Chemistry of f-Block Elements

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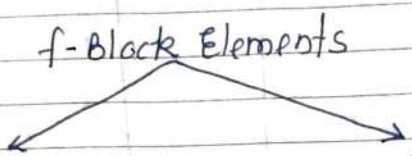
- Also called as Inner-transition Elements.



- Lanthanides or lanthanones (rare earth elements) Ce_{58} to Lu_{71}
- 14 elements
- Actinides or Actinones
- Th_{90} to Lr_{103}
- 14 elements

- f-Block elements may be defined as those elements in which the last electron enter the anti-penultimate energy level i.e. (n-2) sub-shell.

General Characteristics of Lanthanides:

Lanthanides ⇒ $^{54}[Xe]\ 4f^{0-14}\ 5d^{0-1}\ 6s^2$

Element	Z	Electronic configuration	Oxidation states
Lanthanum	57 La	$[Xe]\ 5d^1 6s^2$	+III
Cerium	58 Ce	$[Xe]\ 4f^1\ 5d^1\ 6s^2$	+III +IV
Praseodymium	59 Pr	$[Xe]\ 4f^3\ 6s^2$	+III +IV
Neodymium	60 Nd	$[Xe]\ 4f^4\ 6s^2$	+II +III
Promethium	61 Pm	$[Xe]\ 4f^5\ 6s^2$	+II +III
Samarium	62 Sm	$[Xe]\ 4f^6\ 6s^2$	+II +III
Europium	63 Eu	$[Xe]\ 4f^7\ 6s^2$	+II +III
Gadolinium	64 Gd	$[Xe]\ 4f^7\ 5d^1\ 6s^2$	+III
Terbium	65 Tb	$[Xe]\ 4f^9\ 6s^2$	+III +IV
Dysprosium	66 Dy	$[Xe]\ 4f^{10}\ 6s^2$	+III +IV
Holmium	67 Ho	$[Xe]\ 4f^{11}\ 6s^2$	+III
Erbium	68 Er	$[Xe]\ 4f^{12}\ 6s^2$	+III
Thulium	69 Tm	$[Xe]\ 4f^{13}\ 6s^2$	+II +III
Ytterbium	70 Yb	$[Xe]\ 4f^{14}\ 6s^2$	+II +III
Lutetium	71 Lu	$[Xe]\ 4f^{14}\ 5d^1 6s^2$	+III

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+III ⇒ most common oxidation state
+II ⇒ less important oxidation state
+IV ⇒ unstable or doubtful oxidation state.

Electronic configuration of Actinides:

$[Rn]\ 5f^{1-14}\ 6d^{0-1}\ 7s^2$

Atomic Number	Element	Symbol	Electronic Configuration
89	Actinium	Ac	$[Rn]\ 6d^1\ 7s^2$
90	Thorium	Th	$[Rn]\ 6d^2\ 7s^2$
91	Protactinium	Pa	$[Rn]\ 5f^2\ 6d^1\ 7s^2$
92	Uranium	U	$[Rn]\ 5f^3\ 6d^1\ 7s^2$
93	Neptunium	Np	$[Rn]\ 5f^4\ 6d^1\ 7s^2$
94	Plutonium	Pu	$[Rn]\ 5f^6\ \ 7s^2$
95	Americium	Am	$[Rn]\ 5f^7\ \ 7s^2$
96	Curium	Cm	$[Rn]\ 5f^7\ 6d^1\ 7s^2$
97	Berkelium	Bk	$[Rn]\ 5f^9\ \ 7s^2$
98	Californium	Cf	$[Rn]\ 5f^{10}\ \ 7s^2$
99	Einsteinium	Es	$[Rn]\ 5f^{11}\ \ 7s^2$
100	Fermium	Fm	$[Rn]\ 5f^{12}\ \ 7s^2$
101	Mendelevium	Md	$[Rn]\ 5f^{13}\ \ 7s^2$
102	Nobelium	No	$[Rn]\ 5f^{14}\ \ 7s^2$
103	Lawrencium	Lr	$[Rn]\ 5f^{14}\ 6d^1\ 7s^2$
104	Rutherfordium	Rf	$[Rn]\ 5f^{14}\ 6d^2\ 7s^2$

Oxidation states fo Ln:

- O.S. of +3 is shown by all Ln elements and in most cases is the most stable O.S.
- Some of the lanthanides, in addition to +3, show +2 and +4 O.S. as well.
- +2 and +4 O.S. are less stable than +3 O.S.
- The reason for the unusual O.S. of +2 and +4 can be attributed to the extra stability associated with f^0, f^7 (half-filled) and f^{14} (completely filled) electronic configuration.

