

COPPER GROUP [COINAGE METALS]

Section - 5

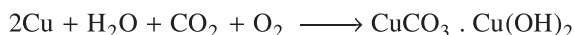
Group 11 consists of the metals copper, gold and silver, all having a completely filled d-shell and one s-electron. They have been known since prehistoric times when they were used to make coins and hence called Coinage Metals. They conduct electricity and heat particularly well and tend to be noble (unreactive). The reason for their noble character is higher ionisation energy and enthalpy of sublimation.

[A] Copper & its Compounds

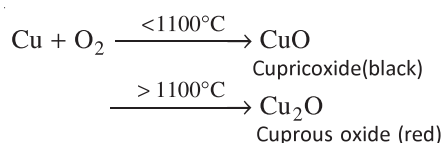
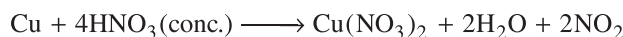
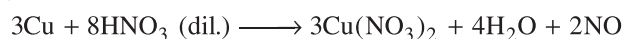
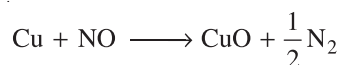
Copper is a reddish coloured, lustrous and soft metal produced on large scale from its ores like chalcopyrite (CuFeS_2), malachite ($\text{CuCO}_3 \cdot \text{Cu(OH)}_2$), cuprite (Cu_2O). The metal is used in the electrical industry because of its high conductivity, electroplating, in manufacture of coins and also as a catalyst.

(i) Reaction with air :

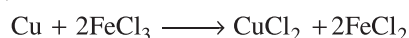
A green coating of basic copper carbonate $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ called 'Verdigris' is formed in presence of moisture and CO_2 in air (O_2).



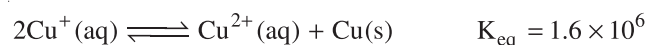
While, when heated it forms two oxides :

**(ii) Copper is inert towards non-oxidising acids (HCl, dil. H_2SO_4) but reacts with concentrated HNO_3 and H_2SO_4 .****(iii) Copper reduces oxides of nitrogen to N_2 and ferric ion to ferrous ion.**

The etching of designs on copper plates using ferric chlorides is based on this property.

**I. Cu^{+1} State**

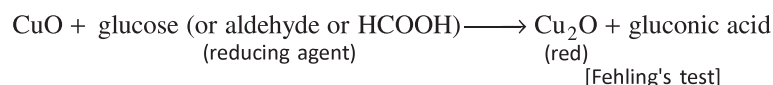
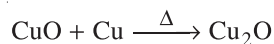
The configuration of copper in (+I) state is $3d^{10}$ to $4s^0$ which is known as 'pseudo-noble gas configuration'. It might thus be expected that the (+I) state would be the most stable but surprisingly this is not so. In fact it disproportionates in aqueous solution as :



The only Cu^+ compounds stable in water are either insoluble (CuCl , CuBr , CuI , CuCN) or present as complexes.

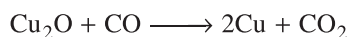
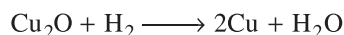
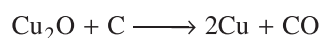
(a) Cuprous Oxide (Cu₂O) :

Cu₂O is a red coloured basic oxide found as the ore cuprite in nature. It is prepared by heating cupric oxide and copper or by reduction of Cu²⁺ by mild reducing agents (as in the *Fehling's Test* for reducing sugars).

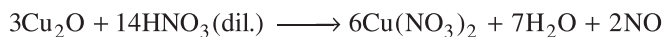
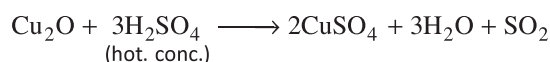
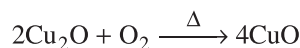


(i) Cu₂O reacts with halogen acids HCl, HBr and HI giving insoluble CuCl(white), CuBr(yellow) and CuI(yellow). CuF is unknown.

