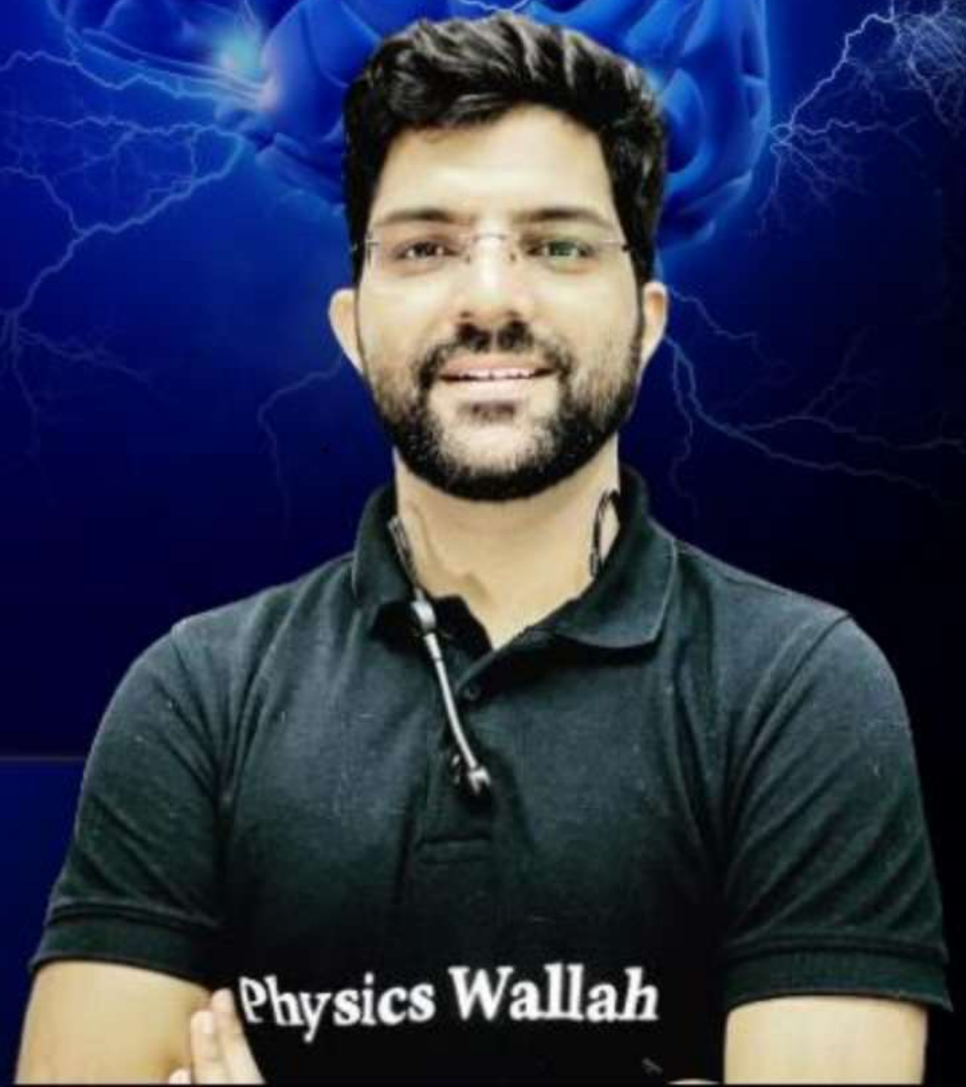
MIND MAP

FOR NEET ASPIRANTS

Inorganic Chemistry

ONESHOT

d & f BLOCK ELEMENTS



By - Mohit Dadheech (MD Sir)

Topics *to be covered*

1. One Shot

Most Imp. topics of chapter.

d & f Block Elements.

d-Block elements

In which last e^- enters into d subshell.

Also known as transition Elements (Partially Filled "d")

$d^1 - d^9$ either in neutral or in any known O.S

d^0, d^{10} → Zn, Cd, Hg, Cn

Transition Element

Atomic properties :-

① gen e^- Configuration

$(n-1)d^{1-10}\ ns^{0-2}$

ns^2 → Normal

ns^0 & ns^1 exceptional.

ns^0 → only one

Pd, Z=46

$[Kr]\ 4d^{10}5s^0$

ns^1 → Cr, Cu, Nb, Mo, Ru, Rh, Ag, Pt, Au.

(2) Size :-

* gen size ↓se L→R in a series.
* Size of ions with same charge ↓se L→R.

3d series Size [Final order]

Sc > Ti > V > Cr < Mn > Fe ≈ Co ≈ Ni < Cu < Zn

(3) I.E :- gen ↑se L→R

Sc < V < Cr < Ti < Mn < Ni < Cu < Co < Fe < Zn

(Final order) deter based

Some imp I.E orders :-

Cr < Mn ($I.E_1$)

Cr > Mn ($I.E_2$)

$3d^5 4s^0$ $3d^5 4s^1$

Cu < Zn ($I.E_1$)

Cu > Zn ($I.E_2$)

$3d^{10} 4s^0$ $3d^{10} 4s^1$

Mn < Fe (IE_1 & IE_2)

Mn > Fe ($I.E_3$)

$3d^5 4s^0$ $3d^6 4s^0$

4) Alloy formation :-

alloys formed by metals having radius within about 15% of each other.

