#### COPPER

Atomic number 29

Electronic configuration: 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>3d<sup>10</sup>4s<sup>2</sup>

#### Ores of copper

| 1. | Copper pyrites | CuFeS <sub>2</sub>                     |
|----|----------------|--|
| 2. | Malachite      | CuCO <sub>3</sub> .Cu(OH) <sub>2</sub> |
| 3. | Copper glance  | $Cu_2S$                                |
| 4. | Cuprite        | Cu <sub>2</sub> O                      |

#### Extraction process

Copper is commonly extracted from copper pyrites.

The ore is first crushed to powder form. The finely divided ore is then mixed with water and frothing agents such as pine oil is added. The earthly materials sink to the bottom because of their density whereas the ore particles float where they are removed, washed and dried.

The ore is then roasted to convert the copper pyrite to copper (I) sulphide, iron(II)oxide and sulphur dioxide.

 $2CuFeS_2(s) + 4O_2(g) \longrightarrow Cu_2S(s) + 2FeO(s) + 3SO_2(g)$ 

The solid product ( $Cu_2S$  (s) and 2FeO (s)) is transferred in to the blast furnace and silica added. The iron (II) oxide is converted in to slag of iron (II) silicate, which is poured away.

 $FeO(s) + SiO_2(s) \longrightarrow FeSiO_3(s)$ 

The copper (I) sulphide is now reduced in the blast furnace to copper (I) oxide

 $Cu_2S(s) + 3O_2(g) \longrightarrow 2Cu_2O(s) + 2SO_2(g)$ The copper (I) oxide produced and unroasted copper (I) sulphide react in the heat of the blast

The copper (1) oxide produced and unroasted copper (1) sulphide react in the heat of the furnance to form copper.

 $2Cu_2O(s) + Cu_2S(s) \longrightarrow 6Cu(s) + SO_2(g)$ The copper formed solidifies on cooling and is called blister copper and contains impurities.

## **EXTRACTION FROM MALACHITE**

#### **Concentration of the ore**

The ore is ground to powder, the finely devided ore particles is mixed with water and frothing agents such as pine off and shaken for a while.

The earthly materials because of their high density sink in to the bottom whereas the ore partcles because of their low density float on the suface where they are removed, washed and dried.

The ore is roasted to form copper (II) oxide

 $CuCO_3.Cu(OH)_2$  (s)  $\rightarrow 2CuO$  (s) +  $CO_2$  (g) +  $H_2O$  (l)

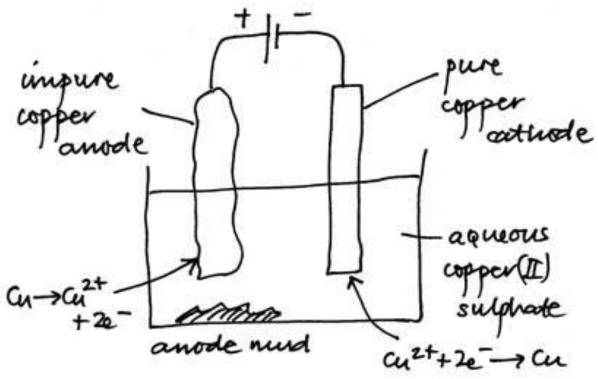
The copper (II) Oxide is reduced with carbon to copper on heating

 $CuO(s) + C(s) \longrightarrow Cu(s) + CO_2(g)$ 

The copper obtained is the purified by electrolysis

#### **Purification of Copper**

This is done by electrolysis. Diagram



- The anode is a block made of impure copper to be purified. The cathode is a thin piece of pure copper .The electrolyte is copper (II) sulphate solution. When electricity is passed thru the cell
- At the Anode: Copper is dissolved by oxidation

Cu (s)  $\longrightarrow$  Cu<sup>2+</sup> (aq) +2e<sup>-</sup> i.e Cu<sup>2+</sup> ions go in to solution

At The Cathode: copper is deposited by reduction.
Cu<sup>2+</sup>(aq) + 2e<sup>-</sup> - Cu (s)

As copper ions move from anode to the cathode the anode gets smaller as the cathode gets bigger:

Discuss the three main processes involved in obtaining pure metals from their ores(Keith Pg 178)

# Uses of copper

Amongst other things copper is used for:

- **Electrical wiring.** It is a very good conductor of electricity and is easily drawn out into wires.
- **Domestic plumbing**. It doesn't react with water, and is easily bent into shape.
- **Boilers** and heat exchangers. It is a good conductor of heat and doesn't react with water.
- **Making brass.** Brass is a copper-zinc alloy. Alloying produces a metal harder than either copper or zinc individually. Bronze is another copper alloy this time with tin.
- **Coinage**. In the UK, as well as the more obvious copper-coloured coins, "silver" coins are also copper alloys this time with nickel. These are known as cupronickel alloys. UK pound coins and the gold-coloured bits of euro coins are copper-zinc-nickel alloys.