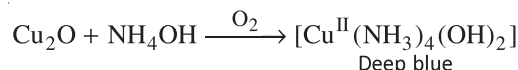
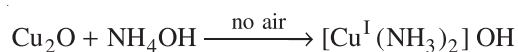
(ii) Cu₂O is reduced to copper when heated in a current of H₂ or CO or with carbon.



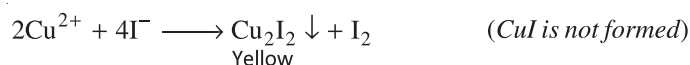
(iii) Oxidation of Cu₂O :



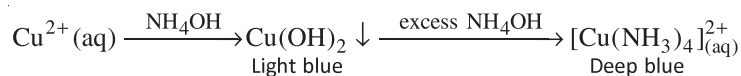
(iv) Reaction with aqueous ammonia :

**II. Cu^{+II} State**

It is the most important and stable state of copper. Since the electronic configuration is *d*⁹, the compounds are typically coloured due to *d-d* spectra and paramagnetic. The hydrated salts are blue due to [Cu(H₂O)₆]²⁺ ions. Cu²⁺ compounds are detected by adding a KI solution which forms yellow precipitate of Cu₂I₂.

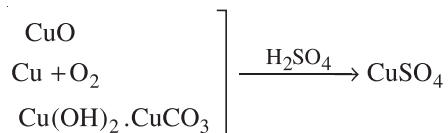


This is also used in the volumetric analysis of Cu^{+II}. Another test is adding the salt to NH₄OH solution.

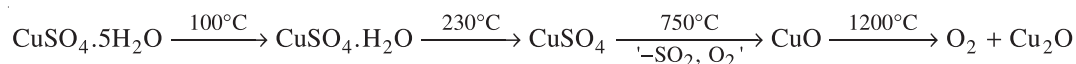


(a) Copper sulphate [$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$] :

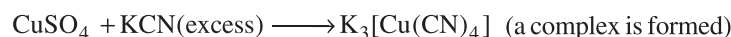
Also known as blue vitriol, copper sulphate solutions are blue coloured. The anhydrous salt is however white. It is prepared by dissolving CuCO_3 , Cu(OH)_2 or CuO in sulphuric acid.



- (i) Hydrated copper sulphate crystals are blue coloured and thus this can be used as a test for the presence of water on heating, the water of crystallisation is lost.



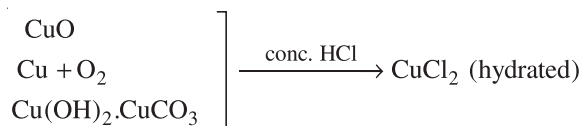
- (ii) $\text{CuSO}_4 + \text{KCN} \longrightarrow \text{CuCN} \downarrow + (\text{CN})_2$
Cyanogen
(extremely poisonous)



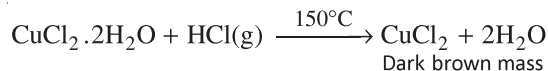
- (iii) A mixture of CuSO_4 and Ca(OH)_2 (milk lime) is used as *Bordeaux Mixture* used for preventing fungus attack on potato leaves and vines. CuSO_4 is also used to make fehling solution.

(b) Cupric Chloride $[\text{CuCl}_2 \cdot 2\text{H}_2\text{O}]$:

Cupric chloride can be obtained by dissolving $\text{Cu}(\text{OH})_2$, CuCO_3 or CuO or the metal in conc. HCl .



The hydrated crystals are green coloured. Anhydrous salt can be obtained by heating in HCl gas.



- (i) It is a deliquescent compound readily soluble in water. Dilute solutions are blue while concentrated solutions are green. It changes to yellow if added to conc. HCl or Cl_2 current is passed.

