THE d & f-BLOCK ELEMENTS

General electronic Configuration of d block elements. ⇒ [Noble gas] $(n-1)d^{1-10}\ ns^{1-2}$

⟹ Transition Series :-

① 1st Transition Series (3d Series) :-

10 elements from Scandium (Sc) to Zinc (Zn)

② IInd Transition Series (4d Series) :-

10 elements from Yittrium (Y) to Cadmium (Cd)

③ IIIrd Transition Series (5d Series) :-

10 elements from Lanthnum (La) to Mercury (Hg)

④ IVth transition Series (6d Series) :-

10 elements from Actinium (Ac) to Unumbium (uub)

⟹ 3d Series :-

Symbol	Atomic No.	Electronic Configu
Sc	21	[Ar] $3d^1 4s^2$
Ti	22	[Ar] $3d^2 4s^2$
V	23	[Ar] $3d^3 4s^2$
Cr	24	✪ [Ar] $3d^5 4s^1$
Mn	25	✪ [Ar] $3d^5 4s^2$
Fe	26	[Ar] $3d^6 4s^2$
Co	27	[Ar] $3d^7 4s^2$.

Ni	28	[Ar] $3d^8 4s^2$
Cu	29	☆ [Ar] $3d^{10} 4s^1$
Zn	30	☆ [Ar] $3d^{10} 4s^2$

⇒ **4d Series :-**

Symbol	Atomic No.	Electronic Configuration
Y	39	[Kr] $4d^1 5s^2$
Zr	40	[Kr] $4d^2 5s^2$
Nb	41	[Kr] $4d^4 5s^1$
Mo	42	[Kr] $4d^5 5s^1$
Tc	43	[Kr] $4d^6 5s^1$
Ru	44	[Kr] $4d^7 5s^1$
Rh	45	[Kr] $4d^8 5s^1$
Pd	46	[Kr] $4d^{10} 5s^0$
Ag	47	[Kr] $4d^{10} 5s^1$
Cd	48	[Kr] $4d^{10} 5s^2$.

⇒ **5d Series :-**

Symbol	Atomic No.	Electronic Configuration
La	57	[Xe] $4f^0 5d^1 6s^2$
Hf	72	[Xe] $4f^{14} 5d^2 6s^2$
Ta	73	[Xe] $4f^{14} 5d^3 6s^2$
W	74	[Xe] $4f^{14} 5d^4 6s^2$
Re	75	[Xe] $4f^{14} 5d^5 6s^2$
Os	76	[Xe] $4f^{14} 5d^6 6s^2$
Ir	77	[Xe] $4f^{14} 5d^7 6s^2$
Pt	78	[Xe] $4f^{14} 5d^9 6s^1$
Au	79	[Xe] $4f^{14} 5d^{10} 6s^1$
Hg	80	[Xe] $4f^{14} 5d^{10} 6s^2$

⇒ Physical properties of d-block elements

→ All are metals
→ Malleable & Ductile (except Hg)
→ High thermal & electrical Conductivity
→ Sonorous (except - Zn, Cd, Hg, Mn)

⇒ **Atomic radii :-** Atomic radii first decrease to the middle, become constant & finally increase across a period.

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

→ 3d < 4d ≈ 5d (except 3rd group)

The Size of 4d & 5d orbital has to be Similar because of Lanthanoid Contraction

⇒ **Lanthanoid Contraction :** The filling of electron in 4f orbital before 5d orbital results regularly decrease atomic radii

Ques ~~Ionic~~ Radii why Zr & Hf has similar Size?

Ans. because of Lanthanoid Contraction.

⇒ **Ionic radii :-**

→ Ionic radii increase with decrease oxidation Number.

→ Ionic radii is different for different oxidation State

→ Ionic Radii of d block is Smaller than s & P block.

→ Ionic Radii regularly decreased for Same oxidation State.

Ex- $Fe^{2+} > Fe^{3+}$

⇒ Metallic character:

→ Hard Metals except Zn, Cd & Hg

→ Cr, Mo, W are hardest metal because of presence of greater no. of balance e⁻

→ Cu, Ag, Au are ductile.

⇒ Density:- The density of D-block elements is higher because of low atomic volume

→ Os & Ir has higher density.

→ Density increase from 3d to 4d Series & just double from 4d to 5d Series.

⇒ Melting & Boiling point:

→ Chromium (Cr), Molibitnum (Mo) & Tungsten (W) have higher boiling point because of greater no. of Valence electron.

→ Zinc (Zn), Cd, Mg has very low melting point because of presence of Stable electrons.

→ Mn & Tc has low boiling point because of high enthalpy of atomisation.

⇒ **Ionisation Enthalpy :-** The first Ionisation Enthalpy of d block is greate than s block but lower than P block. element.

$s < d < p$

→ Successive Ionisation Enthalpy of d-block is lower than s & P block. because electrons enter in (n-1) d orbital provide Screening effect.

