# D and F Block Elements: V

# **EXEMPLAR PROBLEMS:**

- 5. On addition of small amount of  $KMnO_4$  to concentrated  $H_2SO_4$ , a green oily compound is obtained which is highly explosive in nature. Identify the compound from the following.
  - (i) Mn<sub>2</sub>O<sub>7</sub>
  - (ii) MnO<sub>2</sub>
  - (iii) MnSO,
  - (iv) Mn<sub>2</sub>O<sub>3</sub>

Ans. (i)

- 8. Which of the following reactions are disproportionation reactions?
  - (a)  $Cu^+ \longrightarrow Cu^{2+} + Cu$
  - (b)  $3\text{MnO}_4^- + 4\text{H}^+ \longrightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}$
  - (c)  $2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$
  - (d)  $2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$
  - (i) a, b
  - (ii) a, b, c
  - (iii) b, c, d
  - (iv) a, d

8. (i)

- 11.  ${\rm KMnO_4}$  acts as an oxidising agent in acidic medium. The number of moles of  ${\rm KMnO_4}$  that will be needed to react with one mole of sulphide ions in acidic solution is
  - (i)  $\frac{2}{5}$
  - (ii)  $\frac{3}{5}$
  - (iii)  $\frac{4}{5}$
  - (iv)  $\frac{1}{5}$

16.	${\rm KMnO_4}$ acts as an oxidising agent in alkaline medium. When alkaline ${\rm KMnO_4}$
	is treated with KI, iodide ion is oxidised to
	(i) $I_2$
	(ii) IO
	(iii) $IO_3^-$
	(iv) IO <sub>4</sub>
16. (i	ii)
	<b>18.</b> When acidified K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> solution is added to Sn <sup>2+</sup> salts then Sn <sup>2+</sup> changes to
	(i) Sn
	(ii) Sn <sup>3+</sup>
	(iii) Sn <sup>4+</sup>
	(iv) Sn*
18. (i	ii)
	,
21	. Why is HCl not used to make the medium acidic in oxidation reactions of
	KMnO <sub>4</sub> in acidic medium?
	(i) Both HCl and KMnO <sub>4</sub> act as oxidising agents.
	<ul><li>(ii) KMnO<sub>4</sub> oxidises HCl into Cl<sub>2</sub> which is also an oxidising agent.</li></ul>
	(iii) KMnO <sub>4</sub> is a weaker oxidising agent than HCl.
	(iv) KMnO <sub>4</sub> acts as a reducing agent in the presence of HCl.
21. (i	i)
32.	Why does copper not replace hydrogen from acids?
32. C	Cu shows positive E value.
38	When a brown compound of manganese (A) is treated with HCl it gives a gas
36.	(B). The gas taken in excess, reacts with NH <sub>3</sub> to give an explosive compound
	(C). Identify compounds A, B and C.
	(e). Identify compounders, 2 and e.
38. A	= MnO2 B = Cl2 C = NCl3
MnO	2 + 4HCl
NH3	+ 3Cl2 ②→ NCl3 + 3HCl (excess) (C)
45.	When orange solution containing Cr <sub>2</sub> O <sub>2</sub> <sup>2</sup> ion is treated with an alkali, a yellow
	solution is formed and when H <sup>+</sup> ions are added to yellow solution, an orange solution is obtained. Explain why does this happen?

**46.** A solution of KMnO<sub>4</sub> on reduction yields either a colourless solution or a brown precipitate or a green solution depending on pH of the solution. What different stages of the reduction do these represent and how are they carried out?

46. Oxidising behaviour of KMnO<sub>4</sub> depends on pH of the solution.

In acidic medium (pH < 7)

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$
(Colourless)

In alkaline medium (pH>7)

$$MnO_4^- + e^- \longrightarrow MnO_4^{-2-}$$
(Green)

In neutral medium(pH=7)

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$
(Brown precipitate)