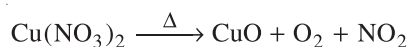
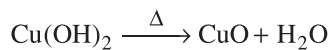
The blue colour is due to $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ and yellow colour due to complex ion $[\text{CuCl}_4]^{2-}$

- $$\text{(ii) } \text{CuCl}_2 + \text{NaOH} \longrightarrow \underset{\text{Light blue}}{\text{Cu(OH)}_2} \downarrow + 2\text{NaCl}$$

- (iii) $\text{CuCl}_2 + \text{Cu} \xrightarrow{\Delta} \text{Cu}_2\text{Cl}_2$

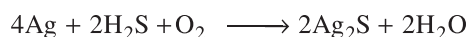
(c) Cupric Oxide [CuO] :

It is black coloured and formed by heating cuprous oxide or copper in air (O_2). In fact, all oxosalts, such as $Cu(NO_3)_2$ decompose into black CuO on strong heating.

**[B] Silver & its Compounds**

Silver is a white lustrous, ductile and malleable metal. It is the best known conductor of electricity and heat. The chemical properties of silver are :

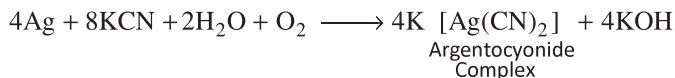
- (i) It is quite unreactive and has no effect of air and alkalies. However, air contaminated with H_2S tarnishes silver due to formation of black Ag_2S .



- (ii) On heating the molten mass of silver absorbs oxygen which is again released on cooling. This is called as 'SPITTING OF SILVER'.

- (iii) Ag dissolves in conc. HNO_3 and conc. H_2SO_4 producing NO_2 and SO_2 respectively. Dilute H_2SO_4 has no effect on silver but dilute HNO_3 react to form NO (Ag being a poor reducing agent). In each case Ag is oxidised to Ag^+ ion.

- (iv) Cyanide complexes are used in the extraction of silver.



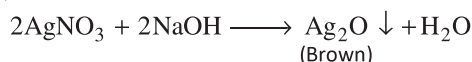
(i.e. excess KCN)

- (v) Silver finds its use as $AgCl$ and $AgBr$ in photographic emulsions. Other uses include in making jewellery and ornaments, silver mirrors and for batteries.

The most stable and common oxidation state of silver is the (+I) state. Some compounds in this state are :

(a) Silver oxide [Ag_2O] :

Ag_2O is mainly basic and prepared from silver salts like $AgNO_3$



- (i) On heating silver oxide decomposes to silver and oxygen at $160^\circ C$.
- (ii) Aqueous solutions of Ag_2O consist of $Ag(OH)$ making the solution strongly basic. Thus the moist Ag_2O can hydrolyse alkyl halides.

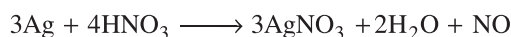


Moist Ag_2O also absorbs carbon dioxide and forms Ag_2CO_3 .

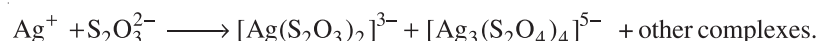
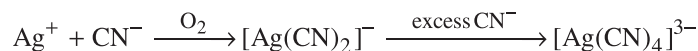
3. Ag_2O forms black coloured AgO with sodium thiosulphate. This oxide actually exists as $Ag^I[Ag^{III}O_2]$ and hence is diamagnetic not paramagnetic.

(b) Silver Nitrate [AgNO₃] (Lunar Caustic) :

Silver nitrate is one of the most important salts of silvers. It can be formed by simply dissolving Ag in nitric acid.



1. In crystalline form it is colourless. Heating AgNO₃ dissociates it into Ag, NO₂ and O₂.
2. All simple compounds of Ag⁺ (Ag₂O, AgCl, AgBr, AgNO₃) form complexes with alkali cyanide and sodium thiosulphate.