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for Ln O.S.

+3 O.S.
La^{3+}, Gd^{3+} & Lu^{3+}
$La^{3+} \rightarrow f^0$ (empty f-subshell)
$Gd^{3+} \rightarrow f^7$ (half-filled)
$Lu^{3+} \rightarrow f^{14}$ (fully-filled)

+4 O.S.
Ce^{4+} & Tb^{4+}
$Ce^{4+} \Rightarrow f^0 d^0 s^0$
$Tb^{4+} \Rightarrow [Xe] 4f^7$ (half filled)

+2 O.S.
Eu^{2+} & Yb^{2+}
Eu^{2+} [Xe] $4f^7$
Yb^{2+} [Xe] $4f^{14}$

Colour and Spectra of Lanthanides:

Colour of Ln

f-f transitions
→ Colours are pale due to Laporte forbidden nature
→ Spectra are sharp
→ Colour is unaffected by nature of ligands

f-d transitions
→ colours are dark
→ spectra are broad
→ Affected with ligands

Charge transfer transition
e.g. Ce^{4+}, Sm^{2+}
→ Allowed transitions.

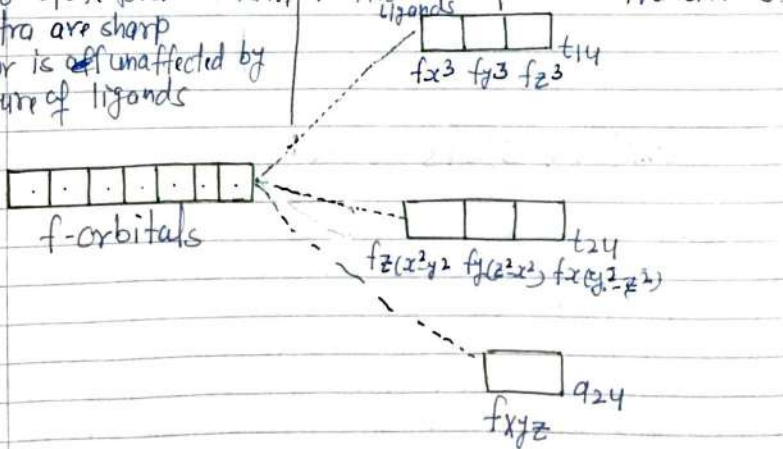

fig: Crystal field splitting of f-orbitals in octahedral field

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Colour of Lanthanide, Ln^{3+} ions:

Ion	No. of 4f Electrons	Colour
La^{3}	0	Colourless
Ce^{3+}	1	Colourless
Pr^{3+}	2	Green
Nd^{3+}	3	Lilac
Pm^{3+}	4	Pink
Sm^{3+}	5	Yellow
Eu^{3+}	6	Pale pink
Gd^{3+}	7	Colourless
Tb^{3+}	8	Pale Pink
Dy^{3+}	9	Yellow
Ho^{3+}	10	Pale Yellow
Er^{3+}	11	Pink
Tm^{3+}	12	Pale Green
Yb^{3+}	13	Colourless
Lu^{3+}	14	Colourless

Colours of Ln^{4+}, Ln^{2+} and their Isoelectronic Ln^{3+} Counterparts:

Ion	Colour	Electronic Configuration	No. of Unpaired Electrons	Isoelectronic M^{3+}
Ce^{4+}	Orange-Red C.T.	$4f^{0}$	0	La^{3+} Colourless
Sm^{2+}	Blood-red C.T.	$4f^{6}$	6	Eu^{3+} Pale Pink
Eu^{2+}	Pale greenish Yellow	$4f^{7}$	7	Gd^{3+} Colourless
Yb^{2+}	Yellow	$4f^{14}$	0	Lu^{3+} Colourless

1. f-f transition:
   - The colour of the lanthanide ion depends primarily on the number of unpaired f-electrons.
   - The colour of the lanthanide ion remains same even on changing the counter ion.
   - Thus, colour of the lanthanide ion is characteristic of the cation.
   - It has been found lanthanide ion containing nf