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## **Reactions of Copper**

## 1. With Air

Copper reacts with moist air to form a green outer layer of copper (II) carbonate (protective). Heated copper reacts with oxygen enriched air (below  $800^{\circ}$ c) to form black copper (II) oxide.

 $2Cu(s) + O_2(g) \longrightarrow 2CuO(s)$ 

At very high temperature >800°C copper reacts with oxygen to form copper (I) oxide.

 $4Cu(s) + O_2(g) \longrightarrow 2Cu_2O(s)$ 

## 2. With Halogens

 $Cu(s) + Cl_2(g) \longrightarrow CuCl_2(s)$ 

Heated copper reacts with halogens to form copper (II) halide. However copper reacts with iodine to form copper (I) iodide.

# 3. With Sulphur

 $Cu (s) + S (s) \longrightarrow CuS (s)$ When heated copper forms a sulphide

#### 4. With Acids

(a) Dilute nitric acid reacts with copper to form copper (II) nitrate, nitrogen monoxide and water.

 $3Cu(s) + 8 HNO_3(aq) \longrightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$ 

(b) Copper reacts with concentrated nitric acid to form copper (II) nitrate, nitrogen dioxide gas and water.

 $Cu(s) + 4HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$ 

(c) Copper reacts with concentrated sulphuric acid to form copper (II) sulphate, sulphur dioxide, and water.

 $Cu (s) + 2H_2SO_4(aq) \longrightarrow CuSO_4(aq) + SO_2(g) + 2H_2O (l)$ 

#### **Compounds of copper**

Copper shows 2 oxidation states of +1 and +2, however compounds in +1 oxidation state are unstable.

#### *Compounds in +2 oxidation state:*

This is the most stable oxidation state of copper and in aqueous solutions exists as  $[Cu(H_2O)_4]^{2+}$  which is blue. It slowly undergoes hydrolysis forming acidic solution

 $[Cu(H_2O)_4]^{2+}(aq) \qquad \leftrightarrows \qquad [Cu(H_2O)_3OH]^{-}_{(aq)} + H^{+}(aq)$ 

#### 1. Copper (II) Hydroxide

*Prepn:* By precipitation It's a blue ppt formed when aqueous NaOH is added to copper ions

 $Cu^{2+}(aq) + 2OH^{-}(aq) \longrightarrow Cu(OH)_{2}(s)$ 

Copper (II) hydroxide does not dissolve in excess sodium hydroxide. However dissolve in excess ammonia solution to form a deep blue solution

 $Cu(OH)_{2}(s) + 4 NH_{3}(aq) \longrightarrow [Cu(NH_{3})_{4}]^{2+} (aq) + 2OH^{-}$ 

tetraammine copper (II) ions

#### 2. Copper (II)Chloride

Prepn: By adding a stream of dry chlorine gas over heated copper metal.

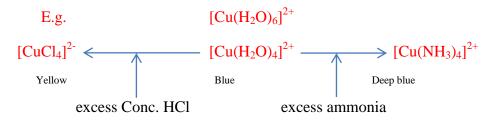
 $Cu(s) + Cl_2(g) \longrightarrow CuCl_2(s)$ 

In aq solution it exists as  $[Cu(H_2O)_4]^{2+}$ . It slowly undergoes hydrolysis forming acidic solution

 $[Cu(H_2O)_4]^{2+} \qquad \leftrightarrows \qquad [Cu(H_2O)_3OH]^{-}_{(aq)} + H^{+}(aq)$ 

 $CuCl_2(s)$  dissolves in conc. HCl acid to form a yellow solution of tetrachlorocuprate (II) ions  $[CuCl_4]^{2-}$ 

A complex ion may undergo ligand exchange whereby all its ligands are replaced by a different ligand which is more willing to donate the pair of electrons more readily. Altering a ligand around a central metal ion brings about a marked color change.



## Determination of Cu in a given copper (II) salt

There are two possible methods depending on the copper salt:

# Method 1

In this first method which is *applicable to any soluble copper salt*, or starting from copper ore dissolve the ore in dilute sulphuric acid.

Procedure:

To a solution containing copper (II) ions is added excess potassium iodide. A white precipitate of copper (I) iodide is formed which is stained brown by the liberated iodine.

