Chapter_08

The *d*-and *f*-Block Elements

1. Transition elements having partially or fully filled d-orbitals in ground or most common oxidation state are called *d*-block elements. These are also called transition elements (having incomplete d-orbitals in ground or most common oxidation state), because their properties are intermediate of s- and p-block elements. General electronic configuration of this block is $(n-1)d^{1-10}ns^{1-2}$.

Zn, Cd, Hg of group 12 have full

 d^{10} configuration in their ground state as well as in their common oxidation states, thus, they are not regarded as transition metals.

2. General Properties

- The transition metals have high enthalpy of atomisation. It first increases, reaches to the maximum in the middle of each series and then decreases. It can be explained on the basis of strong interatomic interaction due to unpaired electrons. Greater is the number of unpaired electrons, stronger is the resultant bonding
- Metals of second (4d) and third (5d) series have high enthalpy of atomisation than the corresponding elements of 3d-series because of stronger metal-metal bond.
- Ionisation enthalpy increases from left to right in a series, but irregularities are observed due to irregular trends in electronic configuration. Members show little difference in values and are fairly close. Zn shows quite high value due to extra stability of completely filled orbital.
- There is a fall in IE₂ from Cr to Mn and from Cu to Zn because after the removal of first electron, Cr and Cu acquire a stable configuration, i.e. d^{5} and d^{10} . The high values of IE₃ for Cu, Ni and Zn explains, why they show a maximum oxidation state of +2.
- Cu⁺ is unstable in aqueous solution and undergoes disproportionation.

 $2Cu^+ \longrightarrow Cu^{2+} + Cu; Cu^{2+}$ is more stable than Cu^+ due to much more (–)ve ΔH (hydration) of Cu²⁺ (aq)

than Cu⁺. This is more than that required to compensate high IE₂ of Cu.

- The values of E° across the series are less negative because of general increase in the sum of the first and second ionisation enthalpies.
- E° value for any metal depends on three factors; hydration enthalpy, ionisation enthalpy, enthalpy of atomisation

Copper has high value of enthalpy of atomisation and low value of hydration enthalpy and also then high energy to transform Cu(s) to $Cu^{2+}(aq)$ is not balanced by its hydration enthalpy, therefore it has positive E° .

- Transition elements exhibit colour due to d-d transition, structure defects and charge transfer. Electrons of lower energy level of *d*-orbital absorb energy from visible region for excitation to higher level.
- Many transition metals and their compounds are used as catalyst because of their ability to adopt multiple oxidation states and to form complexes.

- · Both oxygen and fluorine being highly electronegative can increase the oxidation state of a particular transition metal. In certain oxides, the element oxygen is involved in multiple bonding with the metal and this is responsible for the higher oxidation state of the metal.
- Magnetic properties The magnetic moment is determined by the number of unpaired electrons and is calculated by using the 'spin-only' formula, i.e. $\mu = \sqrt{n(n+2)}$ BM.
- The compounds in which small atoms like H, C, N etc., occupy interstitial sites in the crystal lattice are called interstitial compounds. These compounds are well known for transition metals because small atoms can easily occupy the positions in the interstitial sites present in the crystal lattices of transition metals.
- · Acidic strength of oxides of transition elements increases with the increase in oxidation state of the element, e.g. MnO (Mn²⁺) is basic, whereas $Mn_2O_7 (Mn^{7+})$ is acidic in nature.
- 3. Important Compounds of Transition Elements
 - Potassium dichromate is obtained from chromite ore as: $4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \longrightarrow 2\text{Fe}_2\text{O}_3$ Iron chromate

$$2Na_{2}CrO_{4} + 2H^{+} \longrightarrow Na_{2}Cr_{2}O_{7} + 2Na^{+} + H_{2}O$$
Sodium
chromate
$$Na_{2}Cr_{2}O_{7} + 2KCI \longrightarrow K_{2}Cr_{2}O_{7} + 2NaCI$$
Potassium
dichromate
$$\int_{0}^{2} \int_{0}^{2} \int_{0}^$$



Dichromate ion

· Potassium dichromate is used as a primary standard solution in volumetric analysis. In acidic medium,

$$\begin{array}{l} \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \\ \text{Dicromate} & (E^\circ = 1.33 \text{ V}) \end{array}$$

Thus, acidified potassium dichromate oxidises, iodides to iodine, sulphides to sulphur, iron (II) salts to iron (III) and tin (II) to tin (IV).

Effect of pH on
$$\operatorname{Cr}_2 \operatorname{O}_7^{2^-}$$
, $\operatorname{Cr}_2 \operatorname{O}_7^{2^-} \xrightarrow[H^+]{\operatorname{OH}^-} \operatorname{Cr}\operatorname{O}_4^{2^-}$

· When pyrolusite ore is fused with alkali in the presence of air or an oxidising agent like KNO3, potassium permanganate is formed.

$$2MnO_{2} + 4KOH + O_{2} \longrightarrow 2K_{2}MnO_{4} + 2H_{2}O$$
Potassium
manganate
$$3MnO_{4}^{2^{-}} + 4H^{+} \longrightarrow 2MnO_{4}^{-} + MnO_{2} + 2H_{2}O$$
Permanganate
ion
$$MnO_{4}^{2^{-}} \xrightarrow{\text{Electrolytic oxidation}} MnO_{4}^{-}$$
Permanganate ion
$$MnO_{2} \xrightarrow{\text{Fused with KOH, oxidised}} MnO_{4}^{2^{-}}$$
With air or KNO₃

$$MnO_{4}^{2^{-}}$$
Manganate ion
$$MnO_{4}^{2^{-}} \xrightarrow{\text{Min}O_{4}^{-}} O$$

$$Manganate ion
$$O^{-} O$$

$$O^{-}$$$$

(Purple)

(Green)

• In acidic medium, KMnO₄ oxidises Fe²⁺ to Fe³⁺, SO_3^{-2} to SO_4^{-2} , I⁻ to I₂ whereas in neutral medium, it converts I⁻ to IO₃⁻ and S₂O₃²⁻ to SO₄²⁻.

4. Inner-transition Elements

- The f-block consists of the two series, lanthanoids and actinoids.
- The electronic configuration of all the tripositive ions (the most stable oxidation state of all the lanthanoids) are of the form 4^{*n*}.
- Due to the poor shielding effect of 4 *f*-electrons, effective nuclear charge increases and radius decreases from lanthanum to lutetium. Ionic radii decreases in regular pattern but atomic radii follow irregular pattern because configuration is irregular. The gradual and steady decrease in radii across the period is known as **lanthanoid contraction**.
- Due to lanthanoid contraction, the basic character of oxides and hydroxides decreases from La(OH)₃ to Lu(OH)₃. Zr/Hf; Nb/Ta and Mo/W are almost identical in size.
- Misch metal is an alloy of rare earth elements (94%), iron (5%) and traces of C, S, Ca and Al. It is used in making bullets, shells and lighter flint. Pyrophoric alloys contain Ce (40.5%), La + Nd (44%) Al, Ca and S.
- .Actinoids ions are generally coloured due to f- f transition. It depends upon the number of electrons in 5f-orbitals.
- The decrease in atomic (or ionic) radii in actinoid elements (actinoid contraction) is greater than lanthanoid contraction because 5 *f*-electrons have poor shielding effect as compared to 4 *f*-electrons. Therefore, the effect of increased nuclear charge leading to contraction in size is more in case of actinoid elements.
- Actinoids exhibit more number of oxidation states than lanthanoids. This is due to the fact that 5f, 6d and 7s levels are of comparable energies.
- Actinoids have stronger tendency towards complex formation as compared to lanthanoids.