^0 7S^2$
100	Fm	$[Rn]\ 5f^{12} 6d^0 7S^2$
101	md	$[Rn]\ 5f^{13} 6d^0 7S^2$
102	No	$[Rn]\ 5f^{14} 6d^0 7S^2$
103	Lr	$[Rn]\ 5f^{14} 6d^1 7S^2$

⊙ Properties of Actinides :-

- All these are radioactive elements.
- Th have half life time $t_{1/2}$ 1.39×10^{10} yrs.
- U have the half life time $t_{1/2}$ 4.50×10^{9} yrs ^{238}U
- For rest of the element $t_{1/2}$ it do not occure in nature. It prepared artifically in lab.
- All the actinides are silvery white.
- They resist the attack of alkalies & less reactive towards acids.
- Actinides are paramagnetic
- Except Th & Am have high densities.

⊙ Comparison with Lanthanides.

Lanthanides	Actinides
It is first inner transition series	It is second inner transition series
The outer E.C. of Lanthanide is $4f^{1-14} 5d^{0-1} 6s^2$	The outer E.C. of actinide is $5f^{0-14} 6d^1 7s^2$
It shows +3 oxid^n state	It shows variable oxid^n state varies from +2 to +6
In Lanthanide series, lanthanide contraction occurs	In actinide series no any contraction occurs.
Lanthanum is prototype of lanthanides	Actinium is prototype of actinides.
Monazite sand is the most imp. mineral contains lanthanides	The sources of actinides are monazite sands & pitchblende & carnotite which is the main source of uranium

⊙ Extraction of Uranium from Pitchblend.

There are two steps
First step – U_3O_8
second step – U

Isolation of uranium oxide

ore is crushed to fine pwd.

↓ Conc. by gravity process.

conc. ore is roasted in furnance
in the presence of air

↓ excess air
(To remove S, As, other volatile imp

Roasted ore contains U_3O_8

Δ heated to fusion ↓ mixed with sod. carbonate & sod. nitrate

sod. uranate (fused)
Na_2UO_4

↓ This is extracted with Hot H_2O

Treated with excess of Ammonium carbonate

↓

The impurities such as Al, Ni, Co, Mn get ppt as basic carbonate and uranium remains in soln.

↓ O.S

uranyl carbonate
$[(NH_4)_4UO_2(CO_3)_3]$

↓ Neutralised with dil. H_2SO_4 & evaporated

Ammonium diuronate
$(NH_4)_2U_2O_7$ (yellow ppt)

↓ Calcination

Uranium oxide
(U_3O_8)

Second process - Klaproth's process

In this process, the pitchblende ore is treated with HNO_3 or aqua regia & the resulting soln is evaporated to dryness. The dry mass is then extracted with HCl. The Filtrate is then treated with HNO_3 & neutralised with ammo. carbonate. on boiling this soln uranium, Zn & Co get ppt as oxides.

The ppt is again treated with HCl when the oxides of Zn & Co get dissolved leaving behind the oxide of U which is insoluble in HCl.

⊙ Preparation of metal from the oxide.

From the black oxide of uranium U_3O_8 the metal is obtained as follows.

① The oxide is heated with charcoal or hydrogen to reduce into UO_2

$$U_3O_8 \xrightarrow[\Delta]{charcoal} UO_2$$

it can't be reduced further to uranium on heating with hydrogen even at high temp. as 2500°C

② The dioxide is heated with chlorine to form Uranyl chloride UO_2Cl_2

$UO_2 + Cl_2 \longrightarrow UO_2Cl_2$ (yellow solid)

③ $UO_2Cl_2 + Cl_2 \longrightarrow UCl_4 + O_2$

④ $UCl_4 + 4Na \xrightarrow{\Delta} U + 4NaCl$

② or $UO_2 + 4HF \xrightarrow{\Delta} UF_4 + 2H_2O$

$UF_4 + 2Mg \longrightarrow U + \underset{(slag)}{2MgF_2}$

③ or $3UO_2 + 4Al \longrightarrow 3U + 2Al_2O_3$

(Gold schmidt Process)

⊙ Physical & chemical Properties of Uranium.

Physical Properties :-

- Uranium has a silvery white lusture.
- It melts at 1132°C
- It is malleable and ductile
- It's specific gravity is 19.05
- It Forms a wide range of intermetallic compound such as U_6Mn, U_6Ni, USn_3 etc
- It has several isotope of which ^{235}U and ^{233}U are important for nuclear chemistry

Chemical properties :-

- Uranium is highly reactive.
- It easily gets tarnished in moist air to form the oxide.
- It burns in oxygen at 170°c with a brilliant flame forming U_3O_8
- It reacts with steam betn 150°-250°c to form mix of oxide & hydride.

$$7U + 6H_2O \longrightarrow 3UO_2 + 4UH_3$$

- It dissolves readily in dil. HCl.
- In HNO_3 it dissolves at moderate rate while in H_2SO_4 & HF the rate of dissolution is very slow.
- It does not react with alkali
- It combine directly with halogen
- It burns in fluorin forming green volatile tetrafluoride.
- It catches fire in chlorine at 180°c & in bromine at 240°c forming the corresponding halide.
- It reacts with hydrogen at 600°c under pressure to form UH_3 hydride.

⊙ Separation of Neptunium, Plutonium, Americium from Uranium.

- It is produced mainly from U in nuclear reactors.

- Natural uranium contains large proportion of ^{238}U where as ^{235}U is present only to 0.7%.

- When ^{238}U is bombarded with neutrons of a certain critical velocity, one neutron is captured per atom of Uranium giving rise to an element of a higher mass no.

$$^{238}_{92}U + ^{1}_{0}n \longrightarrow ^{239}_{92}U + \Gamma\text{-rays}$$

This new isotope of uranium is much more radioactive than the natural uranium. It emits a beta particle and gives a new element of atomic no. 93 which does not occur in nature. This element is named neptunium.

$$^{239}_{92}U \longrightarrow ^{239}_{93}Np + ^{0}_{-1}e + \beta\text{-rays}$$

Neptunium also is radioactive & emits a beta particle giving another new element of atomic no. 94. Known as plutonium.

$$^{239}_{93}Np \longrightarrow ^{239}_{94}Pu + ^{0}_{-1}e + \beta\text{-rays}$$

Actually three isotopes of plutonium with mass no. 236, 238 and 239 are formed. The next element Americium were obtained from plutonium by the following reaⁿ:

$$^{241}_{94}Pu \longrightarrow ^{241}_{95}Am + ^{0}_{-1}e$$