D & F Block

- last e^- → $(n-1)d$ penultimate shell
- GEC → $(n-1)d^{1-10}\ ns^{0-2}$
- <u>Transition element</u> : d block → incompletely filled d orbital (In ground state or in any oxidation state)

  Zn, Cd, Hg → $(n-1)d^{10}\ ns^2$ → completely filled always (ground state / any oxid^n state)

- D-Block → [Group 3-12] & Transition → [3-11]

  4th Period → 3d series → (21) Sc – Zn (30)

  5th " → 4d " → (39) Y – Cd (48)

  6th " → 5d " → (57) La , $\overset{72}{Hf}$ – $\overset{80}{Hg}$

  7th " → 6d " → (89) Ac , $\underset{104}{Rf}$ – $\underset{112}{Cn}$

Sc	Ti	V	Cr*	Mn	Fe	Co	Ni	Cu*	Zn
$3d^1\ 4s^2$	$3d^2\ 4s^2$	$3d^3\ 4s^2$	$3d^5\ 4s^1$	$3d^5\ 4s^2$	$3d^6\ 4s^2$	$3d^7\ 4s^2$	$3d^8\ 4s^2$	$3d^{10}\ 4s^1$	$3d^{10}\ 4s^2$
Y	Zr	Nb*	Mo	Tc	Ru	Rh	Pd	Ag	Cd
$4d^1\ 5s^2$	$4d^2\ 5s^2$	$4d^4\ 5s^1$	$4d^5\ 5s^1$	$4d^6\ 5s^1$	$4d^7\ 5s^1$	$4d^8\ 5s^1$	$4d^{10}\ 5s^0$	$4d^{10}\ 5s^1$	$4d^{10}\ 5s^2$
La	Hf	Ta	W	Re	Os	Ir	Pt*	Au*	Hg
$5d^1\ 6s^2$	$5d^2\ 6s^2$	$5d^3\ 6s^2$	$5d^4\ 6s^2$	$5d^5\ 6s^2$	$5d^6\ 6s^2$	$5d^7\ 6s^2$	$5d^9\ 6s^1$	$5d^{10}\ 6s^1$	$5d^{10}\ 6s^2$

General properties of Transition elements

- Generally, all d block → metallic property show.
  1) Tensile → high.
  2) Ductile.
  3) malleable.
  4) Thermal & electrical conductivity.
  5) metallic lusture. 6) Hard 7) low volatile

Except Zn, Cd, Hg, Mn, all have metallic lattice str : → hcp, bcc, hcp, ccp (Fe)

Sc hcp	Ti hcp	V bcc	Cr bcc	Mn ✗	Fe bcc	Co ccp	Ni ccp	Cu ccp	Zn ✗
Y hcp	Zr hcp	Nb bcc	Mo bcc	Tc hcp	Ru hcp	Rh ccp	Pd ccp	Ag ccp	Cd ✗
La hcp	Hf hcp	Ta bcc	W bcc	Re hcp	Os hcp	Ir ccp	Pt ccp	Au ccp	Hg ✗

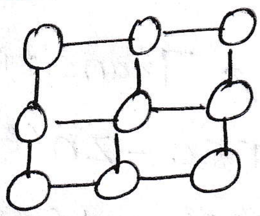
① **MP & B.P** → ~~Greater~~ more valence e^- ⇒ more strong bonding ⇒ more MP & B.P

[Cr, Mo, W] → Highest MP & BP

[Zn, Cd, Hg] → Low MP & BP

[exception → Mn & Tc] → MP & B.P is low.

② **Enthalpy of atomiz^n** :



→ Energy req to Break all bonds of lattice & then convert atoms into gaseous form, (enthalpy of atomiz^n)

• more ve → more strong bond ⇒ more enthalpy of atomiz^n. (follows almost same trend as MP & BP) [max → Vandium]

③ **Atomic size**

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

- Sc > Ti > V > Cr > Mn : decrease — Z_{eff} > screening effect
- Fe = Co = Ni : const — Z_{eff} = Screening effect
- Cu < Zn : increase — Z_{eff} < screening effect.

