d&f BLOCK ELEMENTS

d – Block transition elements (group 3–12)

- Electronic configuration : $(n-1)d^{1-10}\ ns^{1-2}$

Exceptions: $Cr = 4s^1 3d^5$; $Cu = 4s^1 3d^{10}$, $Pd = 5s^0 4d^{10}$

Non-typical transition elements: Zn, Cd & Hg

- Physical properties:

-High melting and boiling point

$\boxed{\text{Melting point : s-block metals < d-block metals}}$

Sc < Ti < V < Cr > Mn < Fe > Co > Ni > Cu > Zn (3d Series)

Melting point: Zn > Cd > Hg; Cu > Ag ≤ Au

-High enthalpies of atomization(Highest for V in 3d, series)

Atomic Radius:

3d series: Sc > Ti > V > Cr > Mn ≥ Fe = Co ≈ Ni ≤ Cu < Zn

In a group 3d < 4d ≈ 5d (Lanthanide contraction)

eg : Ti < Zr ≈ Hf — Smallest radius - Ni; Largest radius - La

Density:

s-Block < d-Block

3d series: Sc < Ti < V < Cr < Mn < Fe < Co ≤ Ni < Cu > Zn

In a group 3d < 4d << 5d

- Ionisation enthalpy:increases from left to right
- Oxidation states : Variable; higher O.S. stable down the group
- Trends in $E^\circ_{M^{2+}/M}$: E° for Mn, Ni and Zn are more negative than expected.
- Trends in $E^\circ_{M^{3+}/M^{2+}}$: variable
- Chemical reactivity and E° values : Variable Ti^{2+} , V^{2+} and Cr^{2+} are strong reducing agents
- Magnetic properties : Diamagnetism and paramagnetism. $\boxed{\mu = \sqrt{n(n+2)}\ \text{BM}}$
- Formation of coloured ions : due to d – d transitions
- Form a large number of complex compounds
- Forms interstitial compounds : Non - stoichiometric and are neither ionic nor covalent.
- Alloy formation : Due to similar atomic sizes.(15% difference in metallic radius)

Uses

- In production of iron and steels.
- TiO in pigment industry
- MnO_2 in dry battery cells.
- As catalysts in industry.
- Ni complexes:polymerization of alkynes and other organic compounds
- AgBr in photographic industry.

