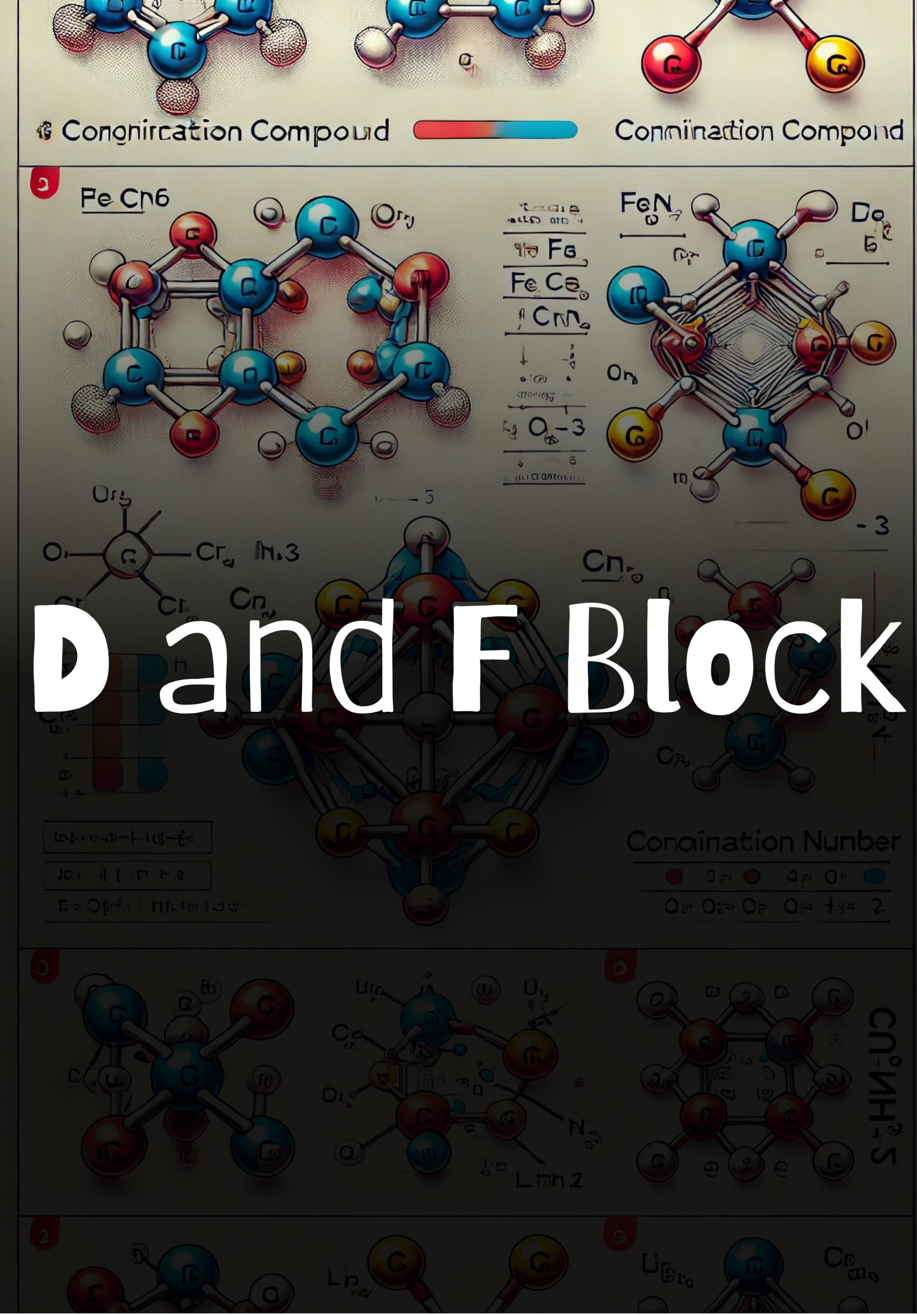


# D and F Block

# * D and F Block *

→ last $e^-$ → $(n-1)d$ orbital → penultimate shell
→ GEC → $(n-1)d^{1-10}\ ns^{0-2}$
→ Transition element - d block having incompletely filled d orbital (either in ground state or in any other oxdn state)

