THE D-AND F-BLOCK ELEMENTS
COMPOUND OF D-BLOCK ELEMENTS

FORMATION OF ALLOY

(a) Alloys are most likely to be formed by transition elements.

(b) Transition elements exhibit low reactivity and nearly identical sizes, allowing easy replacement of one transition metal atom by another in the lattice. This accounts for their high tendency to form alloys.

(c) The ratio of component metals in alloys remains constant.

(d) Alloys characterized by extreme hardness and a 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)

(o) 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 can create interstitial compounds with smaller nonmetal elements such as hydrogen, carbon, boron, nitrogen, and others.

(b) Smaller atoms become trapped within the interstitial spaces of the metal lattices, resulting in non-stoichiometric interstitial compounds that lack a specific formula.

(c) Weak Vander Waals forces of attraction hold the smaller elements in the interstitial spaces of transition elements.

(d) Interstitial compounds share the same chemical properties as their parent metals but exhibit differences in physical properties, including density and hardness. The absorption of excess hydrogen atoms by transition metals like Pd and Pt is termed occlusion.

Non-stoichiometry

(a) Transition elements may exhibit variable valency, leading to the formation of nonstoichiometric compounds.

(b) These compounds possess an indefinite structure and proportion.

(c) For example, lron (II) Oxide FeO should be written as a bar over the formula $\bar{Fe}O$ to indicate the ratio of Fe & O atom is not exactly 1:1 ($Fe_{0.94}O$ & $Fe_{0.84}O$), $V\bar{S}e$ ($VSe_{0.98}VSe_{1.2}$),

(d) Non stoichiometry is shown particularly among transition metal compounds of the group 16 elements (O, S, Se, Te).

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

Potassium Dichromate ($K_2Cr_2O_7$)

PREPARATION

It is derived from Chromite ore, Ferrochrome, or Chrome iron ($FeO.Cr_2O_3$ or $FeCr_2O_4$). The process encompasses several steps.

(a) **Preparation of sodium chromate (Na_2CrO_4):**

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

$$4FeCr_2O_4 + 16NaOH + 7º_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8H_2O$$

or $$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

Following the reaction, the roasted substance is extracted with water, causing complete dissolution of sodium chromate, while ferric oxide remains as a residue.

(b) **Formation of sodium dichromate ($Na_2Cr_2O_7$) from sodium chromate (Na_2CrO_4):**

The solution of sodium chromate is filtered and acidified with dil./con. H_2SO_4 acid giving its dichromate.

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

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.

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

The hot solution undergoes filtration to separate the least soluble compound, sodium chloride, which precipitates. Upon cooling, the remaining liquid yields orange-red crystals of potassium dichromate through crystallization.

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.

$$4K_2Cr_2O_7 \xrightarrow{\text{Heat}} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

Potassium chromate   Chromic oxide

(D) **Action of Alkalies: -** Upon exposure to alkalies, the dichromate solution undergoes a color transformation from orange to yellow, attributed to the creation of chromate ions.

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

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

This chromate on acidifying reconverts into dichromate.

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

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.

$$Cr_2O_7^{2-} + H_2O \xrightleftharpoons{HCrO_4^-} 2CrO_4^{2-} + 2H^+$$

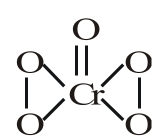
When alkali added, H^+ consumed so forward direction. When acid added, H^+ increases so backward direction.

(E) **Chromyl chloride Test: -** When potassium dichromate is heated with conc. H_2SO_4 acid and a soluble metal chloride (ex. NaCl) orange red vapours of chromyl chloride (CrO_2Cl_2) are formed.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \rightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$$

(F) **Reaction with H_2O_2: -** Acidified solution of dichromate ions give deep blue colour solution with H_2O_2 due to the formation of $[CrO(O_2)_2]$ or CrO_5. The blue colour fades away gradually due to the decomposition of CrO_5 into Cr^{+3} ions and oxygen.

$$Cr_2O_7^{2-} + 4H_2O_2 + 2H^+ \rightarrow 2CrO_5 + 5H_2O$$



(Butterfly structure)

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

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

(H) **Action of con. H_2SO_4**

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

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

(ii) On heating the mixture oxygen is evolved.

