D-Block Elements

Series											
3d	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4d	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
5d	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

Coinage metals

Cr, Mo, W → max^m unpaired e^⊖ (6)
→ Strong metallic bond

Highest O.S. (+8)

Cu, Ag, Au → no unpaired e^⊖
→ volatile metal

Physical Properties :-

① Metallic character :-

order of metallic ch^r $s > d > p$

In d-block elements as the no of unpaired e^⊖s ↑ strength of metallic bonding increases.

So. Cr, Mo, W → 6 unpaired e^⊖. (max^m)
→ Strong metallic bond.

- they possesses high value of m.p. & b.p
- high densities
- high heat of Atomization

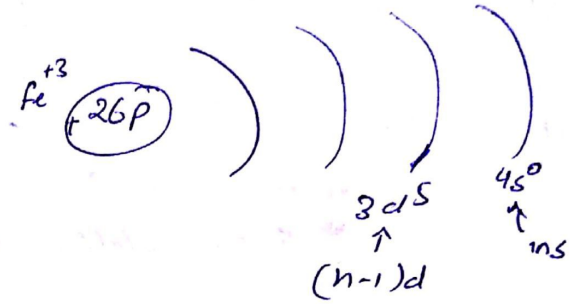
Zn, Cd, Hg → 0 unpaired e^⊖
→ very weak metallic bond
→ so these are volatile metals.

② Oxidation states :-

d-block elements show variable O.S due to participation of $e^{\ominus}$'s from both ns as well (n-1)d orbitals.

Fe^{2+} => $3d^6\ 4s^0$

Fe^{3+} => $3d^5\ 4s^0$



Some imp. points regarding O.S. of d-block elements

① In 3d series Sc & Zn do not show variable O.S.

Sc ⟶ +3 only

Zn ⟶ +2 only.

(II) In 3d series, Mn shows highest O.S. (+7)

(III) Osmium (Os) & Ruthenium (Ru) show highest O.S. in Periodic table (+8).

(IV) In metal carbonyls like $Ni(CO)_4$, $Fe(CO)_5$ & $Cr(CO)_6$ The O.S. on metal is zero.

(V) as O.S. on metal ↑ Acidic ch^r in Oxides ↑

$$Mn^{+2}O < Mn^{+4}O_2 < Mn_2^{+6}O_6 < Mn_2^{+7}O_7$$

order of Acidic character.

(3) Metallic Character :-

- due to presence of unpaired $e^{\ominus}$, d-block elements show paramagnetism.

$$\mu = \sqrt{n(n+2)}$$ unit :- B M (Bohr Magneton)

μ = magnetic moment.

n = no of unpaired $e^{\ominus}$.

→ paramagnetic $\propto \mu \propto$ no of unpaired $e^{\ominus}$

Q. Arrange the following complex in ↑ order of magnetic moment.

① $[MnCl_4]^{2-} < [CoCl_4]^{2-} < [NiCl_4]^{2-}$

② $[NiCl_4]^{2-} < [CoCl_4]^{2-} < [MnCl_4]^{2-}$

③ $[CoCl_4]^{2-} < [MnCl_4]^{2-} < [NiCl_4]^{2-}$

④ $[MnCl_4]^{2-} < [NiCl_4]^{2-} < [CoCl_4]^{2-}$

Ans. Mn^{2+} — $3d^5$ $4s^0$ — $n = 5$

Co^{2+} — $3d^7$ $4s^0$ — $n = 3$

Ni^{2+} — $3d^8$ $4s^0$ — $n = 2$

$\mu \propto n$

Ans (2).

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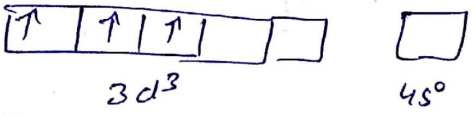
Q Which of the following complex show highest paramagnetic Behaviour ?

① $[Cr(H_2O)_6]^{3+}$

② $[Fe(H_2O)_6]^{2+}$

③ $[Cu(H_2O)_6]^{2+}$

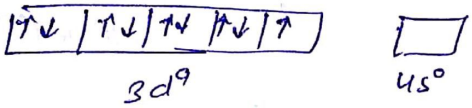
④ $[Zn(H_2O)_6]^{2+}$

Cr^{3+} →  $n = 3$

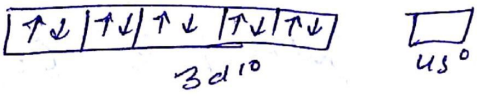
$3d^3$ $4s^0$

Fe^{2+} →  $n = 4$

$3d^6$ $4s^0$

Cu^{2+} →  $n = 1$

$3d^9$ $4s^0$

Zn^{2+} →  $n = 0$

$3d^{10}$ $4s^0$

paramagnetism $\propto$ n

Ans (2)

(4) ***

Colour :-

all complexes having configuration from d^1 to d^9 show color due to d-d transition.

