

# 22

## CHEMISTRY OF SOME IMPORTANT COMPOUNDS OF TRANSITION ELEMENTS

### 22.1 INTRODUCTION

You have learnt in lesson 19 about transition elements these elements are characterised by their high tendency to form large number of binary and ternary compounds in which the metal atom exists in either of the various possible oxidation states. In this lesson we shall learn about a few industrially important, compounds of transition elements of the first series. The metal in all these compounds is in the highest oxidation state. As such some of these compounds are good oxidising agents. Uses, in brief, are also mentioned.

### 22.2 OBJECTIVES

After reading this chapter you will be able to

- describe the production on large scale of potassium dichromate from chromite ore.
  - recall the chemical properties and uses of potassium dichromate.
  - describe the preparation and use of chromic acid.
  - explain the process preparation of potassium permanganate from pyrolusite ore
  - describe the conversion of potassium manganate into potassium permanganate.
  - describe the oxidation properties and uses of potassium permanganate.
-

- describe the laboratory and commercial scale preparation of 'blue vitriol'.
- recall the properties and uses of copper sulphate.
- describe the laboratory preparation and manufacture of potassium ferrocyanide.
- describe the properties, laboratory and commercial uses of potassium ferrocyanide.
- describe the preparation, properties and uses of calamine.
- calculate the oxidation number of an atom in a compound.

## IMPORTANT COMPOUNDS OF TRANSITION ELEMENTS

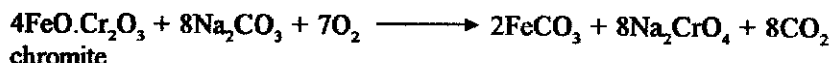
The preparation, properties and applications of the important compounds of transition elements is discussed below.

### 22.3 POTASSIUM DICHROMATE ( $K_2Cr_2O_7$ )

**General:** Mineral chromite or chrome iron stone, ( $FeCr_2O_4$ ) (Ferrous chromite) is the starting material for the manufacture of all chromates and dichromates. Soluble chromates are prepared using alkali metal oxides, hydroxides or carbonates whereas insoluble chromates are made by double decomposition involving soluble chromates. All soluble chromates are poisonous.

#### Large scale production of potassium dichromate from chromite ore.

A mixture of finely powdered concentrated chromite, sodium carbonate and quick lime is heated to redness in a reverberatory furnace in free supply of air. Carbon dioxide is evolved and sodium chromate is formed. The function of quick lime is to keep the mass porous and prevent fusion.



The mass after roasting is extracted with water which dissolves soluble sodium chromate leaving behind insoluble ferric oxide,  $Fe_2O_3$ . After concentrating the solution containing sodium chromate, concentrated sulphuric acid is added.

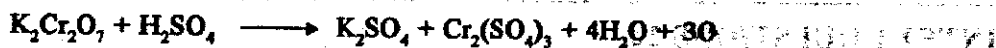


Sodium sulphate produced, crystallizes out and is removed. On further concentrating the solution, deliquescent red crystals of sodium dichromate, ( $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ) slowly separate out on cooling. When a red hot saturated solution of sodium dichromate is mixed with a saturated solution of potassium chloride, sodium chloride is separated out, followed by separation of garnet red triclinic crystals of potassium dichromate with melting point 677 K. Since potassium dichromate is moderately soluble in cold water ( $100\text{g L}^{-1}$  at  $15^\circ\text{C}$ ) but easily soluble in hot water ( $1000\text{g L}^{-1}$ ) at  $100^\circ\text{C}$  it is readily purified by recrystallization from water.

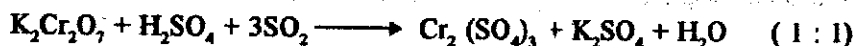
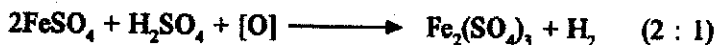
#### Chemical properties

1. Since chromium forms stable compounds in low oxidation state as well, potassium dichromate in which oxidation number of chromium is +6, acts as a powerful

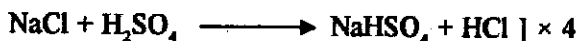
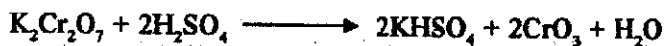
oxidising agent. For this purpose, it is used as a primary standard in volumetric analysis. In acidic solutions, one molecule of potassium dichromate furnishes three atoms (i.e., six equivalents) of available oxygen as follow:



The available oxygen then oxidizes ferrous and iodide ion or molecule of  $\text{SO}_2$  as follows:



2. Potassium dichromate when heated with concentrated sulphuric acid and an ionic chloride (such as  $\text{NaCl}$ ,  $\text{KCl}$ , etc.) forms red vapours of chromyl chloride, ( $\text{CrO}_2\text{Cl}_2$ ) as follow.