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

(I) **Oxidising properties**

The dichromats act as powerful oxidising agent in acidic medium. In presence of dill H_2SO_4, $K_2Cr_2O_7$ liberates Nascent oxygen and therefore acts as an oxidising agent.

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

From an electronic perspective, the ion acquires electrons in an acidic medium, thereby functioning as an oxidizing agent.

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

(i) **It oxidizes iodides to iodine: -**

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

$$[2I^- \rightarrow I_2 + 2e^-] \times 3$$

$$+ 14H^+ + 6I^- \rightarrow 2Cr^{+3} + 3I_2 + 7H_2O$$

Or $$K_2Cr_2O_7 + 7H_2SO_4 + 6KI \rightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$$

(ii) **Acidified ferrous sulphate to ferric sulphate**

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

$$Fe^{+2} \rightarrow Fe^{3+} + e^-] \times 6$$

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

or $$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O + K_2SO_4$$

(iii) **Oxidises H_2S to sulphur**

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

$$H_2S \rightarrow S + 2H^+ + 2e^-] \times 3$$

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

or $K_2Cr_2O_7 + 3H_2S + 4H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3S + 7H_2O + K_2SO_4$

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.

$$3SO_3^{-2} + Cr_2O_7^{2-} + 8H^+ \longrightarrow 3SO_4^{2-} + 2Cr^{3+} + 4H_2O$$
$$3NO_2^- + Cr_2O_7^{2-} + 8H^+ \longrightarrow 3NO_3^- + 2Cr^{3+} + 4H_2O$$
$$3S_2O_3^{2-} + Cr_2O_7^{2-} + 8H^+ \longrightarrow 3SO_4^{2-} + 3S + 2Cr^{3+} + 4H_2O$$
$$6Cl^- + Cr_2O_7^{2-} + 14H^+ \longrightarrow 3Cl_2 + 2Cr^{3+} + 7H_2O$$
$$3Sn^{+2} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 3Sn^{+4} + 2Cr^{3+} + 7H_2O$$

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) Employed for volumetric determination of ferrous salts, iodides, and sulphites.

(b) Utilized in the synthesis of various chromium compounds, such as chrome alum ($K_2SO_4, Cr_2(SO_4)_3.24H_2O$), chrome yellow ($PbCrO_4$), and chrome red ($PbCrO_4.PbO$).

(c) Found in photography for the toughening of gelatin film.

(d) Applied in the leather industry for chrome tanning.

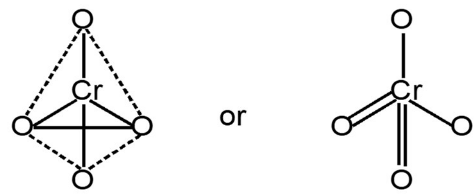
(e) The chromic acid mixture, comprising $K_2Cr_2O_7$ and concentrated H_2SO_4, is utilized for cleaning glassware.

(f) In organic chemistry, it serves as an oxidizing agent.

(g) Employed in dyeing and calico printing.

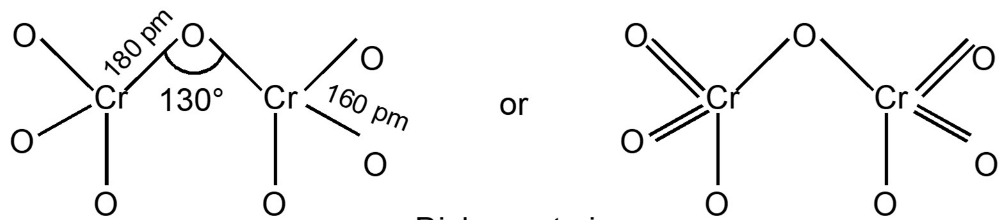
STRUCTURE

The chromate ion exhibits a tetrahedral structure, with four atoms surrounding the chromium atom arranged in a tetrahedral configuration.