Catalysts

Contact process = V_2O_5

Haber process = $Fe_2O_3 + Al_2O_3 + K_2O$

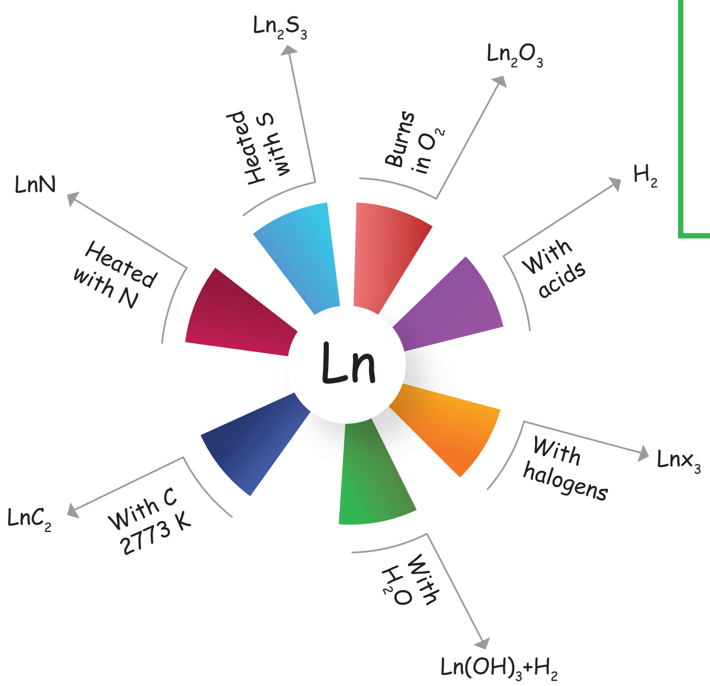
Decomposition of $KClO_3$ = MnO_2

Ostwald process = Pt/Rh

Zeigler Natta catalyst = $TiCl_4 + (C_2H_5)_3Al$

Hydrogenation of Alkene = Ni/Pd

Wilkinson's catalyst=$RhCl(PPh_3)_3$



Lanthanoids

- Electronic configuration: $4f^{1-14}\ 5d^{0-1}\ 6s^2$ (Gd: $4f^7\ 5d^1\ 6s^2$)
- Atomic and ionic sizes: Decreases from La to Lu(Eu is the largest)
- Oxidation states: Most common is +3.
- Some elements: exhibit +2 and +4.
- General characteristics
- Silvery white soft metals and tarnish rapidly in air.
- Hardness increases with increasing atomic number.
- Metallic structure and good conductors of heat and electricity.
- Variable density
- Trivalent Lanthanoid ions are coloured.
- Ionisation Enthalpies : Low third ionisation enthalpies.
- Good reducing agents.

MISCH METAL-Alloy of Ln (95%), Fe (5%) & S,C,Ca,Al etc..

Compounds of d-block elements

Potassium dichromate $K_2Cr_2O_7$

Preparation :

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

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

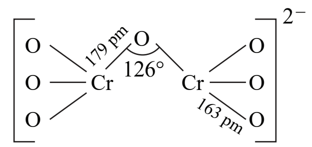
$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

Properties : Strong oxidising agent

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

$Cr_2O_7^{2-}$ (Orange) → Cr^{+3} (green)

- $SO_2 \rightarrow SO_4^{2-}$
- $H_2S \rightarrow S$
- $SO_3^{2-} \rightarrow SO_4^{2-}$
- $NO_2^- \rightarrow NO_3^-$
- $I^- \rightarrow I_2$
- $Br^- \rightarrow Br_2$
- $S_2O_3^{2-} \rightarrow SO_4^{2-}$
- $C_2H_5OH \rightarrow CH_3COOH$
- $Sn^{2+} \rightarrow Sn^{4+}$
- $Fe^{2+} \rightarrow Fe^{3+}$



CrO_4^{2-} (Yellow) $\underset{OH^-}{\overset{H^+}{\rightleftharpoons}}$ $Cr_2O_7^{2-}$ (Orange)

Potassium permanganate $KMnO_4$

- Preparation : $2MnO_2 + 4KOH + O_2 \rightarrow 2KMnO_4 + 2H_2O$

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

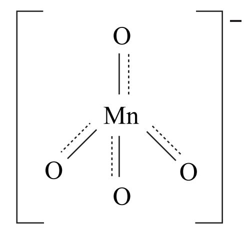
$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$

- Intense colour
- Paramagnetism
- Strong oxidising agent

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

MnO_4^- (Purple) → Mn^{+2} (Purple colour decolourises)

- $C_2O_4^{2-} \rightarrow CO_2$
- $SO_2 \rightarrow SO_4^{2-}$
- $H_2S \rightarrow S$
- $S_2O_3^{2-} \rightarrow SO_4^{2-}$
- $NO_2^- \rightarrow NO_3^-$
- $I^- \rightarrow I_2$
- $Br^- \rightarrow Br_2$
- $Cl^- \rightarrow Cl_2$
- $C_2H_5OH \rightarrow CH_3\text{-}COOH$
- $Sn^{+2} \rightarrow Sn^{+4}$
- $Fe^{+2} \rightarrow Fe^{+3}$



MnO_4^- (purple) $\xrightarrow[\text{solution}]{\text{Strongly Basic}}$ MnO_4^{2-} (green)

$MnO_4^- \xrightarrow[\text{medium}]{\text{neutral}} MnO_2 \downarrow$ Brown ppt

Actinoids

- Electronic configuration : $[Rn]5f^{1-14}\ 6d^{0-1}\ 7s^2$
- Ionic sizes : Gradual decrease along the series
- Oxidation states : Most common is +3 . They show O.S. of +4, +5, +6 and +7.
- General characteristics :

-Highly reactive metals

-Irregularities in metallic radii,greater than in Lanthanoids.

-Magnetic properties more complex than lanthanoids

Actinoid Contraction > Lanthanoid Contraction

PHYSICS WALLAH

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The element that usually does not show variable oxidation state is ?

a) Cu b) Ti

c) Sc d) V

Which of the following is not formed when H_2S reacts with acidic $K_2Cr_2O_7$ solution ?

a) $CrSO_4$ b) $Cr_2(SO_4)_3$

c) K_2SO_4 d) S