Zn, Cd, Hg } $(n-1)d^{10}\ ns^2$ — $Zn^{+2}$ → $(n-1)d^{10}$

↳ These elements are not transition elements

$Cu \rightarrow 3d^{10}\ 4s^1$
$Cu^{+1} \rightarrow 3d^{10}$
$Cu^{+2} \rightarrow 3d^9$

D Block - G3 - G12
Transition metal G3 - G11

~~D Blo~~

| | | | |
|---|---|---|---|
| n=4 | 4th Period | 3d series | → 21 Sc – Zn 30 |
| n=5 | 5th " | 4d series | → 39 Y – Cd 48 |
| n=6 | 6th " | 5d Series | → 57 La, 72 Hf – Hg 80 |
| n=7 | 7th " | 6d Series | → 89 Ac, Rf 104 – Cn 112 |

| Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|
| $3d^1$ | $3d^2$ | $3d^3$ | $3d^5$ | $3d^5$ | $3d^6$ | $3d^7$ | $3d^8$ | $3d^{10}$ | $3d^{10}$ |
| $4s^2$ | $4s^2$ | $4s^2$ | $4s^1$ | $4s^2$ | $4s^2$ | $4s^2$ | $4s^2$ | $4s^1$ | $4s^2$ |

| Y | Zr | Nb * | Mo | Tc | Ru | Rh | Pd | Ag | Cd |
|---|---|---|---|---|---|---|---|---|---|
| $4d^1$ | $4d^2$ | $4d^4$ | $4d^5$ | $4d^6$ | $4d^7$ | $4d^8$ | $4d^{10}$ | $4d^{10}$ | $4d^{10}$ |
| $5s^2$ | $5s^2$ | $5s^2$ | $5s^2$ | $5s^1$ | $5s^1$ | $5s^1$ | $5s^0$ | $5s^1$ | $5s^2$ |

| La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg |
|---|---|---|---|---|---|---|---|---|---|
| $5d^1$ | $5d^2$ | $5d^3$ | $5d^4$ | $5d^5$ | $5d^6$ | $5d^7$ | $5d^9$ | $5d^{10}$ | $5d^{10}$ |
| $6s^2$ | $6s^2$ | $6s^2$ | $6s^2$ | $6s^2$ | $6s^2$ | $6s^2$ | $6s^1$ | $6s^1$ | $6s^2$ |

* General properties (Transition metals
→ Metallic property show.
→ High Tensile
→ malleable & ductile
→ High thermal & electrical conductivity
→ metallic lustre
→ hard
→ less volatile

① # Except Zn, Cd, Hg all have metallic lattice

② MP & BP → more no. of valence $e^-$
→ more strong bonding.

| Cr, Mo, W | → Highest MP & BP | | Zn, Cd, Hg | → lowest MP & BP |
|---|---|---|---|---|

(Cr, Mo, W) 6 valence $e^-$

| Mn, Tc, Re | → exception - MP & BP is less |
|---|---|

③ Enthalpy of atomization → Energy required to break all bonds of lattice and then convert to gases form

maximum is of Vanadium (V)

④ Atomic size

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

period: Sc to Mn: zeff > screening effect; Fe = Co = Ni: zeff = screening effect; Cu, Zn: zeff < screening effect.

| Grp - | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 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 |
| ^ AC | | | | | | | | | |

} Lanthanoid contraction

⑤ IE

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

general - L to R IE ↑

Change at 2, 6, 7

$IE_1$ of Zn, Cd, Hg → fulfilled - highest

$IE_2$ of Cr, Cu → High filled - high

↳ $3d^5$ ↘ $3d^{10}$

$IE_3$ of Mn → $3d^5$ → High

6) Oxidation state - All d block elements show variable oxidation state (Sc & Zn) → exception

↳ very less energy gap betn (n-1) d & ns orbital

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

max O.S = +8

Ru, Os $OsO_4$

$M^{+2}/M$ electrode potential

Mn, Ni, Zn → electrode potential → highly negative
↓ $3d^5$ ↓ $3d^{10}$
∴ High Hydration Enthalpy