Chromate ion

The dichromate ion's structure comprises two tetrahedra that share an oxygen atom at their common corner.



Dichromate ion

POTASSIUM PERMANGANATE ($KMnO_4$)

PREPARATION

The production of potassium permanganate involves the utilization of mineral pyrolusite (MnO_2) and includes the following steps.

(a) **Conversion of pyrolusite ore to potassium manganate**

The Pyrolusite (MnO_2) is melted with either caustic potash (KOH) or potassium carbonate in the presence of air or oxidizing agents like KNO_3 or $KClO_3$. This process results in the formation of a green mass, attributed to the creation 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 dissolved in water, yielding a green solution of potassium manganate. This solution is subsequently subjected to a current of Cl_2, ozone, or CO_2 to oxidize K_2MnO_4 to $KMnO_4$. Following concentration, dark purple crystals of KMnO4 precipitate from the solution.

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KCl + 2KMnO_4$$

$$2K_2MnO_4 + O_3 + H_2O \longrightarrow 2KMnO_4 + 2KOH + O_2$$

$$3K_2MnO_4 + 2CO_2 \longrightarrow 2K_2CO_3 + MnO_2\downarrow + 2KMnO_4$$

Alternatively, alkaline potassium manganate is electrolytically oxidised.

Electrolytic method: - The electrolytic cell, housing an iron cathode and nickel anode, is filled with the potassium manganate solution. Upon passing a current, the manganate ions are oxidized to permanganate ions at the anode, and concurrently, hydrogen is liberated at the 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 $KMnO_4$ gives KOH, MnO and water vapours, when heated in current of hydrogen.

$$2KmnO_4 + 5H_2 \xrightarrow{\Delta} 2KOH + 2MnO + 4H_2O$$

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

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

(e) **Action of con. H_2SO_4:** With cold H_2SO_4, it gives Mn_2O_7 which on heating decomposes into MnO_2.

$$2KMnO_4 + 2H_2SO_4 \longrightarrow Mn_2O_7 + 2KHSO_4 + H_2O$$

$$2Mn_2O_7 \longrightarrow 4MnO_2 + 3O_2$$

(f) **Oxidising character: -** $KMnO_4$ 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. $= \frac{M}{5}$]

Neutral solution :- MnO_2 is formed

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

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

In the course of the reaction, the alkali produced induces the formation of an alkaline medium, even when commencing from a neutral medium.

Alkaline medium: - Manganate ions are formed.

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

Reactions in Acidic Medium: In acidic medium $KMnO_4$ 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:**

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

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-] \times\ 5$$

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{+2} + 10CO_2 + 8H_2O$$

(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 H_2S 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 SO_2 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

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

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

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

Reactions in Neutral Medium:

(a) It oxidizes H_2S to sulphur:

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

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

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

(b) It oxidizes Manganese sulphate ($MnSO_4$ to MnO_2) manganese dioxide:

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

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

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

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

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

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

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

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

Reactions in Alkaline Medium

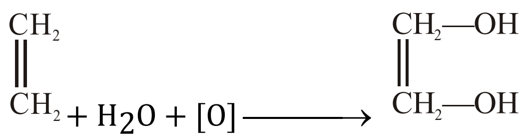
(a) It oxidizes Iodides to Iodates in alkaline medium:

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

$$KI + 3O \longrightarrow KIO_3$$

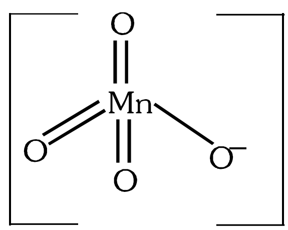
$$2KMnO_4 + KI + H_2O \longrightarrow 2MnO_2 + 2KOH + KIO_3$$

(b) Alkaline $KMnO_4$ (Baeyer's reagent) oxidizes ethylene to ethylene glycol.



STRUCTURE

MnO_4^-



USES

(a) Employed in volumetric analysis to estimate ferrous salts, oxalates, and other reducing agents, though it is not utilized as a primary standard due to challenges in obtaining it in a pure state.

