THE D-AND F-BLOCK ELEMENTS

COMPOUND OF D-BLOCK ELEMENTS

FORMATION OF ALLOY

- (a) Transition elements have maximum tendency to form alloys.
- (b) The reactivity of transition elements is very less and their sizes are almost similar. Due to this a transition metal atom in the lattice can be easily replaced by other transition metal atom and hence they have maximum tendency to form alloys.
- (c) In the alloys, ratio of component metals is fixed.
- (d) These are extremely hard and have high melting point.

SOME IMPORTANT ALLOY

| (a) | Bronze | Cu (75 - 90 %) +Sn (10 - 25 %) |
|-----|-------------------|--|
| (b) | Brass | Cu (60 - 80 %) +Zn (20 - 40 %) |
| (c) | Gun metal | (Cu + Zn + Sn) (87 : 3 : 10) |
| (d) | German Silver | Cu + Zn + Ni (2 : 1 : 1) |
| (e) | Bell metal | Cu (80 %) + Sn (20 %) |
| (f) | Nichrome | (Ni + Cr + Fe) |
| (g) | Alnico | (Al, Ni, Co) |
| (h) | Type Metal | Pb + Sn + Sb |
| (i) | Alloys of steel | |
| | l Vanadium steel | V (0.2 - 1 %) |
| | l Chromium steel | Cr (2 - 4 %) |
| | l Nickel steel | Ni (3 -5 %) |
| | l Manganese steel | Mn (10 - 18 %) |
| | l Stainless steel | Cr (12 - 14 %) & Ni (2 - 4 %) |
| | l Tungsten steel | W (10 - 20 %) |
| | l Invar | Ni (36 %) |
| (j) | 14 Carat Gold | 54 % Au + Ag (14 to 30 %) + Cu (12 - 28 %) |
| (k) | 24 Carat Gold | 100 % Au |
| (l) | Solder | Pb + Sn |
| (m) | Magnalium | Mg (10%) + Al (90%) |
| (n) | Duralumin | (Al + Mn + Cu) |
| (0) | Artificial Gold | Cu (90 %) + Al (10%) |

(p) Constantan Cu(60%) + Ni(40%)

% of Carbon in Different Type of Iron

| | Name | % of C |
|-----|--------------|-------------|
| (a) | Wrought Iron | 0.1 to 0.25 |
| (b) | Steel | 0.25 to 2.0 |
| (c) | Cast Iron | 2.6 to 4.3 |
| (d) | Pig Iron | 2.3 to 4.6 |

Formation of Interstitial Compounds

- (a) Transition elements form interstitial compounds with smaller sized nonmetal elements like hydrogen, carbon, boron, nitrogen etc.
- (b) The smaller sized atoms get entrapped in between the interstitial spaces of the metal lattices.

These interstitial compounds are non-stoichiometric in nature and hence cannot be given any definite formula.

- (c) The smaller sized elements are held in interstitial spaces of transition elements by weak Vander Waals forces of attractions.
- (d) The interstitial compounds have essentially the same chemical properties as the parent metals but they differ in physical properties such as density and hardness.The process of adsorption of excess of H atom by the transition metals like Pd, Pt etc is called occlusion.

Non-stoichiometry

- (a) The transition elements sometimes form nonstoichiometric compounds due to variable valency.
- (b) These are the compounds of indefinite structure & proportion.
- (c) For example, Iron (II) Oxide FeO should be written as a bar over the formula FeO to indicate the ratio of Fe & O atom is not exactly 1:1 (FeO .94 O & FeO.84 O), V Se (VSe0.98VSe1.2),
- (d) Non stoichiometry is shown particularly among transition metal compounds of the group 16 elements (0, S, Se, Te).

(e) Sometimes nonstoichiometric is caused by defect in the solid structure.

```
Potassium Dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>)
PREPARATION
```

It is prepared from Chromite ore or Ferrochrome or Chrome iron. (Fe $0.Cr_2O_3$ or Fe Cr_2O_4). The various steps involved are.

(a) Preparation of sodium chromate (Na_2CrO_4) :

The powdered chromite ore in fused with sodium hydroxide or sodium carbonate in the presence of air in a reverberatory furnace.

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

or $4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \longrightarrow 8\text{Na}_2\text{Cr}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2$

After the reaction the roasted mass is extracted with water. So sodium chromate is completely dissolved while ferric oxide is left behind.

(b) Formation of sodium dichromate (Na₂Cr₂O₇) from sodium chromate (Na₂CrO₄): The solution of sodium chromate is filtered and acidified with dil./con. H₂SO₄ acid giving its dichromate.

 $2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O_4$

On cooling, sodium sulphate being less soluble crystallizes out as $Na_2SO_4.10H_2O$ and is removed. The resulting solution contains sodium dichromate ($Na_2Cr_2O_7$).

(c) Formation of potassium dichromate from sodium dichromate:

The hot concentrate solution of sodium dichromate is heated with calculated amount of KCl.

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

Sodium chloride, being the least soluble precipitates out from the hot solution and is removed by filtration. Orange red crystals of potassium dichromate separate out from mother liquid on cooling.

PROPERTIES

- (A) Colour and Melting Point: Orange red crystals. 670 K
- (B) Solubility: Moderately soluble is cold water but readily soluble in hot water.

(C) Action of Heat: - It decompose on heating to give potassium chromate, chromic oxide and oxygen.

 $\begin{array}{c} 4\text{K}_2\text{Cr}_2\text{O}_7 \xrightarrow[\text{Heat}]{} 4\text{K}_2\text{Cr}\text{O}_4 + 2\text{Cr}_2\text{O}_3 + 3\text{O}_2\\ & \text{Potassium} \quad \text{Chromic}\\ & \text{chromate} \quad \text{oxide} \end{array}$

(D) Action of Alkalies: - On heating with alkalies the orange colour of dichromate solution changes to yellow due to the formation of chromate ions.