Group

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

→ Lanthanide Contra^n (poor sheilding of f orbital e^-)

④ **I.E**

Period : generally increase from L to R (But change at 2, 6, 7)

Sc < Ti < V < Cr < Mn < Fe < Co < Ni < Cu < Zn
(↑ 2 at Ti < V, ↑ 6 at Fe < Co, ↑ 7 at Co < Ni)

Sc < Ti > V < Cr < Me < Fe > Co > Ni < Cu < Zn

IE_1 of Zn, Cd, Hg → Highest → full filled

IE_2 of Cr, ~~Mn~~ Cu → High → $3d^5$, $3d^{10}$

IE_3 of Mn → High → d^5 ~~con~~

<u>Group</u>

G3	→	3d > 4d > 5d
G 4 5 6 10	→	5d > 4d > 3d
G 7 8 9 11 12	→	5d > 3d > 4d

⑤ <u>Oxidation state</u> : All d block shows variable oxidation state. except G3 & G12

↳ why variable oxdⁿ state?? → very less energy gap b/w (n-1)d & ns orbital. (e^- easy excited from (n-1)d to ns)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+3	+2	+2	+2	+2	+2	+2	+2	+1	+2
	+3	+3	+3	+3	+3	+3	+3	+2	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

- Highest num of oxdⁿ state → Mn (+2 — +7)
- Low oxdⁿ state is found with π acceptor ligand $Fe(CO)_5$, $Ni(CO)_4$
- elements with d^0, d^5, d^{10} configuration are more stable. Sc^{+3}, Ti^{+4}, V^{+5}, Fe^{+3}, Mn^{+2}, Zn^{+2} etc.
- ~~Cu^{+2} more stable than Cu^+ due to lower redⁿ potential & high hydⁿ enthalpy of Cu^{+2}.~~
- Highest oxidation state in entire d block is +8. (Ru, Os) ↳ OsO_4.

⑥ <u>M^{2+}/M standard electrode potential</u> → E^0 value will be more -ve if M^{+2} is stable

E^0 values of Mn, Ni, Zn are more negative.

Mn ↓ d^5; Zn ↓ d^{10}

↓ High ~~negative~~ hydration enthalpy.

E^0 value of Cu is +ve. (→ Cu can't liberate H_2 from acid.) (→ low hydration enthalpy)

⑦ M^{+3}/M^{+2} standard electrode potential :-

$Sc^{+2} \longrightarrow Sc^{+3}$ (stable) → High negative (low)

$Zn^{+2} \longrightarrow Zn^{+3}$ → positive (high)
d^{10} stable

$Mn^{+2} \longrightarrow Mn^{+3}$ → positive (high)
d^5 stable

$Fe^{+2} \longrightarrow Fe^{+3}$ → High negative (low)
d^5 stable

⑧ Higher oxidation state in Halides & oxides

Halides

Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
TiX_2	VX_2	CrX_2	MnX_2	FeX_2	CoX_2	NiX_2	CuX, CuX_2	ZnX_2
TiX_3	VX_3	CrX_3	MnF_3	FeX_3	CoF_3			
TiX_4	~~VX_4~~	CrX_4	MnF_4					
	VF_5	CrF_5						
		CrF_6						
			MnO_3F					

- only VF_5 is known, which on hydrolysis gives VOX_3.
- ~~all~~ CuX_2 is formed except iodide.

$$Cu^{+2} + I^- \rightarrow Cu_2I_2 + I_2$$

- In aq soln Cu^{+2} is more stable than Cu^{+1}
  ↳ very high hydration energy released which compensates 2nd I.E

Oxide

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	TiO	VO	CrO	MnO					
Sc_2O_3	Ti_2O_3	V_2O_3	Cr_2O_3	Mn_2O_3	FeO	CoO	NiO	CuO	ZnO
	TiO_2	V_2O_4	CrO_2	MnO_2	Fe_2O_3	Co_3O_4		Cu_2O	
		V_2O_5	CrO_3	Mn_3O_4	Fe_3O_4				
				Mn_2O_7					

- In Higher oxidation state, oxides are more stable than fluorides

⑨ Magnetic properties

diamagnetic
Repelled by magnetic field
→ no unpaired e^-

Paramagnetic
attracted by magnetic field
→ presence of unpaired e^-

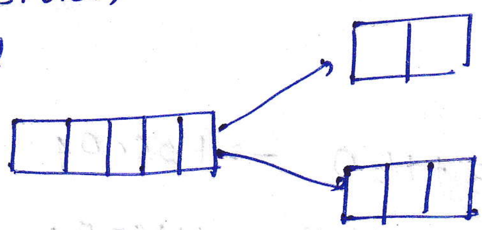
Ferromagnetic
Very strongly attracted by magnetic field.

