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PHYSICAL PROPERTIES :-

Metallic character :-

order of metallic chr $\boxed{s > d > p}$

In d-block elements as the no of unpaired $e^{\ominus}s$ ↑ strength of metallic bonding increases.

$\boxed{Cr, Mo, W}$ → →

↓

they

reat Atomi

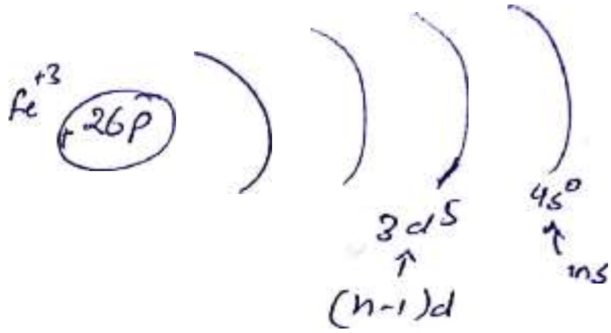
$\boxed{Zn, Cd, Hg}$ → →

weak

show

from

Fe -› za' vz°



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

i) In 3d series Sc & Zn do not show variable

D• s• Sc ⟶ -/-s only

⟶

@ & sp so•a‹ , x*^ ‹••• * “#*‘"** D'S <* ^*

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

iv) In metal carbonyls $Ni(CO)_4$, $Fe(CO)_5$ & $Cr(CO)_6$

on zero

v) as O.S. on metal ↑ ›P>k£•'c v i* n xfi£"

$$\boxed{\overset{+2}{Mn}O < \overset{+4}{Mn}O_2 < \overset{+6}{Mn_2}O_6 < \overset{+7}{Mn_2}}$$

order of Acidic character.

3 Metallic Character :-

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

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

μ = magnetic moment.

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

→ $\boxed{\text{paramagnetis} \propto \mu \propto \text{no of unpaired } e^{\ominus}}$

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

Ans. Mn^{2+} [↑ | ↑ | ↑ | ↑ | ↑] $3d^5$ [ ] $4s^0$ $n=5$

Co^{2+} [↑↓ | ↑↓ | ↑ | ↑ | ↑] $3d^7$ [ ] $4s^0$ $n=3$

Ni^{2+} [↑↓ | ↑↓ | ↑↓ | ↑ | ↑] $3d$ [ ] $4s^0$ $n=2$

$\boxed{\mu \propto n}$

Ans (2).

$\frac{IIT}{Q}$ 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 $[Zn(H_2O)_6]^{2+}$

$Cr^{3+} \rightarrow$ | ↑ | ↑ | ↑ | | | $3d^3$ | | $4s^0$ $n = 3$

$Fe^{2+} \rightarrow$ | ↑↓ | ↑ | ↑ | ↑ | ↑ | $3d^6$ | | $4s^0$ $n = 4$

$Cu^{2+} \rightarrow$ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑ | $3d^9$ | | $4s^0$ $n = 1$

$Zn^{2+} \rightarrow$ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | $3d^{10}$ | | $4s^0$ $n = 0$

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

IIT

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+} $n=0$

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

$Cu^{+} \to n=0$

$V^{3+} \to n=2$ Ans 2 & 4

colour.

not

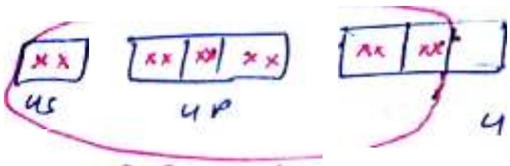
but they colours

"*'^" * '"''*''*• '' /°^ *J•& •«eD›«<a«f › d *¿y'y**t<

O_2 $\rightarrow$ $O^{\ominus}$

$[Fe(H_2O)_5NO]SO_4$ $\rightarrow$ Brown colored complex

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



sp^3d^2, outer

* >^'^M * t•'i•fzi› .z @•< ‹=/ cii» A•e*"n •'*-''¿;'° •-4»'

Nature. It is a orbital complex in
iron

5 Catalytic Behaviours :-

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

(a) 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.

$$\overset{+5}{V_2}O_5 + SO_2 \longrightarrow SO_3 + \underset{\uparrow}{\overset{+4}{V_2}O_4}$$

unstable intermediate species

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

(b) 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 <u>complex forming tendency</u>:-

d- block elements have tendency to forms 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^- pair donated by ligands.

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

⑦ <u>Alloy formation</u> :-

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

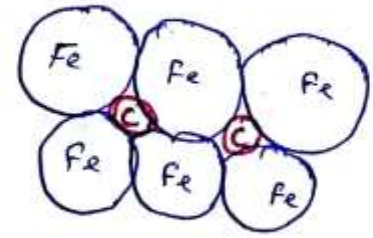
eg :→ Brass , Bronze etc.