 $K_2Cr_2O_7 + 2KOH \longrightarrow 2K_2CrO_4 + H_2O$ $Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$

or

 $Cr_2 0_7^{2-}$

This chromate on acidifying reconverts into dichromate.

$$2K_2CrO_4 + H_2SO_4 \longrightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O_5$$

or $2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$

The interconversion is explained by the fact that dichromate ion and chromate ion exist in equilibrium at a pH of about 4.

$$\operatorname{Cr}_2 \operatorname{O}_7^{2-} + \operatorname{H}_2 \operatorname{O} \xrightarrow{\operatorname{HCrO}_4^{2-}} 2\operatorname{CrO}_4^{2-} + 2\operatorname{H}^+$$

When alkali added, H⁺ consumed so forward direction. When acid added, H⁺ increases so backward direction.

(E) Chromyl chloride Test :- When potassium dichromate is heated with conc. H₂SO₄ acid and a soluble metal chloride (ex. NaCl) orange red vapours of chromyl chloride (CrO₂Cl₂) are formed.

 $K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \longrightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O_2Cl_2 + 3H_2O_2CCl_2 + 3H_$

(F) Reaction with H₂O₂:- Acidified solution of dichromate ions give deep blue colour solution with H₂O₂ due to the formation of [CrO(O₂)₂] or CrO₅. The blue colour fades away gradually due to the decomposition of CrO₅ into Cr⁺³ ions and oxygen.

$$+ 4H_2O_2 + 2H^+ \rightarrow 2CrO_5 + 5H_2O$$

(Butterfly structure)

Chemistry

(G) Action with HCl: - Potassium dichromate reacts with hydrochloric acid and evolves chlorine.

 $K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$

(H) Action of con. H₂SO₄

(i) In cold, red crystals of chromic anhydride are formed.

 $K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow 2CrO_3 + 2KHSO_4 + H_2O$

(ii) On heating the mixture oxygen is evolved.

 $2K_2Cr_2O_7 + 8H_2SO_4 \longrightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$

(I) Oxidising properties

The dichromats act as powerful oxidising agent in acidic medium. In presence of dil H₂SO₄, K₂Cr₂O₇ liberates Nascent oxygen and therefore acts as an oxidising agent.

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

In terms of electronic concept, the ion takes up electrons in the acidic medium and hence acts as an oxidising agent.

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

(i) It oxidizes iodides to iodine: -

(ii) Acidified ferrous sulphate to ferric sulphate

+
$$14H^+ + 6e^- \longrightarrow 2Cr^{+3} + 7H_20$$

Fe⁺² \longrightarrow Fe³⁺ + e⁻] × 6
+ $14H^+ + 6Fe^{+2} \longrightarrow 2Cr^{+3} + 6Fe^{+3} + 7H_20$
K₂Cr₂O₇ + $6FeSO_4 + 7H_2SO_4 \longrightarrow Cr_2 (SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_20 + K_2SO_4$

or

0r

Chemistry

(iii) Oxidises H₂S to sulphur

$$+ 14H^{+} + 6e^{-} \longrightarrow 2Cr^{+3} + 7H_2O$$

$$H_2S \longrightarrow S + 2H^{+} + 2e^{-}] \times 3$$

$$+ 3H_2S + 8H^{+} \longrightarrow 2Cr^{+3} + 3S + 7H_2O$$
or
$$K_2Cr_2O_7 + 3H_2S + 4H_2SO_4 \longrightarrow Cr_2 (SO_4)_3 + 3S + 7H_2O + K_2SO_4$$

Similarly, it oxidizes sulphites to sulphates, chlorides to chlorine, nitrites to nitrates, thiosulphates to sulphates and sulphur and stannous (Sn^{+2}) salts to stannic (Sn^{+4}) salts.

$$3SO_{3}^{-2} + Cr_{2}O_{7}^{2-} + 8H^{+} \rightarrow 3SO_{4}^{2-} + 2Cr^{3+} + 4H_{2}O$$

$$3NO_{2}^{-} + Cr_{2}O_{7}^{2-} + 8H^{+} \rightarrow 3NO_{3}^{-} + 2Cr^{3+} + 4H_{2}O$$

$$3S_{2}O_{3}^{2-} + Cr_{2}O_{7}^{2-} + 8H^{+} \rightarrow 3SO_{4}^{2-} + 3S + 2Cr^{3+} + 4H_{2}O$$

$$6Cl^{-} + Cr_{2}O_{7}^{2-} + 14H^{+} \rightarrow 3Cl_{2} + 2Cr^{3+} + 7H_{2}O$$

$$3Sn^{+2} + Cr_{2}O_{7}^{2-} + 14H^{+} \rightarrow 3Sn^{+4} + 2Cr^{3+} + 7H_{2}O$$

It oxidizes SO_2 to sulphuric acid.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$
$$SO_2 + O + H_2O \longrightarrow H_2SO_4$$

USES

- (a) For volumetric estimation of ferrous salts, iodides and sulphites.
- **(b)** For preparation of other chromium compounds such as chrome alum (K_2SO_4 , $Cr_2(SO_4)_3.24H_2O$), chrome yellow (PbCrO₄) and chrome red (PbCrO₄.PbO).
- (c) Used in photography for hardening of gelatin film.
- (d) It is used in leather industry (chrome tanning)
- (e) Chromic acid mixture is used for cleaning glassware, consist of K₂Cr₂O₇ and Con.
 H₂SO₄.
- (f) In organic chemistry, it is used as an oxidising agent.
- (g) In dyeing and calico printing.

STRUCTURE

The chromate ion has tetrahedral structure in which four atoms around chromium atom are oriented in a tetrahedral arrangement.



Chromate ion

The structure of dichromate ion consists of two tetrahedra sharing an oxygen atom at the common corner.



POTASSIUM PERMANGANATE (KMnO₄) PREPARATION

Potassium permanganate is prepared from mineral pyrolusite (MnO_2) . The preparation involves the following steps.

(a) Conversion of pyrolusite ore to potassium manganate

The pyrolusite MnO_2 is fused with caustic potash (KOH) or potassium carbonate in the presence of air or oxidising agents, such as KNO_3 or $KClO_3$ to give a green mass due to the formation of potassium manganate (K_2MnO_4).