**65.** When a chromite ore (A) is fused with sodium carbonate in free excess of air and the product is dissolved in water, a yellow solution of compound (B) is obtained. After treatment of this yellow solution with sulphuric acid,

$$\begin{array}{lll} 65. & A = \mathrm{FeCr_2O_4} & B = \mathrm{Na_2CrO_4} & C = \mathrm{Na_2Cr_2O_7.2H_2O} & D = \mathrm{K_2Cr_2O_7} \\ & 4\mathrm{FeCr_2O_4} + 8\mathrm{Na_2CO_3} + 7\mathrm{O_2} \longrightarrow 8\mathrm{Na_2CrO_4} + 2\mathrm{Fe_2O_3} + 8\mathrm{CO_2} \\ & (A) & (B) \\ & 2\mathrm{NaCrO_4} + 2\mathrm{H}^* \longrightarrow \mathrm{Na_2Cr_2O_7} + 2\mathrm{Na}^* + \mathrm{H_2O} \\ & \mathrm{Na_2Cr_2O_7} + 2\mathrm{KCl} \longrightarrow \mathrm{K_2Cr_2O_7} + 2\mathrm{NaCl} \\ & (C) & (D) \end{array}$$

66. When an oxide of manganese (A) is fused with KOH in the presence of an oxidising agent and dissolved in water, it gives a dark green solution of compound (B). Compound (B) disproportionates in neutral or acidic solution to give purple compound (C). An alkaline solution of compound (C) oxidises potassium iodide solution to a compound (D) and compound (A) is also formed. Identify compounds A to D and also explain the reactions involved.

66. 
$$A = MnO_2$$
 (B)  $K_2MnO_4$  (C)  $KMnO_4$  (D)  $KIO_3$ 

$$2 MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$
(A) (B)
$$3MnO_4^{2-} + 4H^* \longrightarrow 2MnO_4^{-} + MnO_2 + 2H_2O$$
(C)
$$2MnO_4^{-} + H_2O + KI \longrightarrow 2MnO_2 + 2OH^{-} + KIO_3$$
(A) (D)

71. A violet compound of manganese (A) decomposes on heating to liberate oxygen and compounds (B) and (C) of manganese are formed. Compound (C) reacts with KOH in the presence of potassium nitrate to give compound (B). On heating compound (C) with conc. H<sub>2</sub>SO<sub>4</sub> and NaCl, chlorine gas is liberated and a compound (D) of manganese along with other products is formed. Identify compounds A to D and also explain the reactions involved.

# NCERT PROBLEMS

(iii) The transition metals generally form coloured compounds.

Most of the complexes of transition metals are colored. This is because of the absorption of radiation from visible light region to promote an electron from one of the d-orbitals to another. In the presence of ligands, the d orbitals split up into two sets of orbitals having different energies. Therefore, the transition of electrons can take place from one set to another. The energy required for these transitions is quite small and falls in the visible region of radiation. The ions of transition metals absorb the radiation of a particular wavelength and the rest is reflected, imparting color to the solution.

## Q14:

Describe the preparation of potassium dichromate from iron chromite ore.

What is the effect of increasing pH on a solution of potassium dichromate?

#### Answer:

Potassium dichromate is prepared from chromite ore  ${\rm (FeCr_2O_4)}_{\rm in}$  in the following steps.

Step (1): Preparation of sodium chromate

$$4\text{FeCr}_{2}\text{O}_{4} + 16\text{NaOH} + 7\text{O}_{2} \longrightarrow 8\text{Na}_{2}\text{CrO}_{4} + 2\text{Fe}_{2}\text{O}_{3} + 8\text{H}_{2}\text{O}$$

Step (2): Conversion of sodium chromate into sodium dichromate

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

Step(3): Conversion of sodium dichromate to potassium dichromate

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

Potassium dichromate being less soluble than sodium chloride is obtained in the form of orange coloured crystals and can be removed by filtration.

#### Q15:

Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with:

(i) iodide (ii) iron(II) solution and (iii) H2S

### Answer:

 ${
m K_2Cr_2O_7}$  acts as a very strong oxidising agent in the acidic medium.

$$\mathrm{K_2Cr_2O_7} + 4\mathrm{H_2SO_4} \longrightarrow \mathrm{K_2SO_4} + \mathrm{Cr_2} \big(\mathrm{SO_4}\big)_3 + 4\mathrm{H_2O} + 3\big[\mathrm{O}\big]$$

 $K_2Cr_2O_7$  takes up electrons to get reduced and acts as an oxidising agent. The reaction of  $K_2Cr_2O_7$  with other iodide, iron (II) solution, and  $H_2S$  are given below.