(b) Functions as a potent oxidizing agent in both laboratory and industrial settings.

(c) Used as a disinfectant and germicide.

(d) Found in dry cells.

(e) Utilized for washing wounds in the form of a highly diluted $KMnO_4$ solution.

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, 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 ($K_2Cr_2O_7$):

PREPARATION

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

$$4FeO.\,Cr_2O_3 \text{ (chromite ore)} + 8Na_2CO_3 + 7O_2 \xrightarrow[\text{in air}]{\text{Roasting}} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

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 Na_2SO_4 crystallizes out. The solution is further concentrated when crystals of $Na_2Cr_2O_7$ are obtained. Hot saturated solution of $Na_2Cr_2O_7$ is then treated with KCl when orange red crystals of $K_2Cr_2O_7$ are obtained on crystallization.

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

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:

This crystalline compound exhibits an orange-red color and displays moderate solubility in cold water, becoming freely soluble in hot water. Its melting point is 398°C.

(b) **Chemical:**

(i) Effect of heating:

On heating strongly, it decomposes liberating oxygen.

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

Upon exposure to alkalies, it undergoes conversion to chromate, resulting in a color change from orange to yellow. Upon acidification, the yellow color reverts to orange.

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

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

Orange Yellow

$$2CrO + 2H^+ \rightarrow Cr_2O + H_2O$$

Yellow Orange

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

$$2CrO + 2H^+ \rightleftharpoons 2HCrO_4^- \rightleftharpoons Cr_2O + H_2O$$

Chromate ions are present in alkaline solutions, whereas dichromate ions are present in acidic solutions.

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

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

(iii) Acidified $K_2Cr_2O_7$ solution reacts with H_2O_2 to give a deep blue solution due to the formation of CrO_5.

$$Cr_2O_7{}^{2-} + 2H^+ + 4H_2O_2 \rightarrow 2CrO_5 + 5H_2O$$

The gradual fading of the blue color in an aqueous solution is attributed to the decomposition of CrO_5 into Cr^{3+} ions and oxygen. In a less acidic solution, the combination of $K_2Cr_2O_7$ and H_2O_2 produces a violet-colored and diamagnetic salt due to the formation of $[CrO(O_2)(OH)]^-$. In an alkaline medium with 30% H_2O_2, a red-brown K_3CrO_8 (diperoxo) is formed, representing a tetra-peroxy species $[Cr(O_2)_4]^{3-}$, and thus, chromium is in the +V oxidation state. In an ammoniacal solution, a dark red-brown compound, $(NH_3)_3CrO_4$, which is a diperoxo compound with Cr(IV), is generated.

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

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

(v) It acts as a powerful oxidising agent in acidic medium (dilute H_2SO_4)

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

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

(a) Iodine is liberated from potassium iodide:

$$Cr_2O + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

$$2I^- \rightarrow I_2 + 2e^- \times [3]$$

$$Cr_2O + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

(b) Ferrous salts are oxidised to ferric salts:

$$6Fe^{2+} + Cr_2O + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

(c) Sulphites are oxidised to sulphates:

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

(d) H_2S is oxidised to sulphur:

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

(e) SO_2 is oxidised to H_2SO_4:

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

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

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

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

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

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) $+ 3H_2O$

$$CrO_2Cl_2 + 4OH^- \rightarrow CrO_4^{2-} \text{ (yellow)} + 2Cl^- + 2H_2O$$

$$CrO_4^{2-} \text{ (yellow)} + Pb^{2+} \rightarrow PbCrO_4 \downarrow \text{ (yellow)}$$

(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 CH_3COONa is added, precipitate becomes quantitative.

USES

It is used:

(i) Employed as a volumetric reagent for estimating reducing agents like oxalic acid, ferrous ions, iodide ions, etc., and serves as a primary standard.

(ii) Utilized in the synthesis of various chromium compounds such as chrome alum, chrome yellow, chrome red, zinc yellow, etc.