 $2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$ $2MnO_2 + 2K_2CO_3 + O_2 \longrightarrow 2K_2MnO_4 + 2CO_2$

(b) Oxidation of potassium manganate to potassium permanganate

The green mass is extracted with water resulting is green solution of potassium manganate. The solution is then treated with a current of Cl_2 or ozone or CO_2 to

Chemistry

oxidize K_2MnO_4 to $KMnO_4$. The solution is concentrated and dark purple crystals of $KMnO_4$ separate out.

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KCl + 2KMnO_4$$
$$2K_2MnO_4 + O_3 + H_2O \longrightarrow 2KMnO_4 + 2KOH + O_2$$
$$3K_2MnO_4 + 2CO_2 \longrightarrow 2K_2CO_3 + MnO_2\downarrow + 2KMnO_4$$

Alternatively, alkaline potassium manganate is electrolytically oxidised.

Electrolytic method :- The potassium manganate solution is taken in an electrolytic cell which contains iron cathode and nickel anode. When current is passed the manganate ion in oxidised to permanganate ion at anode and hydrogen is liberated at cathode.

$$K_2MnO_4 \longrightarrow 2K^+ + MnO_4^2 -$$

At anode: $MnO_4^{-2} \longrightarrow MnO_4^{-} + e^{-}$

Green Purple

At cathode: $2H^+ + 2e^- \longrightarrow 2H$

$$2H \longrightarrow H_2$$

PROPERTIES

- (a) Colour and M.P.: Dark violet crystalline solid, M.P. 523 K
- **(b) Solubility: -** Moderately soluble is room temperature, but fairly soluble in hot water giving purple solution.
- (c) Heating: When heated strongly it decomposes at 746 K to give K_2MnO_4 and O_2 .

$$2KMnO_4 \xrightarrow{746 k} K_2MnO_4 + MnO_2 + O_2$$

Solid KMnO₄ gives KOH, MnO and water vapours, when heated in current of hydrogen.

$$2KMnO_4 + 5H_2$$
 $2KOH + 2MnO + 4H_2O$

(d) Action of alkali :- On heating with alkali, potassium permanganate changes into potassium manganate and oxygen gas is evolved.

 $4KMnO_4 + 4KOH \longrightarrow 4K_2MnO_4 + 2H_2O + O_2$

Chemistry

(e) Action of con. H₂SO₄: - With cold H₂SO₄, it gives Mn₂O₇ which on heating decomposes into MnO₂.

 $2KMnO_4 + 2H_2SO_4 \longrightarrow Mn_2O_7 + 2KHSO_4 + H_2O$ $2Mn_2O_7 \longrightarrow 4MnO_2 + 3O_2$

(f) Oxidising character: - KMnO₄ acts as powerful oxidising agent in neutral, alkaline or acidic solution because it liberates nascent oxygen as :-

Acidic solution :- Mn⁺² ions are formed

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

or
$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O$$
 [equal wt. $= \frac{M}{r}$]

Neutral solution :- MnO₂ is formed

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

or $MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$ [equal wt. $= \frac{M}{3}$]

During the reaction the alkali produced generates the alkaline medium even if we start from neutral medium.

Alkaline medium :- Manganate ions are formed.

 $2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + [0]$

Reactions in Acidic Medium : In acidic medium KMnO4 oxidizes -

(a) Ferrous salts to ferric salts

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

$$Fe^{+2} \longrightarrow Fe^{+3} + e^{-}] \times 5$$

$$MnO_4^- + 5Fe^{+2} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{+3} + 4H_2O$$

(b) Oxalates to CO_2 :

 $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O] \times 2$

 $C_2 O_4^{2-} \longrightarrow 2CO_2 + 2e^{-}] \times 5$

Chemistry

$$2MnO_4^- + 5C_2O_4^2^- + 16H^+ \longrightarrow 2Mn^{+2} + 10CO_2 + 8H_2O_2^-$$

(c) Iodides to Iodine

 $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O] \times 2$ $2I^- \longrightarrow I_2 + 2e^-] \times 5$ $10I^- + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{+2} + 5I_2 + 8H_2O$

(d) Sulphites to sulphates

 $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O] \times 2$ $SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-] \times 5$

$$5SO_3^{2-} + 2MnO_4^{-} + 6H^+ \longrightarrow 2Mn^{+2} + 5SO_4^{2-} + 3H_2O$$

(e) It oxidizes H₂S to S

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O] \times 2$$

$$S^{2-} \longrightarrow S + 2e^-] \times 5$$

$$2MnO_4^- + 16H^+ + 5S^{-2} \longrightarrow 2Mn^{+2} + 5S + 8H_2O$$

(f) It oxidizes SO₂ to sulphuric acid

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

 $SO_2 + H_2O + [O] \longrightarrow H_2SO_4] \times 5$

 $2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$

(g) It oxidizes Nitrites to nitrates

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

 $KNO_2 + 0 \longrightarrow KNO_3] \times 5$

 $2KMnO_4 + 5KNO_2 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5KNO_3 + 3H_2O$

Reactions in Neutral Medium:

(a) It oxidizes H₂S to sulphur:

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

 $H_2S + 0 \longrightarrow H_2O + S] \times 3$

 $2KMnO_4 + 3H_2S \longrightarrow 2KOH + 2MnO_2 + 2H_2O + 3S$

(b) It oxidizes Manganese sulphate (MnSO₄ to MnO₂) manganese dioxide:

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3 [0]$$

$$MnSO_4 + H_2O + O \longrightarrow MnO_2 + H_2SO_4] \times 3$$

$$2KOH + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O$$

$$2KMnO_4 + 3MnSO_4 + 2H_2O \longrightarrow 5MnO_2 + K_2SO_4 + 2H_2SO_4$$

(c) It oxidizes Sodium thiosulphate to sulphate and sulphur :

 $2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3[0]$

 $Na_2S_2O_3 + 0 \longrightarrow Na_2SO_4 + S] \times 3$

 $2KMnO_4 + 3Na_2S_2O_3 + H_2O \longrightarrow 2MnO_2 + 3Na_2SO_4 + 2KOH + 3S$

Reactions in Alkaline Medium

(a) It oxidizes Iodides to Iodates in alkaline medium:

 $2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3 [O]$ KI +30 \longrightarrow KIO₃

 $2KMnO_4 + KI + H_2O \longrightarrow 2MnO_2 + 2KOH + KIO_3$

(b) Alkaline KMnO₄ (Baeyer's reagent) oxidizes ethylene to ethylene glycol.