Magnetic moment $\mu = \sqrt{n(n+2)}$ BM
n = no of unpaired e^-.

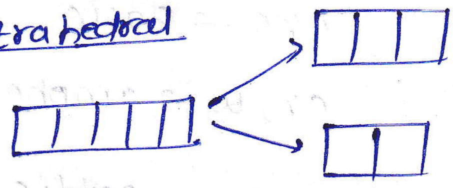
⑩ Formation of Colored ions

if an unpaired electron is present, it will show color due to d-d transition.

octahedral



tetrahedral



- electron is excited from lower energy to higher energy d orbital

⑪ Catalytic properties

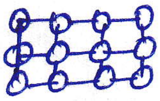
→ It has multiple oxidation state so, shows Catalytic property.

Contact process → V_2O_5
Haber process → Finely divided Iron
Catalytic hydrogenation → Ni

$Fe^{+3} + I^- \longrightarrow Fe^{+2} + I_2$
$Fe^{+2} + S_2O_8^{-2} \longrightarrow Fe^{+3} + SO_4^{-2}$

(12) Formation of Interstitial compd :-

These are metals & form lattice. (voids are created in the lattice)



Small atoms like B, H, C, N are accomodated in these empty spaces & form interstitial compound.

TiC, Mn_4C, Fe_3H, $VH_{0.5}$, $TiH_{1.7}$

- High melting point, very hard, chemically inert & have metallic conductivity.

(13) Alloy formation

Due to similar size of d block metals, these metals form alloy

alloy of copper

- Brass → Cu (70-80%) + Zn (20-30%)
- Bronze → Cu (80-90%) + Sn (10-20%)
- Bell-metal → Cu (72-80%) + Zn (20-28%)
- Gun-" → Cu (85%) + Zn (10%) + Sn (5%)

Some imp compounds of Transition elements

oxides

oxides of d-block elements in low oxidation state are basic in high oxidation state is acidic & intermediate oxidation state → amphoteric.

V_2O_3 → Basic

V_2O_5 → amphoteric

$$V_2O_5 + NaOH \rightarrow Na_3VO_4 + H_2O$$

$$V_2O_5 + HCl \rightarrow VO_2Cl + H_2O$$

CrO → Basic

Cr_2O_3 → amphoteric

CrO_3 → acidic → $CrO_3 + H_2O \rightarrow H_2CrO_4$

$$Mn_2O_7 + H_2O \rightarrow HMnO_4$$

$$2CrO_3 + H_2O \rightarrow H_2Cr_2O_7$$

Potassium dichromate ($K_2Cr_2O_7$)

(1) Preparation

chromite ore ($FeCr_2O_4$) + सोडा ऐश + O_2 के साथ

$FeCr_2O_4 + Na_2CO_3 + O_2 \longrightarrow Na_2CrO_4 + Fe_2O_3 + CO_2$

($FeCr_2O_4$: chromite ore; Na_2CrO_4: sodium chromate)

$Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

($Na_2Cr_2O_7$: sodium dichromate)

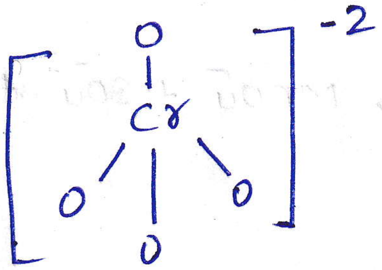
$Na_2Cr_2O_7 + KCl \longrightarrow K_2Cr_2O_7 + NaCl$

($K_2Cr_2O_7$: potassium dichromate)