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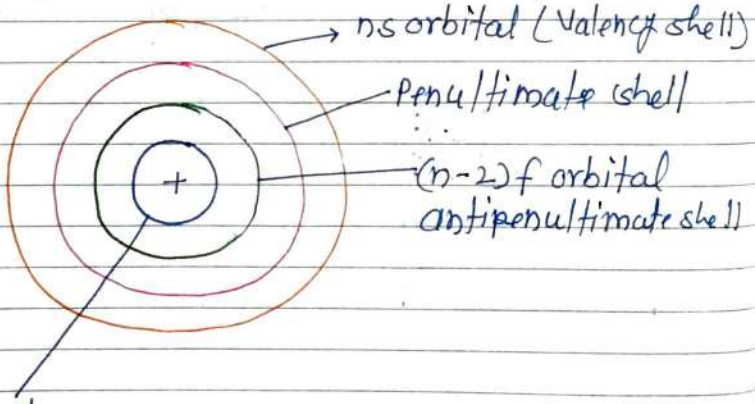
electrons often have a similar colour to those with (14-n) electrons.

- The colour of the lanthanide ion is due to absorption of light from the visible region of the spectrum that results in the electronic transition within 4f level.
- This type of transition is called f-f transition.
- f-f transition are forbidden transition.
- A unique feature of the spectra of tripositive lanthanide ions is that the absorption bands are sharp line-like bands in the UV, visible or near IR regions. This behaviour is in contrast to the absorption bands of d-d type transition metals which appear as broad absorption bands. The bands of lanthanide ions are so much sharp that they are used for characterising lanthanides.
- The reason for very sharp absorption band is that the 4f orbitals are located deep inside the atom.



Thus, they are effectively shielded from environmental factors such as nature and number of ligands which forms the complexes and from vibrations of the ligands.

Thus the colour of the lanthanide ion does not change with different ligands.

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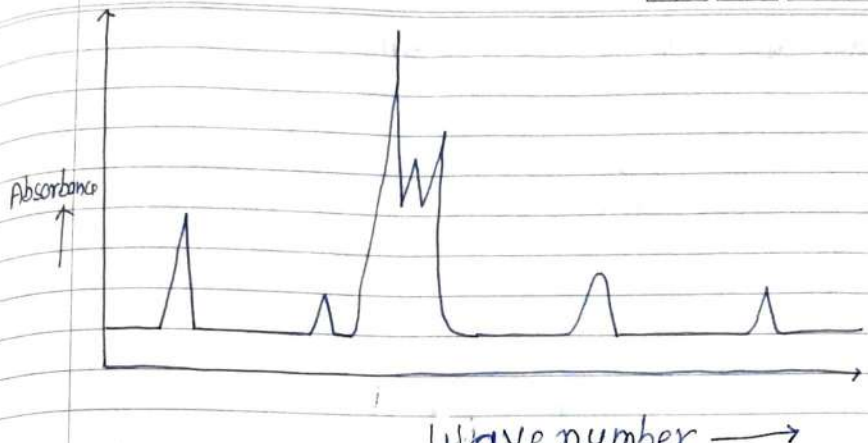

fig: UV-visible spectrum of Ho^{3+}

It is important to mention here that this behaviour is in contrast with transition elements where d-d transition give absorption band whose position changes from ligand to ligand and width of the peak is greatly broadened because of the vibrations of the ligands.

2. f-d Transition:
- → f-d transitions are allowed transition.
- → Because of allowed nature they show very intense absorption bands.
- Transitions due to f-d bands are broad in contrast to narrow f-f bands.

eg. Ce^{3+}, Tb^{3+} ($4f \rightarrow 5d$ transition)

3. Charge transfer:

Charge transfer spectra are possible due to the transfer of an electron from ligand to metal.
- This is more probable if the metal is in a high oxidation state or the ligand has reducing character.
- → Charge transfer produces intense colour.

eg. Yellow colour of Ce^{4+}
Sm^{2+} Blood red colour

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Magnetic Properties of Lanthanides:

- **Diamagnetic**
  - La^{3+} & $Ce^{4+} \Rightarrow f^0$
  - Lu^{3+}, Yb^{2+}] f^{14}
- **Paramagnetic**
  - Except La^{3+}, Ce^{4+}, Lu^{3+} & Yb^{2+}