STRUCTURE

 MnO_4^-



USES

- (a) Used in volumetric analysis for estimation of ferrous salts, oxalates, and other reducing agents. It is not used as primary standard because it is difficult to obtain it in the pure state.
- (b) It is used as strong oxidising agent in the laboratory as well as industry.
- (c) As disinfectant and germicide.
- (d) In dry cells.
- (e) A very dilute solution of KMnO₄ is used for washing wounds.
- **Ex.** Potassium permanganate acts as an oxidant in neutral, alkaline as well as acidic media. The final products obtained from it in three conditions are respectively:

(A)
$$MnO_4^{2-}$$
, Mn^{3+} and Mn^{2+} (B) MnO_2 , MnO_2 and Mn^{2+}

(C)
$$MnO_2$$
, MnO_2^+ and Mn^{3+} (D) MnO_1 , MnO_2^+ and Mn^{2+}

Sol.

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

 $e^- + MnO_4^- \longrightarrow MnO_4^{-2}$ (dilute alkaline medium)

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

Therefore, (B) option is correct.

POTASSIUM DICHROMATE (K₂Cr₂O₇) :

PREPARATION

The chromite ore is roasted with sodium carbonate in presence of air in a reverberatory furnace

Chemistry

$$4\text{FeO. } \text{Cr}_2\text{O}_3 \text{ (chromite ore)} + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \frac{\text{Roasting}}{\text{in air}}$$
$$8\text{Na}_2\text{Cr}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2$$

The roasted mass is extracted with water when Na_2CrO_4 goes into the solution leaving behind insoluble Fe_2O_3 . The solution is then treated with calculated amount of H_2SO_4 .

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

The solution is concentrated when less soluble Na₂SO₄ crystallizes out. The solution is further concentrated when crystals of Na₂Cr₂O₇ are obtained. Hot saturated solution of Na₂Cr₂O₇ is then treated with KCl when orange red crystals of K₂Cr₂O₇ are obtained on crystallization.

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

Note: $K_2Cr_2O_7$ is preferred over $Na_2Cr_2O_7$ as a primary standard in volumetric estimation because $Na_2Cr_2O_7$ is hygroscopic in nature but $K_2Cr_2O_7$ is not.

PROPERTIES

(a) Physical:

It is orange-red coloured crystalline compound. It is moderately soluble in cold water but freely soluble in hot water. It melts at 398°C.

- (b) Chemical:
- (i) Effect of heating:

On heating strongly, it decomposes liberating oxygen.

$$2K_2Cr_2O_7 \rightarrow 2K_2CrO_4 + Cr_2O_3 + O_2$$

On heating with alkalies, it is converted to chromate, i.e., the colour changes from orange to yellow. On acidifying, yellow colour again changes to orange.

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

 $Cr_2O + 2OH^- \rightarrow 2CrO + H_2O$
Orange Yellow

Chemistry

$$2\text{Cr}0 + 2\text{H}^+ \rightarrow \text{Cr}_20 + \text{H}_20$$

Yellow Orange

Thus CrO_4^{2-} and $Cr_2O_7^{2-}$ exist in equilibrium and are interconvertible by altering the pH of solution.

$$2\text{Cr}0 + 2\text{H}^+ \rightleftharpoons 2\text{HCr}0_4^- \rightleftharpoons \text{Cr}_20 + \text{H}_20$$

In alkaline solution, chromate ions are present while in acidic solution, dichromate ions are present.

(ii) $K_2Cr_2O_7 + 2H_2SO_4$ (conc. & cold) $\longrightarrow 2CrO_3 \downarrow$ (bright orange/red) + 2KHSO_4 + H_2O

 $2K_2Cr_2O_7 + 8H_2SO_4 \text{ (conc. & Hot)} \longrightarrow 2K_2SO_4 + 8H_2O + 2Cr_2(SO_4)_3 + 3O_2$

(iii) Acidified K₂Cr₂O₇ solution reacts with H₂O₂ to give a deep blue solution due to the formation of CrO₅.

$$Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \longrightarrow 2CrO_5 + 5H_2O_2$$

Blue colour in aqueous solution fades away slowly due to the decomposition of CrO_5 to Cr^{3+} ions and oxygen. In less acidic solution $K_2Cr_2O_7$ and H_2O_2 give salt which is violet coloured and diamagnetic due to the formation of $[CrO(O_2)(OH)]^-$. In alkaline medium with 30% H_2O_2 , a red-brown K_3CrO_8 (diperoxo) is formed. It is tetra per oxo species $[Cr(O_2)_4]^{3-}$ and thus the Cr is in +V oxidation state. In ammoniacal solution a dark red-brown compound, (NH₃)₃CrO₄ - diperoxo compound with Cr(IV) is formed.

(iv) Potassium dichromate reacts with hydrochloric acid and evolves chlorine gas.

 $\text{K}_2\text{Cr}_2\text{O}_7 + 14\text{HCl} \rightarrow 2\text{KCl} + 2\text{Cr}\text{Cl}_3 + 7\text{H}_2\text{O} + 3\text{Cl}_2$

(v) It acts as a powerful oxidising agent in acidic medium (dilute H₂SO₄)

$$Cr_2O + 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O. (E^{\circ} = 1.33 V)$$

Chemistry

The oxidation state of Cr changes from + 6 to +3.

(a) Iodine is liberated from potassium iodide:

 $Cr_20 + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_20$

$$\frac{2I - \rightarrow I_2 + 2e - \times [3]}{Cr_2 0 + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 3I_2 + 7H_2 0}$$

(b) Ferrous salts are oxidised to ferric salts:

$$6Fe^{2+} + Cr_20 + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_20$$

(c) Sulphites are oxidised to sulphates:

$$Cr_2O + 3SO + 8H^+ \rightarrow 3SO + 2Cr^{3+} + 4H_2O$$

(d) H₂S is oxidised to sulphur:

$$Cr_2O + 3H_2S + 8H^+ \rightarrow 2Cr^{3+} + 7H_2O + 3S$$

(e) SO_2 is oxidised to H_2SO_4 :

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

Chrome alum is obtained when acidified $K_2Cr_2O_7$ solution is saturated with SO_2 .

