Chapter 21

d and *f*-Block Elements

*The **transition elements** may be defined as elements whose atoms or simple ions in their most common oxidation state contain partially filled d-orbitals.* This definition does not cover zinc, cadmium and mercury. However, these are studied with transition elements.

The general electronic configuration of these elements is $(n-1)d^{1-10}\,ns^{0-2}$.

ATOMIC AND PHYSICAL PROPERTIES

The important properties of the transition metals are given below :

1. Metallic Character

(a) Transition elements exhibit good mechanical properties, i.e, they are hard, malleable and ductile. They have high enthalpies of atomization, high melting and boiling points, they have high thermal and electrical conductivity as well as lustre.

(b) Their mechanical properties and high melting as well as boiling points indicate the presence of strong metallic bond.

2. Ionisation Energies

(a) The ionisation energies of transition metals increases as we move across each series though not quite regularly.

(b) It is evident that first ionisation energies of most of the 5*d* elements are higher than those of 3*d* and 4*d*-elements. This is due to the fact that the outer valence electrons of 5*d*-elements experience greater effective nuclear charge due to poor shielding of the nucleus by 4*f*-electrons.

3. Electrode Potential

In general, transition elements have low negative values of standard reduction electrode potential due to high ionisation energies, high heat of sublimation which are more than offset with large heats of hydration. Consequently, transition elements are **weak reducing agents** and are **less reactive** than *s*-block elements.

4. Variable Oxidation States

(a) Transition metals exhibit a wide range of oxidation states. When '*ns*' electrons are involved, then compounds with lower oxidation states are formed. In compounds with higher oxidation states, (*n*–1) *d* electrons are also involved.

(b) The highest oxidation state exhibited by any transition metal is +8, *i.e*, Ruthenium tetroxide (RuO_4) and Osmium tetroxide (OsO_4)

(c) The highest oxidation state are shown by transition metal when they combine with most electronegative elements such as fluorine or oxygen, *i.e*., CrO_3, Mn_2O_7 and VF_5.

(d) Maximum number of variable oxidation states are shown by Mn (+2, +3, +4, +5, +6, +7).

(e) The most common oxidation state for first transition series is +2 which arises from the loss of 4*s* electrons (except Sc).

(f) In lower oxidation states as +2 and +3, the bonds are mostly ionic while in higher oxidation states such as +6 or +7, the bonds are essentially covalent as in MnO_4^- (Mn= +7), $Cr_2O_7^{2-}$ (Cr = +6)

5. Formation of Complexes :

By virtue of their small size, comparatively high nuclear or ionic charge and availability of vacant d-orbitals of suitable energy, these metals exert strong electrostatic attraction on the ligands. The species formed on interaction of metal and the ligand (or ligands) is known as a complex.

Formation of Coloured Compounds : The transition metal ions have unpaired d-electrons, which on absorbing visible light can jump from one *d*-orbital to another *i.e.*, *d-d* transitions take place. Thus when light falls certain visible wavelengths are absorbed. The reflected light appears coloured and gives the colour of compound. The ions having no *d-d* transitions are ($KMnO_4$ & $K_2Cr_2O_7$) coloured due to charge transfer spectra. Some compounds are coloured due to polarisation e.g., AgI.

6. Catalytic Properties

Most of the transition metals and their compounds are found to act as catalysts.

Transition Metals as Catalyst : Catalytic power of transition metals is believed to operate by the formation of interstitial compounds to adsorb and activate the reacting substances e.g. hydrogenation of alkenes in presence of palladium or platinum is thought to take place through this mechanism.

7. Magnetic Properties

(a) Most of the transition elements show paramagnetism. Paramagnetism arises from the presence of unpaired electrons in atoms, ions or molecules.

(b) The magnetic character is comparable in terms of magnetic moment given as $\mu = \sqrt{n(n+2)}$ Bohr magnetons. In general, more is the number of unpaired electrons greater is the magnetic character.

(c) The maximum paramagnetism is seen in d^5 cases, having the maximum unpaired electrons.

8. Formation of Nonstoichiometric Compounds and Interstitial Compounds

Transition metals can trap some of the small size atoms like hydrogen, boron, carbon, nitrogen, etc in the vacant spaces between the crystal lattice forming interstitial compounds.

9. Alloy Formation

(a) Molten transition metals are miscible with one another. Therefore, on cooling a mixture of the transition metals results in the formation of alloys.