Origin of Magnetism

- **Spin-motion**
  - → Due to spin motion of electron.
  - $\mu_S = \sqrt{4S(S+1)}$
- **orbital motion**
  - Due to orbital motion of electron
  - $\mu_L = \sqrt{L(L+1)}$

$$\mu = \sqrt{4S(S+1) + L(L+1)}$$

→ Orbital motion is not Quenched in case of Lanthanide elements

→ This is because of presence of f-orbital into the antipenultimate shell.

for lanthanide

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

$J = L - S$ when the shell is less than half filled

$J = L + S$ when the shell is more than half filled

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

S = Total spin quantum number

L = Total orbital magnetic quantum number

Lande splitting factor

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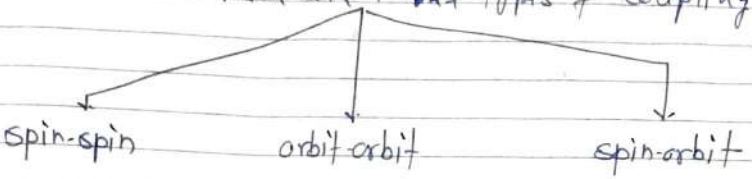
There are three types of coupling



- In Ln all types of coupling are present

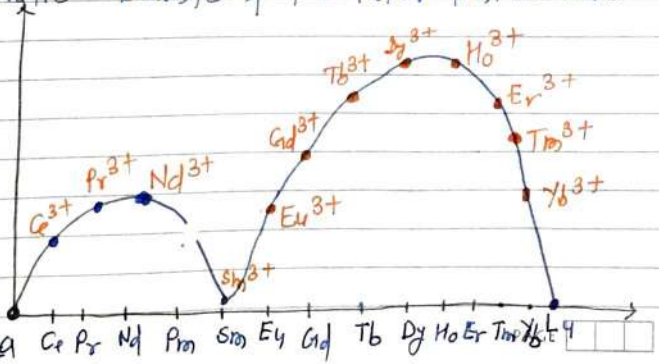
$$\mu = g\sqrt{J(J+1)}$$

J = Total angular momentum Quantum number

- If spin-orbit coupling is non-existent then

$$\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}$$

- All the tripositive lanthanide ion exapt La^{3+} and Lu^{3+} contain unpaired electrons and are, therefore paramagnetic.
- A plot of the magnetic values of the tripositive lanthanide ions reveal that the magnetic moment values increases frist upto Nd^{3+} and then decreases upto Sm^{3+}.
- It ... increases steadily again and reaches a maximum value for Dy^{3+} ion then starts decreasing till it reaches zero value for Lu^{3+} ion which is diamagnetic.
- It is important to remark that the high values of the magnetic moment for Tb^{3+}, Dy^{3+} and Ho^{3+} clearly demonstrate the role of orbital contribution towards the magnetic moments of the later lanthanides.



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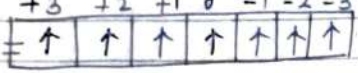
Q. Calculate the magnetic moment of Gd^{3+} ion in Bohr Magneton (Z for Gd is 64).

Solution: $Gd_{64}: [Xe]\ 4f^7 5d^1 6s^2$

$Gd^{3} = [Xe]\ 4f^7$

$\mu = \sqrt{4S(S+1) + L(L+1)}$



$L = +3+2+1+0-1-2-3$

$L = 0$

$S = \frac{7}{2}$

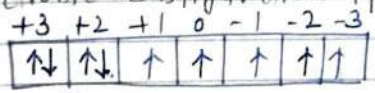
$\mu = \sqrt{4 \times \frac{7}{2}\left(\frac{7}{2}+1\right) + 0(0+1)}$

$= \sqrt{4 \times \frac{7}{2} \times \frac{9}{2}}$

$= \sqrt{63}$

$\boxed{\mu = 7.9\ B.M}$

Q. Calculate the magnetic moment of Dy^{3+} with outer electronic configuration $4f^9 6s^0$



$S = \frac{5}{2}$

$L = 5$

$J = L + S$ (more than half-filled)

$= 5 + 2.5$

$J = 7.5$

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

$g = 1\frac{1}{2} + \frac{7.5(7.5+1) + 2.5(2.5+1) - 5(5+1)}{2 \times 7.5\ (7.5+1)}$

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$g = 1.33$

$\mu_{S+L} = 1.33\sqrt{7.5(7.5+1)}$

$= 1.33 \times 7.98$

$\mu_{S+L} = 10.62$ B.M.