Cu → +ve value → electrode potential
↳ Cu can't liberate $H_2$ from acid
↳ low Hydration enthalpy

$M^{+3}/M^{+2}$ Electrode potential

$Sc^{+2}$ → $Sc^{+3}$ (stable) → High negative electrode potential (low)

$Zn^{+2}$ → $Zn^{+3}$ → Positive electrode potential (high)

$Mn^{+2}$ → $Mn^{+3}$ → Positive " " (high)

$Fe^{+2}$ → $Fe^{+3}$ (stable) → Negative " " (low)

Higher oxidation state in halide & oxide

Halides

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

# only $VF_5$ is known → on hydrolysis → $VOF_3$

# $CuX_2$ is formed except $CuI_2$ / $Cu^{+2} + I^- \rightarrow Cu_2I_2 + I_2$

→ In aq soln $Cu^{+2}$ is more stable than $Cu^{+1}$
↳ because HE is more in $Cu^{+2}$

Oxide

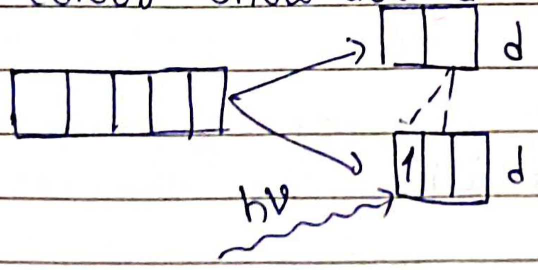
| Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|
| $Sc_2O_3$ | $TiO$ | $VO$ | $CrO$ | $MnO$ | $FeO$ | $CoO$ | $NiO$ | $CuO$ | $ZnO$ |
| | $Ti_2O_3$ | $V_2O_3$ | $Cr_2O_3$ | $Mn_2O_3$ | $Fe_2O_3$ | $Co_3O_4$ | | $Cu_2O$ | |
| | $TiO_2$ | $V_2O_4$ | $CrO_2$ |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

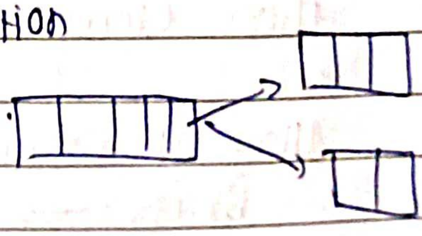
Magnetic Property

| → diamagnetic | Paramagnetic | Ferromagnetic |
|---|---|---|
| Repelled by MF | attracted by MF | very strongly attracted by MF |
| → 0 unpaired $e^-$ | → presence of unpaired $e^-$ | |
| → all $e^-$ are paired | → Magnetic moment | $\mu = \sqrt{n(n+2)}$ B.M |
| | | n = no. of unpaired $e^-$ |

Formation of colored ions.

→ unpaired e- is present & it shows colour
→ colour show due d-d transition



$Sc^{+3}$ → no colour
$Zn^{+2}$ → no colour

* Catalytic property due to variable oxidation state it shows catalytic property.
  Contact process — $V_2O_5$
  Haber's process → Fe (Finely divided)
  Catalytic hydrogenation → Ni, Pt, Pd

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

* Interstitial compound. [H, C, N, B] → small size elements
→ Transition elements are metal & hence form metallic lattice (voids)
Small size element like B, H, C, N are accomodated in this empty spaces (voids) & form interstitial comp.
→ High melting point
→ very hard
→ chemically inert.
→ Have metallic conductivity.

* Alloy Formation Due to similar size of d block elements these elements form alloy.

Alloy of Copper
  Brass → Cu (70-80%) + Zn (20-30%)

  Bronze → Cu (80-90%) + Sn (10-20%)

  Gun metal → Cu (85%) + Zn (10%) + Sn (5%)

  Bell metal → Cu (72-80%) + Zn (20-28%)

* Some imp compounds of Transition elements

Oxides

low oxidation state oxide → Basic
High " " " → Acidic
Intermediate " " → Amphoteric

$V_2O_3$ → Basic
$V_2O_5$ → Amphoteric → $V_2O_5 + HCl \rightarrow VO_2Cl + H_2O$
$CrO$ → Basic → $V_2O_5 + NaOH \rightarrow Na_3VO_4 + H_2O$
$Cr_2O_3$ → Amphoteric
$CrO_3$ → Acidic