Eg:- $[Ti(H_2O)_6]^{3+}$ is a violet colored complex due to d-d transition.

** → complexes having d^0 & d^{10} configuration are colorless complexes because d-d transition is not possible.

Q. which of the following complexes are colorless

(i) $[Sc(H_2O)_6]^{3+}$ (ii) $[Zn(H_2O)_6]^{2+}$

(iii) $[Ti(H_2O)_6]^{4+}$ (iv) All of these

Ans $Sc^{3+} \rightarrow n=0$, $Zn^{2+} \rightarrow n=0$, $Ti^{4+}, n=0$ Ans (iv)

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Q. which of the following complexes are colored?

(1) $[Ti(NO_3)_4]$ (2) $[Cr(NH_3)_6]Cl_3$

(3) $[Cu(NCCH_3)_4]^+$ (4) $K_3[VF_6]$

Ans Ti^{4+} $n=0$

$Cr^{3+} \Rightarrow n=3$

$Cu^+ \Rightarrow n=0$

$V^{3+} \rightarrow n=2$ Ans (2) & (4)

$KMnO_4$ & $K_2Cr_2O_7$ shows color :-

$KMnO_4$ & $K_2Cr_2O_7$ do not have unpaired $e^\ominus$ in d-orbital but they shows colors. this is due to special phenomenon known as Charge Transfer Spectrum (CTS)

→ in $KMnO_4$ which is purple colored, Oxygen transfer it's $e^\ominus$ to Mn thus converting Mn^{+7} to Mn^{+6} while itself get converted from O^{2-} to $O^\ominus$. this is known as Charge Transfer Spectrum. (CTS)

$$O_2^{2-} \xrightarrow{+e^\ominus} O^\ominus$$

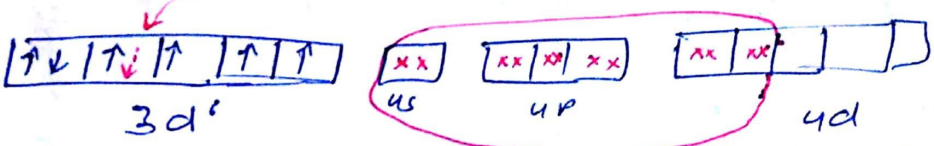
$$Mn^{+7} + e^\ominus \longrightarrow Mn^{+6}$$

$[Fe(H_2O)_5NO]SO_4$ → Brown colored complex.

$$NO \longrightarrow NO^+ + e^\ominus$$

$$Fe^{2+} + e^\ominus \longrightarrow Fe^\oplus$$

Fe^{2+}



sp^3d^2, outer orbital complex

This complex which is found in Brown Ring Test (confirmatory test for nitrates) is paramagnetic in Nature. It is a outer orbital complex in which iron is sp^3d^2 hybridised.

⑤ Catalytic Behaviour :-

Most of the d-block elements are used as catalyst due to following 2 reasons -

ⓐ d-block elements show variable O.S. and hence they are converted to unstable intermediate species while they convert reactants to products. This reaction occurs via a path of lower activation energy due to which rate of rxn is increased.

eg :- in Contact Process, for manufacture of H_2SO_4 V_2O_5 is used as a catalyst.

$$\overset{+5}{V_2O_5} + SO_2 \longrightarrow SO_3 + \overset{+4}{V_2O_4}$$

(V_2O_4 : unstable intermediate species)

$$V_2O_4 + \tfrac{1}{2}O_2 \longrightarrow V_2O_5$$

ⓑ d-block elements absorb the reactant molecule and provide a suitable surface area to them for the reaction.

eg :- in Hydrogenation of alkenes Nickel or Palladium is used to absorb hydrogen gas at high Pressure.

$$CH_2 = CH_2 + H_2 \xrightarrow{Ni/Pd} CH_3 - CH_3$$

⑥ **Complex forming tendency :-**

d-block elements have tendency to form complex due to two reasons -

ⓐ Small size and high charge density on metal cations so that they polarize ligands effectively.

