D & F BLOCK ELEMENTS

D-Block elements

General Configuration = $(n-1)d^{1-10} ns^{1-2}$

- Zn, Cd, Hg and Cn are not regarded as transition metal elements due to completely filled orbitals
- Shows a variety of oxidation states.
- They are paramagnetic in nature

Physical Properties

Crystal lattices	**BCC**	Sc, Ti, V, Cr, Mn, Fe
	HCP	Sc, Ti, Fe, Ni, Cu, Zn
	CCP	Mn, Co, Ni, Cu

- **Melting points** (usually high due to metallic bonding)
  - Sc<Ti < V < Cr > Mn < Fe > Co > Ni > Cu
- **Enthalpy of Atomisation**
  - Sc < Ti < V > Cr > Mn < Fe < Co < Ni > Cu > Zn
- **Atomic Size :** 3d < 4d ≃ 5d (Lanthanoid Contraction)
  - Sc > Ti > V > Cr < Mn > Fe > Co≃ Ni < Cu < Zn
- **Density**
  - Sc < Ti < V < Cr < Mn < Fe < Co < Ni ≃ Cu > Zn
- **Ionisation enthalpy (Less variation)**
  - Sc < Ti > V < Cr < Mn < Fe > Co > Ni < Cu < Zn
- **Standard Electrode Potential**
  - Sc < Cr < Ti < V < Fe < Mn < Co < Zn

Important points about Oxidation states

- $3d^0$ configuration metals are stable : Sc^{+3}, Ti^{+4}, V^{+5}
- $3d^5$ configuration metals are stable : Mn^{+2}, Fe^{+3}
- Cr^{+3} is stable in aqueous medium.
- $3d^{10}$ Cu^{+1} is stable (Cu^{+2} is more stable in aq. med.)
- Most common O.S. = +2
- Highest O.S. = +8 for Ru & Os.
- Zero O.S. is also found in metal carbonyls : $Ni(CO)_4$
- Ti^{+2}, V^{+2}, Co^{+2}, Fe^{+2} are oxidising agents
- Cr^{+6}, Mn^{+7}, Mn^{+4}, Mn^{+5}, Mn^{+6} are reducing agents

Coloured ions

• Colourless	Sc^{+3}, Ti^{+4}, Zn^{+2}
• Purple	Ti^{+3}
• Blue	V^{+4}, Cr^{+2}, Cu^{+2}
• Green	V^{+3}, Fe^{+2}, Ni^{+2}
• Violet	V^{+2}, Cr^{+3}, Mn^{+3}
• Pink	Mn^{+2}
• Yellow	Fe^{+3}

Complex formation

- Due to small size
- High ionic Charges
- Vacant d-orbitals

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

Catalytic activity

- Due to their ability to adopt multiple O.S.

Catalyst	Used in
V2O5	Contacts process
Fe	Haber's Process
Ni	Catalytic hydrogenation
Fe^{+3}	Catalytic reaction b/w I^- and $S_2O_8^{2-}$
$TiCl_4$	used in Vinyl Polymerisation

Interstitial compounds formation

- Trapping of small atoms in crystal lattices
- Non Stoichiometric, Neither ionic nor covalent
- Hard and have high Melting points
- Inert in Nature, shows metallic Conductivity
    - TiC, Mn_4N, Fe_3H, $TiH_{1.7}$

Some Alloys

Brass : Cu-Zn	**Bronze :** Cu-Sn	**Gun Metal :** Cu-Zn-Sn
UK Copper : Copper coated steel		**Silver UK :** Cu-Ni

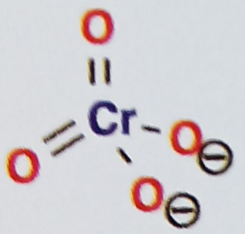
Potassium Dichromate ($K_2Cr_2O_7$)

Preparation :

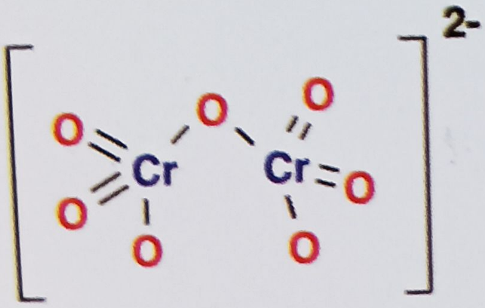
$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow \mathbf{8Na_2CrO_4} + 2Fe_2O_3 + 8CO_2$$

$$2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$$

$$Na_2Cr_2O_7 + 2KCl \rightarrow \mathbf{K_2Cr_2O_7} + 2NaCl$$



Chromate ion



Dichromate ion

- **Chromate ion**
    - Tetrahedral
    - Yellow in colour
- **Dichromate ion**
    - Two tetra units joined
    - Orange Colour
    - Bridging Cr–O bond is larger than terminal

$$\underset{\textbf{Yellow}}{CrO_4^{-2}} \underset{ph > 7}{\overset{ph < 7}{\rightleftharpoons}} \underset{\textbf{Orange}}{Cr2O_7^{-2}}$$

Chemical Reaction of Potassium Dichromate:

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

Potassium Permanganate ($KMnO_4$)

Preparation

$$MnO_2 \xrightarrow[\text{Oxidised with air}]{\text{Fused with KOH}} MnO_4^{2-} \xrightarrow[\text{Alkaline sol.}]{\text{Electrolytic ox.}} MnO_4^-$$

- **Manganate ion is** Tetrahedral, Paramagnetic in nature and π bond b/w O and Mn.
- **Permanganate ion is** Diamagnetic with Temp. dependence paramganetism.

