CHAPTER

10 The d & f-Block Elements

Definition

Transition elements are those d-block elements which have partially filled (n – 1)d subshell either in their ground state or in their most stable oxidation states. Therefore, Zn, Cd & Hg are d-block elements and not transition elements.

General electronic configuration

$ns^{0-2}\,(n-1)d^{1-10}$

$$\text{Exceptions}\begin{cases} Cr = 3d^5\,4s^1 \\ Cu = 3d^{10}\,4s^1, Pd = 4d^{10}\,5s^0 \end{cases}$$

Transition Series

1st	3d series	Sc_{21} — Zn_{30}	9 + 1 = 10
2nd	4d series	Y_{39} — Cd_{48}	9 + 1 = 10
3rd	5d series	La_{57}, Hf_{72} — Hg_{80}	9 + 1 = 10
4th	6d series	Ac_{89}, Unq_{104} — Uub_{112}	9 + 1 = 10

Atomic Radius

3d series: Sc > Ti > V > Cr > Mn ≥ Fe ≃ Co ≃ Ni ≤ Cu < Zn. In a group from 3d to 4d series, atomic radius increases but 4d and 5d series have nearly same atomic radius due to poor shielding of f electrons (Lanthanide contraction).

$$\boxed{3d < 4d \simeq 5d}$$

$$\text{e.g}: Ti < Zr \simeq Hf \left| \begin{array}{l} \text{Smallest radius} - Ni \\ \text{Largest radius} - La \end{array} \right.$$

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

In a series, on increasing number of unpaired electrons, melting point increases upto Cr and then decreases.

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

Cr ↓ Half filled d^5 ∴ weak metallic bond

Zn ↓ Fully filled d^{10} ∴ weak metallic bond

$$\text{Melting point}\left| \begin{array}{l} Zn > Cd > Hg \\ Cu > Ag \le Au \end{array} \right. \text{(data based)}$$

E.N. Exception: Zn < Cd < Hg

$$\boxed{\textbf{Density}: \text{s} - \text{block metals} < \text{d} - \text{block metals.}}$$

3d series

$$\boxed{Sc < Ti < V < Cr < Mn < Fe < Co \le Ni < Cu > Zn}$$

Density in a Group: 3d < 4d << 5d

Metallic character: They are solid, hard, ductile, malleable, good conductor of heat and electricity and exhibit metallic lusture, high tensile strength. Hg is a liquid.

Electrical conductivity:-

$$\underbrace{Ag > Cu > Au}_{d-block} > \underset{p-block}{Al}$$

Oxidation State

Transition elements exhibit variable oxidation states due to small energy difference of ns and (n–1)d orbitals.

- Sc(+3) and Zn(+2) exhibit only one oxidation state.
- Common oxidation state is +2 & +3.
- In 3d series, highest oxidation state is +7 (Mn).
- In d-block series, highest oxidation state is +8 (Os, Ru).
- In carbonyl compounds, oxidation state of metals is zero due to synergic effects.
- Their higher oxidation states are more stable in fluorides and oxides.
- Higher oxidation states in oxides are normally more stable than fluorides due to capability of oxygen to form multiple bonds.

  Eg. stable fluoride in higher oxidation state of Mn is MnF_4 while oxide is Mn_2O_7.
- Mn shows maximum number of oxidation states (+2 to +7) among 3d series.
- Beyond Mn, trihalides are not observed except in FeX_3 (X = Cl/Br/I) & CoF_3.

⇒ V_2O_3 Basic, V_2O_4 Basic, V_2O_5 Amphoteric

⇒ CrO — Cr_2O_3 — CrO_3

Basic — Amphoteric — Acidic

⇒ MnO — MnO_2 — Mn_2O_7

Basic — Amphoteric — Acidic

⇒ CuI_2 does not exist as it decomposes to give CuI & I_2 at room temperature

$$CuI_2 \longrightarrow CuI + \frac{1}{2}I_2$$

⇒ In aqueous solution, Cu^+ disproportionates into Cu & Cu^{2+}. In p-block, lower oxidation states of heavier elements are more stable, while in d-block higher oxidation state of heavier elements are more stable.

Eg. In VIB group, Mo(+6) & W(+6) are more stable than Cr(+6).