$\overset{+6}{Cr}O_3 + H_2O \rightarrow H_2\overset{+6}{Cr}O_4$

$\overset{+7}{Mn_2}O_7 + H_2O \rightarrow H\overset{+7}{Mn}O_4$

$2CrO_3 + H_2O \rightarrow H_2Cr_2O_7$

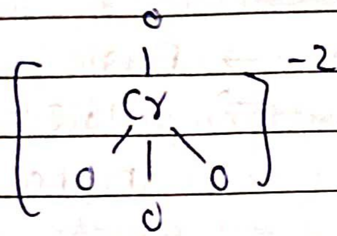
Potassium dichromate ($K_2Cr_2O_7$)
Preparation - Chromite ore + धो डालो
($FeO \cdot Cr_2O_3$) ← $FeCr_2O_4$

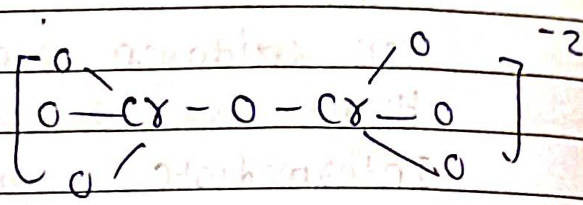
i) $FeCr_2O_4 + Na_2CO_3 + O_2 \rightarrow Na_2CrO_4 + Fe_2O_3 + CO_2$
$Fe^{+2}$ $Cr_2O_4^{-2}$ $Na^+$ 0 Sodium Chromate (yellow)

② $Na_2CrO_4 + H_2SO_4 \rightarrow Na_2SO_4 + Na_2Cr_2O_7$
Sodium dichromate

③ $Na_2Cr_2O_7 + KCl \rightarrow K_2Cr_2O_7 + NaCl$
potassium dichromate

| Str. | Chromate | Dichromate |
|---|---|---|
| | $CrO_4^{-2}$ | $Cr_2O_7^{-2}$ |





Chromate - dichromate Equilibrium

$\overset{+6}{Cr}\overset{-2}{O_4}{}^{-2} \rightleftharpoons \overset{+6}{Cr_2}\overset{-2}{O_7}$

Yellow — Orange

$PH < 7$ [C → d]
Acidic → आगे - Rxn forward

Basic → Backward [d → c]
$PH > 7$

* Strong oxidizing agent in acidic medium

$\overset{+6}{Cr_2O_7^{-2}} + H^+ \longrightarrow Cr^{+3}$

$I^- \longrightarrow I_2$

$H_2S \rightarrow S$ — $Cr_2O_7^{-2} + H^+ + I^- \rightarrow Cr^{+3} + I_2 + H_2O$

$Sn^{+2} \rightarrow Sn^{+4}$ — $Cr_2O_7^{-2} + H^+ + H_2S \rightarrow Cr^{+3} + S + H_2O$

$Fe^{+2} \rightarrow Fe^{+3}$

* Chromyl chloride test

Metal chloride + conc. $H_2SO_4 + K_2Cr_2O_7 \longrightarrow CrO_2Cl_2 + KHSO_4 + H_2O$
(Red vapour)

* Potassium permagnate ($KMnO_4$)

Prep$^n$ $MnO_2$ (pyrolusite ore)

$MnO_2 + KOH + O_2 \longrightarrow K_2MnO_4 + H_2O$
Magnate ion (green)

$\overset{+6}{MnO_4^{-2}} \xrightarrow{H^+} \overset{+7}{MnO_4} + MnO_2 + H_2O$

green — Permagnate (Purple) dark pink

DATE

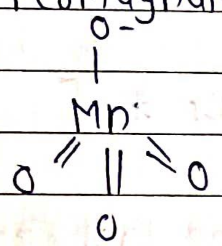
commercial prep$^n$ — $MnO_2$ $\xrightarrow[\text{air or } KNO_3]{\text{Fused with KOH \& oxidise with}}$ $MnO_4^{-2}$

$MnO_4^{-2}$ $\xrightarrow[\text{oxd}^n]{\text{electrolytic}}$ $MnO_4^-$

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

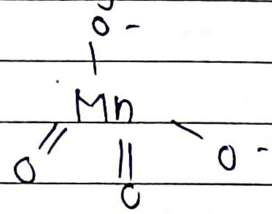
Str.