(iii) Applied in various industries including dyeing, chrome tanning, calico printing, photography, etc.

(iv) Functions as a cleansing agent for glassware 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 H_2SO_4 to yield red crystals (B). In presence of dilute H_2SO_4 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. H_2SO_4 (A) yields blue colour. (A) and concentrated H_2SO_4 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. H_2SO_4 gives red crystals and a suffocating gas (SO_2) turns its solution in water in to green coloured solution, therefore compound (A) may be $K_2Cr_2O_7$.

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \longrightarrow KHSO_4 + 2\ CrO_3\ \text{(red crystals)} + H_2O$$

(A) (B)

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \longrightarrow K_2SO_4 + Cr_2\ (SO_4)_3 + 7H_2O + 3S\downarrow\ \text{(Yellow)}$$

(C) (D)

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow Cr_2\ (SO_4)_3\ \text{(Green solution)} + K_2SO_4 + H_2O$$

(E) (F)

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

I_2 + Starch Blue colour

COMPOUNDS OF IRON

Ferrous Sulphate (Green Vitriol), $FeSO_4 \cdot 7H_2O$:

This ferrous salt is widely acknowledged, occurring naturally as copper and produced through the oxidation of pyrites influenced by water and atmospheric air.

$$2FeS_2 + 7O_2 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4$$

It is commonly known as harikari's.

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 loses its water content, becoming anhydrous. The colorless anhydrous ferrous sulfate, when intensely heated, decomposes to produce ferric oxide, releasing SO_2 and SO_3.

$$\underset{\text{Green}}{FeSO_4 \cdot 7H_2O} \xrightarrow[-7H_2O]{300^\circ C} \underset{\text{White}}{2FeSO_4} \xrightarrow[\text{temperature}]{\text{High}} Fe_2O_3 + SO_2 + SO_3$$

(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.

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

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

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

(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 sulfate finds application in the production of blue-black ink.

(b) Utilized as a mordant in the dyeing process.

(c) Also employed as an insecticide in agriculture.

(d) Finds use as a laboratory reagent and in the synthesis of Mohr's salt.

Ferrous-Oxide FeO (BLACK)

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

PROPERTIES: It is stable at high temperature and on cooling slowly disproportionate into Fe_3O_4 and iron

Ferrous Chloride ($FeCl_2$)

PREPARATION: $Fe + 2HCl \xrightarrow[\text{a current of HCl}]{\text{heated in}} FeCl_2 + H_2$

PROPERTIES: $2FeCl_3 + H_2 \xrightarrow{\Delta} 2FeCl_2 + 2HCl$

(a) Similar to $FeCl_3$, it deliquesces in the air.

(b) Its solubility extends to water, alcohol, and ether due to its considerable covalent nature.

(c) Volatilization occurs around 1000°C, and the vapor density suggests the existence of Fe_2Cl_4. Beyond 1300°C, the density normalizes.

(d) It oxidises on heating in air

$$12FeCl_2 + 3O_2 \longrightarrow 2Fe_2O_3 + 8FeCl_3$$

(e) H_2 evolves on heating in steam

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

(f) It can exist as different hydrated form

$$FeCl_2 \cdot 2H_2O \longrightarrow \text{colourless}$$

$$FeCl_2 \cdot 4H_2O \longrightarrow \text{pale green}$$

$$FeCl_2 \cdot 6H_2O \longrightarrow \text{green}$$

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)

$$2Zn + O_2 \longrightarrow 2ZnO$$

PROPERTIES

(a) ZnO appears white at low temperatures, making it suitable as a pigment in paints. However, its color shifts to a pale yellow when heated, attributed to a alteration in the lattice structure.

(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)
$$ZnO + C \xrightarrow[>1000^\circ C]{\Delta} Zn + CO$$
$$ZnO + CO \xrightarrow{\Delta} Zn + CO_2$$

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 ($ZnSO_4$)

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. H_2SO_4

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

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)
$$ZnSO_4 \cdot 7H_2O \xrightarrow[\Delta]{100^\circ C} ZnSO_4 \cdot 6H_2O \xrightarrow[\Delta]{280^\circ C} ZnSO_4 \xrightarrow{T>760^\circ C} ZnO + SO_3$$

It slowly effloresces when exposed to air.