Imp Ex :-

Brass (Cu + Zn)

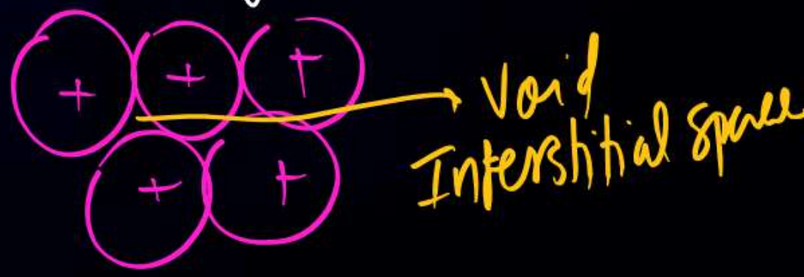
Germen Silver (Cu, Zn, Ni)

Bronze (Cu + Sn)

5. Interstitial Compounds

Prepared by trappin Small Size atoms (C, N, B, H) into Interstitial Space of metallic Lattice

- Non Stoichiometric
- Hard than pure metal
- M.P is more
- Conductance remains Same
- Chemically inert.



6. Magnetic Moment :-

Unpaired e^- (n) → Para.
Present

absent → diamagnetic

*/MDJ

Magnetic Moment = n point something

$$\mu = \sqrt{n(n+2)}$$

7. Melting Point :-

generally
no. of Unpaired e↑
atomic Interaction ↑, M.P ↑
atomisation Enthalpy ↑se.

M.P orders

For group 3rd & 12th
$3d > 4d > 5d$

group 11th
$3d > 5d > 4d$. $Cu > Au > Ag$.

group 4th to 10th
$3d < 4d < 5d$

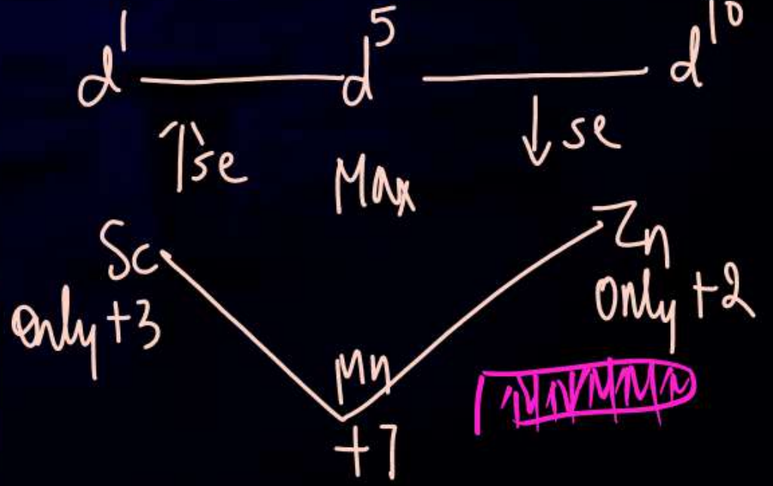
Max incl → W
Max in each series → group 6th (Cr, Mo, W)

8. Variable O.S

× due to more availability of e^- (n-1) d^- in addition to ns e^-
× due to Low Energy gap b/w (n-1)d & ns subshell
× Fe^{+5}, Co^{+5}, Sc^{+2} ~~Ex~~ ~~t~~ X
Max in 3d series :-

(Mn) From +2 to +7.

First ↑se upto d^5 then ↓se



NOTE

Stability of H.O.S ↑se down the group in d-Block

Ex

Cr^{+6} | Stability of +6 ↑se

Mo^{+6}

W^{+6}

$\overset{+6}{Cr_2O_7}$ / $\overset{+6}{CrO_3}$ — not stable in +6, Can work as O.A

$\overset{+6}{MoO_3}$ $\overset{+6}{WO_3}$ — stable in +6, ~~O.A~~

NOTE

H.O.S of d-Block elements Stable with High E.N: O & F only.

More stable with Oxygen due to its ability to form multiple Bonds

MnF_2 ✓ Mn_2O_7 ✓

MnF_3 ✓ Mn_3O_4 ✓

MnF_4 ✓ MnO_3F ✓

Mn_2O_3 ✓

MnF_5, MnF_6, MnF_7 ✗ due to steric hindrance

⑨ Complex Formation Tendency :—

due to: Small size & High Ø Nature of d-Block Metals ions

⑩ Colour of aq. ions :—

d^0, d^{10} Colourless due to absence of d-d transition.

(11) SRP (E^0)

$E^0_{M^{2+}/M}$

In 3d series all have -ve value except Cu.

$E^0_{Cu^{2+}/Cu}$ = +Ve.

Reason High IE$_2$

thats why Cu can not librate H_2 gas From acids.

$E^0_{M^{3+}/M^{2+}}$

$E^0_{Sc^{3+}/Sc^{2+}}$ Low value (-Ve) $\because$ Sc^{3+} Noble gas confi

$E^0_{Zn^{3+}/Zn^{2+}}$ High Value (+Ve) Zn^{2+} d^{10} Confi

$E^0_{Mn^{3+}/Mn^{2+}}$ High Value Mn^{2+} d^5 Half filled Stable.

Values of $E^0_{M^{3+}/M^{2+}}$

Show that :-

Mn^{3+}, Co^{3+} } Strong O.A $M^{3+} \longrightarrow M^{2+}$

Ti^{2+}, V^{2+}, Cr^{2+} } Strong R.A

$M^{2+} \rightleftharpoons M^{3+}$

OXIDES OF d-BLOCK

Imp Points :-

* All $\overset{+2}{MO}$ type oxides are ionic in nature ∵ Low O.S → Ionic Nature.

NOTE → ScO do not Exist.

* O.S ↑se, EN ↑se, Acidic Nature of O^{2-} ↑se

+1, +2, +3 → Basic.
+4 ⟶ Amphoteric
+5, +6, +7, +8 → Acidic

NOTE $\overset{+3}{Cr_2O_3}$, $\overset{+2}{ZnO}$ } Amphoteric

$\overset{+5}{V_2O_5}$ → Mainly acidic But show Ampho also.

