

## DEFINITION

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

### GENERAL ELECTRONIC CONFIGURATION

$$\label{eq:constraint} \begin{split} ns^{0-2} & (n{-}1)d^{1{-}10} \\ Exceptions \begin{cases} Cr = 4s^1 3d^5 \\ Cu = 4s^1 3d^{10}, Pd = 5s^0 4d^{10} \end{cases} \end{split}$$

### **TRANSITION SERIES**

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

### **ATOMIC RADIUS**

3d series  $Sc > Ti > V > Cr > Mn \ge Fe \simeq Co \simeq Ni \le Cu \le Zn$ 

**In a group** 3d to 4d series increases but 4d and 5d series nearly same due to poor shielding of f electron. (Lanthanide contraction)

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3d < 4d \simeq 5d
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e.g : Ti < Zr  $\simeq$  Hf  $\begin{vmatrix} \text{Smallest radius} - \text{Ni} \\ \text{Largest radius} - \text{La} \end{vmatrix}$ 

#### Melting point: s-block metals < d-block metals

In a series on increasing number of unpaired e<sup>-</sup> melting point increases upto Cr then decreases.

Sc < Ti < V < Cr > Mn < Fe > Co > Ni > Cu > Zn↓
Half filled d<sup>5</sup>
Fully filled d<sup>10</sup>
∴ weak metallic bond
∴ weak metallic bond

 $\begin{array}{c} \text{Melting point} \\ \text{Melting point} \\ \hline \\ \text{Cu} > \text{Ag} \le \text{Au} \end{array} (\text{data based})$ 

E.N. Exception Zn < Cd < Hg

**Density**: -s - block metals < d - block metals.

3d series

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

**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 liquid

Electrical conductor

$$\frac{Ag}{d-block} > Cu > Au > Al \\ p-block$$

#### **OXIDATION STATE**

Transition elements exhibit variable oxidation state due to small energy difference of ns and (n-1)d electrons.

- 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 compound oxidation state of metals is zero due to synergic effects.
- Their higher oxidation states are more stable in fluoride 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<sub>4</sub> while oxide is Mn<sub>2</sub>O<sub>7</sub>

- $\Rightarrow$  Mn show maximum number of oxidation state (+2 to +7) among 3d series.
- $\Rightarrow$  Beyond Mn, trihalide are not observe except FeX<sub>3</sub> (X = Cl/Br/I) & CoF<sub>3</sub>

⇒	$V_2O_3$	$V_2O_4$	V <sub>2</sub> O <sub>5</sub>
	basic	basic	amphoteric
⇒	CrO	Cr <sub>2</sub> O <sub>3</sub>	CrO <sub>3</sub>
	basic	amphoteric	acidic
⇒	MnO	MnO <sub>2</sub>	Mn <sub>2</sub> O <sub>7</sub>
	basic	amphoteric	acidic
_	Cul does not evis	t	

ul, uses not exis

$$\operatorname{CuI}_2 \longrightarrow \operatorname{CuI} + \frac{1}{2}\operatorname{I}_2$$

 $\Rightarrow$  In aqueous, Cu<sup>+</sup> disproportinated into Cu & Cu<sup>+2</sup>. 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 gp Mo(+6) & W(+6) are more stable than Cr(+6)

## MAGNETIC PROPERTY

All transition elements are paramagnetic due to presence of unpaired electrons. They attract when magnetic field is applied. Magnetic moment of unpaired electron is due to spin and orbital angular momentum.

"Spin only" magnetic moment can be calculated by using formula  $\mu = \sqrt{n(n+2)}$  Bohr magneton. (n is number of unpaired e<sup>-</sup>.)

If n is 1  $\mu$  = 1.73 BM n is 2  $\mu$  = 2.84 BM n is 3  $\mu$  = 3.87 BM n is  $4 \mu = 4.90 BM$ n is 5  $\mu$  = 5.92 BM

Substances that are not attracted by applied magnetic field are diamagnetic. They have all the electrons paired. d-block element and ions having d<sup>0</sup> and d<sup>10</sup> configuration are diamagnetic.

## COLOUR

Colour in transition metal ions is associated with d-d transition of unpaired electron 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<sup>4+</sup>, Zn<sup>2+</sup> etc

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

## ALLOYS

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

eg. Brass (Cu + Zn)

Bronze (Cu + Sn) etc.

Hg when mix with other metals from semisolid amalgam except Fe, Co, Ni, Pt.

#### **Interstitial compound**

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

They are nonstoichiometric compounds.

They have high melting point than metals.

They are chemically inert.

## **CATALYTIC PROPERTIES**

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

#### Example:

Contact process =  $V_2O_5$ Haber process =  $Fe_2O_3 + Al_2O_3 + K_2O$ Fenton's reagent =  $FeSO_4 + H_2O_2$ Decomposition of KCIO<sub>3</sub> = MnO<sub>2</sub> Ostwald process = Pt/Rh Zeigler Natta = TiCl<sub>4</sub> + (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> Al Hydrogenation of Alkene = Ni/Pd Wilkinson's catalyst = RhCl + PPh<sub>3</sub>

#### Important reactions of d-block elements

(a) 
$$Cu^{2^{+}} + 4\Gamma \longrightarrow Cu_2I_{2(s)} + I_2$$
  
(b)  $CuSO_4 + KCN \longrightarrow K_2SO_4 + Cu(CN)_2$   
 $2Cu(CN)_2 \longrightarrow 2CuCN + (CN)_2$   
 $Cyanogen$   
 $CuCN + 3KCN \longrightarrow K_3[Cu(CN)_4]$   
(c)  $Cu \xrightarrow{H_2O + CO_2}{moist air} > CuCO_3.Cu(OH)_2$   
 $Au \xrightarrow{Aqua regia}{(3HCI + HNO_3)} H[AuCl_4] + NOCI + H_2O$ 

(d) 
$$AgNO_{3}(s) \xrightarrow{Heating} Ag + NO_{2} + \frac{1}{2}O_{2}$$
  
 $AgCO_{3}(s) \xrightarrow{Heating} Ag + CO_{2} + \frac{1}{2}O_{2}$   
(e)  $CuSO_{4}.5H_{2}O \xrightarrow{100^{\circ}C} CuSO_{4}.H_{2}O \xrightarrow{720^{\circ}C} CuSO_{4}$   
 $iight greenish blue \xrightarrow{Colourless} -\frac{230^{\circ}C}{Cl} CuO + SO_{2} + \frac{1}{2}O_{2}$   
(f)  $Hg_{2}Cl_{2} + NH_{4}OH \longrightarrow Hg \swarrow_{Cl}^{NH_{2}} + Hg$   
 $g) NO_{3}/NO_{2} \xrightarrow{FeSO_{4} + H_{2}SO_{4}} [Fe(H_{2}O)_{5} NO^{+}]SO_{4}$   
Brown ring complex  
(h)  $AgBr + 2Na_{2}S_{2}O_{3} \longrightarrow Na_{3}[Ag(S_{2}O_{3})_{2}] + NaBr$   
Photographic  
complex  
(i) Chemical volcano:

$$(\mathrm{NH}_4)_2\mathrm{Cr}_2\mathrm{O}_7 \rightarrow \mathrm{N}_2 + 4\mathrm{H}_2\mathrm{O} + \mathrm{Cr}_2\mathrm{O}_3$$

# **Reactions of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>**