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 + 23H_2O \xrightarrow{T < 70^{\circ}C} K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$$

(f) It oxidises ethyl alcohol to acetaldehyde and acetaldehyde to acetic acid

$$C_2H_5OH \xrightarrow{[0]} CH_3CHO \xrightarrow{[0]} CH_3COOH$$

ethyl alcohol acetaldehyde acetic acid

(g) It also oxidises nitrites to nitrates, arsenates to arsenates, HBr to Br_2 . HI to I_2 , etc.

(h)
$$K_2Cr_2O_7 + 2C$$
 (charcoal) $\xrightarrow{\Delta} Cr_2O_3 + K_2CO_3 + CO^{\uparrow}$

(vi) Chromyl chloride test:
$$4Cl^- + Cr_2O_7^{2-} + 6H^+ \rightarrow 2CrO_2Cl_2 \uparrow (deep red) + 3H_2O_2^{2-}$$

$$\operatorname{CrO}_2\operatorname{Cl}_2 + 4\operatorname{OH}^- \to \operatorname{CrO}_4^{2-} (\text{yellow}) + 2\operatorname{Cl}^- + 2\operatorname{H}_2\operatorname{O}_2^{2-1} (\text{yellow}) + 2\operatorname{Cl}_2^{2-1} (\text{yellow}) + 2\operatorname{$$

$$CrO_4^{2-}$$
 (yellow) + Pb²⁺ \rightarrow PbCrO₄ \downarrow (yellow)

(vii) $Cr_2O_7^{2-}$ (concentrated solution) + $2Ag^+ \rightarrow Ag_2Cr_2O_7 \downarrow$ (reddish brown)

$$Ag_2Cr_2O_7 + H_2O \rightarrow Ag_2CrO_4 + CrO_4^{2-} + 2H^+$$
.

(viii)

$$Cr_2O_7^{2-} + Ba^{2+} + H_2O \rightleftharpoons 2BaCrO_4 \downarrow + 2H^+$$

As strong acid is produced, the precipitation is only partial. But if NaOH or CH₃COONa is added, precipitate becomes quantitative.

USES

It is used:

- (i) As a volumetric reagent in the estimation of reducing agents such as oxalic acid, ferrous ions, iodide ions, etc. It is used as a primary standard.
- (ii) For the preparation of several chromium compounds such as chrome alum, chrome yellow, chrome red, zinc yellow, etc.
- (iii) In dyeing, chrome tanning, calico printing, photography etc.
- (iv) As a cleansing agent for glass ware in the form of chromic acid.
- Ex. An inorganic compound (A) has garnet red prismatic crystals.(A) is moderately soluble in water and dissolves in cold concentrated H₂SO₄ to yield red crystals (B). In presence of dilute H₂SO₄ it converts a pungent gas(C) into a yellow turbidity (D) and converts a suffocating gas (E) into a green solution (F). The gas (C)and (E) also combine to produce the yellow turbidity (D). With KI and starch in presence of dilute. H₂SO₄ (A) yields blue colour. (A) and concentrated H₂SO₄ mixture is used as a cleansing agent for glassware in the laboratory. Identify (A)and explain the reactions.
- **Sol.** As compound (A) has garnet red prismatic crystals which with cold conc. H₂SO₄ gives red crystals and a suffocating gas (SO₂) turns its solution in water in to green coloured solution, therefore compound (A) may be K₂Cr₂O₇.

$$\begin{array}{ccc}
\text{K}_2\text{Cr}_2\text{O}_7 + 4\text{H}_2\text{SO}_4 + 3\text{H}_2\text{S} &\longrightarrow & \text{KHSO}_4 + 2 \text{ CrO}_3 \text{ (red crystals)} + \text{H}_2\text{O} \\
\textbf{(A)} & \textbf{(B)} \\
\text{K}_2\text{Cr}_2\text{O}_7 + 4\text{H}_2\text{SO}_4 + 3\text{H}_2\text{S} &\longrightarrow & \text{K}_2\text{SO}_4 + \text{Cr}_2 \text{ (SO}_4\text{)}_3 + 7\text{H}_2\text{O} + 3\text{S} \downarrow \text{ (Yellow)} \\
\textbf{(C)} & \textbf{(D)} \\
\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 + 3\text{SO}_2 &\longrightarrow & \text{Cr}_2 \text{ (SO}_4\text{)}_3 \text{ (Green solution)} + \text{K}_2\text{SO}_4 + \text{H}_2\text{O} \\
\end{array}$$

(E) (F)

 $K_2Cr_2O_7 + 7H_2SO_4 + 6KI \longrightarrow 4K_2SO_4 + Cr_2 (SO_4)_3 + 7H_2O + 3I_2$ I₂ + Starch Blue colour

COMPOUNDS OF IRON

Ferrous Sulphate (Green Vitriol), FeSO4·7H2O:

This is the best known ferrous salt. It occurs in nature as copper and is formed by the oxidation of pyrites under the action of water and atmospheric air.

 $2\text{FeS}_2 + 70_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4$

It is commonly known as harakasis.

PREPARATION

It is obtained by dissolving scrap iron in dilute sulphuric acid.

 $Fe + H_2SO_4 \longrightarrow 2FeSO_4 + H_2$

The solution is crystallized by the addition of alcohol as ferrous sulphate is sparingly soluble in it.

PROPERTIES

(a) Action of heat: At 300°C, it becomes anhydrous. The anhydrous ferrous sulphate is colourless. The anhydrous salt when strongly heated, breaks up to form ferric oxide with the evolution of SO₂ and SO₃.

 $\begin{array}{cccc} FeSO_4 \cdot 7H_2O & \xrightarrow{300^\circ C} & 2FeSO_4 & \xrightarrow{High} \\ Green & \overrightarrow{-7H_2O} & White & \xrightarrow{temperature} \\ \end{array} Fe_2O_3 + SO_2 + SO_3 \end{array}$

(b) The aqueous solution of ferrous sulphate is slightly acidic due to its hydrolysis.

 $FeSO_4 + 2H_2O \rightleftharpoons Fe(OH)_2 + H_2SO_4$

Weak base Strong acid

(c) It reduces gold chloride to gold.