Magnetic Property

All transition elements are paramagnetic due to the presence of unpaired electrons. Magnetic moment of unpaired electrons is due to spin and orbital angular momentum.

"Spin only" magnetic moment can be calculated by using the formula,

$\mu = \sqrt{n(n+2)}$ Bohr magneton. (n is the number of unpaired e^-s)

If n is 1, μ = 1.73 BM

n is 2, μ = 2.84 BM

n is 3, μ = 3.87 BM

n is 4, μ = 4.90 BM

n is 5, μ = 5.92 BM

Substances, that are not attracted by applied magnetic field are diamagnetic. They have all the electrons paired. d-block elements and ions, having d^0 and d^{10} configuration are diamagnetic.

Colour

Colour in transition metal ions is associated with d-d transitions of unpaired electrons from t_{2g} to e_g set of energies. This is achieved by absorption of light in the visible spectrum, rest of the light is no longer white.

Colourless – Sc^{3+}, Ti^{4+}, Zn^{2+} etc.

Coloured – Fe^{3+} yellow, Fe^{2+} green, Cu^{2+} blue, Co^{3+} blue etc.

Alloys

Solid mixture of metals in a definite ratio (15% difference in metallic radius). They are hard and have high melting point.

Eg. Brass (Cu + Zn)

Bronze (Cu + Sn) etc.

Hg when mixed with other metals form semisolid amalgam except Fe, Co, Ni, Pt.

Interstitial compound

When less reactive non-metals of small atomic size eg. H, B, N, C are trapped in the interstitial space of transition metals, interstitial compounds are formed, like: TiC, Mn_4N, Fe_3H etc.

They are non-stoichiometric compounds.

They have high melting point than the metals from which they are formed.

They are chemically inert.

Catalytic Properties

Most of the d-block compounds act as catalyst due to their variable oxidation state, complex formation tendency and adsorption of gases on their surface.

Example:

Contact process = V_2O_5

Haber's process = $Fe_2O_3 + Al_2O_3 + K_2O$

Fenton's reagent = $FeSO_4 + H_2O_2$

Decomposition of $KClO_3$ = MnO_2

Ostwald's process = Pt/Rh

Zeigler Natta = $TiCl_4 + (C_2H_5)_3Al$

Hydrogenation of Alkene = Ni/Pd

Wilkinson's catalyst = RhCl + PPh_3

Important reactions of d-block elements

(*a*) $Cu^{2+} + 4I^- \rightarrow Cu_2I_2(s) + I_2$

(*b*) $CuSO_4 + \underset{\text{Excess}}{KCN} \rightarrow K_2SO_4 + \underset{\text{Unstable}}{Cu(CN)_2}$

$2Cu(CN)_2 \rightarrow 2CuCN + \underset{\text{Cyanogen}}{(CN)_2}$

$CuCN + 3KCN \rightarrow K_3[Cu(CN)_4]$

(*c*) $Cu \xrightarrow[\text{moist air}]{H_2O + CO_2} \underset{\text{Green}}{CuCO_3.Cu(OH)_2}$

$Au \xrightarrow[(3HCl + HNO_3)]{\text{Aqua regia}} H[AuCl_4] + NOCl + H_2O$

(*d*) $AgNO_3(s) \xrightarrow{\text{Heating}} Ag + NO_2 + \frac{1}{2}O_2$

$Ag_2CO_3(s) \xrightarrow{\text{Heating}} Ag + CO_2 + \frac{1}{2}O_2$

(*e*) $CuSO_4.5H_2O \xrightarrow{100^\circ C} \underset{\text{Light greenish blue}}{CuSO_4.H_2O} \xrightarrow{720^\circ C}$

$\underset{\text{Colourless}}{CuSO_4} \xrightarrow{230^\circ C} CuO + SO_2 + \frac{1}{2}O_2$

(*f*) $Hg_2Cl_2 + NH_4OH \longrightarrow Hg\begin{matrix} NH_2 \\ Cl \end{matrix} + \underset{\text{Black}}{Hg}$

(*g*) $NO_3^-/NO_2^- \xrightarrow{FeSO_4 + H_2SO_4} \underset{\text{Brown ring complex}}{[Fe(H_2O)_5 NO^+]SO_4}$

