d – Block Elements

1. **Reactivity** : The *d*- block elements are unreactive due to the following factors:
   - i) **High ionisation energies** : on account of small size of their atoms, ionisation energies of d- block elements are fairly high
   - ii) **High heats of sublimation**: Due to presence of covalent bonding, these have high heats of sublimation.

   The tendency to remain unreactive is more pronounced in platinum and gold in the third transition series.

2. **Standard Electrode Potential**: The standard reduction potential of all the transition elements (except Cu and Hg in 3d-series etc.) is lower (negative) than that of hydrogen (taken as Zero). thus all the transition elements, with negative reduction potential, liberate hydrogen from dilute acids

   However, some metals evolve hydrogen very slowly because they are protected from the attack of acids by the formation of an impervious layer of an inert oxide. For example, chromium is so unreactive that it can be used as a protective non-oxidising metal.

3. **Reducing Properties**: Transition metals with sufficiently negative standard reduction potential should be good reducing agents i.e, they should be oxidised easily to their ions.

$$M \rightarrow M^{2+} + 2e^-$$

   However they are not good reducing agents as compared to elements of Group 1, 2 and 13 . This is because the transition metals have fewer tendencies to form ions due to their low reactivity.

PREPARATION, PROPERTIES AND USES OF $KMnO_4$ AND $K_2Cr_2O_7$:

Potassium dichromate, $K_2Cr_2O_7$:

Preparation: It is prepared from chromite ore or Ferro chromes ($FeCr_2O_4$ or $FeOCr_2O_3$) by following steps.

(a) Fusion of the ore with molten alkali in presence of air

$$4FeCr_2O_4 + 16\ NaOH + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8H_2O.$$

The fused mass is extracted with water and filtered.

(b) Conversion of sodium chromate into sodium dichromate by treating the filtrate with dil H_2SO_4

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

Na_2SO_4 being less soluble is separated as $Na_2SO_4 10H_2O$ by fractional crystallization.

(c) Conversion of sodium dichromate into potassium dichromate by heating with KCl.

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

Potassium dichromate being less soluble is obtained by fractional crystallization.

Properties:

(i) **Physical state** : Potassium dichromate forms orange red crystals which melts at 669

K. It is moderately soluble in cold water but freely soluble in hot water.

(ii) **Action of heat** : When heated strongly to white heat, it decomposes with the evolution of oxygen.

$$\underset{\text{Pot. Dichromate}}{4K_2Cr_2O_7} \xrightarrow{\Delta} \underset{\text{Pot. Chromate}}{4K_2CrO_4} + \underset{\text{chromic oxide}}{2Cr_2O_3} + 3O_2$$

(iii) **Action of alkalis**: When an alkali is added to an orange red solution containing dichromate ions, a yellow solution is obtained due to the formation of chromate ions. For example,

$$K_2Cr_2O_7 + 2KOH \rightarrow 2K_2CrO_4 + H_2O$$

Pot. Dichromate Pot. Chromate

On acidifying the above yellow solution containing chromate ions, it again changes to orange red due to the formation of dichromate ions.

$$2K_2CrO_4 + H_2SO_4 \rightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$$

Pot. Chromate Pot. Dichromate

In fact, in any given solution, dichromate ions and chromate ions exist in equilibrium and are interconvertible by altering the *p*H of the solution.

(iv) **Action of concentrated sulphuric acid** : In cold, red crystals of chromic anhydride (CrO_3) are formed

$$K_2Cr_2O_7 + 2H_2SO_4 \text{ (conc.)} \rightarrow 2CrO_3 + 2KHSO_4 + H_2O$$

(v) **Oxidising properties**: Potassium dichromate is a powerful oxidizing agent. In acidic solution, its oxidizing action can be represented as follows.

Ionic equation:

$$CrO_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \quad [E^0 = +1.31V]$$

Molecular equation :

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

Thus, equivalent mass of $K_2Cr_2O_7 = \frac{294}{6} = \frac{49}{6}$

(a) It oxidises iodides to iodine

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 7H_2O + 3I_2 \text{ (Ionic Equation)}$$

This reaction is used in the estimation of iodide ions in the volumetric analysis.

(b) It oxidises ferrous salts of ferric salts:

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

This reaction is used in the estimation of ferrous ions in the volumetric analysis.

(c) In oxidises H_2S to S :

$$Cr_2O_7^{2-} + 8H^+ + 3H_2S \rightarrow 2Cr^{3+} + 7H_2O + 3S$$

(d) It oxidises sulphur dioxide to sulphuric acid :

$$Cr_2O_7^{2-} + 2H^+ + 3SO_2 \rightarrow 2Cr^{3+} + H_2O + 3SO_4^{2-}$$

(e) If oxidises ethyl alcohol to acetaldehyde and acetic acid :

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

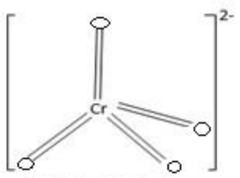
$$C_2H_5OH + [O] \rightarrow CH_3CHO + H_2O$$

$$CH_3CHO + [O] \rightarrow CH_3COOH$$

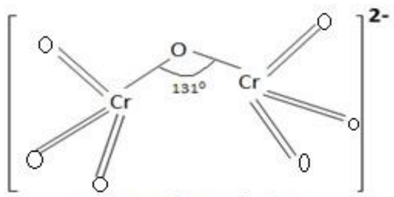
(vi) **With hydrogen peroxide**: Acidified potassium dichromate forms a deep blue colour with hydrogen peroxide due to the formation of CrO_5.

$$K_2Cr_2O_7 + H_2SO_4 + 4H_2O_2 \rightarrow 2CrO_5 + K_2SO_4 + 5H_2O$$

The blue colour fades away gradually due to decomposition of CrO_5 into Cr^{3+} ions and oxygen.



Tetrahedral structure of CrO_4^{2-} ions



Structure of $Cr_2O_7^{2-}$ ions containing two tetrahedra

(vii) **Structure of chromate and dichromate ions** :

Uses.

(i) In volumetric estimation of reducing agents e.g., ferrous salts, iodides and sulphites. This is due to the fact that $K_2Cr_2O_7$ is obtained in a much higher degree of purity than $Na_2Cr_2O_7$

(ii) In the preparation of chromium compounds e.g., chrome alum.

(iii) In photography for hardening of gelatin.

(iv) In dyeing for producing $Cr(OH)_3$ as mordant.

(v) Chromic acid mixture ($K_2Cr_2O_7$ + conc. H_2SO_4) is used for cleaning glass wares in the laboratory.

(vi) As an oxidizing agent.

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