K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> oxidizes iodide to iodine.

$$\begin{array}{c} Cr_{2}O_{7}^{2-} + 14H^{+} + 6e^{-} \longrightarrow 2Cr^{3+} + 7H_{2}O \\ & 2I^{-} \longrightarrow I_{2} + 2e^{-}] \times 3 \\ \hline Cr_{2}O_{7}^{2-} + 6I^{-} + 14H^{+} \longrightarrow 2Cr^{3+} + 3I_{2} + 7H_{2}O \end{array}$$

(ii)  $K_2Cr_2O_7$  oxidizes iron (II) solution to iron (III) solution i.e., ferrous ions to ferric ions.

$$\begin{array}{c} Cr_2O_7^{2^-} + 14H^+ + 6e^- &\longrightarrow 2Cr^{3^+} + 7H_2O \\ & Fe^{2^+} &\longrightarrow Fe^{3^+} + e^-] \times 6 \\ \hline Cr_2O_7^{2^-} + 14H^+ + 6Fe^{2^+} &\longrightarrow 2Cr^{3^+} + 6Fe^{3^+} + 7H_2O \\ \hline (iii) & K_2Cr_2O_7 \text{ oxidizes H}_2S \text{ to sulphur.} \\ \hline Cr_2O_7^{2^-} + 14H^+ + 6e^- &\longrightarrow 2Cr^{3^+} + 7H_2O \\ & \underline{H_2S} &\longrightarrow S + 2H^+ + 2e^-] \times 3 \\ \hline Cr_2O_7^{2^-} + 3H_2S + 8H^+ &\longrightarrow 2Cr^{3^+} + 3S + 7H_2O \\ \hline \end{array}$$

#### Q16:

Describe the preparation of potassium permanganate. How does the acidifiedpermanganate solution react with (i) iron(II) ions (Ii) SO2and (Iii) oxalic acid?

Write the ionic equations for the reactions.

#### Answer:

Potassium permanganate can be prepared from pyrolusite (MnO<sub>2</sub>). The ore is fused with KOH in the presence of either atmospheric oxygen or an oxidising agent, such as KNO<sub>2</sub>or KClO<sub>4</sub>, to give K<sub>2</sub>MnO<sub>4</sub>.

$$2MnO_2 + 4KOH + O_2 \xrightarrow{heat} 2K_2MnO_4 + 2H_2O$$
(Green)

The green mass can be extracted with water and then oxidized either electrolytically or by passing chlorine/ozone into the solution.

Electrolytic oxidation

$$K_2MnO_4 \longleftrightarrow 2K^+ + MnO_4^{2-}$$
  
 $H_2O \longleftrightarrow H^+ + OH^-$ 

At anode, manganate ions are oxidized to permanganate ions.

$$MnO_4^{2-} \longleftrightarrow MnO_4^- + e^-$$
  
Green Purple

Oxidation by chlorine

$$2 \text{ K}_2 \text{MnO}_4 + \text{Cl}_2 \longrightarrow 2 \text{ KMnO}_4 + 2 \text{ KCl}$$
  
 $2 \text{ MnO}_4^{2-} + \text{Cl}_2 \longrightarrow 2 \text{MnO}_4^{-} + 2 \text{ Cl}^{-}$ 

. . . . .

$$2K_2MnO_4 + O_3 + H_2O \longrightarrow 2KMnO_4 + 2KOH + O_2$$
  
 $2MnO_4^{2-} + O_1 + H_2O \longrightarrow 2MnO_4^{2-} + 2OH^- + O_3$ 

(i) Acidified KMnO<sub>4</sub>solution oxidizes Fe (II) ions to Fe (III) ions i.e., ferrous ions to ferric ions.

$$\frac{MnO_{4}^{-} + 8H^{+} + 5e^{-} \longrightarrow Mn^{2+} + 4H_{2}O}{Fe^{2+} \longrightarrow Fe^{3+} + e^{-}] \times 5}$$

$$\frac{MnO_{4}^{-} + 5Fe^{2+} + 8H^{+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_{2}O}{MnO_{4}^{-} + 5Fe^{3+} + 4H_{2}O}$$

(ii) Acidified potassium permanganate oxidizes SO<sub>2</sub> to sulphuric acid.