ⓑ Presence of vacant orbitals of same or nearly same energy to accept $e^{\ominus}$ pair donated by ligands.

eg :→ $[Ni(CN)_4]^{2-}$, $[NiCl_4]^{2-}$ $[Fe(CN)_6]^{4-}$ etc

⑦ **Alloy formation :-**

d-block elements due to their nearly similar atomic size can substitute their position easily in ~~crystallic~~ crystal latice and form alloys.

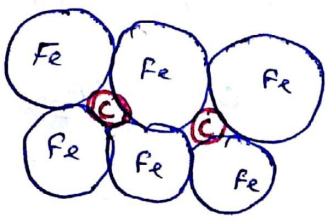
eg :→ Brass, Bronze etc.

⑧ **Formation of interstitial compound :-**

d-block elements entraps small non-metals like B, C & N in their interstitial spaces or voids for their crystal lattice & forms interstitial compounds.

for eg :- **in formation of steel**

Fe entraps small C-atoms in voids of its crystal lattice & form interstitial compound



stainless steel

Some Important compounds of d-block elements

① Pottassium Dichromate :-

Preparation :- It is obtained from chromite ore [$Fe\,Cr_2O_4$]

Step I :- $Fe\,Cr_2O_4 + Na_2CO_3 + O_2 \longrightarrow Na_2CrO_4 + Fe_2O_3 + 3CO_2$

Step II :- $2Na_2CrO_4 + H_2SO_4 \xrightarrow{(Conc.)} Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

Step III :- $Na_2Cr_2O_7 + KCl \longrightarrow K_2Cr_2O_7 + NaCl$

Properties of $K_2Cr_2O_7$:-

① The crystals of $K_2Cr_2O_7$ are orange red in color.

② In aq. medium, $Cr_2O_7^{2-}$ ions occur in equilibrium with chromate ion, CrO_4^{2-}.

at pH = 4.

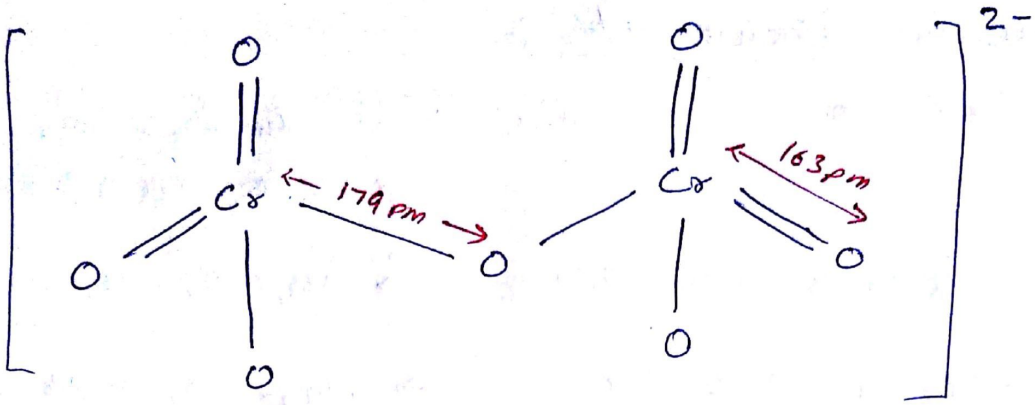
$$\underset{\text{Orange}}{Cr_2O_7^{2-}} + H_2O \underset{H^{\oplus}}{\overset{OH^{\ominus}}{\rightleftharpoons}} 2\,\underset{\text{Yellow}}{CrO_4^{2-}} + 2H^{\oplus}$$

***

when pH > 4 or medium is basic due to formation of chromate ion colour of solution becomes Yellow.

but when pH < 4 or medium is acidic due to formation of dichromate color of solution becomes orange

Str. of $Cr_2O_7^{2-}$



➡ In $Cr_2O_7^{2-}$ two tetrahedral units are joined by a common oxygen atom.