Ionic Radii and Lanthanide Contraction:

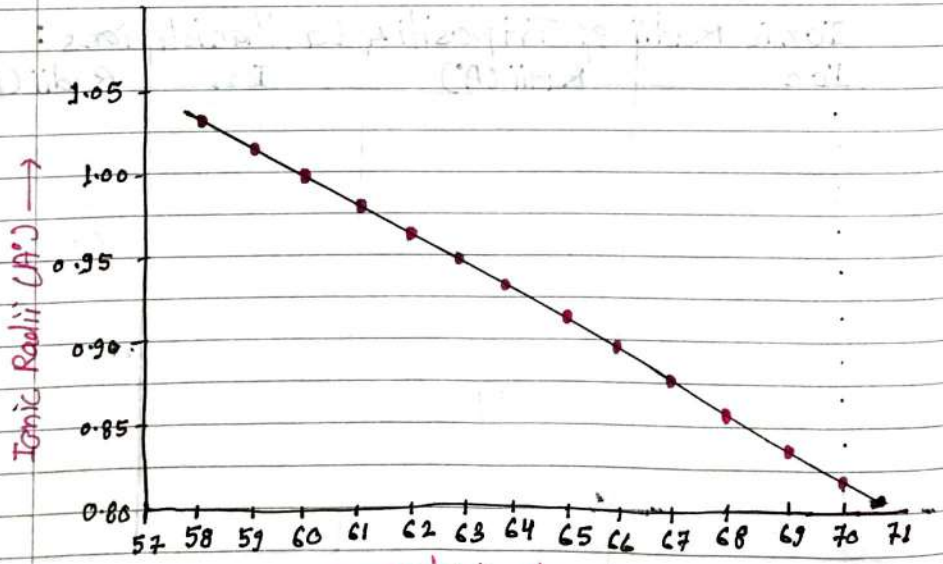
- Covalent and ionic radii increase on moving down a group in the periodic table
- This is due to presence of additional shells between the successive periods.
- On the other hand, on moving from left to right across a period, the covalent and ionic radii decrease. This is due to increased Z_{eff} as a consequence of which the outermost electrons are attracted more and more.
- This results in the outermost electrons being pulled more and more closer.
- We also know that the shielding effect of electrons decrease in the order $s > p > d > f$.

Ionic Radii of Tripositive Lanthanide ions:

Ion	Radii (A°)	Ion	Radii (A°)
La^{3+}	1.03	Er^{3+}	0.89
Ce^{3+}	1.02	Tm^{3+}	0.88
Pr^{3+}	0.99	Yb^{3+}	0.87
Nd^{3+}	0.98	Lu^{3+}	0.86
Pm^{3+}	0.97		
Sm^{3+}	0.96		
Eu^{3+}	0.95		
Gd^{3+}	0.94		
Tb^{3+}	0.92		
Dy^{3+}	0.91		
Ho^{3+}	0.90		

- A careful inspection of the Table reveals that as we move along the lanthanides series from La^{3+} to Lu^{3+}, there is a gradual decrease in the size of the atoms and ions with the increase in atomic number.
- It has been observed that in case of tripositive lanthanide ions from Ce^{3+} ($Z=58$) to Lu^{3+} ($Z=71$), the ionic radii decreases from 1.03 A° to 0.86 A°. This shows that the overall decrease of 0.17 A° occurs in going from Ce^{3+} to Lu^{3+} ion. This is indeed a very small decrease in comparision to elements of other groups and periods.
- The atomic radii of the elemental lanthanides also decreases from 1.83 A° (Ce) to 1.73 (Lu). The total decreace of atomic radii from Ce to Lu comes out to be 0.10 A°.

This small steady decrease in atomic or ionic radii of the lanthanide elements with increase in atomic number is called lanthanide contraction.