$$\frac{MnO_{4}^{-}+6H^{+}+5e^{-}\longrightarrow Mn^{2+}+3H_{2}O]\times 2}{2H_{2}O+2SO_{2}+O_{2}\longrightarrow 4H^{+}+2SO_{4}^{2-}+2e^{-}]\times 5}$$

$$\frac{2MnO_{4}^{-}+10SO_{2}+5O_{2}+4H_{2}O\longrightarrow 2Mn^{2+}+10SO_{4}^{2-}+8H^{+}}{2MnO_{4}^{-}+10SO_{2}^{-}+5O_{2}+4H_{2}O\longrightarrow 2Mn^{2+}+10SO_{4}^{2-}+8H^{+}}$$

(III) Acidified potassium permanganate oxidizes oxalic acid to carbon dioxide.

$$\frac{MnO_{4}^{-} + 8H^{+} + 5e^{-} \longrightarrow Mn^{2+} + 4H_{2}O] \times 2}{C_{2}O_{4}^{2-} \longrightarrow 2CO_{2} + 2e^{-}] \times 5}$$

$$\frac{2MnO_{4}^{-} + 5C_{2}O_{4}^{2-} + 16H^{+} \longrightarrow 2Mn^{2+} + 10CO_{2} + 8H_{2}O}{266}$$

Indicate the steps in the preparation of:

- (i) K2Cr2O7 from chromite ore.
- (ii) KMnO4 from pyrolusite ore.

### Answer:

(i)

Potassium dichromate ( $K_2Cr_2O_7$ ) is prepared from chromite ore  $(FeCr_2O_4)_{in}$  the following steps.

Step (1):Preparation of sodium chromate

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

Step (2):Conversion of sodium chromate into sodium dichromate

$$2Na_{2}Cr_{2}O_{4} + conc.H_{2}SO_{4} \longrightarrow Na_{2}Cr_{2}O_{7} + Na_{2}SO_{4} + H_{2}O$$

Step(3):Conversion of sodium dichromate to potassium dichromate

$$Na_{2}Cr_{2}O_{2} + 2KCl \longrightarrow K_{2}Cr_{2}O_{2} + 2NaCl$$

Potassium chloride being less soluble than sodium chloride is obtained in the form of orange coloured crystals and can be removed by filtration.

The dichromate ion  $\left(Cr_2O_7^{2-}\right)_{\text{exists in equilibrium with chromate}} \left(CrO_4^{2-}\right)_{\text{ion at pH 4. However, by changing the pH, they can be interconverted.}}$ 

$$\begin{array}{cccc} 2CrO_4^{2-} & \xleftarrow{Acid} & 2HCrO_4^{-} & \xleftarrow{Acid} & Cr_2O_7^{2-} \\ Chromate & Hydrogen & Dichromate \end{array}$$

Potassium permanganate ( $^{KMnO_4}$ ) can be prepared from pyrolusite ( $^{MnO_2}$ ). The ore is fused with KOH in the presence of either atmospheric oxygen or an oxidising agent, such as  $^{KNO_3}$ or  $^{KClO_4}$ , to give  $^{K_2}$ MnO<sub>4</sub>.

$$2MnO_2 + 4KOH + O_2 \xrightarrow{heat} 2K_2MnO_4 + 2H_2O$$
(Green)

The green mass can be extracted with water and then oxidized either electrolytically or by passing chlorine/ozone into the solution.

Electrolytic oxidation

$$K_2MnO_4 \longleftrightarrow 2K^+ + MnO_4^{2-}$$
  
 $H_2O \longleftrightarrow H^+ + OH^-$ 

At anode, manganate ions are oxidized to permanganate ions.

$$MnO_4^{2-} \longleftrightarrow MnO_4^{-} + e^{-}$$
  
Green Purple

Oxidation by chlorine

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$$
  
 $2MnO_4^{2-} + Cl_2 \longrightarrow 2MnO_4^{-} + 2Cl^{-}$ 

Oxidation by ozone

$$2 \text{ K}_2 \text{MnO}_4 + \text{O}_3 + \text{H}_2 \text{O} \longrightarrow 2 \text{ KMnO}_4 + 2 \text{ KOH} + \text{O}_2$$

$$2 \text{ MnO}_4^{2-} + \text{O}_3 + \text{H}_2 \text{O} \longrightarrow 2 \text{ MnO}_4^{2-} + 2 \text{ OH}^- + \text{O}_2$$