(2) str

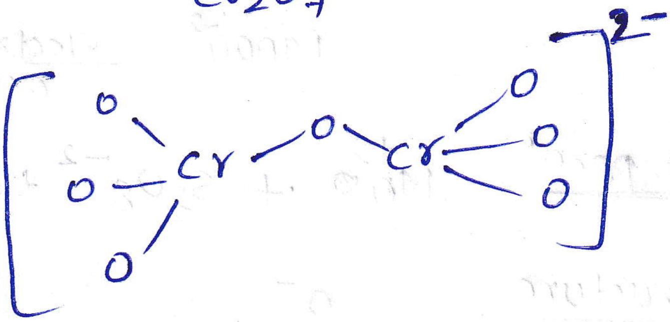
chromate ion

CrO_4^{-2}



dichromate ion

$Cr_2O_7^{-2}$



(3) chromate-dichromate eqm

$CrO_4^{-2} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} Cr_2O_7^{-2}$

~~(orange)~~ (yellow) ~~(yellow)~~ (orange)

Acid → आगे

Basic → Backward

(4) Strong oxidizing agent in acidic medium

$\overset{+6}{Cr_2}O_7^{-2} + H^+ \longrightarrow Cr^{+3}$

so it oxidizes, I^- to I_2, H_2S to S, Sn^{+2} to Sn^{+4}, Fe^{+2} to Fe^{+3}

$Cr_2O_7^{-2} + I^- + H^+ \longrightarrow I_2 + Cr^{+3} + H_2O$

" " Fe^{+2} + " $\longrightarrow Fe^{+3}$ ——

—— H_2S —— $\longrightarrow S$ ——

—— Sn^{+2} —— $\longrightarrow Sn^{+4}$ ——

(5) chromyl chloride Test

any metal chloride + conc H_2SO_4 + $K_2Cr_2O_7 \longrightarrow CrO_2Cl_2 + KHSO_4 + H_2O$

eg → (KCl)

(CrO_2Cl_2: Red vapours)

① Potassium permagnate ($KMnO_4$)

Preparation ore → pyrolusite ore MnO_2

$$MnO_2 + KOH + O_2 \longrightarrow K_2MnO_4 + H_2O$$

magnate ion (green)

&

$$MnO_4^{-2} \xrightarrow{H^+} MnO_4^- + MnO_2 + H_2O$$

Green → purple

Commercial ppr^n

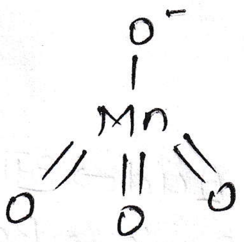
$$MnO_2 \xrightarrow[\text{or } KNO_3]{\text{Fused with KOH \& oxidized with air}} MnO_4^{-2}$$

$$MnO_4^{-2} \xrightarrow{\text{Electrolytic oxidation}} MnO_4^-$$

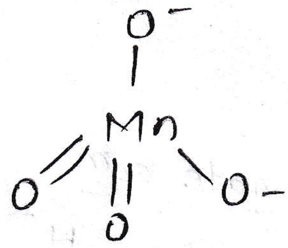
Lab ppr^n

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

② Structure



Per-magnate
Purple
diamagnetic



magnate
Green
Paramagnetic

③ properties

$$\underset{\text{purple}}{KMnO_4} \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2\uparrow$$

→ decompose.

• Potassium per magnate in acidic medium oxidizes. ($Mn^{+7} \rightarrow Mn^{+2}$)

1. oxalate → CO_2 — $\overset{+3}{C_2O_4^{-2}} \longrightarrow CO_2$
2. $Fe^{+2} \longrightarrow Fe^{+3}$.
3. Nitrite → nitrate — $\overset{+3}{NO_2^-} \longrightarrow \overset{+5}{NO_3^-}$
4. Iodide → Iodine — $I^{-1} \longrightarrow I_2^0$
5. $S^{-2} \longrightarrow S^0$
6. $\overset{+4}{SO_3^{-2}} \longrightarrow \overset{+6}{SO_4^{-2}}$