V_2O_5 with acid gives ⇒ VO_2^+

V_2O_5 with Base gives ⇒ VO_4^{3-}

Potassium Permanganate ($KMnO_4$)

$K_2\overset{+6}{Mn}O_4$ → Pot. Manganate. ($\overset{+6}{Mn}O_4^{2-}$)

$K\overset{+7}{Mn}O_4$ → Pot. Permanganate. ($\overset{+7}{Mn}O_4^{-}$)

$$\overset{+6}{Mn}O_4^{2-} \xrightarrow{H^+} \overset{+7}{Mn}O_4^{-} + \overset{+4}{Mn}O_2$$

dark green Colour.

dark purple or Violet.

Preparation of $KMnO_4$

From Pyrolusite ore (MnO_2)

$Mn^{+4}O_2$ ore (Pyrolusite) $\xrightarrow[\text{Fused with KOH}]{\text{Oxidation}}$ $K_2Mn^{+6}O_4$

O.A → Air or KNO_3

$K_2Mn^{+6}O_4 \xrightarrow{H^+} KMn^{+7}O_4 + Mn^{+4}O_2$

$K_2Mn^{+6}O_4 \xrightarrow{\text{Electrolysis}} KMn^{+7}O_4$ (Commercial Preph)

$K_2Mn^{+6}O_4 \xrightarrow{O_3\ (\text{strong O.A})} KMn^{+7}O_4$

Laboratory Method

(O_2^{2-}) O.A Peroxide

Mn^{2+} (Colourless) $+ S_2O_8^{2-} \longrightarrow MnO_4^{-} + SO_4^{2-}$

Peroxodisulphate (O.A)

MnO_4^- Violet

SO_4^{2-} sulphate.

MnO_4^{2-}

⇒ * Manganate ion.

⇒ * Mn^{+6} d^1

⇒ n=1, Paramagnetic

⇒ * dark green colour.

⇒ Structure

tetrahedral.

MnO_4^-

Permanganate ion.

Mn^{+7} ⇒ d^0 ⇒ n=0 "diamagnetic"

But Temp. dependent

Weak Paramagnetism

dark purple or Violet

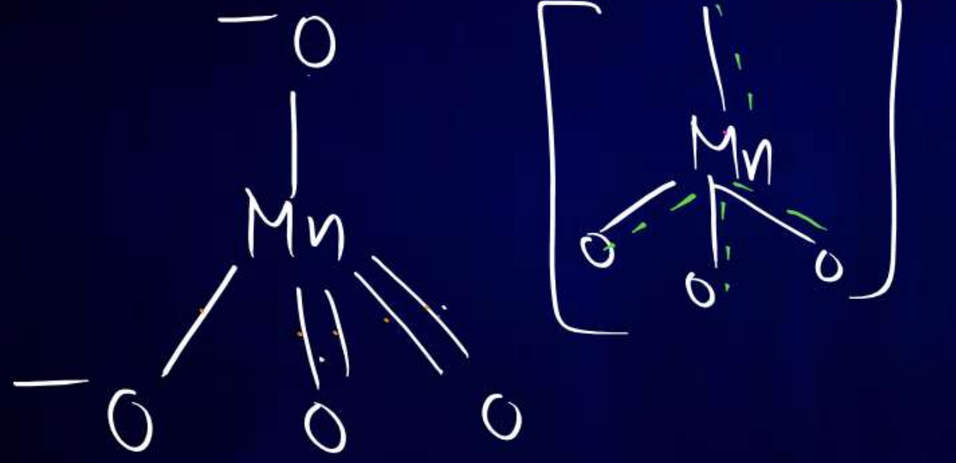
↳ Colour due to ~~d-d~~ ~~transition~~.

∵ d^0

Colour due to LMCT Charge transfer

tetrahedral

MnO_4^{2-}



Avg. Mn–O Bond order $= \frac{6}{4}$

All Mn–O B.L → equal.

no. of $d\pi$–$p\pi$ Bonds ⇓ 2

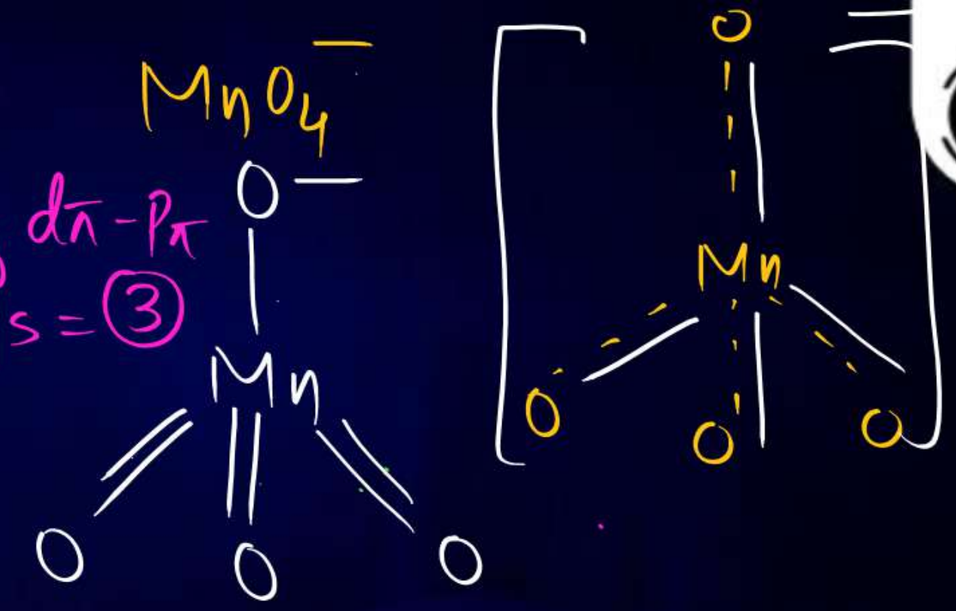
B.O ↑ B.L ↓ ⟹

$MnO_4^- < MnO_4^{2-}$ (Mn–O B.L)

$MnO_4^- > MnO_4^{2-}$ (Mn–O B.O)

MnO_4^-

no. of $d\pi$–$p\pi$ Bonds = ③



Avg Mn–O B.O ⇒ $\frac{7}{4}$

All Mn–O B.L are equal.