⑧ <u>formation of interstitial compound</u>:-

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 <u>eg</u> :- in <u>formation of steel</u>

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 $[FeCr_2O_4]$

step I :- $FeCr_2O_4 + Na_2CO_3 + O_2 \longrightarrow Na_2CrO_4 + Fe_2O_3 + 3CO_2$

Step II :- $2Na_2CrO_4 + \underset{(conc.)}{H_2SO_4} \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

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 equillibirium with chromate ion, CrO_4^{2-}.

at $\boxed{pH = 4}$.

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

***

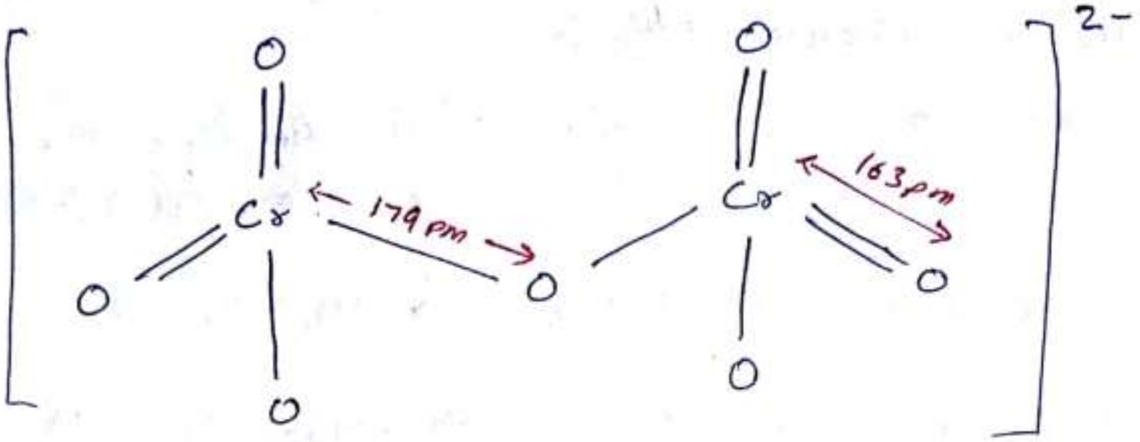
when pH>4 or medium is basic

due to formation of chromate ion colour of solution becomes Yellow.

but when pH < 4 or medium is acidic

due to fromation of dichromate color of solution becomes orange

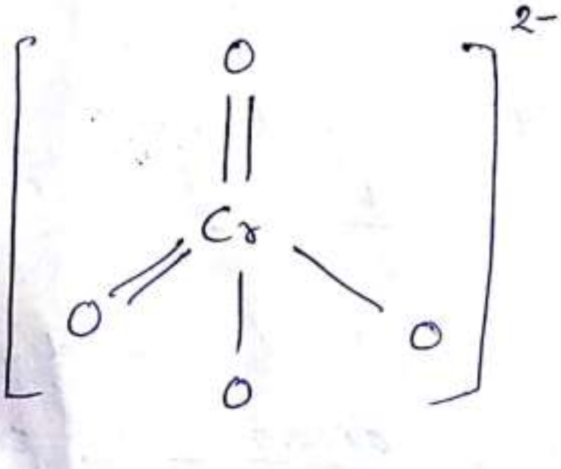
Str. of $Cr_2O_7^{2-}$



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

IIT ➡ 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 ~~prensce 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.

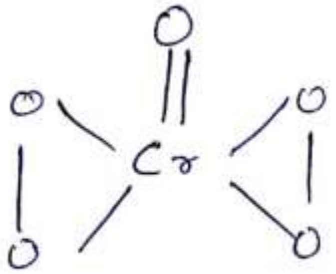
④ *** Rxn. with H_2O_2

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

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

pottassium chromate

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

Pottassium Permanganate ($KMnO_4$) :-

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 permangnate.

$$2MnO_2 + 4KOH + \underset{\uparrow \atop (KNO_3)}{O_2} \longrightarrow \underset{\text{dark green}}{2K_2MnO_4} + H_2O$$

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

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)

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

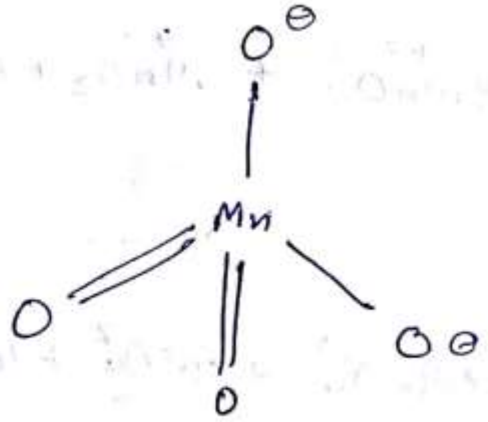
MnO_4^{2-}

manganate

→ (green)