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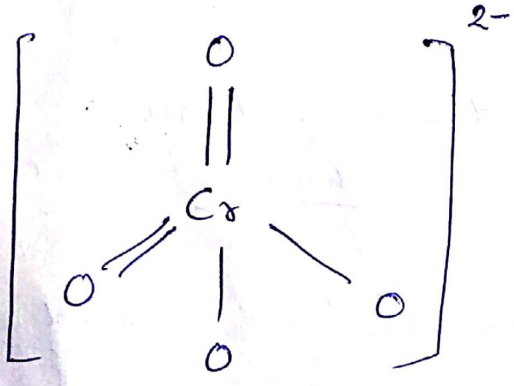
➡ In $Cr_2O_7^{2-}$, 6 Cr-O bond length are same due to resonance while two Cr-O bond length are found to be different.

Str. of CrO_4^{2-}



③ *** **Chromyl Chloride Test :-**

When any chloride is ~~treated~~ with $K_2Cr_2O_7$ in ~~presence of~~ presence of conc. H_2SO_4 then due to formation of CrO_2Cl_2 (Chromyl chloride) orange red fumes are obtained. This is known as chromyl chloride Test.

$$NaCl + K_2Cr_2O_7 + H_2SO_4 \longrightarrow NaHSO_4 + KHSO_4 + \boxed{CrO_2Cl_2} + H_2O$$

Orange red fumes

When these Orange Red fumes are passed through NaOH then due to formation of Na_2CrO_4 (sodium Chromate) color becomes Yellow.

$$CrO_2Cl_2 + NaOH \longrightarrow \boxed{Na_2CrO_4} + NaCl$$

Yellow.

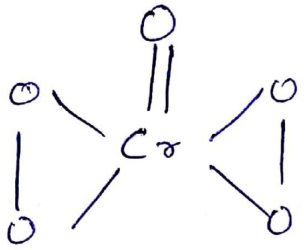
④ *** Rxn. with H_2O_2

when $Cr_2O_7^{2-}$ (dichromate ions) are treated with H_2O_2 in acidic medium then due to formation of CrO_5 (chromic peroxide) color of solution becomes deep blue.

$$Cr_2O_7^{2-} + H_2O_2 \xrightarrow[\text{medium}]{\text{acidic}} \boxed{CrO_5} + H_2O$$

deep blue

Str. of CrO_5 :-



butter fly like str.

$\boxed{Cr^{+6}}$

⑤ Action of heat :-

when $K_2Cr_2O_7$ is strongly heated then it decomposes to K_2CrO_4

$$4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

potassium chromate

** ⑥ $K_2Cr_2O_7$ is used in volumetric analysis instead of $Na_2Cr_2O_7$ because of its hygroscopic nature.

Potassium Permanganate ($KMnO_4$) :- ⑦

It is prepared by fusion of MnO_2 with an alkali metal hydroxide and an oxidising agent like KNO_3

This produces dark green K_2MnO_4 which disproportionates in neutral or acidic medium to give permanganate.

$$2MnO_2 + 4KOH + O_2 \xrightarrow{(KNO_3)} 2K_2MnO_4 + H_2O$$

dark green.

$$3\overset{+6}{Mn}O_4^{2-} + 4H^{\oplus} \longrightarrow 2\overset{+7}{Mn}O_4^{\ominus} + \overset{+4}{Mn}O_2 + H_2O$$

preparation II

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \longrightarrow 2MnO_4^{\ominus} + 10SO_4^{2-} + 16H^{\oplus}$$

Properties :-

① It is dark purple in color.

② It is paramagnetic.

$KMnO_4$ do not have unpaired $e^{\ominus}$ but it is colored due to a special phenomenon charge Transfer spectrum (CTS)

$$O_2^{2-} \longrightarrow O_2^{-} + e^{\ominus}$$

$$Mn^{+7} + e^{\ominus} \longrightarrow Mn^{+6}$$

Oxygen transfer its $e^{\ominus}$ to Mn

③ On heating it decomposes to manganate (MnO_4^{2-}) and ~~permanganate (MnO_4^-)~~ MnO_2 (Manganese dioxide)

$$KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$$

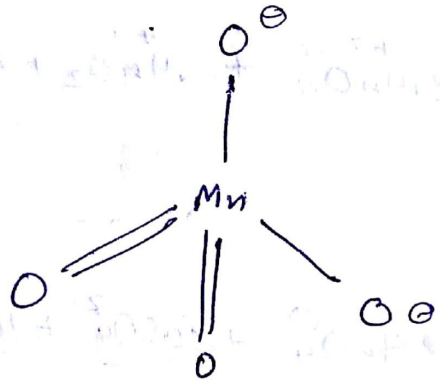
MnO_4^{2-}

manganate

→ (green)