(*h*) $AgBr + 2Na_2S_2O_3 \longrightarrow \underset{\text{Photographic complex}}{Na_3[Ag(S_2O_3)_2]} + NaBr$

(*i*) Chemical volcano:

$\underset{\text{orange solid}}{(NH_4)_2Cr_2O_7} \xrightarrow{\Delta} N_2 + 4H_2O + \underset{\text{Green residue}}{Cr_2O_3}$

Reactions of $Cr_2O_7^{2-}$

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

$SO_2 \longrightarrow SO_4^{2-}$

$H_2S \longrightarrow S$

$SO_3^{2-} \longrightarrow SO_4^{2-}$

$NO_2^- \longrightarrow NO_3^-$

$I^- \longrightarrow I_2$

$Br^- \longrightarrow Br_2$

$S_2O_3^{2-} \longrightarrow S + SO_4^{2-}$

$C_2H_5OH \longrightarrow CH_3COOH$

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

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

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

$Cr_2O_7^{-2}/H^+$ (Orange)

$H_2O_2 \longrightarrow H_2O$

$\underset{\text{(Blue)}}{CrO_5}$

Reaction of MnO_4^-

MnO_4^-(Purple)/H^+ → Mn^{+2}(Purple colour is decolourised)

$C_2O_4^{2-} \longrightarrow CO_2$

$SO_2 \longrightarrow SO_4^{2-}$

$H_2S \longrightarrow S$

$S_2O_3^{2-} \longrightarrow S + SO_4^{2-}$

$NO_2^- \longrightarrow NO_3^-$

$I^- \longrightarrow I_2$

$Br^- \longrightarrow Br_2$

$Cl^- \longrightarrow Cl_2$

$C_2H_5OH \longrightarrow CH_3COOH$

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

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

$$\underset{\text{Purple}}{MnO_4^-} \xrightarrow[\text{Basic Solution}]{\text{Strongly }\Delta} \underset{\text{Green}}{MnO_4^{2-}}$$

MnO_4^-/OH^- → $\underset{\text{(Brown ppt)}}{MnO_2}$

$I^- \longrightarrow IO_3^-$

$CH_2 = CH_2 \longrightarrow CH_2(OH) - CH_2(OH)$

Some important d-Block metal compounds

Ferrous sulphate, $FeSO_4.7H_2O$ (Green Vitriol)

Commonly known as harkasis.

Heating effect:

$$FeSO_4.7H_2O \xrightarrow{140°C} FeSO_4.H_2O \xrightarrow{300°C} 2FeSO_4 \xrightarrow[\text{Temp.}]{\text{High}} Fe_2O_3 + SO_2\uparrow + SO_3\uparrow$$

$$\text{Fe (from iron scrap)} \xrightarrow[-H_2\uparrow]{H_2SO_4} FeSO_4$$

$$FeSO_4 \xrightarrow[-K_2SO_4]{KCN} K_4[Fe(CN)_6]$$

$$FeSO_4 \xrightarrow{\text{Hydrolysis}} Fe(OH)_2 + H_2SO_4$$

(Solution is acidic)

Uses : For making laboratory reagents, like Mohr's salt etc.

$$FeSO_4 + (NH_4)_2SO_4 + 6H_2O \longrightarrow FeSO_4.(NH_4)_2SO_4.6H_2O$$

(Mohr's salt)

$FeSO_4 + H_2O_2$ known as Fenton's reagent is used as catalyst.

2. Zinc Sulphate, $ZnSO_4.7H_2O$ (White Vitriol)

$$ZnSO_4 \xrightarrow[-Na_2SO_4]{NaOH} \underset{\text{White}}{Zn(OH)_2\downarrow} \xrightarrow[-H_2O]{NaOH} \underset{\text{Soluble Complex}}{Na_2ZnO_2}$$

$$ZnSO_4 \xrightarrow{100°} ZnSO_4 \cdot 6H_2O \xrightarrow{200°} ZnSO_4 \xrightarrow{800°C} ZnO + SO_3\uparrow$$

3. Copper sulphate, $CuSO_4.5H_2O$ (Blue vitriol)

Also known as 'Nilathotha'