→ ~~diamagnetic~~

→ paramagnetic



tetrahedral

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

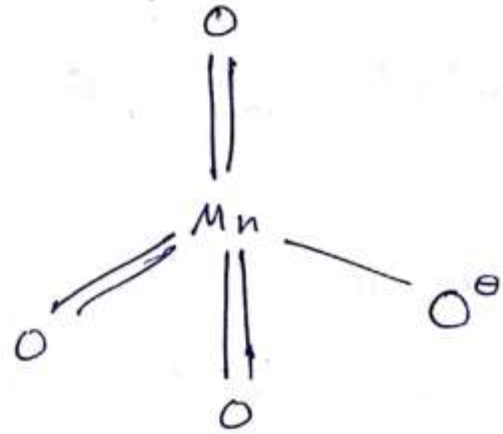
MnO_4^-

permanganate

→ (purple)

→ ~~paramagnetic~~

→ diamagnetic



tetrahedral.

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

in

°6!g !»Y- + « a• o¿ + ib »'+' $\longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$

ⓑ $5Fe^{2+} + MnO_4^{\ominus} + 8H^{\oplus} \quad Mn^{2+} + 4H_2O + 5Fe^{3+}$

green yellow

$\longrightarrow$

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

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

ppt

ⓔ sulphurous acid or sulphite is oxidised to

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

“A>’/’ e ’-* • ^’

d/*A/ O y -/- 1/ x/n dt -r- 6 f* $\longrightarrow 2Mn^{2+} + 5NO_3^{\ominus} +$,

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

(a) <u>iodide to iodate</u>

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

(b) Oxidation of thiosulphate to sulphate

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

(c) <u>Manganous salt to MnO_2</u>

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

<u>Note</u>:- titration of Permanganate is not done in persence of HCl because it oxidise HCl to chlorine (Cl_2).

<u>Uses</u>:-

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

some Important points Regarding d block elements @

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

② Etard's Reagent ⇒ CrO_2Cl_2 (chromyl chloride)

③ Barfoed's Regent ⇒ $Cu(CH_3COO)_2$ + 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 ⓐ Blue vitrol ⇒ $CuSO_4 \cdot 5H_2O$

*** ⓑ Green vitrol ⇒ $FeSO_4 \cdot 7H_2O$

ⓒ White vitrol ⇒ $ZnSO_4 \cdot 7H_2O$

⑩ ⓐ Brown's catalyst ⇒ Nickel Boride

ⓑ Permagnic acid ⇒ $HMnO_4$

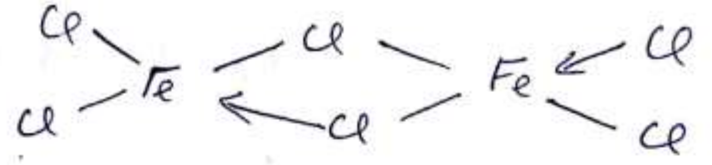
(11) Corrosive Sublimate $HgCl_2$

* (12) Calomel Hg_2Cl_2

* (13) Lunar Caustic $AgNO_3$

$AgNO_3$ is used in hair dyes.
It is kept in colored bottle because ~~its~~ 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

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

(15) Cu^+ salts undergo disproportination in aqeous medium.

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

⇒ 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.

$$\boxed{CuSO_4 + KCN \longrightarrow K_3[Cu(CN)_4]}$$

Cu^+ → diamagnetic

(16) Bor

f - block elements * d^-^! -f "' (^-i)d »‹ "')

(Inner Transition Elements)

Lanthanoids | Actinoids

Lanthanoids :-

in the

are

there are also earth

K-e fi'» ^^'=* Pm s;w f;, (â *-> 'il "° " "" "' Lu

(z = 58) (z=71)

berties

Lanthanoids are heavier elements and they

from 6.77 to 9.74 g/c.c.

Oxidation state :-

All Lanthanoids show stable O.S. of +3 bco

value of their $(IE_1 + IE_2 + IE_3)$ very

Some Lanthanoids also shows +2 & +4 D'S

but they

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

aqeous medium

$\Rightarrow$ $\boxed{Ce^{4+} \text{ salt act as good oxidising agent}}$ 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+}

NEET II 2016

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.