 $AuCl_3 + 3FeSO_4 \longrightarrow Au + Fe_2(SO_4)_3 + FeCl_3$

(d) It reduces mercuric chloride to mercurous chloride.

 $[2HgCl_2 \longrightarrow Hg_2Cl_2 + 2Cl] \times 3$

 $[3FeSO_4 + 3Cl \longrightarrow Fe_2(SO_4)_3 + FeCl_3] \times 2$

Chemistry

$$6HgCl + 6FeSO_4 \longrightarrow 3Hg_2Cl_2 + 2Fe2(SO_4)_3 + 2FeCl_3$$

(e) A cold solution of ferrous sulphate absorbs nitric oxide forming dark brown addition compound, nitroso ferrous sulphate.

 $FeSO_4 + NO \longrightarrow FeSO_4 \cdot NO$

Nitroso ferrous sulphate (Brown)

The NO gas is evolved when the solution is heated.

USES

- (a) Ferrous sulphate is used for making blue black ink.
- (b) It is used as a mordant in dyeing.
- (c) It is also used as an insecticide in agriculture.
- (d) It is employed as a laboratory reagent and in the preparation of Mohr's salt.

Ferrous-Oxide FeO (BLACK)

PREPARATION: $FeC_2O_4 \xrightarrow[In absence of air]{\Delta} FeO + CO + CO_2$

PROPERTIES: It is stable at high temperature and on cooling slowly disproportionate into Fe₃O₄ and iron

Ferrous Chloride (FeCl₂)

PREPARATION: Fe + 2HCl $\xrightarrow{\text{heated in}}_{a \text{ current of HCl}}$ FeCl₂ + H₂ **PROPERTIES:** 2FeCl₃ + H₂ $\xrightarrow{\Delta}$ 2FeCl₂ + 2HCl

- (a) It is deliquescent in air like FeCl₃
- (b) It is soluble in water, alcohol and ether also because it is sufficiently covalent in nature
- (c) It volatilizes at about 1000°C and vapour density indicates the presence of Fe₂Cl₄.
 Above 1300°C density becomes normal
- (d) It oxidises on heating in air

 $12FeCl_2 + 30_2 \longrightarrow 2Fe_2O_3 + 8FeCl_3$

(e) H₂ evolves on heating in steam

 $3FeCl_2 + 4H_2O \longrightarrow Fe_3O_4 + 6HCl + H_2$

Chemistry

(f) It can exist as different hydrated form

 $FeCl_2 \cdot 2H_2O \longrightarrow colourless$

 $FeCl_2 \cdot 4H_2O \longrightarrow pale green$

 $FeCl_2 \cdot 6H_2O \longrightarrow green$

COMPOUND OF ZINC Zinc Oxide (ZnO) Zinc White PREPARATION

(a) ZnO is formed when ZnS is oxidised

 $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$

(b) Zn(OH)₂ on strongly heating gives ZnO

 $Zn(OH)_2 ZnO + H_2O$

(c) Zinc on burning in air gives ZnO (commercial method)

 $2Zn + 0_2 \longrightarrow 2Zn0$

PROPERTIES

- (a) ZnO is white when it is cold, a property that has given it a use as a pigment in paints. However, it changes colour, when hot, to a pale yellow. This is due to change in the structure of lattice.
- (b) ZnO is soluble both in acid and alkali and is thus amphoteric in nature.

 $ZnO + 2H^+ \longrightarrow Zn^{2+} + H_2O$ $ZnO + 2OH^- + H_2O \longrightarrow [Zn(OH)_4]^2-$

or

zincate ion

$$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$$

$$ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$$

sodium zincate

(c)
$$\operatorname{ZnO} + \operatorname{C} \frac{\Delta}{>1000^{\circ}\mathrm{C}} \operatorname{Zn} + \operatorname{CO}$$

 $\operatorname{ZnO} + \operatorname{CO} \xrightarrow{\Delta} \operatorname{Zn} + \operatorname{CO}_2$

It is preferred to white lead as it is not blackened by H_2S . It is also used in medicine and in the preparation of Riemann's green ($ZnCo_2O_4$)

Zinc Sulphate (ZnSO₄)

PREPARATION

(a) $ZnSO_4 \cdot 7H_2O$ (also called white vitriol) is formed by decomposing $ZnCO_3$ with dil. H_2SO_4

 $ZnCO_3 + H_2SO_4 \longrightarrow ZnSO_4 + H_2O + CO_2$

(b) By heating ZnS (zinc blende) in air at lower temperature and dissolving the product in dil. H₂SO₄

$$2ZnS + 3.5O_2 \xrightarrow{\Delta} ZnO + ZnSO_4 + SO_2$$
$$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$$

PROPERTIES

(a) Highly soluble in water and solution is acidic in nature due to hydrolysis

 $ZnSO_4 + 2H_2O \longrightarrow Zn(OH)_2 + H_2SO_4$

(b)
$$\operatorname{ZnSO}_4 \cdot 7H_2O \xrightarrow{100^{\circ}C} \operatorname{ZnSO}_4 \cdot 6H_2O \xrightarrow{280^{\circ}C} \operatorname{ZnSO}_4 \xrightarrow{T > 760^{\circ}C} \operatorname{ZnO} + \operatorname{SO}_3$$

It slowly effloresces when exposed to air.

(c) It is isomorphous with Epsom salt and used in the manufacture of lithophone (which is a mixture of BaS + ZnSO₄ and is used as white pigment).