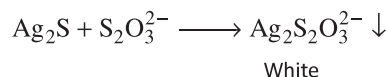
3. A solution of AgNO₃ and alkaline aqueous ammonia is used as *Tollens Reagent* (ammonical AgNO₃ or [Ag(NH₃)₂][OH⁻])
4. $5\text{AgNO}_3 + 3\text{H}_2\text{O} + \text{I}_2 \text{ (excess)} \longrightarrow \text{HIO}_3 + 5\text{AgI} \downarrow + 5\text{HNO}_3$
 $6\text{AgNO}_3 \text{ (excess)} + 3\text{I}_2 + 3\text{H}_2\text{O} \longrightarrow \text{AgIO}_3 + 5\text{AgI} \downarrow + 6\text{HNO}_3$

(c) Silver Halides :

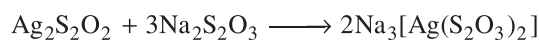
Silver halides (AgX) are insoluble solids used in photography. AgCl is white, AgBr pale yellow and AgI yellow. Presence of halide ions in solutions is tested by adding AgNO₃ solution and dil. HNO₃ which forms silver halide precipitates. The colour indicates the type of halide ion present. This can be confirmed by testing solubility of these precipitates in ammonium hydroxide. AgCl is soluble in dilute NH₄OH. AgBr fully dissolves only in strong ammonia solution while AgI is insoluble in NH₄OH. (AgCl and AgBr form the soluble ammine complex Ag(NH₃)₂⁺ which is linear).

(d) Silver thiosulphate [Ag₂S₂O₃] :

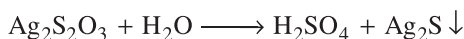
It forms white needle like crystals precipitated when Ag₂S or AgNO₃ reacts with hypo.



On adding excess of sodium thiosulphate, it dissolves.

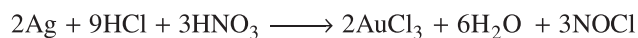


- Ag₂S₂O₃ is decomposed by water giving a variety of colours changing from black through yellow and brown.



[C] Gold

Gold(Au) is a soft, heavy and yellow metal with high lustre. It is inert to air and all acids except aqua regia (a 3 : 1 mixture of concentrated HCl and HNO₃). The HNO₃ acts as an oxidising agent and the chloride ions as a complexing agent.



The most stable oxidation state for gold is Au(+III)

IN-CHAPTER EXERCISE - D

1. Explain the following facts :

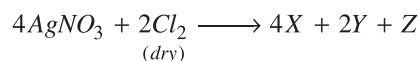
- (i) Silver nitrate is kept in dark coloured bottles :
- (ii) Copper hydroxide is soluble in ammonium hydroxide but not in sodium hydroxide.
- (iii) Cuprous chloride is insoluble in water and dilute HCl but dissolves in concentrated HCl.
- (iv) The species $[\text{CuCl}_4]^{2-}$ exists but $[\text{CuI}_4]^{2-}$ does not .
- (v) Addition of an alkali to cuprous chloride solution gives a yellow precipitate which gradually changes to a red colour.

Choose the correct alternative. Only One choice is Correct.

2. Hydrazine reduces Fehling's solution to form :

- (A) $\text{Cu}(\text{OH})_2$ (B) Cu_2O (C) CaO (D) $\text{Cu} + \text{O}_2$

3. In the following reaction Y and Z are respectively :



- (A) $\text{AgCl}_2, \text{O}_2$ (B) $\text{NO}_2, \text{N}_2\text{O}_4$ (C) $\text{N}_2\text{O}_5, \text{O}_2$ (D) None of these

4. AgCl precipitate dissolves in NH_3 due to the formation of

- (A) $[\text{Ag}(\text{NH}_3)]\text{Cl}$ (B) $[\text{Ag}(\text{NH}_3)_2]\text{OH}$ (C) $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ (D) $[\text{Ag}(\text{NH}_4)_2]\text{OH}$

5. In the reaction, $\text{CuS} \xrightarrow[\text{air}]{\text{roast in}} (\text{P}) \xrightarrow[\text{air}]{\text{roast without}} (\text{Q})$ which of the statement(s) is/are false ?

- (A) It is self reduction
- (B) It involves disproportionation
- (C) (P) is mixture of CuO and CuS, (Q) is a mixture of Cu and SO₂
- (D) All are false