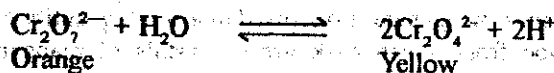
Reaction  
steps



Overall  
Reaction

Red vapours of chromyl chloride, a derivative of chromic acid is absorbed in dilute solution of sodium hydroxide or water. A yellow solution of sodium chromate is formed. On acidifying this solution with acetic acid and adding lead acetate, a yellow precipitate of lead chromate, which is soluble on heating and reappears on cooling, is formed. This is used as confirmatory test to detect the presence of chloride ions in qualitative analysis.

3. When concentrated sulphuric acid is added to a solution of chromate or dichromate, a red coloured solution of chromic trioxide ( $\text{CrO}_3$ ) often called "chromic acid", is obtained. In the acidic solution it exists only as dichromic acid, ( $\text{H}_2\text{Cr}_2\text{O}_7$ ). Chromium trioxide is a very powerful oxidising agent.
4. Oxidation number of chromium is +6 in both chromates and dichromates. However, in neutral aqueous solutions, dichromate ions exists in equilibrium with chromate ions as:



Thus in acidic medium, equilibrium shifts to the left and dichromate ions exists whereas in alkaline medium, only monomeric chromate ions exist.

uses:

- 1) Potassium dichromate is used as an important volumetric reagent for the estimation of  $\text{Fe}^{2+}$ ,  $\text{I}^-$ ,  $\text{SO}_3^{2-}$  etc

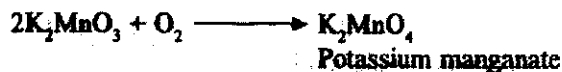
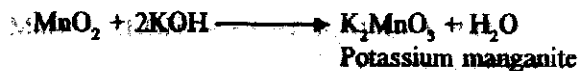
- 2) It is used in the manufacture of chrome alum,  $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$  an important compound used in the tanning of leather and dyeing of fabrics.

### INTEXT QUESTIONS 22.1

- Name the starting materials used in the preparation of soluble chromates and dichromates.  
.....
- How is sodium chromate converted into sodium dichromate.  
.....
- Calculate the equivalent weight of potassium dichromate.  
.....
- What happens when potassium dichromate is heated with a chloride and concentrated sulphuric acid.  
.....
- Give the molecular formula of chromalum. What are its uses?  
.....

### 22.4 POTASSIUM PERMANGANATE

**General :** When pyrolusite ore of manganese dioxide is fused with hydroxide of sodium or potassium in presence of air or an oxidising agent such as potassium nitrate or chlorate, the potassium or sodium manganite first formed is converted into a dark green mass of corresponding manganate as follows.



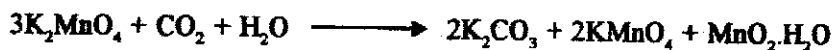
The dark green mass of potassium manganate is dissolved in a small quantity of cold water to form a dark green solution from which dark green crystals of manganate can be obtained on concentration.

#### Conversion of potassium manganate into potassium permanganate

Any of the following methods can be used for preparing potassium permanganate.

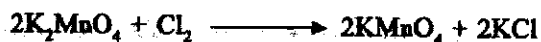
- When green concentrated solution of potassium manganate is gently warmed, or largely diluted with water, the green colour changes to pink owing to the formation of

potassium permanganate. Potassium manganate is not hydrolyzed in alkaline solutions or in pure water. Even a trace of acid, like carbonic acid, is enough to bring about the hydrolysis.

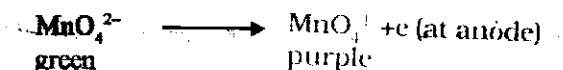


- (2) Potassium manganate may also be converted into potassium permanganate by oxidation either chemically with chlorine or ozone or electrolytically at the anode.