Zinc Chloride (ZnCl₂)

PREPARATION

 $ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$

 $ZnCO_3 + 2HCI \longrightarrow ZnCl_2 + H_2O + CO_2$

 $Zn(OH)_2 + 2HCI \longrightarrow ZnCl_2 + 2H_2O$

Anhydrous $ZnCl_2$ cannot be made by heating $ZnCl_2 \cdot 2H_2O$ because

 $ZnCl_2 \cdot 2H_2O Zn(OH)Cl + HCl + H_2O$

Zn(OH)Cl ZnO + HCl



 $\operatorname{Zn} + \operatorname{Cl}_2 \longrightarrow \operatorname{ZnCl}_2$

 $Zn + 2HCl(dry) \longrightarrow ZnCl + H_2$

 $\operatorname{Zn} + \operatorname{HgCl}_2 \longrightarrow \operatorname{ZnCl}_2 + \operatorname{Hg}$

PROPERTIES

- (a) It is deliquescent white solid (when anhydrous)
- **(b)** $ZnCl_2 + H_2S \longrightarrow ZnS$

 $ZnCl_2 + NaOH \longrightarrow Zn(OH)_2 \text{ excess } Na_2[Zn(OH)_4]$

 $ZnCl_2 + NH_4OH \longrightarrow Zn(OH)_2 excess [Zn(NH_3)_4]^2 +$

USES

- (a) Used for impregnating timber to prevent destruction by insects
- (b) As dehydrating agent when anhydrous
- (c) $ZnO \cdot ZnCl_2$ used in dental filling
- **Ex.** $\operatorname{Zn}(\operatorname{OH})_2 \xrightarrow{\Delta} [X].$

Select the correct statement (s) for the compound X.

- (A) X on heating with cobalt nitrate gives green mass
- (B) X on heating alone, becomes yellow but turns white on cooling.
- **(C)** Solution of X in dilute HCl gives bluish white/white precipitate with excess potassium ferrocyanide.
- (D) X is insoluble in aqueous sodium hydroxide.

Sol.

- (A) X is ZnO which on heating with cobalt nitrate gives ZnO. CoO, the Riemann's green.
- **(B)** It turns yellow on heating and becomes white on cooling.
- (C) $ZnCl_2$ forms bluish white/white precipitate. $Zn_3K_2[Fe(CN)_6]_2$.

 $3 \text{Zn}^{2+} + 2 \text{K}^{+} + 2 [\text{Fe}(\text{CN})_6]^{4-} \text{K}_2 \text{Zn}_3 [\text{Fe}(\text{CN})_6]_2 \downarrow$

(D) $ZnO + 2NaOH Na_2ZnO_2$ (soluble complex) + H₂O.

So options A, B & C are correct and (D) is incorrect.

COMPOUND OF SILVER Silver Nitrate (Lunar Caustic) AgNO₃ PREPARATION

(a) When Ag is heated with dil HNO₃, AgNO₃ is formed. Crystals separate out on cooling the concentrated solution of AgNO₃

 $3Ag + 4HNO_3 \xrightarrow{\Delta} 3AgNO_3 + NO + 2H_2O$

Colourless crystalline compound soluble in $\rm H_2O$ and alcohol; m.p. 212°C

(b) When exposed to light, it decomposes hence, stored in a brown-coloured bottle:

$$2Ag + 2NO_2 + O_2 \xrightarrow{\Delta, red hot} 2AgNO_3 \xrightarrow{\Delta, T > 212^\circ C} 2AgNO_2 + O_2$$

PROPERTIES

(a) It is reduced to metallic Ag by more electropositive metals like Cu, Zn, Mg and also by PH₃.

$$2AgNO_3 + Cu \longrightarrow Cu(NO_3)_2 + 2Ag$$

 $6AgNO_3 + PH_3 + 3H_2O \longrightarrow 6Ag + 6HNO_3 + H_3PO_3$

(b) It dissolves in excess of KCN:

 $AgNO_{3} \xrightarrow{KCN} AgCN \xrightarrow{KCN} K[Ag(CN)_{2}]$

white ppt soluble potassium argent cyanide

AgNO₃ gives white precipitate with $Na_2S_2O_3$; white precipitate changes to black.

 $2AgNO_3 + Na_2S_2O_3 \longrightarrow Ag_2S_2O_3 + 2NaNO_3$

white ppt

$$Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S + H_2SO_4$$

black

(c) Ammoniacal AgNO₃ is called Tollen's reagent and is used to identify reducing sugars (including aldehydes):

$$\text{RCHO} + 2\text{Ag}^+ + 30\text{H}^- \xrightarrow{\Delta} \text{RCOO}^- + 2\text{Ag}^{\downarrow} + 2\text{H}_2\text{O}$$

It is called 'silver mirror test' of aldehydes and reducing sugar (like glucose, fructose).

Some important reaction of AgNO3



COMPOUND OF COPPER

Cupric Oxide (CuO)

It is called black oxide of copper and is found in nature as tenorite.

PREPARATION

(a) By heating Cu₂O in air or by heating copper for a long time in air (the temperature

should not exceed above 1100°C)

$$Cu_2 0 + \frac{1}{2} 0_2 \longrightarrow 2Cu 0$$

$$2cu + 02 \longrightarrow 2cuc$$

(b) By heating cupric hydroxide,

 $Cu(OH)_2 \longrightarrow CuO + H_2O$

(c) By heating copper nitrate,

 $2Cu(NO_3)_2 \longrightarrow 2CuO + 4NO_2 + O_2$

(d) On a commercial scale, it is obtained by heating molachite which is found in nature.

 $CuCO_3 \cdot Cu(OH)_2 \longrightarrow 2CuO + CO_2 + H_2O$

PROPERTIES

- (a) It is black powder and stable to moderate heating.
- (b) The oxide is insoluble in water but dissolves in acids forming corresponding salts.

Class-12th

 $CuO + 2HCl \longrightarrow CuCl_2 + H_2O$

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

 $CuO + 2HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O$

(c) When heated to 1100 – 1200°C, it is converted into cuprous oxide with evolution of oxygen.

 $4Cu0 \longrightarrow 2Cu_20 + 0_2$

(d) It is reduced to metallic copper by reducing agents like hydrogen, carbon and carbon monoxide.

 $Cu0 + H_2 \longrightarrow Cu + H_20$ $Cu0 + C \longrightarrow Cu + C0$ $Cu0 + C0 \longrightarrow Cu + C0_2$

USES

It is used to impart green to blue colour to glazes and glass.