$$\overset{+7}{MnO_4^-} + C_2O_4^{-2} + H^- \rightarrow Mn^{+2} + CO_2 + H_2O$$

$$MnO_4^- + H^+ + Fe^{+2} \rightarrow Mn^{+2} + Fe^{+3} + H_2O$$

$$MnO_4^- + H^+ + NO_2^- \rightarrow Mn^{+2} + NO_3^- + H_2O$$

$$MnO_4^- + H^+ + I^- \rightarrow Mn^{+2} + I_2 + H_2O$$

$$MnO_4^- + H^+ + S^- \rightarrow Mn^{+2} + S + H_2O$$

$$MnO_4^- + H^+ + SO_3^{-2} \rightarrow Mn^{+2} + SO_4^{-2} + H_2O$$

Potassiumpermanganate (neutral / faintly alkaline)
less alkaline

$$MnO_4^- + I^- + ~~H_2O~~ \longrightarrow MnO_2 + IO_3^-$$

$$MnO_4^- + S_2O_3^{-2} \longrightarrow MnO_2 + SO_4^{-2}$$

$$MnO_4^- + Mn^{+2} \longrightarrow MnO_2$$

NOTE → In titration we use dil H_2SO_4 & not HCl [illegible]

bcoz $HCl^- + MnO_4^- \longrightarrow Cl_2 + Mn^{+2}$

f-Block element

- last e^- → (n-2) f orbital ⇒ anti penultimate shell → Rare earth metal 58 – 71 Ce – Lu
  - → Lanthanoids (14) → Lanthanum के आगे
  - → Actanoids (14) → Actinium के आगे 90 – 103 Th – Lr → Radioactive

① Electronic Configuration

				M	M^{+3}
				$4f^1 5d^1 6s^2$	$4f^1$
58	Ce	Cerium	सीने		$4f^2$
59	Pr	Praseodymium	पर	$4f^3 6s^2$	$4f^3$
60	Nd	Neodymium	नदियाँ	$4f^4$ "	$4f^4$
61	Pm	Promethium	प्रेम	$4f^5$ "	$4f^5$
62	Sm	Samarium	शरमाए	$4f^6$ "	$4f^6$
63	Eu	Europium	यूँ	$4f^7$ "	$4f^7$
64	Gd	Gadolinium	जाग-जग	$4f^7 5d^1 6s^2$	$4f^7$
65	Tb	Terbium	तब	$4f^9$	$4f^8$
66	Dy	Dysprosium	दिल	$4f^{10}$	$4f^9$
67	Ho	Holmium	हुआ	$4f^{11}$	$4f^{10}$
68	Er	Erbium	अरे	$4f^{12}$	$4f^{11}$
69	Tm	Thulium	तुम	$4f^{13}$	$4f^{12}$
70	Yb	Ytterbium	ऐसी	$4f^{14}$	$4f^{13}$
71	Lu	Lutetium	लुटा मो	$4f^{14} 5d^1 6s^2$	$4f^{14}$

② Atomic / Ionic Size

from La to Lu → decrease in atomic/ionic radii (due to lanthanide contraction)

- ↳ from La to Lu → atomic number ↑
  - → number of Protons in nucleus ↑
  - → electrons are added to 4f orbital
  - → very poor sheilding
  - → so radius ↓.

- Atomic radius of 4d and 5d series are same due to lanthanoid contraction

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

Oxidation state : Generally +3 oxd^n state,
but +2 and +4 also exist due to
$4f^0$, $4f^7$, $4f^{14}$ configuration.

$Ce^{+4} \rightarrow 4f^0$ → oxidizing agent → Ce^{+3}
$Tb^{+4} \rightarrow 4f^7$
$Eu^{+2} \rightarrow 4f^7$] Reducing agent → Eu^{+3}
$Yb^{+2} \rightarrow 4f^{17}$] Reducing agent → Yb^{+3}

Samarium → exhibits +2 & +3 oxidation state.

General characteristics

① **Reaction with air** :- Lanthanoids are silvery white (soft) & tarnish in moist air. In air it forms Ln_2O_3 type oxide.