→ ~~diamagnetic~~

→ paramagnetic



tetrahedral

Mn^{+6} $3d^1$ $4s^0$

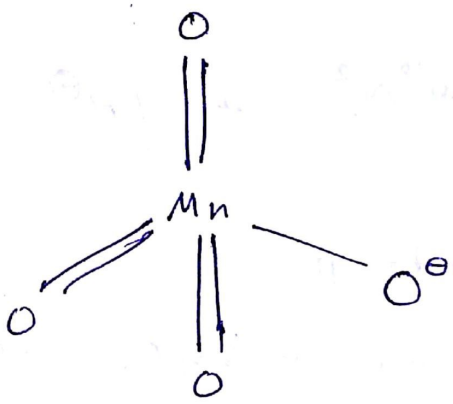
MnO_4^-

permanganate

→ (purple)

→ ~~paramagnetic~~

→ diamagnetic



tetrahedral.

Mn^{+7} $3d^0$ $4s^0$

④ It act as good oxidising agent in Acidic medium. ⑧

eg:- ⓐ $10I^{\ominus} + 2MnO_4^- + 16H^{\oplus} \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$

ⓑ $5Fe^{2+}$ (green) $+ MnO_4^{\ominus} + 8H^{\oplus} \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$ (yellow)

ⓒ $5C_2O_4^{2-}$ (oxolate ion) $+ 2MnO_4^- + 16H^{\oplus} \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

ⓓ oxidation of H_2S

$H_2S \longrightarrow 2H^+ + S^{-2}$

$5S^{2-} + 2MnO_4^- + 16H^{\oplus} \longrightarrow 2Mn^{2+} + 8H_2O + 5S$ (ppt)

ⓔ Sulphurous acid or sulphite is oxidised to a sulphate or sulphuric acid

$5SO_3^{2-} + 2MnO_4^- + 6H^{\oplus} \longrightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-}$

ⓕ Nitrite is oxidised to Nitrate

$5NO_2^- + 2MnO_4^- + 6H^{\oplus} \longrightarrow 2Mn^{2+} + 5NO_3^{\ominus} + 3H_2O$

(5) Oxidation by $KMnO_4$ in neutral or slightly alkaline medium.

(a) iodide to iodate

$$2MnO_4^- + H_2O + I^\ominus \longrightarrow 2MnO_2 + 2OH^\ominus + IO_3^\ominus$$

(b) Oxidation of thiosulphate to sulphate

$$8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^\ominus$$

(c) Manganous salt to MnO_2

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \xrightarrow[\text{catalyst.}]{ZnSO_4/ZnO} 5MnO_2 + 4H^\oplus$$

Note:- titration of Permanganate is not done in presence of HCl because it oxidise HCl to chlorine (Cl_2).

Uses :-

- Strong oxidising agent in organic chemistry
- used in bleaching of wool, cotton, silk etc.

some Important points Regarding d block elements (a)

① Bayer's Reagent ⇒ 1% alkaline solution of $KMnO_4$

② Etard's Reagent ⇒ CrO_2Cl_2 (chromyl chloride)

③ Barfoed's Reagent ⇒ $Cu(CH_3COO)_2 + CH_3COOH$

④ Fenton's Reagent ⇒ $FeSO_4 + H_2O_2$

⑤ Luca's Reagent ⇒ Anhyd. $ZnCl_2$ + conc. HCl.

⑥ Titanox ⇒ mix of $TiO_2 + BaSO_4$
↳ It is white coloured pigment.

⑦ philosopher wool ⇒ ZnO

⑧ Rinman's green ⇒ $CoO \cdot ZnO$
↳ It is green colored pigment.

⑨
- (a) Blue vitrol ⇒ $CuSO_4 \cdot 5H_2O$
- (b) Green vitrol ⇒ $FeSO_4 \cdot 7H_2O$
- (c) White Vitrol ⇒ $ZnSO_4 \cdot 7H_2O$

⑩
- (a) Brown's catalyst ⇒ Nickel Boride
- (b) Permagnic acid ⇒ $HMnO_4$

(11) Corrosive Sublimate $HgCl_2$

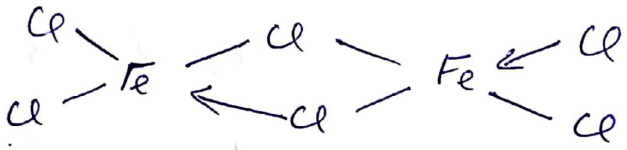
(12) Calomel Hg_2Cl_2

(13) Luna's Caustic $AgNO_3$

$AgNO_3$ is used in hair dyes.