Cupric Chloride, $(CuCl_2 \cdot 2H_2O)$

PREPARATION

(a) $2Cu + 4HCl + O_2 \longrightarrow 2CuCl_2 + 2H_2O$ $CuO + 2HCl \longrightarrow CuCl_2 + H_2O$ $Cu(OH)_2CuCO_3 + 4HCl \longrightarrow 2CuCl_2 + 3H_2O + CO_2$

(b) $Cu + Cl_2 \longrightarrow CuCl_2$

$$CuCl_2 \cdot 2H_2O_{HCl\,gas}^{150^{\circ}C} CuCl_2 + 2H_2O$$

PROPERTIES

(a) The aqueous solution is acidic due to its hydrolysis.

 $CuCl_2 + 2H_2O \rightleftharpoons Cu(OH)_2 + 2HCl$

(b) The anhydrous salt on heating forms Cu_2Cl_2 and Cl_2

 $2CuCl_2 \rightleftharpoons Cu_2Cl_2 + Cl_2$

(c) It is readily reduced to Cu₂Cl₂ by copper turnings or SO₂ gas, or hydrogen (Nascentobtained by the action of HCl on Zn) or SnCl₂.

 $CuCl_{2} + Cu \longrightarrow Cu_{2}Cl_{2}$ $2CuCl_{2} + SO_{2} + 2H_{2}O \longrightarrow Cu_{2}Cl_{2} + 2HCl + H_{2}SO_{4}$ $2CuCl_{2} + 2H \longrightarrow Cu_{2}Cl_{2} + 2HCl$ $2CuCl_{2} + SnCl_{2} \longrightarrow Cu_{2}Cl_{2} + SnCl_{4}$

(d) A pale blue precipitate of basic cupric chloride, $CuCl_2 \cdot 3Cu(OH)_2$ is obtained when NaOH is added.

 $CuCl_2 + 2NaOH \longrightarrow Cu(OH)_2 + 2NaCl$

 $CuCl_2 + 3Cu(OH)_2 \longrightarrow CuCl_2 \cdot 3Cu(OH)_2$

It dissolves in ammonium hydroxide forming a deep blue solution. On evaporating of this solution deep blue crystals of tetraamine cupric chloride are obtained.

 $CuCl_2 + 4NH_4OH \longrightarrow Cu(NH_3)_4Cl_2 \cdot H_2O + 3H_2O$

USES

It is used as a catalyst in Deacon's process. It is also used in medicines and as an oxygen carrier in the preparation of organic dyestuffs.

Copper Sulphate (Blue Vitriol), $CuSO_4 \cdot 5H_2O$

Copper sulphate is the most common compound of copper. It is called as blue vitriol or nilathotha.

PREPARATION

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

$$Cu(OH)_2 + H_2SO_4 \longrightarrow CuSO_4 + 2H_2O$$

$$Cu(OH)_2CuCO_3 + 2H_2SO_4 \longrightarrow 2CuSO_4 + 3H_2O + CO_2$$

(b) On commercial scale : it is prepared from scrap copper. The scrap copper is placed in a perforated lead bucket which the dipped into hot dilute sulphuric acid. Air is blown through the acid. Copper sulphate is crystallised from the solution.

$$Cu + H_2SO_4 + \frac{1}{2}O_2(air) \longrightarrow CuSO_4 + H_2O_4$$

PROPERTIES

- (a) It is a blue crystalline compound and is fairly soluble in water.
- (b) Heating effect

CuSO₄ ·
$$\underbrace{\text{Exposure}}_{230^{\circ}\text{C}}$$
 5H₂O CuSO₄ · $\underbrace{100^{\circ}\text{C}}_{230^{\circ}\text{C}}$ 3H₂O CuSO₄ ·
 $\underbrace{230^{\circ}\text{C}}_{230^{\circ}\text{C}}$ H₂O CuSO₄
Blue Pale blue Bluish white
White
CuSO₄ 720°C CuO + SO₃
 \downarrow
SO₂ + $\frac{1}{2}$ O₂
(c) Action of NH₄OH : With ammonia solution, it forms the soluble blue complex. First it
forms a precipitate of Cu(OH)₂ which dissolves in excess of ammonia solution

$$CuSO_4 + 2NH_4OH \longrightarrow Cu(OH)_2 + (NH_4)SO_4$$

$$Cu(OH)_2 + 2NH_4OH + (NH_4)_2SO_4 \longrightarrow Cu(NH_3)_4SO_4 + 4H_2O$$

Tetraammine cupric
sulphate

The complex is known as Schwitzer's reagent which is used for dissolving cellulose in the manufacture of artificial silk.

(d) Action of alkalies : Alkalies form a pale blue precipitate of copper hydroxide.

 $CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$

(e) Action of potassium iodide: First cupric iodide is formed which decomposes to give white cuprous iodide and iodine.

 $[CuSO_4 + 2KI \longrightarrow CuI_2 + K_2SO_4] \times 2$

 $2CuI_2 \longrightarrow Cu_2I_2 + I_2$

$$2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$$

(f) Action of H₂S : When H₂S is passed through copper sulphate solution, a black precipitate of copper sulphide is formed.

Chemistry

 $CuSO_4 + H_2S \longrightarrow CuS + H_2SO_4$

The black precipitate dissolves in conc. HNO_3

 $3CuS + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 3S + 4H_2O$

(g) Action of potassium sulphocyanide: Cupric sulphocyanide is formed.

 $CuSO_4 + 2KCNS \longrightarrow Cu(CNS)_2 + K_2SO_4$

If SO₂ is passed through the solution, a white precipitate of cuprous sulphocyanide is formed.

 $2CuSO_4 + 2KCNS + SO_2 + 2H_2O \longrightarrow Cu_2(CNS)_2 + K_2SO_4 + 2H_2SO_4$

[This is the general method for obtaining cuprous compounds.]

(h) Action of sodium thiosulphate etc.

$$CuSO_4 + Na_2S_2O_3 \longrightarrow CuS_2O_3 + Na_2SO_4$$

$$2CuS_2O_3 + Na_2S_2O_3 \longrightarrow Cu_2S_2O_3 + Na_2S_4O_6$$

$$3Cu_2S_2O_3 + 2Na_2S_2O_3 \longrightarrow Na_4[Cu_6(S_2O_3)_5]$$
Sodium cuprothiosulphate

USES

- (a) Copper sulphate is used for the preparation of other copper compounds.
- (b) It is used in agriculture as a fungicide and germicide.
- (c) It is extensively used in electric batteries.