Permagnate



diamagnetic (purple)

magnate



Paramagnetic (Green)

Potassium per magnate in acidic medium

$Mn^{+7} \longrightarrow Mn^{+2}$

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

$KMnO_4 + H^+ + C_2O_4^{-2} \rightarrow Mn^{+2} + CO_2$

$KMnO_4 + H^+ + Fe^{+2} \rightarrow Mn^{+2} + CO_2$

$KMnO_4 + H^+ + NO_2^- \rightarrow NO_3^- + Mn^{+2}$

Neutral / faintly alkaline soln

$\overset{+7}{Mn}O_4^- + I^- \longrightarrow \overset{+4}{Mn}O_2 + IO_3^-$

$\overset{+7}{Mn}O_4^- + S_2O_3^{-2} \longrightarrow \overset{+4}{Mn}O_2 + SO_4^{-2}$

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

→ we dont use HCl in acidic medium/ titration

$HCl + KMnO_4 \longrightarrow Mn^{+2} + Cl_2$

## * F-Block *

The elements in which the last e- enters into f- orbital of atoms are called f- block elements i.e antipenultimate Shell (n-2) f.

Also called inner transition elements

Two series of f - block - 4f series & 5f series

General Electronic configuration $(n-2)f^{1-14}\ (n-1)d^{0-1}\ ns^2$

4 f series (Lanthanoid)

Last electron enters into 4f orbital & properties are almost similar to lanthanum - Exception in 4f = 2,8

| | | | | |
|---|---|---|---|---|
| La | 57 | Lanthanum | | $[Xe]\ 6s^2\ 4f^0\ 5d^1$ |
| Ce | 58 | Cerium | सिने | $[Xe]\ 6s^2\ 4f^1\ 5d^1$ |
| Pr | 59 | Praseodymium | पर | $[Xe]\ 6s^2\ 4f^3\ 5d^0$ |
| Nd | 60 | Neodymium | नदियाँ | $[Xe]\ 6s^2\ 4f^4\ 5d^0$ |
| Pm | 61 | Promethium | प्रेमिका | $[Xe]\ 6s^2\ 4f^5\ 5d^0$ |
| Sm | 62 | Samarium | समाई | $[Xe]\ 6s^2\ 4f^6\ 5d^0$ |

| | | | | |
|---|---|---|---|---|
| Eu | 63 | Europium | यू | [xe] $6s^2$ $4f^7$ $5d^0$ |
| Gd | 64 | Gadolinium | गदगद | [xe] $6s^2$ $4f^7$ $5d^1$ |
| Tb | 65 | Terbium | तन | [xe] $6s^2$ $4f^9$ $5d^0$ |
| Dy | 66 | Dyprosium | दिल | [xe] $6s^2$ $4f^{10}$ $5d^0$ |
| Ho | 67 | Holmium | हुआ | [xe] $6s^2$ $4f^{11}$ $5d^0$ |
| Er | 68 | Erbium | अरे | [xe] $6s^2$ $4f^{12}$ $5d^0$ |
| Tm | 69 | Thulium | तुम | [xe] $6s^2$ $4f^{13}$ $5d^0$ |
| Yb | 70 | Yterbium | यारमी | [xe] $6s^2$ $4f^{14}$ $5d^0$ |
| Lu | 71 | Lutetium | लुटवातो | [xe] $6s^2$ $4f^{14}$ $5d^1$ |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Position of Elements | 1 | (2) | 3 | 4 | 5 | 6 | 7 | (8) | 9 | 10 | 11 | 12 | 13 | 14 |
| $e^-$ in f-subshell | 1 | 3 | 4 | 5 | 6 | 7 | 7 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |

Note- half fill (7) & Ful fill (14) are stable in f subshell

Cerium is 26th most abundant Lanthanoid element on earth and most common occuring lanthanoid.