It is kept in colored bottle because it get decomposes in presence of sunlight.

(14) $FeCl_3$ exist as dimer in form of Fe_2Cl_6



aq. solution of $FeCl_3$ is acidic due to its hydrolysis

$$FeCl_3 + H_2O \longrightarrow \underset{\text{weak Base}}{Fe(OH)_3} + \underset{\text{Strong Acid}}{HCl}$$

(15) Cu^+ salts undergo disproportionation in aqueous medium

$$Cu^+ \longrightarrow Cu^{+2} + Cu$$

$\Rightarrow$ Cu^{2+} ions are more stable as compare to Cu^+ ion in aq medium because Cu^{2+} ions undergo more hydration due to their small size and high charge density.

$$CuSO_4 + KCN \longrightarrow \underset{Cu^+ \rightarrow \text{diamagnetic}}{K_3[Cu(CN)_4]}$$

(16) Brv

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

(Inner Transition Elements)

Lanthanoids Actinoids

Lanthanoids :-

Those element which involve the filling of electrons in 4f orbital are known as Lanthanoids or Lanthanons these are also known as "rare earth metals"

Ce (z=58) Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu (z=71)

Physical Properties :-

① **Density :-**

Lanthanoids are heavier elements and they possesses density from 6.77 to 9.74 g/c.c.

② **Oxidation state :-**

All Lanthanoids show stable O.S. of +3 because value of their ($IE_1 + IE_2 + IE_3$) are very low.

Some Lanthanoids also shows +2 & +4 O.S but they readily convert to their stable O.S (+3) in aqueous medium.

eg:- Cerium shows +4 O.S. which convert to +3 O.S. in aqueous medium

⇒ Ce^{4+} salt act as good oxidising agent — NEET II 2016

other Lanthanoid which shows +4 OS ⇒ Pr^{4+} & Tb^{4+}

Lanthanoid which show +2 OS. ⇒ Sm^{2+}, Eu^{2+}, Tm^{2+}, Yb^{2+}

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③ Atomic Radii & Lanthanoid contraction :-

There is a steady decrease in atomic as well as ionic size as we move from Ce to Lu in case of Lanthanoids. This is due to Lanthanoid contraction.

$Ce^{3+} > Pr^{3+} > Nd^{3+} > Pm^{3+} > \dots\dots\dots > Lu^{3+}$

Lanthanoid contraction

Cause of Lanthanoid contraction :-

As we move from Cerium (z=58) to lutetium (z=71) there is a increase in nuclear charge due to progressive addition of protons. Thus nucleas charge ↑ by +14 unit

In case of Lanthanoids 14 $e^{\ominus}$'s are filled in 4f orbitals which possesses poorest shield / screening effect due to their highly diffused shape.

As a result of which the increase in nucleas charge pulls the electron cloud of 5d & 6s towards itself thus causing contraction in size known as Lanthanoid contraction.

Consequences of Lanthanoid contraction :-

① similarity in size of 5d & 4d series elements

4d	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn
		‖	‖	‖	‖	‖	‖	‖	‖	‖	‖	‖
5d	La ...	Hf	Ta	W.	Re	Os	Ir	Pt	Au	Hg	Tl	Pb

$Z=57$ ↑ $Z=72$

Ce (58) to Lu (71).

$3d > 4d \tilde{>} 5d$

Those elements which are coming after Lu ($Z=71$) i.e. from Hf ($Z=72$) to Pb ($Z=82$) are having the effect of Lanthanoids contraction. due to which atomic size of 5d series elements is nearly equal to 4d elements.

② Effect on the Basic characters of hydroxides in case of Lanthanoids :-

As we move from Ce ($Z=58$) to Lu ($Z=71$) with the ↓ in atomic and ionic radii M–OH bond length ↓ from Ce to Lu thus tendency to give $OH^{\ominus}$ ions ↓ and hence basic characters of hydroxides ↓.