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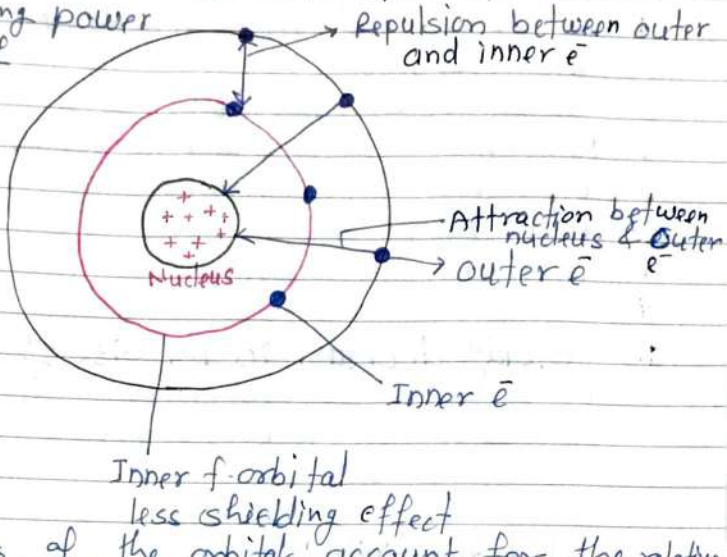
Cause of Lanthanide contraction:

Order of Screening power
s > p > d > f



- The shapes of the orbitals account for the relative atomic radii of f-block elements.
- The lanthanides, involve the gradual filling of 4f-orbitals. The lobes of the f-orbitals occupy markedly different regions of spaces and are therefore far apart from each other.
- Consequently, f orbitals repel one another very weakly.
- Secondly, electron density in f-orbital is low near the nucleus.
- As a result of being away from the nucleus, 4f-orbitals are not very effective at shielding other electrons from the nucleus.
- Thus, with the increase in atomic number and the nuclear charge, the Z_{eff} experienced by each 4f electron increases. This increases the inward pull of 4f electrons and results in the reduction of the size of the atom/ion.

This contraction in the size of the atom or ion by pulling the valence electrons inward due to high nuclear charge and the poor shielding effect of the f-electron is the main cause of lanthanide contraction.

Consequences of Lanthanide Contraction:

1. Steady decrease in the size of lanthanide ions
2. Electronegativity
3. Electrode potential value (E°)
4. Resemblance of IInd and IIIrd transition series
5. Difficulty in separation
6. High density
7. Difference in Basicity
8.

1. **Steady decrease in the size of Lanthanide ions:** As a result of lanthanide contraction, there is a gradual or steady decrease in the ionic radi of lanthanides.

2. **Electronegativity:** There is a slight increase in the electronegativity of the trivalent ions.

3. **Electrode Potential values (E°):** There is a small but regular increase in the electrode potential values E° for the process.

$$M^{3+} + 3e^- \longrightarrow M$$

4. **Resemblance of Second and Third Transition Series:** The atomic radii of elements of second transition series (period 5) are typically greater than those of the first transition series (Period 4).
- However, the radii of the third transition series elements (period 6) are about the same size as that of second transition series.

This similarity in the atomic radii is due to t presence of f-block near the begining of per period 6.

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Table: Atomic radii of the elements (A°) before and after lanthanides

Sc	Ti	V	Cr	Mn	Fe	Co	Ni
1·44	1·32	1·22	1·17	1·17	1·17	1·16	1·15
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
1·62	1·45	1·34	1·29	–	1·24	1·25	1·28
La	Hf	Ta	W	Re	Os	Ir	Pt
1·69	1·44	1·34	1·30	1·28	1·26	1·26	1·29

→ 14 Lanthanide Elements

There is a pronounced decrease in the atomic radii along the lanthanides.

- When the d-block resume at Lu, the atomic radius has fallen from 2·24 A° for Ba to 1·72 A° for La. As a result of this, the atoms of all the following elements are smaller than expected.

In brief, as a result of lanthanide contraction, the chemistry of second and third transition series resemble each other more than the elements of ~~first~~ second transition series

5. **Difficulty in Separation:**
Because of the very small change in the size of the lanthanide ions in the lanthanide series their chemical properties are alike. This causes the separation of elements a difficult task.

6. **High Density:** The lanthanide contraction is responsible for the high density of the third transition series.

7. **Difference in Basicity:** The size of the lanthanide ion decreases regularly with the increase in atomic number the lanthanides. This decrease in the size of the cation tends to increase the covalent character according to Fajan's rule.

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As a result, the bonding of the smallest cation and the hydroxide ion become mostly covalent.

$La(OH)_3 \longrightarrow Lu(OH)_3$

strongest base — weakest base

→ Similarly basic strength of oxides also decreases.