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

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 nuclear charge ↑ by +14 unit

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

As a result of which the increase in nuclear 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

$Z=57$ ↑ $Z=72$

$_{58}Ce$ to $_{71}Lu$

$$\boxed{3d > 4d \simeq 5d}$$

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 character 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 character of hydroxides ↓.

$$\boxed{Ce(OH)_3 > Pr(OH)_3 > Nd(OH)_3 > \text{------} > Lu(OH)_3}$$

M —— OH   M–OH

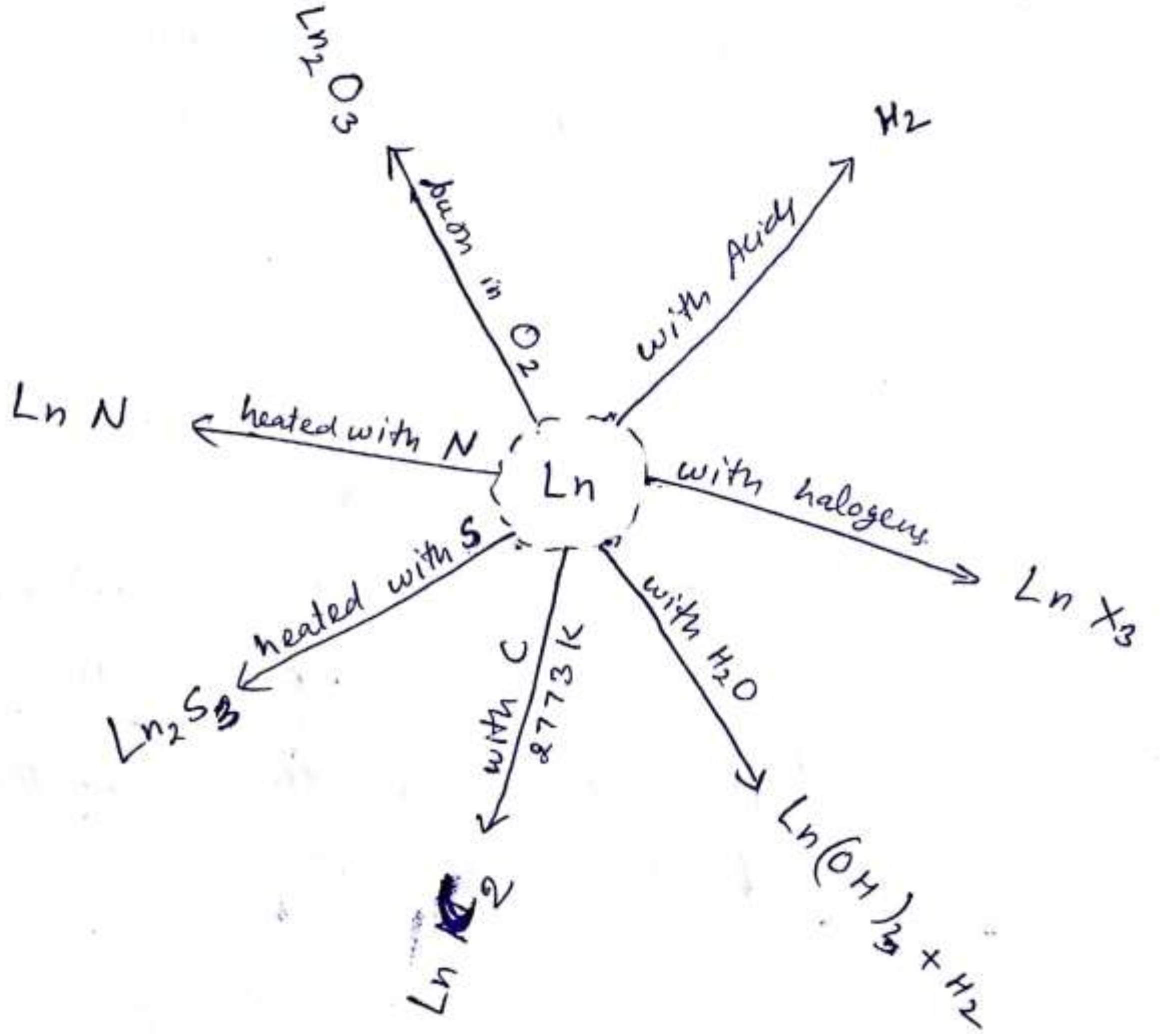
order of Basic ch^r

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)



$e^{\ominus}$ in 5f orbital are known as actinoids.

(Z=90) (Z=103)

are elements.

there

from

case

due

show O.S. like of

but actinoid show more O.S. as compare to Lanthanoid.

because case of Actinoid electrons participate from

5f orbital also ~~known~~ which is extended beyond

while in case of Lanthanoids, e

from 4f orbitals which is

totally shielded from