$Ce(OH)_3 > Pr(OH)_3 > Nd(OH)_3 > \cdots\cdots > Lu(OH)_3$

M—OH (Ce) ... M–OH (Lu)

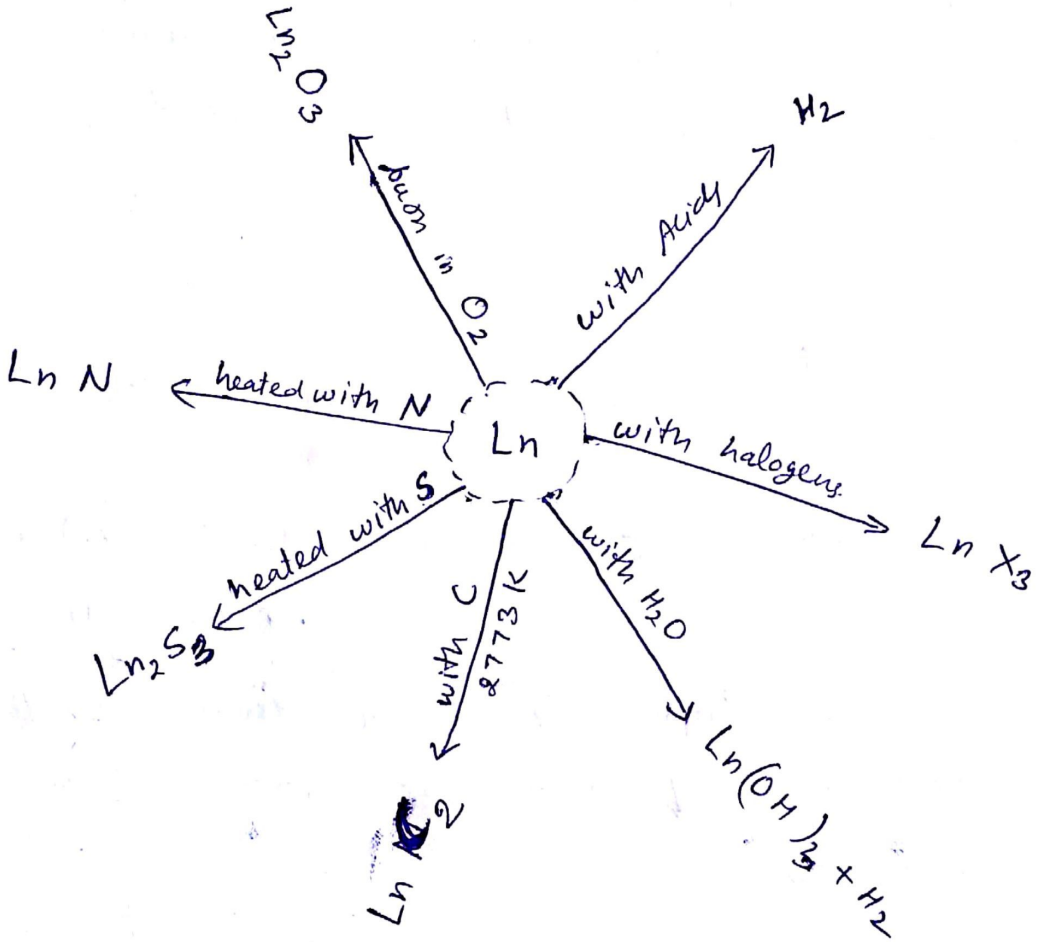
order of Basic Nature

④ Colour :-

like that of d-block elements Lanthanoids also show color due to f-f transition,

⇒ La^{3+} (f^0) & Lu^{3+} (f^{14}) do not show f-f transition and are colorless.

⑤ Rxns of Lanthanoids (Ln)



Actinoids :-

Those elements which involve the filling of $e^{\ominus}$ in 5f orbital are known as actinoids.

Th (Z=90) Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr (Z=103)

* Actinoids are radioactive elements.

Actinoid contraction :-

Like that of Lanthanoids there is a decrease in atomic and ionic radii. As we move from Th (Z=90) to Lr (Z=103) in case of actinoids, this is known as Actnoid contraction.

⇒ It is due to poor shielding effect of 5f electron

Oxidation state :-

Actinoids show +3 O.S. like that of Lanthanoids but actinoid show more O.S. as compare to Lanthanoid.

Because in case of Actinoid electrons participate from 5f orbital also ~~known as~~ which is extended beyond 6p & 7s orbitals.

while in case of Lanthanoids, ~~element~~ $e^{\ominus}$ do not take part from 4f orbitals which is totally shielded from 5d & 6s orbitals.

Hence actinoids show more O.S. as compare to Lanthanoids