→ Second Ionisation Enthalpy of Cr & Cu has higher

⇒ **Oxidation State :-**

- They show variable oxidation state
- Most Common oxidation State of first Series is +2 (except Sc) → Scandium
- The metal in lower oxidation state form ionic bond & in higher oxidation State form Covalent bond.

Ex - $\overset{+2}{Zn}Cl_2$, $\overset{+2}{Cd}Cl_2$ ⟶ Ionic

Ex — $\overset{+6}{Cr_2}O_7^{2-}$, $\overset{+7}{Mn}O_4^{-}$ ⟶ Covalent bond.

- Metal in heigher oxidation State form Oxo Acid.
- Osmium has heighest oxidation State (+8)
- Metal exist more than 1 oxidation state then the relative Stability is known as standard Reduction potential
- Cu^{2+} is more stabe in aq. solⁿ then Cu^{1+} becaus of there low Value of Eo

$Cu^{2+} = (0.34)$

$Cu^{+} = (0.54)$

⇒ **Standard Reduction potential :-** E The E_o value depends on enthalpy of Sublimation, Ionisation & hydration enthalpy.

- More (+ve) E_o Value, greater Stable Compound
- Zn has low E_o Value because of there higher their ionisation enthalpy.

⇒ **Trends of M^{+2}/M & M^{3+}/M^{2+} :-**

- Cu has positive E_o Value because of high enthalpy of Atomisation & low enthalpy of hydration hence large amount of energy required for the Conversion of Cu to Cu^{2+} is not balanced by hydration energy.

→ M^{3+}/M^{2+} has positive E_o Value because Mn^{2+} is in $3d^5$ Stable electronic configuration & third Ionisation enthalpy of Mn^{3+} is very high.

⇒ **Magnetic property :-** The compound having unpaired electron is known as para-magnetic Compound

→ The Compound having

→ The magnetic property can be calculated by

$$\mu = \sqrt{n(n+2)}$$ BM → Bhor magneton

n = no. of unpaired e^-

⇒ **Coloured Ions** :- Most of the d-block metal ion are coloured in both solid as well as aqueous state.

→ Coloured is due to d-d Transition [More than 1 unpaired e^-]

ex - Sc^{3+}, Ti^{4+}, Zn^{2+}, Cu^{+} ← colourless.
V^{4+}, Cr^{2+}, Fe^{2+} ← Coloured.

⇒ **Complex formation** :- Most of the d-block elements forms complex because of small size, high charge & Availability of vacant d-orbital

Ex :- $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $[Cu(NH_3)_4]^{2+}$ etc

⇒ **Catalytic property** :-

→ Most of the d-block elements and there compounds used as catalyst.

Ex - Pt, Pd, Ni, Mo, W, Co etc.

① V_2O_5 :- Manufacture of H_2SO_4 by contact process.

V_2O_5/Pt :- Oxidation of SO_2 to SO_3 by contact process.

② Fe + Mo :- Manufacture by NH_3 :- (Haber's process

③ Ni :- Hydrogenation of unsaturated organic compound.

④ MnO_2 :- decomposition of H_2O_2

⑤ Co Salt :- Decomposition of Bleaching powder

⑥ $[(Ph_3P)_3RhCl]$:- Wilkinson Catalyst used for hydrogenation of Alkene.

⑦ $FeSO_4 + H_2O_2$:- fenton's reagent used for alcohol to Aldehyde.

⑧ $TiCl_4 + Al(C_2H_5)_3$:- Zieglear Natta Catalyst used for polymerisation of ethylene.

⇒ Interstitial Compound :

→ d - block elements form a large no. of interstitial compound in which shall atom Such as H, C, B, N etc. occupied at their Interstitial site.

→ These Compounds are generally non-stoicheometric in nature.

Ex → TiC, TiH, TiH_2, WC, Mn_4N etc.

⇒ Alloy formation :

→ Most of the Alloys of d-block are very hard & at high melting points.

→ They are solid Substitutional.

Ex - Benzene (Cu + Sn)

Brass (Cu + Zn)

Dental Alloys (Ag + Hg + Cu + Zn + Sn)

Stainless steel (Fe + Cr)

Nickel Steel (i) Ni + C : Used for Shaving

(ii) Fe + Ni in drilling Machine

⇒ Oxides & Oxoacids:

$\overset{+2}{CrO}$	$\overset{+3}{Cr_2O_3}$	$\overset{+4}{CrO_2}$.
Basic	Amphotenic	Acidic.

Covalent ↑

$MnO < Mn_2O_3 < Mn_2O_4 < MnO_2 < Mn_2O_7$

Acidic character ↑

Imp.