Reactions of $KMnO_4$

(i) Thermal decomposition

$$\overset{+7}{K}\overset{+7}{Mn}O_4{}_{(s)} \xrightarrow{\Delta} K_2\overset{+6}{Mn}O_4 + \overset{+4}{Mn}O_2 + \overset{0}{O_2}$$

(ii) Oxidising Reactions :—

$KMnO_4$ Can work as strong O.A in Acidic as well as weak basic & Medium. (faintly) Neutral.

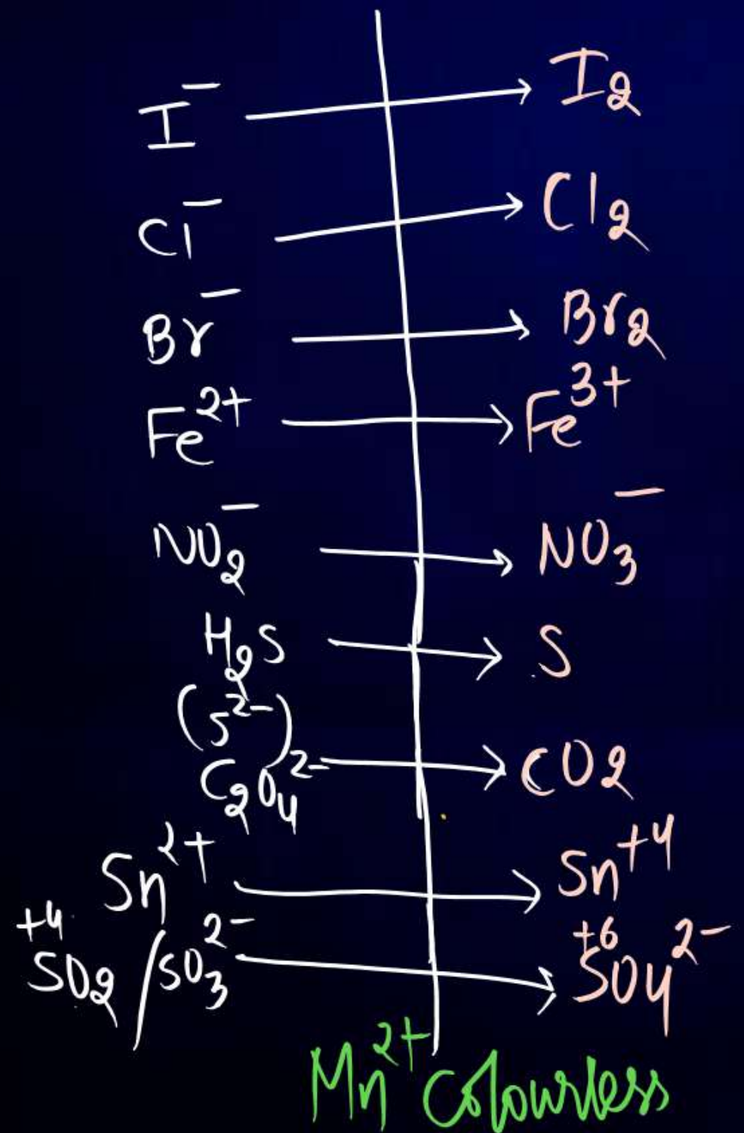
$\overset{+7}{Mn}O_4^-$ (Acidic) → get easily Reduced to achive d^5 stable configuration → Mn^{+2} (d^5 stable)

∵ In MnO_4^- Mn is present in (+7) H.O.S

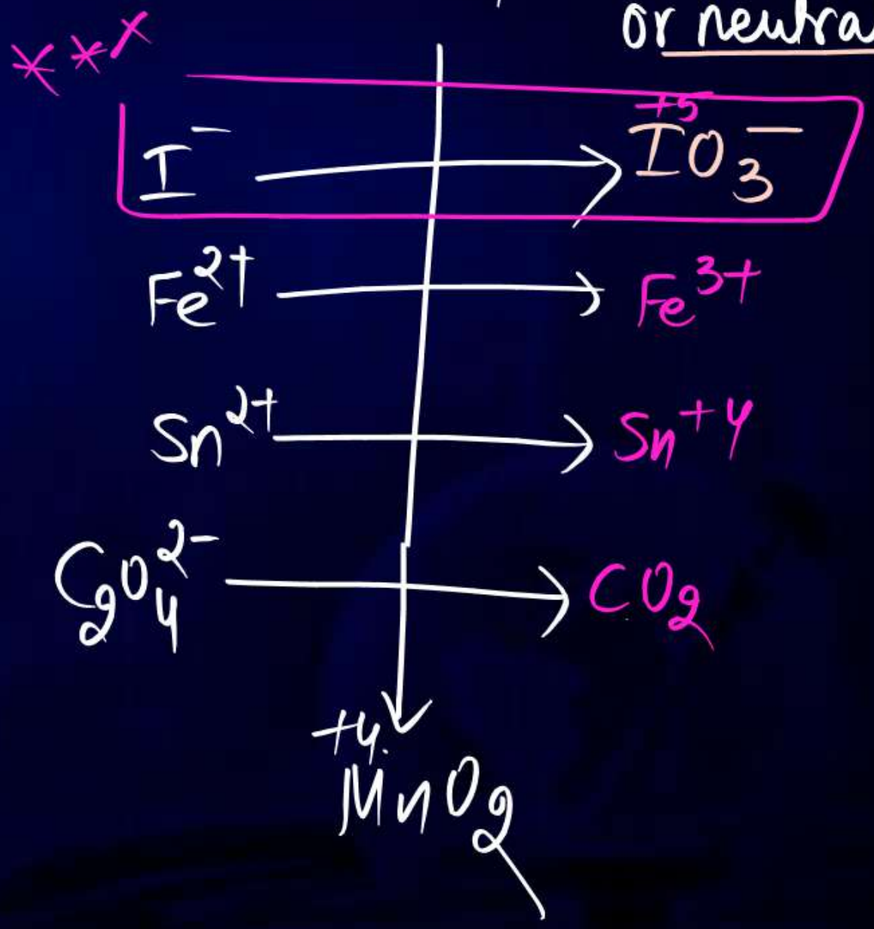
Can work as O.A.