(b) Such alloys are usually harder, have higher melting points and are more resistant to corrosion than the parent metals.

IMPORTANT COMPOUNDS OF TRANSITION METALS

Potassium Dichromate ($K_2Cr_2O_7$) :

Preparation : From Chromite ore:

The preparation is completed in the following three steps:

(a) Preparation of sodium chromate :

$$4[FeO.Cr_2O_3] + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2 \uparrow$$

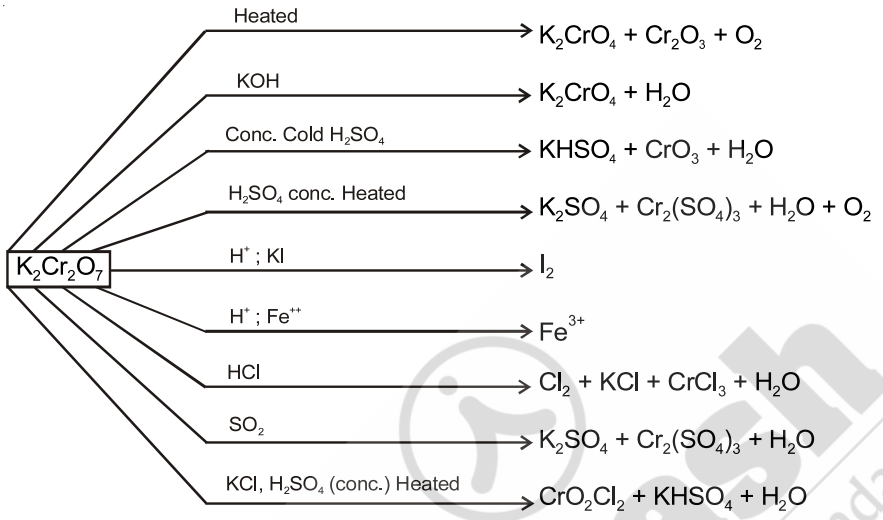
(b) Conversion of sodium chromate into sodium dichromate :

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

(c) Conversion of sodium dichromate into potassium dichromate :

$$Na_2Cr_2O_7 + 2KCl \longrightarrow \underset{\text{(less soluble)}}{K_2Cr_2O_7} + 2NaCl$$

Properties of $K_2Cr_2O_7$: Potassium dichromate is orange coloured compound. The important reactions are given below



Potassium Permanganate ($KMnO_4$)

Preparation :

It is prepared by fusing pyrolusite ore (MnO_2) with KOH in the presence of atmospheric oxygen or an oxidising agent like KNO_3 or $KClO_3$ to get potassium manganate K_2MnO_4, (green mass). The green mass is oxidised to potassium permanganate, electrolytically or by passing chlorine or ozone into the solution.

Step-I:

$$2MnO_2 + 4KOH + \underset{\substack{\text{(From } KNO_3 \\ \text{or } KClO_3\text{)}}}{2[O]} \xrightarrow{\text{Heat}} 2K_2MnO_4 + 2H_2O$$

Step-II:

Electrolytic Oxidation

At the cathode $2H^+ + 2e^- \longrightarrow H_2$

At the anode $\underset{\text{(Green)}}{MnO_4^{2-}} \longrightarrow \underset{\text{(Purple)}}{MnO_4^-} + e^-$

Properties of $KMnO_4$: The important properties are given below:

1. **Oxidising Nature in Neutral Medium**

   $[2KMnO_4 + H_2O \rightarrow 2KOH + 2MnO_2 + 3[O]]$.

   In this medium $MnSO_4$ is oxidised to MnO_2 and $Na_2S_2O_3$ to Na_2SO_4.

2. Oxidising Nature in Alkaline Medium :

$[2KMnO_4 + 2KOH \rightarrow 2K_2MnO_4 + H_2O + [O]]$.

In this medium KI is oxidised to KIO_3 and alkenes are oxidised to glycols.

3. Oxidising Nature in Acidic Medium :

$[2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]]$.

In this medium it oxidises

$H_2S + [O] \rightarrow H_2O + S$

$SO_2 + H_2O + [O] \rightarrow H_2SO_4$

$H_2C_2O_4 + [O] \rightarrow 2CO_2 + H_2O$

$2FeSO_4 + H_2SO_4 + [O] \rightarrow Fe_2(SO_4)_3 + H_2O$

$2KI + [O] + H_2O \rightarrow I_2 + 2KOH$

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