Physical Properties: Blue crystalline compound, soluble in water.

$$CuSO_4.5H_2O \xrightarrow[\text{effloresces}]{\text{air}} CuSO_4.4H_2O \xrightarrow{100°C} CuSO_4.H_2O \xrightarrow{250°C} CuSO_4 \xrightarrow{750°C} CuO + SO_2\uparrow + O_2\uparrow$$

$$Cu + H_2SO_4 + O_2 \xrightarrow[-H_2O]{} CuSO_4$$

$$CuSO_4 \xrightarrow[-Na_2SO_4/-Na_2SO_4,\ CO_2]{NaOH/Na_2CO_3} \underset{\text{blue}}{Cu(OH)_2\downarrow}$$

$$CuSO_4 \xrightarrow{KSCN + SO_2 + H_2O} CuSCN\downarrow(\text{white}) + K_2SO_4 + H_2SO_4$$

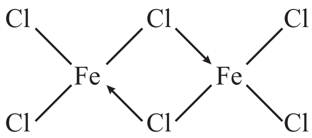
4. Ferric Chloride, $FeCl_3$

$$FeCl_3(\text{anhyd.}) + O_2 \xrightarrow[-Fe_2O_3]{\Delta} \boxed{FeCl_3}$$

$$Fe + Cl_2\ (\text{dry}) \xrightarrow{\Delta} \boxed{FeCl_3}$$

$$FeCl_3.6H_2O + SOCl_2 \xrightarrow{-HCl,\ SO_2} \boxed{FeCl_3}$$

It sublimes at 300°C giving a dimeric gas.



Two 3C-4e^- bond
Four 2C-2e^- bond

5. **Zinc Chloride**

   Prepration of hydrated $ZnCl_2(ZnCl_2.2H_2O)$

   $$ZnO + HCl \longrightarrow ZnCl_2.2H_2O \xrightarrow[-HCl,\ H_2O]{\Delta} Zn(OH)Cl \xrightarrow{\Delta} ZnO + HCl$$

6. **Cupric chloride, $CuCl_2$, $2H_2O$**

   Heating effect: $CuCl_2.2H_2O \xrightarrow[\text{HCl gas}]{150°C} CuCl_2 + 2H_2O$

7. **Silver nitrate, $AgNO_3$ (Lunar Caustic)**

$$Ag + HNO_3\,(\text{dil.}) \xrightarrow{\Delta} \boxed{AgNO_3}$$

$$AgNO_3 \xrightarrow{\text{Heating above M.pt.}} AgNO_2 + O_2$$

$$AgNO_3 \xrightarrow{\text{Red Hot}} Ag + NO_2 + O_2$$

Photography

(*i*) A photographic film consists of a light sensitive emulsion of fine particles (grains) of silver salts in gelatin, spread on a clear celluloid strip or a glass plate. AgBr is mainly used as the light sensitive material.

(*ii*) The film is placed in a camera. When the photograph is exposed, light from the subject enters the camera and is focussed by the lens to give a sharp image on the film. The light starts a photochemical reaction by exciting a halide ion, which loses an electron. The electron moves in a conduction band to the surface of the grain, where it reduces Ag^+ ion to metallic silver. To remove the excess of AgBr, hypo solution is used.

$$2AgBr(s) \xrightarrow{\text{light}} 2Ag + Br_2$$

$$AgBr + 2Na_2S_2O_3(aq.) \xrightarrow{\text{light}} Na_3[Ag\,(S_2O_3)_2] + NaBr$$

f-block elements

Lanthanoids are a series of elements that involve the filling of 4f- subshell. These are fourteen elements, following lanthanum, from Cerium to Lutetium. Actinoids are a series of elements that involve filling of 5f-subshell. These are fourteen elements following Actinium from Thorium to Lawrencium. The common oxidation state of lanthanoids and actinoids is +3.

Some Applications of d- and f-Block Elements

Iron and steels are the most important construction materials. Their production is based on the reduction of iron oxides, the removal of impurities and the addition of carbon and alloying metals, such as Cr, Mn and Ni. TiO for the pigment industry and MnO_2 for use in dry battery cells. The battery industry also requires Zn and Ni/Cd. The 'silver' UK coins are Cu/Ni alloy.