MnO_4^- (O.A) Purple (Violet)

Acidic Medium



MnO_4^- in Faintly Basic or neutral Medium



Potassium Dichromate ($K_2Cr_2O_7$)

Chromate ion.
yellow.
Stable in Basic medium.

dichromate.
Orange.
Stable in Acidic Medium.

~~Redox Rxn~~

pH dependent Interconvertible Reaction.

(O.S Remains Same)

Preparation of $K_2Cr_2O_7$:-

By chromite ore. $FeCr_2O_4$

$FeCr_2O_4$ → Mixed oxide $[FeO + Cr_2O_3]$ (+2, +3)

$FeCr_2O_4 \xrightarrow[\text{oxidation}]{\text{Air } (O_2)} \underset{\text{Basic}}{Fe_2O_3}(+3) + \underset{\text{Acidic}}{CrO_3}(+6)$

$CrO_3 + Na_2CO_3 \rightarrow Na_2CrO_4$ (Basic)

Na_2CrO_4 (+6) — yellow sol. of Sod. chromate

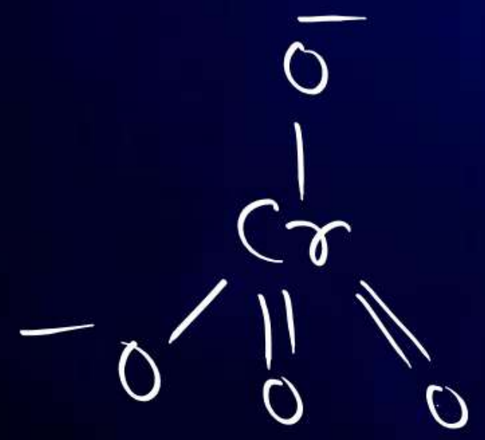
$Na_2CrO_4 \xrightarrow[(H^+)]{H_2SO_4} Na_2Cr_2O_7$ (orange solution)

$Na_2Cr_2O_7 \xrightarrow{KCl} K_2Cr_2O_7$ orange crystals

Structure

Chromate

CrO_4^{2-}



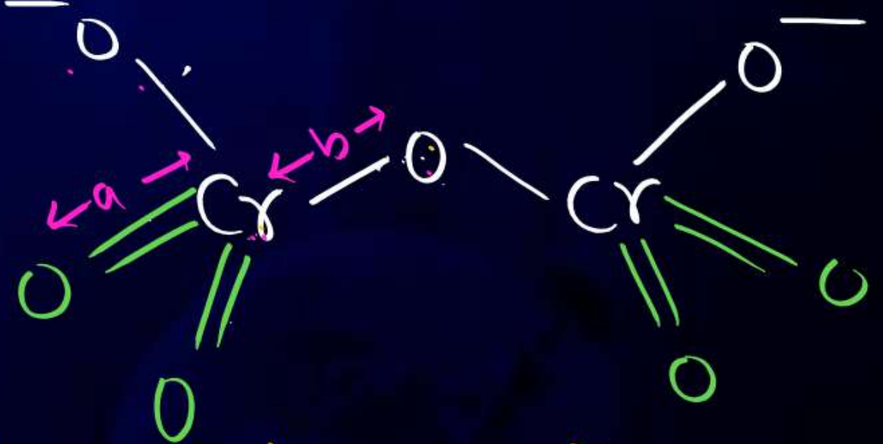
- tetrahedral
- All Cr-O B.L equal.
- Avg Cr-O B.O = $\frac{6}{4}$
- 4 $d\pi - p\pi$ Bonds.

Both are diamagnetic

(n=0)

Cr^{+6}

$Cr_2O_7^{2-}$



- → two tetrahedral Units
- → Cr-O-Cr Bridge
- → 4 $d\pi - p\pi$ Bonds.
- → All Cr-O B.L are not equal.
- → Terminal B.L < Bridging Cr-O B.L
  (a < b)

Imp

NOTE

$Na_2Cr_2O_7$ is more soluble than $K_2Cr_2O_7$.

Imp

NOTE

$K_2Cr_2O_7$ is preferred over $Na_2Cr_2O_7$ as a Primary standard in Volumetric Analysis.