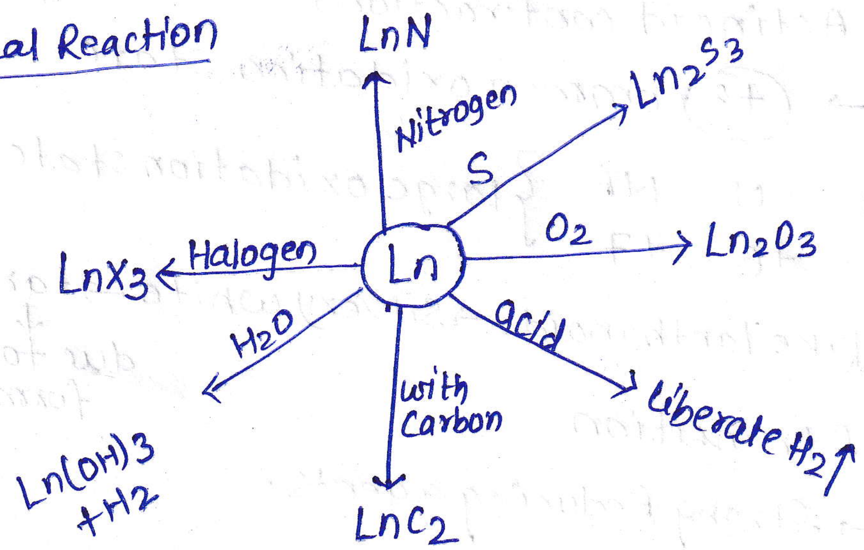
② **Hardness** :- ↑ with ↑ ~~atmo~~ atomic number. (Samarium → exceptionally hard like steel.)

③ **MP** : (1000 – 1200K) (Samarium–exception 1623K)

④ **Conductivity** → metals are, so good conductor of heat & Electricity.

⑤ **Colored ion** → f–f transition, La^{+3} & Lu^{+3} → colorless due to $4f^0$ & $4f^{14}$ configuration.

⑥ **Chemical Reaction**



• The oxide & ~~oh~~ hydroxides are basic like G-2 oxides & hydroxides.

Actinoids

Th —— Lr $5f^{1-14} 6d^{0-1} 7s^2$

90 —— 103

				M^{+3}	M^{+4}
Ac	Actinium	एक	$6d^1 7s^1$	$5f^0$	
Th	Thorium	था	$6d^2 7s^2$	$5f^1$	$5f^0$
Pa	Protactinium	पागल	$5f^2 6d^1 7s^2$	$5f^2$	$5f^1$
U	Uranium	उस	$5f^3 6d^1 7s^2$	$5f^3$	$5f^2$
NP	Neptunium	ने पूछा	$5f^4 6d^1 7s^1$	$5f^4$	$5f^3$
Pu	Plutonium	पुराने	$5f^6 7s^2$	$5f^5$	$5f^4$
Am	Americium	आम	$5f^7 7s^2$	$5f^6$	$5f^5$
Cm	Curium	कितने में	- - - - - -	$5f^7$	$5f^6$
BK	Berkelium	लिकेज़ो	$5f^9 7s^2$	$5f^8$	$5f^7$
Cf	Californium	Cafe	$5f^{10} 7s^2$	$5f^9$	$5f^8$
Es	Einsteinium	Einstein ने	$5f^{11} 7s^2$	$5f^{10}$	$5f^9$
Fm	Fermium	छनाओ	$5f^{12} 7s^2$	$5f^{11}$	$5f^{10}$
Md	Mendelevium	मिरिंडा	$5f^{13} 7s^2$	$5f^{12}$	$5f^{11}$
NO	Nobelium	Nimbupani	$5f^{14} 7s^2$	$5f^{13}$	$5f^{12}$
Lr	Lawrenium	Lao	$5f^{14} 6d^1 7s^2$	$5f^{14}$	$5f^{13}$

- **Size** → Ionic radii decrease across a series. (Actinoid contraction)
- **Oxidation state** → +3 common oxidation state.

Th	Pa	U	NP
+4	+5	+6	+7

} large oxidation state.

- **Action of air** : Like lanthanoid. → Silvery white → tarnish ↓ due to oxide formation.
- **Colored ion** : f-f transition
- Reducing agent → Strong Reducing agents.

—————×—————×—————