⇒ Potassium dichromate ($K_2Cr_2O_7$)

Preparation of $K_2Cr_2O_7$ - from chromite are

$$FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

Chemical properties:

① Action with acid & base.

$$Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$$

$$2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$$

② Oxidising property:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$Cr_2O_7^{2-} + 5Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 5Fe^{3+} + 7H_2O$$

$$Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

⇒ Potassium permagnate ($KMnO_4$)

Preparation of $KMnO_4$:- from pyrolusite are

$$2MnO_2 + 4KOH + O_2 \longrightarrow K_2MnO_4 + 2H_2O$$

$$3MnO_4^{-} + 4H^+ \longrightarrow MnO_4^- + MnO_2 + 2H_2O.$$

Laboratory preparation

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

Chemical properties :-

(1) Action of Heat

$$2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2.$$

(2) Reaction in Acidic medium.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

$$2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$$

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

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

$$2MnO_4^- + 5S^{2-} + 8H^+ \longrightarrow 2Mn^{2+} + 5S + 4H_2O$$

(3) In Neutral Medium :-

$$MnO_4^- + 2H_2O \longrightarrow MnO_2 + 4OH^-$$

$$2MnO_4^- + 3S^{2-} + 8H^+ \longrightarrow 2MnO_2 + 3S + 4H_2O$$

$$8MnO_4^- + 3S_2O_8^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$$

(4) In Basic Medium :-

$MnO_4^- \longrightarrow MnO_4^{2-} + e^-$

$MnO_4^{2-} + 2e^- + 2H_2O \longrightarrow MnO_2 + 4OH^-$

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

F- Block Elements

⇒ **Landthanoids :** Lanthanum $_{57}(La)$
It has 14 elements from Cerium $_{58}(Ce)$ to lutatium $_{71}(Lu)$
general configuration :- $[Xe]\,4f^{1-14}\,5d^{0-1}\,6s^2$

General propeoties -

→ they are highly dense metal.
→ They have high melting point.
→ They form Alloys with metal
→ They are Soft Maleable & Ductile.

⇒ **Oxidation State :-** Most Common oxidation State of Lanthanoid is +3. Some of the element also exibit +2 & +4 Oxidation State.

Colour :- La^{3+} $(4f^0)$ & Lu^{3+} $(4f^{14})$ are Colourless and other are trivalent lanthanoid ions are Coloured due to f-f transition.

⇒ **Magnetic property** :- La^{3+} & Lu^{3+} are generally dimagnetic & other lanthanoid ion are paramagnetic in nature.

Example :-

$_{57}La^{3+}$, $_{58}Ce^{4+}$ > $4f^0$ - Colourless → Diamagnetic

$_{70}Yt^{2+}$, $_{71}Lu^{3+}$ > $4f^{14}$ - Colour → Diamagnetic.

$_{63}Eu^{2+}$, Gd^{3+}, Tb^{4+} > $4f^7$ - Stable Configuration (coloured) → Paramagnetic.

⇒ **Reactivity** :- Lanthanoids are highly electro +ve & they have almost similar chemical Reactivity.

Lanthanoid Contraction :- The filling of e^- in 4f orbital before 5d orbital results regularly decrease atomic radii.

⇒ **Actinoids** : Actinium $_{89}$(Ac) to Lawrencium $_{103}$(Lr)

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

General properties

→ They are highly dense metal with high melting point & form Alloys with other metals.

→ They are Silvery white metal which are highly reactive.

Actinoid Contraction - The filling of e^- in 5f before 6d Series, result attraction towards nucleous & Valence e^- ↓ tends to atomic Size ↓.

Oxidation State:- Common oxidation state of Actinoids is +3. The max. oxidation State increase from +4 In $_{90}Th$ to +5, +6 & +7 $_{91}Pa$, $_{92}U$, $_{93}Np$

→ The most of the Actinoid ions are coloured

Magnetic property:- Many of the Actinoids are paramagnetic except $_{84}(Ac)$ & $_{103}(Lu)$

Reactivity:-

→ They are also highly electro +ve & form oxides as well as Complex.

→ Many of these elements are radioactive.

Uses:-

→ $_{90}Th$ is used in treatment of Cancer

→ $_{91}U$ is used in textile & glass industry nuclear & in Medicine

→ $_{94}Pu$ is used in Atomic Reactor & in atomic bond.

Uses of Lanthanoids:

→ Ce Salt in used in dying cotton and also as Catalyst.

→ Lanthanoid Compounds are used as Catalyst for dehydragenation & petroleum trading.

→ Lanthanoid oxide are used as polishing of glass.

Difference b/w Lanthanoid & Actinoid

① Except Pm lanthanoids are non-radio active except while actinoids are radio Active.

② Lanthanoid do not form of oxocation. where as Actinoid form oxocation.

③ Lanthanoid has less tendency toward Complex formation where as actinoid has greater tendency toward Complex formation.

Similarity b/w Lanthanoid & Actinoid.

→ Both show +3 oxidation State.

→ Actinoid Show Actinoid Contraction as like Lanthanoid Contraction.

→ Both are electro +ve & very Reactive.