Reason

$Na_2Cr_2O_7$ is Hygroscopic

↓

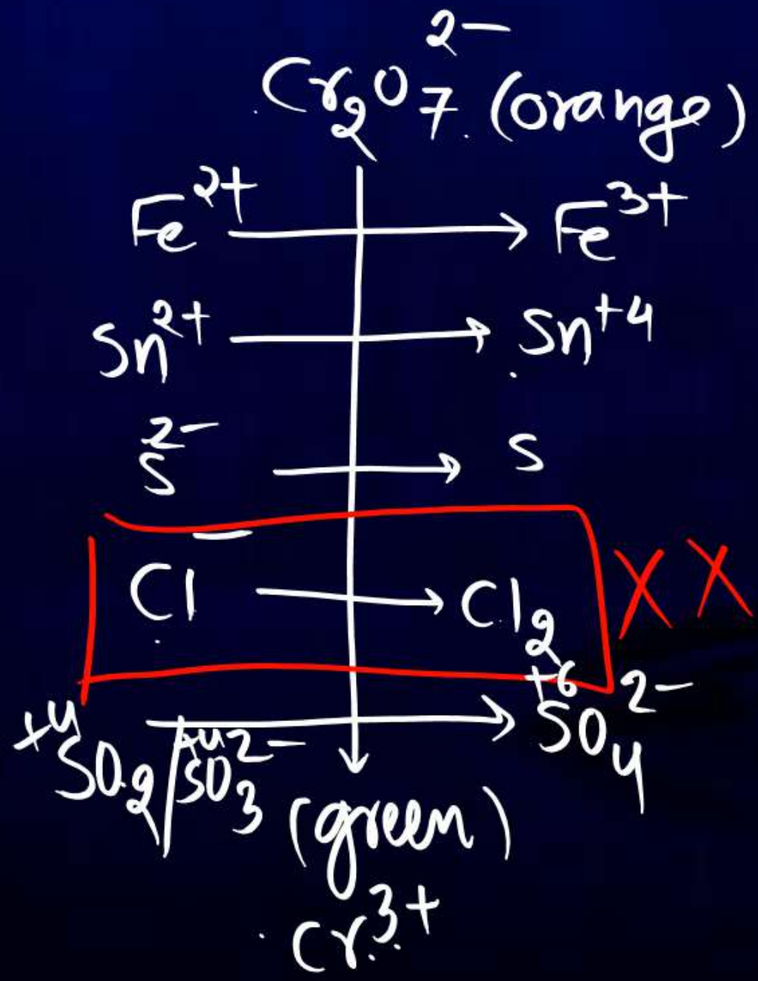
Absorb moisture from atmosphere

~~Primary~~

Secondary standard.

Reactions of $K_2Cr_2O_7$ (O.A)

Oxidising Reaction



∴

Oxidising Power

$Cl_2 > Cr_2O_7^{2-}$

Thermal decomposition of $K_2Cr_2O_7$

(Add in Reactions of $K_2Cr_2O_7$)

$$\overset{+6}{K_2Cr_2O_7}(s) \xrightarrow{\Delta} \overset{+6}{K_2CrO_4} + \overset{+3}{Cr_2O_3} + O_2$$

NOTE Both $KMnO_4$ & $K_2Cr_2O_7$ are O.A because in Both Metals are present in H.O.S.

$MnO_4^- > Cr_2O_7^{2-}$

$MnO_4^- > Cl_2 > Cr_2O_7^{2-}$

$+7$ $+6$
MnO_4^- $Cr_2O_7^{2-}$

get reduced to achive stable Configuration

Mn^{2+} (Colourless)

d^5 stable

Cr^{3+} (green)

d^3 → t_{2g}^3 stable

Half filled

f- Block Elements

Lanthanoids

$n = 6$

group - 3

58 to 71

Ce to Lu

Actinoids

$n = 7$

group - 3

90 to 103

Th to Lr

LANTHANOIDS

① e⁻ Configuration

* $6s^2$ is Common but vairable occupancy of 4f subshell.
*

MDJ

① $5d^0$ Normal

$5d^1$ → Exceptional.

② Ab tak 56 Bhaaro.

$[Xe]\ 6s^2$ Common in all (54 + 2 = 56)

③ Remaining e⁻ in 4f.

④ Ce Gd Lu → $5d^1$

Cinema Gadar Lut o gaye

*58	Ce	$[Xe]\ 6s^2$	$4f^1\ 5d^1$
59	Pr	$[Xe]\ 6s^2$	$4f^3\ 5d^0$
60	Nd	$[Xe]\ 6s^2$	$4f^4\ 5d^0$
61	Pm	$[Xe]\ 6s^2$	$4f^5\ 5d^0$
62	Sm	$[Xe]\ 6s^2$	$4f^6\ 5d^0$
63	Eu	$[Xe]\ 6s^2$	$4f^7\ 5d^0$
*64	Gd	$[Xe]\ 6s^2$	$4f^7\ 5d^1$
65	Tb	$[Xe]\ 6s^2$	$4f^9\ 5d^0$
66	Dy	$[Xe]\ 6s^2$	$4f^{10}\ 5d^0$
67	Ho	$[Xe]\ 6s^2$	$4f^{11}\ 5d^0$
68	Er	$[Xe]\ 6s^2$	$4f^{12}\ 5d^0$
69	Tm	$[Xe]\ 6s^2$	$4f^{13}\ 5d^0$
70	Yb	$[Xe]\ 6s^2$	$4f^{14}\ 5d^0$
*71	Lu	$[Xe]\ 6s^2$	$4f^{14}\ 5d^1$

MDJ

f^0, f^2, f^8 XX

f^7, f^{14} Repeats

$[Xe]\ 4f\ 5d\ 6s^2$

Energy → 6s < 4f < 5d

② Size

Left to right decreases due to increase in Z_{eff} → due to Lanthanoid Contraction or.

$L \rightarrow R$ e^- are filled into 4f subshell.

Which have poor σ, $\sigma \downarrow$ $Z_{eff} \uparrow$

Contraction in Size occours (Lanthanoid Contraction)

Eu > La > Ce > Pr > Nd > Pm > Sm < Eu > Gd > Tb > Dy > Ho > Er > Tm > Yb > Lu

f^7 loose packing

weak Metal-Metal Bonding

$\gamma \uparrow$ Size $\uparrow$

Size in M^{+3}

$La^{3+} > Ce^{3+} > Pr^{3+} > Nd^{3+} > Pm^{3+} > Sm^{3+} > Eu^{3+} > Gd^{3+} > Tb^{3+} > Dy^{3+} > Ho^{3+} > Er^{3+} > Tm^{3+} > Yb^{3+} > Lu^{3+}$.

Reason → Same

Lanthanoid contraction.