(b) It shares isomorphism with Epsom salt and finds application in the production of lithophone, a white pigment consisting of a blend of BaS and $ZnSO_4$.

Zinc Chloride ($ZnCl_2$)

PREPARATION

$$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$$
$$ZnCO_3 + 2HCl \longrightarrow ZnCl_2 + H_2O + CO_2$$
$$Zn(OH)_2 + 2HCl \longrightarrow ZnCl_2 + 2H_2O$$

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

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

$$Zn(OH)Cl \quad ZnO + HCl$$

To get anhydrous $ZnCl_2$

$$Zn + Cl_2 \longrightarrow ZnCl_2$$

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

$$Zn + HgCl_2 \longrightarrow ZnCl_2 + Hg$$

PROPERTIES

(a) It is deliquescent white solid (when anhydrous)

(b) $ZnCl_2 + H_2S \longrightarrow ZnS$

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

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

USES

(a) Employed in impregnating timber to protect against insect damage.

(b) Functions as a dehydrating agent in its anhydrous form.

(c) $ZnO \cdot ZnCl_2$ is utilized in dental fillings.

Ex. $Zn\,(OH)_2 \xrightarrow{\Delta} [X]$.

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. $Zn_3K_2[Fe(CN)_6]_2$.

$$3\,Zn^{2+} + 2\,K^{+} + 2\,[Fe(CN)_6]^{4-} \; K_2Zn_3[Fe(CN)_6]_2 \downarrow$$

(D) $ZnO + 2NaOH\; Na_2ZnO_2$ (soluble complex) $+ H_2O$.

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

COMPOUND OF SILVER

Silver Nitrate (Lunar Caustic) $AgNO_3$

PREPARATION

(a) When Ag is heated with dill HNO_3, $AgNO_3$ is formed. Crystals separate out on cooling the concentrated solution of $AgNO_3$

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

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

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

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

PROPERTIES

(a) It is reduced to metallic Ag by more electropositive metals like Cu, Zn, Mg and also by PH_3.

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

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

(b) It dissolves in excess of KCN:

$$\underset{\text{white ppt}}{AgNO_3} \xrightarrow{KCN} \underset{\text{soluble potassium}}{AgCN} \xrightarrow{KCN} \underset{\text{argent cyanide}}{K[Ag(CN)_2]}$$

$AgNO_3$ gives white precipitate with $Na_2S_2O_3$; white precipitate changes to black.

$$2AgNO_3 + Na_2S_2O_3 \longrightarrow \underset{\text{white ppt}}{Ag_2S_2O_3} + 2NaNO_3$$

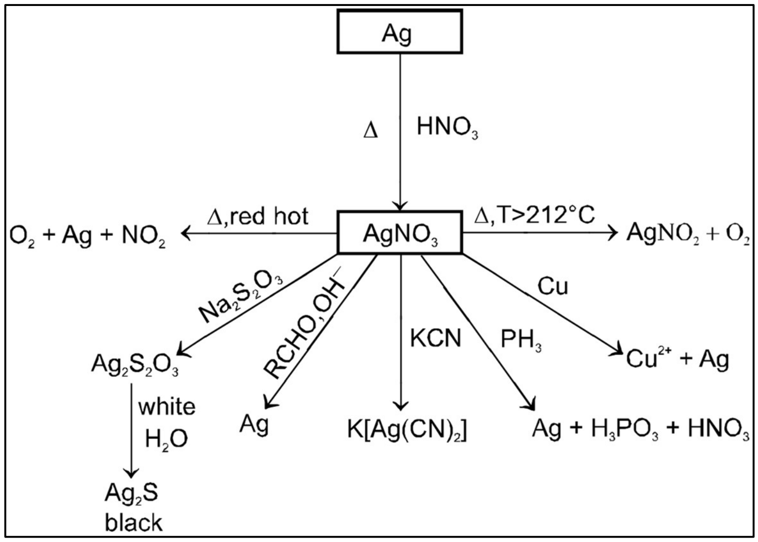
$$Ag_2S_2O_3 + H_2O \longrightarrow \underset{\text{black}}{Ag_2S} + H_2SO_4$$