 $2Cu^{2+}_{(aq)} + 4\Gamma_{(aq)} \longrightarrow Cu_2I_{2(s)} + I_{2(aq),\dots,n}1$ 

The amount of iodine liberated is then determined by titrating the resultant solution with a standard solution of sodium thiosulphate using starch as indicator  $2S_2O_3^{2^-}(aq) + I_{2(aq)} \longrightarrow S_4O_6^{2^-}(aq) + \Gamma_{(aq),...,2}$ 

Combining equation 1 and 2 gives overall equation as follows:  $2S_2O_3^{2-}(aq) + 2\Gamma_{(aq)} + 2Cu^{2+}(aq) \longrightarrow Cu_2I_{2(s)} + S_4O_6^{2-}(aq).....3$  $[Cu^{2+}] = [S_2O_3^{2-}]$ 

The concentration of  $Cu^{2+}$  is now determined by equation (3). Thus knowing the number of moles of thiosulphate ions that reacted, that of copper ions present can be can be determined.

## Questions

- a) Brass is an alloy of which copper is a component. Describe an experiment that can be carried out to determine the percentage of copper in brass.
- b) 2.4g of brass was dissolved to make 250cm<sup>3</sup> of copper (II) nitrate. To 10.0cm<sup>3</sup> of the solution was added excess iodide solution. The iodide liberated required 9.60cm<sup>3</sup> of 0.1M sodium thiosulphate for complete oxidation.

- i. Write an equation of reaction which took place btn KI and the brass solution
- ii. Cal the % of Cu in the sample of brass
- (d) *Explain why CuCl is insoluble in water and dilute HCl but dissolves in conc. HCl. (Keith Pg 196)*

## Method II

Copper (II) iodate is a sparingly soluble salt whose solubility eqtn is;

 $Cu(IO_3)_2 \rightleftharpoons Cu^{2+}_{(aq)} + 2IO_3^{-}_{(aq)}$ 

To the solution of the  $Cu(IO_3)_{2}$ , is added a solution of excess KI in the presences of sulphuric acid. Iodine is liberated as a brown solution.

 $IO_{3(aq)}^{-} + 6H^{+}_{(aq)} + 5\Gamma_{(aq)} \longrightarrow 3I_{2(aq)} + 3H_2O_{(aq)} \dots 1$ 

The iodine liberated is then titrated with a standard solution of sodium thiosulphate

$$I_{2(aq)} + 2S_2O_3^{2^-}(aq) \longrightarrow 2I_{(aq)}^{-} + S_4O_6^{2^-}(aq) \dots 2I_{(aq)}^{-}$$

#### Note:

Since 3 moles of iodine are produced by equation 1, the equation 2 is then multiplied throughout by 3 so as to balance the number of moles of iodine.

 $3I_{2(aq)} + 6S_2O_6^{2}(aq) \longrightarrow 6\Gamma_{(aq)} + 3S_4O_6^{2}(aq) \dots 3$ 

Equation 1 and 3 are now added noting that common species are cancelled to give:

 $IO_{3}^{}_{(aq)} + 6H^{+}_{(aq)} + 6S_{2}O_{3}^{2^{-}}_{(aq)} \longrightarrow 3H_{2}O_{(l)} + 3S_{2}O_{6}^{2^{-}}_{(aq)} + \Gamma_{(aq)}$ Therefore  $[Cu^{2^{+}}] = \frac{1}{2}[IO_{3}] = \frac{1}{2}(\frac{1}{6}[S_{2}O_{6}])$ 

## Test for Cu<sup>2+</sup>

## 1) Use of Sodium Hydroxide.

To the solution containing the cation is added NaOH (aq) drop wise until excess. Obsn: A blue precipitate of Cu(OH)<sub>2</sub>, insoluble in excess NaOH is formed :

# $Cu^{2+}_{(aq)} + 2OH^{-}_{(aq)} \longrightarrow Cu(OH)_2 (s)$

The precipitate turns black on heating due to formation of CuO

### 2) Use of ammonia solution

*Observation:* A blue ppt of Cu(OH)<sub>2</sub> soluble giving a deep blue solution tetraamine copper(II) complex ions

 $\operatorname{Cu}^{2^{+}}_{(aq)} + 4\operatorname{NH}_{3(aq)} \longrightarrow [\operatorname{Cu}(\operatorname{NH}_{3})_{4}]^{2^{+}}_{(aq)}$ 

## 3) Use of KI (aq)

To the solution containing copper ions is added KI (aq)

*Observation:* A white precipitate of Copper (I) iodide and a brown solution of iodine is produced.

 $2Cu^{2+}_{(aq)} + 4I^{-}_{(aq)} \longrightarrow Cu_2I_{2(s)} + I_{2(aq)}$ 

 Use of potassium hexacyanoferrate (II) solution.
To the solution containing Cu<sup>2+</sup> is added potassium hexacyanoferrate(II) solution Observation: A brown precipitate of copper hexacyanoferrate(II)

 $2Cu^{2+}_{(aq)} + [Fe(CN_{6})]^{4-}_{(aq)} \longrightarrow Cu_{2}[Fe(CN_{6})]_{(s)}$ 

Brown precipitate