Monazite sand is most common mineral with contain lanthanoid
Frometbium is only synthetic radioactive element

Oxidation state- All lanthanoid exhibit a common oxdn state of +3
Ce and Tb exhibit +4 oxdn state
Eu and Yb exhibit +2 " "
La, Gd and Lu exhibit only +3 oxdn state
$Eu^{2+}$ is a strong reducing agent.

Colour- Colour of lanthanoid ions arises due to absorption in visible region of spectrum resulting in f-f transition because they have partially filled f-orbitals

$La^{+3}$ and $Lu^{3+}$ don't show any colour but other trivalent lanthanoid show colours.

Magnetic properties- Lanthanoids ion other than $f^0$ type ($La^{3+}$ & $Ce^{4+}$) and $f^{14}$ type ($Yb^{2+}$ & $Lu^{3+}$) are all paramagnetic

Chemical Reactivity

Burns in air, $Ln + O_2 \longrightarrow Ln_2O_2$

Heated with S, $Ln + S \longrightarrow Ln_2S_3$

Heated with N, $Ln + N \longrightarrow LnN$

Rxn with C, $Ln + C \xrightarrow{273\ K} LnC_2$

Rxn with H2O, $Ln + H_2O \longrightarrow Ln(OH)_3 + H_2$

Rxn with halogen, $Ln + X \longrightarrow LnX_3$

Rxn with acid, $Ln + acid \longrightarrow Ln\ salt + H_2$

Similarity among lanthanoids :- Because of very small change in radii of Lanthanoids their chemical properties are quite similar. Thus it is very difficult to separate the elements in pure state.

Basicity difference- The basic strength of hydroxides decreases with ↑ in atomic no.
Thus $Ca(OH)_3$ is most basic while $Cu(OH)_3$ is least basic.

Uses- Used in making mischmetal, an alloy of a lanthanoid metal (~95%) with iron (~5%) and traces of S, C, Ca and Al. It is used to make traces bullet shell

* 5f - series (Actinoids)

Last $e^-$ enters into 5f orbitals. Their properties are almost similar to actinium, thus they are called actinoids.

Exception in 5f = 6, 8.

Electronic configuration $ns^2 (n-2)f^{1-14} (n-1)d^{0-1}$ n=7

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Elements position | 1 | 2 | 3 | 4 | 5 | (6) | 7 | (8) | 9 | 10 | 11 | 12 | 13 | 14 |
| $e^-$ in 5f subshell | 1 | 2 | 3 | 4 | 5 | 7 | 7 | 9 | 10 | 11 | 12 | 13 | 14 | 14 |

Actinoids are radioactive elements and initial members have long life than lower member ranging from a day to 3 min.

Ionic sizes. Just like lanthanoids here is also gradual decrease in size of atom or $M^{3+}$ ions across the series. This is referred as actinoid contraction due to poor shielding of 5f orbitals, the effective nuclear charge ↑ which results in contraction of size.

Actinoid contraction is greater from element to element than lanthanoid contraction because 5f orbitals have or poor shielding effect than 4f orbitals in lanthanoids. Thus effective nuclear charge experienced by valence $e^-$ in case of actinoids is much more than experienced by lanthanoids.

Oxdn state - Most common O.S is +3

The also shows O.S of +4, +5, +6 & +7 in Th, Pa, U and Np respectivay. They have greater range of O.S because 5f, 6d and 7s levels are of comparabr energies.

| Ac | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3 | | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
| | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | | | | | | |
| | | 5 | 5 | 5 | 5 | 5 | | | | | | | | |
| | | | 6 | 6 | 6 | 6 | | | | | | | | |
| | | | | 7 | 7 | | | | | | | | | |

Some more characteristics

→ Silvery appearance and highly reactive

→ HCl can react with all actinoids

→ Most of them are slightly affected by $HNO_3$ because of protective layer formation (oxide layer)

→ Magnetic properties are complex

→ IE are less compared to lanthanoid and cannot be accurately known but as 5f orbital is deeply burried due to which it is more effectivey shielded by nuclear charge than 4f electron and outer electron can easily removed.

→ Actinoids are coloured in ionic form & compounds because of f-f transition