Chemical oxidation:



Anodic oxidation:



### Physical properties

Potassium permanganate forms dark purple red rhombic prisms which have a green iridescence. It is sparingly soluble in water (5.31 g in 100 ml at 15°) giving a deep-purple solution which is opaque until very dilute. The crystals on heating evolve oxygen and form a black powder of potassium manganate and manganese dioxide.



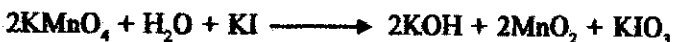
### Chemical properties

Potassium permanganate is a powerful oxidising agent. The action is different in alkaline, neutral and acidic solutions

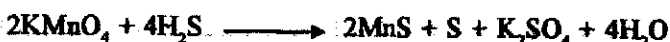
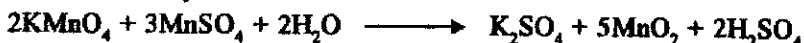
- (i) In alkaline solution: Two molecules of  $KMnO_4$  give three atoms of available oxygen.



Alkaline permanganate oxidises iodides to iodates.



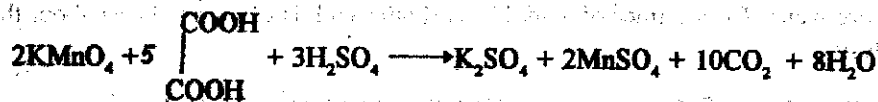
- (ii) In neutral solution,  $KMnO_4$  oxidises  $Mn^{2+}$  salts to  $MnO_2$  and  $H_2S$  to  $S$  as follows:



- (iii) In acidic solution, two molecules of permanganate are reduced to manganese (II) salt and five atoms of oxygen are liberated



Oxalic is oxidized to carbon dioxide.



The reaction is slow at first unless some manganese (II) sulphate is added which acts as a catalyst. The oxidation reaction is usually carried out in presence of  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  is avoided as it is oxidized to  $\text{Cl}_2$  gas.

**Uses:**

1. Potassium permanganate is used as an oxidising agent in the laboratory and in industry.
2. Because of its oxidising properties, it is used for disinfecting wells and lake water, as mouth wash, for washing wounds and gargling during throat infections.
3. It is used as a reagent in volumetric analysis for estimating Iron (II) ion, oxalic acid, oxalate ion, sulphites and hydrogen peroxide.

## INTEXT QUESTIONS 22.2

1. How is potassium manganate converted into potassium permanganate?  
.....
2. Give reactions of  $\text{KMnO}_4$  to show that it acts as an oxidising agent in neutral, alkaline and acidic media.  
.....
3. Why  $\text{KMnO}_4$  is added to wells and lakes from where water is drawn for drinking.  
.....

## 22.5 COPPER SULPHATE

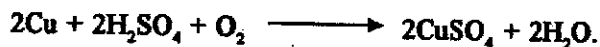
**General:** copper sulphate pentahydrate is commercially known as 'blue vitriol'. It forms large, transparent blue triclinic crystals.

**Preparation**

- (i) Pure copper sulphate is made in the laboratory by dissolving either copper oxide or copper hydroxide or copper carbonate in dilute sulphuric acid and evaporating the solution to crystallization point.
- (ii) On commercial scale it is prepared by either of the following methods.
  - (a) Scrap copper is heated in a reverberatory furnace with sulphur. Copper (II) sulphide thus formed is oxidized to sulphate using air as oxidant. Impure copper

sulphate is leached with dilute sulphuric acid and crystallized; insoluble impurities are separated out during leaching.

- (b) Dilute sulphuric acid is sprayed on the scrap copper in a lead-lined tower in which air is blown upwards. The solution so formed is circulated until sufficient concentration of copper sulphate is reached.



### Properties

1. Copper sulphate pentahydrate loses four water molecules at  $100^\circ\text{C}$ , the residual monohydrate is bluish white. The fifth water molecule is more tightly bound and is lost only at  $230^\circ\text{C}$  when white anhydrous copper sulphate is formed. This is highly hygroscopic and turns blue on absorption of water. On heating at  $750^\circ$  decomposes to give copper oxide and sulphur trioxide.

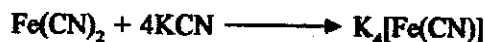
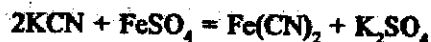


### Uses:

- 1 It is used in the manufacture of green pigments containing copper carbonates.
- 2 It is extensively used in making electroplating baths and in storage batteries.
- 3 It is used as a mordant in the dyeing and printing industry.
- 4 It is used for preserving timber and as fungicide for fruit trees. As fungicide it is applied as solution called Bordeaux mixture formed by mixing copper sulphate solution with milk of lime (CaO).
- 5 It is used in preparing laboratory reagents like Fehlings solution and Benedict's reagent.