NOTE

$La(OH)_3$ - $Lu(OH)_3$ →

Size ↓ EN ↑ Acidic Nature ↑se Basic ↓se.

of OH^-/O^{2-}

(3) Oxidation states

* Common O.S state → +3 ✓
* Most stable O.S is +3 ✓
* Some elements also show +2 & +4
  due to Vacant, Half filled (f^7), Full filled (f^{14}) f stability

Ce

$[Xe]\ 4f^1\ 5d^1\ 6s^2$ ($1e^-$, $1e^-$, $2e^-$)

Ce^{+4}

$[Xe]\ 4f^0\ 5d^0\ 6s^0$

Inertgas Or Vacant f

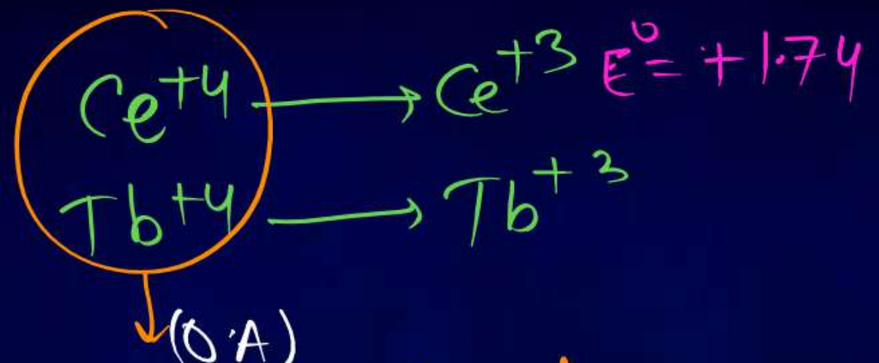
Ex

Ce^{+4} $4f^0$ (inertgas) $[Xe]\ 4f^0\ 5d^0\ 6s^0$

Tb^{+4} $4f^7$ → Halffilled stable

Yb^{+2} $4f^{14}$ Full filled stable

Eu^{+2} $4f^7$ Half filled stable.

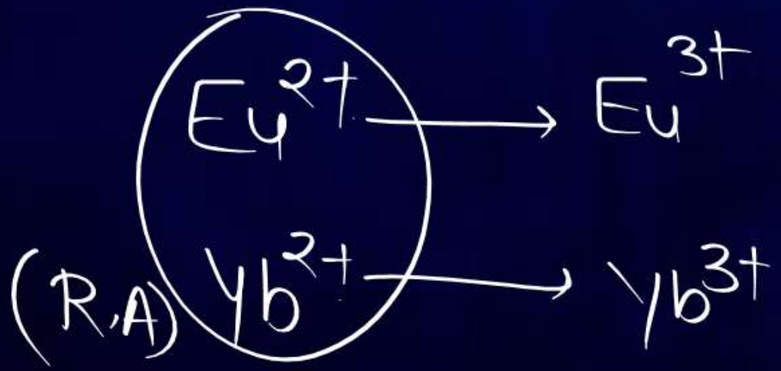


Work as oxidant.

0.5 0.5

$+4 \longrightarrow +3$

(O.A)



(R.A)

$+2 \longrightarrow +3$

Reductant

(4) Gen. Characteristics :-

* Silvery White Metals ✓
* Tarnish Rapidly in air ✓
* Hardness ↑se L → R (Sm → steel Hard)
  1623 K MP (Max in series)
* good Conductors of Heat & electricity ✓
* almost all trivalent (M^{3+}) ions are Coloured in Both solid & aq. But La^{3+} Lu^{3+} Colourless (LaLu)
* f^0 & f^{14} type Lanthanoids are dia magnetic. (n=0)
  → La^{3+}, Lu^{3+}, Ce^{+4}, Yb^{+2} (n=0)

I.E

→ $I.E_1$ & $I.E_2$ of lanthanoids. Similar to Ca

600 & 1200

$(kJ\,mol^{-1})$

→ Abnormal Low value of $I.E_3$ ⇒ La, Gd, Lu

Reason → after removal of 3rd e^- ($I.E_3$) these three species achive empty, Half filled & full filled f orbital stability respectively

f^{14}	f^7	
La $[Xe]\,4f^0\,5d^1\,6s^2$	Gd $[Xe]\,4f^7\,5d^1\,6s^2$	Lu $[Xe]\,4f^{14}\,5d^1\,6s^2$
$\downarrow$	$\downarrow$	$\downarrow -3e^-$
$La^{3+}\,[Xe]\,4f^0$	$Gd^{3+}\,[Xe]\,4f^7$	$Lu^{3+}\,4f^{14}$

Chemical Reactivity :-

Earlier members reactivity → Similar to Ca.