(c) Ammoniacal $AgNO_3$ is called Tollen's reagent and is used to identify reducing sugars (including aldehydes):

$$RCHO + 2Ag^+ + 3OH^- \xrightarrow{\Delta} RCOO^- + 2Ag\downarrow + 2H_2O$$

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

Some important reaction of $AgNO_3$



COMPOUND OF COPPER

Cupric Oxide (CuO)

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

PREPARATION

(a) By heating Cu_2O in air or by heating copper for a long time in air (the temperature should not exceed above 1100°C)

$$Cu_2O + \frac{1}{2}O_2 \longrightarrow 2CuO$$

$$2Cu + O_2 \longrightarrow 2CuO$$

(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.

$$CuO + 2HCl \longrightarrow CuCl_2 + H_2O$$

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

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

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

$$4CuO \longrightarrow 2Cu_2O + O_2$$

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

$$CuO + H_2 \longrightarrow Cu + H_2O$$

$$CuO + C \longrightarrow Cu + CO$$

$$CuO + CO \longrightarrow Cu + CO_2$$

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) $$Cu + Cl_2 \longrightarrow CuCl_2$$

$$CuCl_2 \cdot 2H_2O \xrightarrow[\text{HCl gas}]{150^\circ C} CuCl_2 + 2H_2O$$

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 Cu_2Cl_2 by copper turnings or SO_2 gas, or hydrogen (Nascent–obtained by the action of HCl on Zn) or $SnCl_2$.

$$CuCl_2 + Cu \longrightarrow Cu_2Cl_2$$

$$2CuCl_2 + SO_2 + 2H_2O \longrightarrow Cu_2Cl_2 + 2HCl + H_2SO_4$$

$$2CuCl_2 + 2H \longrightarrow Cu_2Cl_2 + 2HCl$$

$$2CuCl_2 + SnCl_2 \longrightarrow Cu_2Cl_2 + SnCl_4$$

(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 serves as a catalyst in the Deacon's process and finds applications in medicines and as an oxygen carrier in the synthesis of organic dyestuffs. Copper Sulphate (Blue Vitriol), $CuSO_4 \cdot 5H_2O$

Copper sulfate is the most prevalent copper compound, commonly known as blue vitriol or nilathotha.

PREPARATION

(a)

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

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

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

(b) **On commercial scale:** it is derived from recycled copper. The process involves placing scrap copper in a perforated lead bucket, submerging it in hot dilute sulfuric acid, and blowing air through the acid. Copper sulfate is then crystallized from the resulting solution.

$$Cu + H_2SO_4 + \frac{1}{2}O_2(\text{air}) \longrightarrow CuSO_4 + H_2O$$

PROPERTIES

(a) It is a blue crystalline compound and is fairly soluble in water.

(b) Heating effect

$$CuSO_4 \cdot 5H_2O \underset{}{\overset{\text{Exposure}}{\rightleftharpoons}} CuSO_4 \cdot 3H_2O \overset{100°C}{\rightleftharpoons} CuSO_4 \cdot \overset{230°C}{\rightleftharpoons} H_2O \; CuSO_4$$

Blue Pale blue Bluish white

White

$$CuSO_4 \xrightarrow{720°C} CuO + SO_3$$
$$\downarrow$$
$$SO_2 + \frac{1}{2}O_2$$

(c) **Action of NH_4OH:** 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 H_2S:** When H_2S is passed through copper sulphate solution, a black precipitate of copper sulphide is formed.

$$CuSO_4 + H_2S \longrightarrow CuS + H_2SO_4$$

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 SO_2 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 sulfate is employed in the synthesis of various other copper compounds.

(b) In agriculture, it serves as a fungicide and germicide.

(c) It finds widespread use in electric batteries.