## 22.6 POTASSIUM FERROCYANIDE

Preparation : Potassium ferrocyanide is formed by adding excess of potassium cyanide to a solution of Iron (II) sulphate until the brown precipitate, formed initially, redissolves



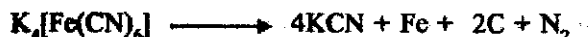
Potassium ferrocyanide is also obtained when crude coal gas is passed through a solution of Iron (II) sulphate and alkali to remove cyanides.

On commercial scale, potassium ferrocyanide is manufactured when nitrogenous refuse (blood, horns, leather scraps etc.) is fused with potassium carbonate and iron fillings. The fused mass is then digested with water and filtered. The solution on evaporation deposits yellow crystals of potassium ferrocyanide,  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$

### Properties

Potassium ferrocyanide crystallizes as laminated sulphur yellow crystals. It is soluble in

water, the aqueous solution is better in taste but not particularly poisonous. The salt decomposes on heating as follows:



When heated with dilute sulphuric acid, HCN is formed whereas carbon monoxide is formed on heating with concentrated acid.

**Uses:**

1. It is used as a laboratory reagent for the qualitative detection of copper, molybdenum etc.
2. It is used in the manufacture of prussian blue.

## 22.7 CALAMINE

**Preparation :** Zinc carbonate occurs native as calamine. In laboratory it is formed when zinc oxide dissolve in water containing carbon dioxide. Zinc carbonate is also precipitated when sodium bicarbonate is added to a soluble zinc salt. However , addition of a sodium carbonate solution precipitates basic carbonate ( $ZnCO_3 \cdot 2Zn(OH)_2 \cdot H_2O$ ).

**Properties**

Calamine is chemically basic zinc carbonate. It is a white powder but the commercial sample is pink because of the presence of traces of iron oxide. It decomposes on heating to form zinc oxide.

**Uses:**

Calamine has mild astringent and antiseptic actions and is used as a lotion and a dusting powder in a variety of skin disorders.

## INTEXT QUESTIONS 22.3

1. Why all the five water molecules present in  $CuSO_4 \cdot 5H_2O$  crystals, not lost on heating at  $100^\circ C$ .  
.....
2.  $CuSO_4 \cdot 5H_2O$  Crystals on heating lose colour to give a white powder. What happens when
  - (i) a drop of water is added to this white powder,
  - (ii) When it is heated to  $750^\circ C$  or more.
 .....
3. What is Bordeaux mixture and what is its use?  
.....

4. How is Potassium ferrocyanide prepared from slaughter house waste.

.....

5. Write two uses of calamine.

.....

## 22.8 WHAT YOU HAVE LEARNT

- Potassium dichromate and potassium permanganate are prepared from chromite and pyrolusite ores respectively.
- Both  $K_2Cr_2O_7$  and  $KMnO_4$  are oxidising agents. The former acts only in acidic medium while the later acts in alkaline, neutral as well as acidic media.
- Potassium ferrocyanide is prepared on large scale from the nitrogen refuse, potassium carbonate and iron fellings.
- Coppersulphate is used to prepare Bordeaux mixture, a fungicide and Fehling and Bannedicts reagents.
- Calamine is an antiseptic.

## 22.9 TERMINAL EXERCISE

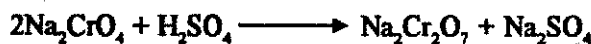
1. Do you think a solution of potassium ferrocyanide gives normal reactions of ferrous ions? Explain.
2. Give uses of calamine.
3. State uses of copper sulphate.
4. Zinc salts are white in colour but calamine is light pink. Comment.
5. What is prussian blue? How is it prepared?
6. Write molecular formula of potassium manganate and calculate oxidation number of manganese in this compound.
7. Under what conditions potassium permanganate will oxidise
  - (i) KI
  - (ii)  $MnSO_4$

## CHECK YOUR ANSWERS

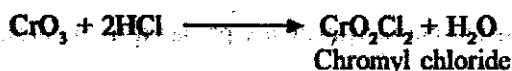
### INTEXT QUESTIONS 22.1

1. Mineral chromite or chrome iron stone (Ferrous chromite,  $FeO.Cr_2O_3$  or  $FeCr_2O_4$ ) and alkali metal oxides, hydroxides or carbonates are starting materials for the preparation of chromates.