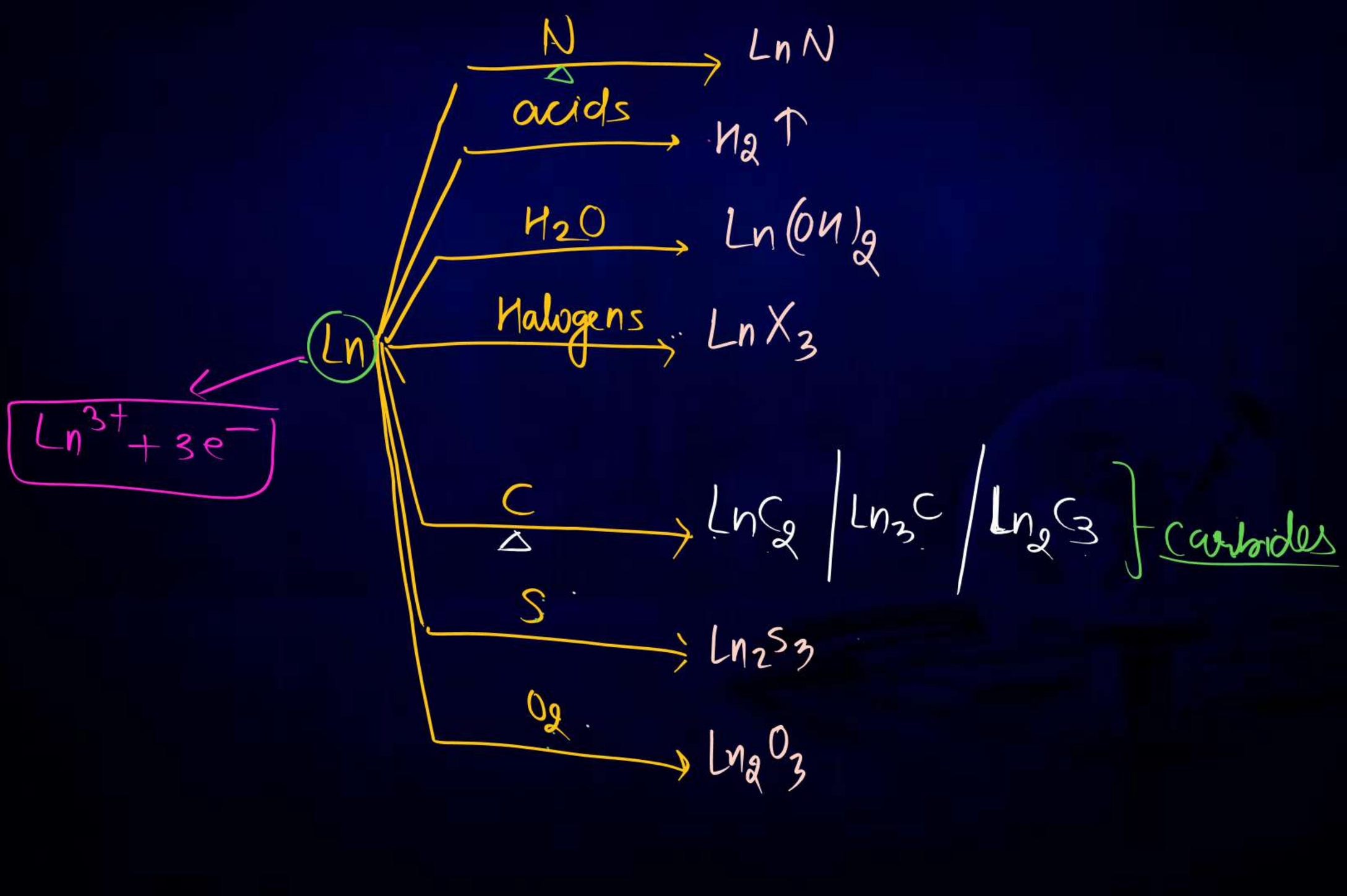
with ↑se in atomic no. they behave like Al

$$Ln^{3+}_{(aq)} + 3e^- \longrightarrow Ln_{(s)} \Rightarrow (E^0 \text{ [} -2.2 \text{ to } -2.4\,V \text{]})$$

Ln

↓

Common Symbol For All Lanthanoids


N
LnN
acids
H_2 ↑
H_2O
$Ln(OH)_2$
Halogens
LnX_3
Ln
$Ln^{3+} + 3e^-$
C
LnC_2 / Ln_3C / Ln_2C_3
carbides
S
Ln_2S_3
O_2
Ln_2O_3

ACTINOIDS

* Radioactive elements
* Earlier members have relatively long Half-lives the latter one have a day to 3 minutes For Lr 103

Electronic Configuration :-

* 5f Subshell is Progressively filled
* $7s^2$ is common in all.

MDJ

⇒ Ab tak 88 fill karo.

$Rn + 7s^2$
$86 + 2 = 88$

⇒ Remaining e^- 5f Mai fill karo.

Note → Th 90 = $6d^2$

$6d^0$ → normal

$6d^{1/2}$ exceptional.

91 92 93 96 103 ⇒ 6d
Pa U Np Cm Lr

90	Th	[Rn] $7s^2$	$5f^0\ 6d^2$
91	Pa		$5f^2\ 6d^1$
92	U		$5f^3\ 6d^1$
93	Np		$5f^4\ 6d^1$
94	Pu		$5f^6\ 6d^0$
95	Am		$5f^7\ 6d^0$
96	Cm		$5f^7\ 6d^1$
97	Bk		$5f^9\ 6d^0$
98	Cf		$5f^{10}\ 6d^0$
99	Es		$5f^{11}\ 6d^0$
100	Fm		$5f^{12}\ 6d^0$
101	Md		$5f^{13}\ 6d^0$
102	No		$5f^{14}\ 6d^0$
103	Lr	[Rn] $7s^2$	$5f^{14}\ 6d^1$

(88) — Same. Same.

f^1, f^5, f^8 XX

f^7, f^{14} Repeats

Size :- gen. ↓se L→R in "M" as well "M^{3+}" due to actinoid: Contraction.

↓

due to poor σ of 5f e^-

$Z_{eff} = Z - \sigma$

$\sigma \downarrow$ Z_{eff} ↑

Shielding order

s > p > d > f

↓

4f > 5f

Contraction strength →

A.C > L.C

↓

Contraction due to more poor σ of 5f e^-

Contraction due to poor σ of 4f e^-

Oxidation states :-

* Common +3 but show Variable O.S. due to Comparable energy levels of **7s, 5f, 6d** subshell.

* Max. O.S ⇒ +7 (Np & Pu)

Other imp points :-

→ gen. I.E are lesser than lanthanoids.

→ Size greater than Ln.

→ Highly Reactive in Powdered form.

→ gen. All **actinoids + $C.HNO_3$** → Passivation

Formation of Protective oxide layer on Metal surface


Thank you