Due to decreased basicity

Hydrolysis of ions	Solubility of the salts	Thermal decomposition of oxy salts
→ Due to rise in basic strength, there is a slight rise in the degree of hydrolysis in solution from La^{3+} to Lu^{3+}. → La^{3+} readily hydrolysed than Lu^{3+} ion.	→ Hydroxides of lanthanides ppts with decreasing p^H values from the NO_3^- of La^{3+} to Lu^{3+}	→ stability of nitrates of lanthanides rise with rise in atomic number.
	La^{3+} ppt at p^H 6.83	$La(NO_3)_3$ → little decomposition
	Gd^{3+} 6.83	
	Lu^{3+} 6.30	$Lu(NO_3)_3$ → more decom.

Complex formation Tendency of Lanthanides:

→ Compared to transition metals lanthanide ions (Ln^{3+}) do not readily form complexes.

→ It is primarily due to larger size of the ions which result into small charge to size (ionic radius) ratio.

Size of Ln^{3+} → 1.03 to 0.86 A°

Transition elements e.g. Cr^{3+} 0.615 A°

Fe^{3+} 0.55 A°

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- Lanthanide ions form complexes preferably with F and O-donor ligands.
- Very few stable complexes are formed with CO, CN^- and organometallic groups.

C.N.	Complex	shape
4	$[Lu(2,6\text{-dimethylphenyl})_4]^-$	Td
6	$[Ce^{IV}Cl_6]^{2-}$	Oh
6	$[Er(NCS)_6]$	Oh
7	$[Y(acetylacetone)_3H_2O]$	Mono-capped trigonal prism
8	$[La(acetylacetone)_3(H_2O)_2]$	Square antiprism
8	$[Ce^{IV}(acetylacetone)_4]$	Square antiprism
8	$[Eu(acetylacetone)_3(phenanthroline)]$	Square antiprism
8	$[Ho(tropolonate)_4]^-$	Dodecahedral
9	$[Nd(H_2O)_9]^{3+}$	Tri-capped trigonal prism
10	$[Ce^{IV}(NO_3)_4(Ph_3PO)_2]$	Complex each NO_3^- is a bidentate
12	$[Ce^{IV}(NO_3)_6]^{2-}$	Icosahedral (Each NO_3^- is bidentate)

Separation of the Lanthanide Elements:

Ion-Exchange Method:

→ Most important and efficient method for the separation and purification of lanthanides.

- In this method, a solution of the lanthanide ions is passed through a column of synthetic ion exchange resin Dowex-50 which contain the functional groups $-COOH$ or $-SO_3H$.
- Lanthanide ions when come in contact with the resin containing the acidic functional group undergo proton exchange as

$$Ln^{3+}_{(aq)} + 3H\text{-}Resin_{(s)} \rightleftharpoons Ln(Resin)_{3(s)} + 3H^+_{(aq)}$$

- In this process, the lanthanide ions are bonded to the resin and the H^+ ions produced are washed through

the column. The bonding of the lanthanide ions to the resin depend on the size of the lanthanide ion.

- Since lanthanide ions are present in aqueous solution these are heavily hydrated.
- The smaller the lanthanide ion, the most heavily hydrated it is.
- Thus Lu^{3+} ion which is the smallest in size is the most heavily hydrated ion.
- It means that the size of hydrated Lu^{3+} is maximum.
- It means that the smaller sized hydrated lanthanide ion binds strongly with the resin and larged sized lanthanide ion binds loosely with the resin.
- The bonded metal ions are eluted that is washed off the column by a complexing agent. The commonly used complexing agent is a buffered solution of citric acid - ammonium citrate at pH=8. During elution, the NH_4^+ ions elutes the metal ions from the resin as

$$Ln(Resin)_3(s) + 3NH_4^+(aq) \longrightarrow 3NH_4Resin + Ln^{3+}(aq)$$

The metal ions in turn the form a complex by combining with citrate ion.

$$Ln^{3+}(aq) + Citrate^{3-}(aq) \longrightarrow Ln\text{-}Citrate\ complex$$

- As hydrated Lu^{3+} ion being the largest size ion will bind less firmly to the resin.
- It is therefore will be eluted first.
- On the other hand hydrated Lu^{3+} being smallest sized hydrated ion will bind strongly to the resin. Therefore it will be eluted the last of all.