2. Sodium chromate on treatment with Concentrate sulphuric acid forms sodium dichromate.

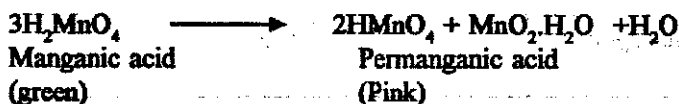
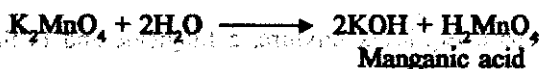


3. Chromyl chloride, an orange red gas is formed.



### INTEXT QUESTIONS 22.2

1. When green solution of potassium manganate is gently warmed, manganese dioxide is precipitated and permanganic acid is formed.



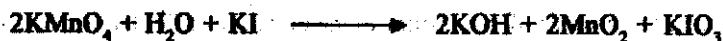
On separation manganese dioxide and evaporating the solution, dark purple red rhombic prisms of  $\text{KMnO}_4$  separate out.

2.  $\text{KMnO}_4$  acts as oxidising agent over a wide pH range.

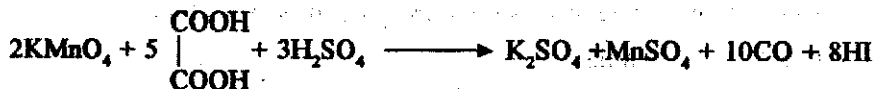
- (i) In neutral medium: It oxidises sulphides to sulphur and  $\text{Mn}^{2+}$  to  $\text{Mn}^{4+}$ .



- (ii) In alkaline medium, it oxidises iodides to iodates.



- (iii) In acidic medium, oxalic acid is oxidised to carbon dioxide.



3. Because of its oxidising properties it is added to wells, lakes etc to destroy microbes. It is an excellent disinfectant.

### INTEXT QUESTIONS 22.3

1. Four of the five water molecules are Water of Crystallisation while the fifth molecule is the Water of Co-ordination. It is lost only above  $230^\circ\text{C}$ .

2. (i) On adding a drop of water, the blue colour is restored.

- (ii) On heating to  $750^\circ\text{C}$ ,  $\text{CuSO}_4$  decomposes to  $\text{CuO}$  and  $\text{SO}_3$ .

3. Bordeaux mixture is formed by mixing copper sulphate solution with milk of lime (CaO). It is a fungicide and is used to pressure timber and fruit.
4. Slaughter house waste contains nitrogenous refuse like blood, horn, leather etc. It is fused with  $K_2CO_3$  and iron filling and the fused mass digested with water and filtered. On evaporating the solution, yellow crystals of  $K_4[Fe(CN)_6]$  separate out.
5. Calamine is an antiseptic. It is used in the form of lotion and dusting powder in a variety of skin disorders.

### TERMINAL EXERCISES

1. Since iron atom is a part of coordination complex species, it does not respond to normal reactions of Iron (II) ions.
2. Calamine has mild astringent and antiseptic actions and is used as a lotion and a dusting powder in a variety of skin disorders.
3. It is used in the manufacture of green pigments containing copper carbonates. It is extensively used in making electroplating baths and in storage batteries. It is used as a mordant in the dyeing and printing industry. It is used for preserving timber and as fungicide for fruit trees. As fungicide it is applied as a solution called Bordeaux mixture formed by mixing copper sulphate solution with milk of lime (CaO). It is used in preparing laboratory reagents like Fehling's solution and Benedict's reagent.
4. Calamine is coloured light pink due to impurities of iron compounds.
5.  $KFe[Fe(CN)_6]$ . It is prepared by reacting an Iron (III) salt solution with potassium ferrocyanide.
6.  $K_2Mn_2O_4$ . Oxidation number of manganese is +6.
7. (i) Alkaline, (ii) neutral, and (iii) acidic.

(i) Alkaline permanganate oxidises iodides to iodates.



(ii) In neutral solution,  $KMnO_4$  oxidises  $Mn^{2+}$  salts to  $MnO_2$ .



(iii) In acidic solution, oxalic is oxidized to carbon dioxide.