Chemical Reactions of $KMnO_4$

- $2Mn^{2+} + S_2O_8^{-2} + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$
- $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$
- $5Fe^{2+}\ MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O + 5Fe^{+3}$
- $5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{+2} + 8H_2O + 10CO_2$
- $MnO_4^- + 3S_2O_3^{2-} + H_2O \rightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$
- $2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + 2OH^- + IO_3^-$

General confoguration of Lanthanoids

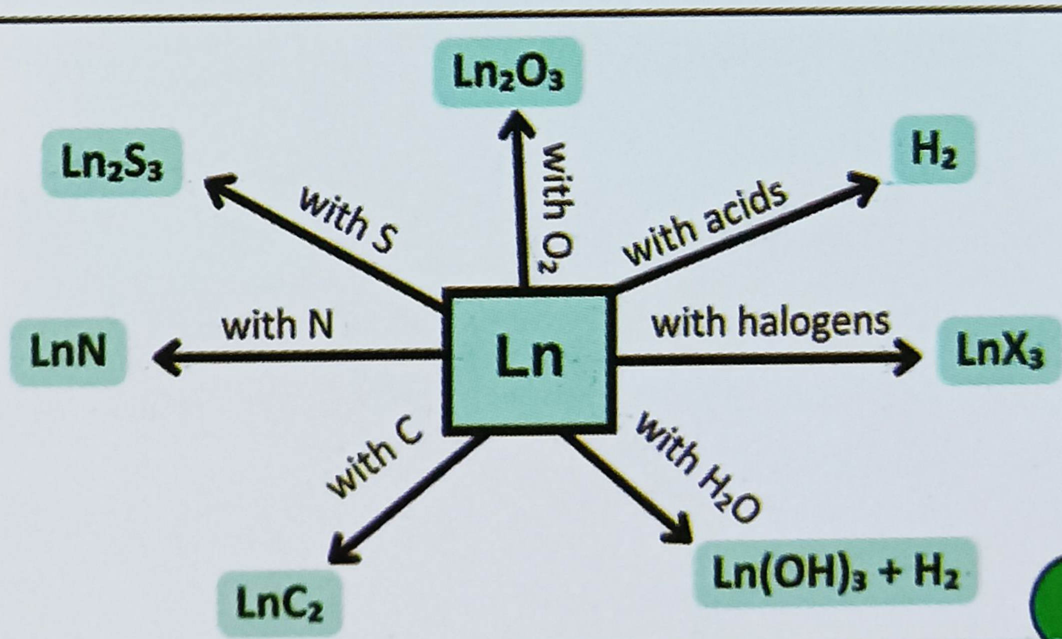
$[Xe]\ 4f^{0-14}\ 5d^{0-1}\ 6s^2$

At. No.	element	Config.	Stable O.S.
57	Lanthanum	$4f^0 5d^1 6s^2$	La^{+3} / f^0
58	cerium	$4f^1 5d^1 6s^2$	Ce^{+4}/ f^0
63	europium	$4f^7 5d^0 6s^2$	Eu^{+2} /f^7
64	gadolinium	$4f^7\ 5d^1\ 6s^2$	Gd^{+3} / f^7
65	terbium	$4f^9\ 5d^0\ 6s^2$	Tb^{+2}/ f^7
70	ytterbium	$4f^{14}\ 5d^0\ 6s^2$	Yb^{+2} / f^{14}
71	lutetium	$4f^{14}\ 5d^1\ 6s^2$	Lu^{+3} / f^{14}

Oxidant	Reductant
Ce^{+4}, Tb^{+4}, Pr^{+4}, Nd^{+4}, Dy^{+4}	Eu^{+2} Yb^{+2}

-Ce^{+4} is good analytical reagent

-Pr, Nd, Tb, Dy forms oxides MO_2



Lanthanoid contraction

- The size from La^{+3} to Lu^{+3} decreases due to poor shielding effect of 4f orbitals.
- Atomic size from La to Lu decreases except Eu which is greatest in size
- 2nd and 3rd transition series show resemblance in size
- Basic character of oxides decreases from left to right
- $La(OH)_3$ most basic ; $Lu(OH)_3$ least basic

General characterstics of lanthanoids

- silvery white, soft metals, tarnish rapidly in air
- hardness atomic number
  [Samarium is the hardest lanthanoid]
- except La^{+3} / Lu^{+3} , all are colored
- La^{+3} , Ce^{+4}, Yb^{+2}, Lu^{+3} are diamagnetic in nature and all other are paramagnetic in nature
- Mischmetal consist of lanthanoids (95%) iron (5%) and some traces of S , C , Ca, Al

Actinoids : (Rn) $5f^{1-14}$ $6d^{0-1}$ $7s^2$

- Atomic size decreases from left to right due to actinoid contraction
- General O.N is +3 , Np and Pu show maximum variation ON [3-7]
- Silvery appearance,
- IE Values lower than lanthanoids due to poor shielding of 5f than 4f
- Their oxides are less basic than oxides of lanthanoids
- All are radioactive in nature