SULPHUR AND ITS COMPOUNDS

1.1. SULPHUR

Sulphur is a non-metallic element with atomic number 16, and electronic configuration 2:8:6 and atomic mass 32.

Sulphur belongs to group VI and period 3 of the Periodic Table.

OCCURANCE

Sulphur exists as free sulphur underground and in compounds in form of sulphites, sulphides and sulphates.

Sulphur is a bright yellow solid normally in powder form at room temperature.

It has a molecular structure made up of eight sulphur atoms, S_8 molecule.

structure

It occurs in a combined state in compounds like lead(II) sulphide, zinc sulphide, iron(II)sulphide and iron(II) disulphide. These are ores of sulphur.

A good proportion of sulphur exists as hydrogen sulphide in petroleum gases and in volcanic regions.

Sulphur has basically two allotropes (monoclinic sulphur and rhombic sulphur).

Sulphur is insoluble in water but soluble in organic solvents

1.2. USES OF SULPHUR

1. manufacture of sulphuric acid
2. vulcanisation of rubber, a process which converts the soft pliable rubber into the hard, tough substance of which motor tyres and similar products are made
3. spraying or dusting of plants and fruits to prevent the growth of fungus.
4. Used in making calcium hydrogen sulphite ($Ca(HSO_3)_2$), which is used as a bleaching agent(bleacher) of wood pulp in manufacture of paper.
5. manufacture of dyes, gunpowder, fireworks, match sticks, Sulphur compounds such as carbon disulphide (CS_2)
6. making ointments for treatment of skin diseases such as ringworms.

1.3. Extraction of Sulphur by the Frasch process

Diagram

Procedure

Three concentric pipes are drilled into the sulphur deposits.

Superheated water at 170^{o}C at high pressure is forced down the outermost pipe into the sulphur deposit to melt the sulphur whose melting point is 115^{o}C, and 10atmospheres.

The Sulphur melts and flows into the reservoir at the base of the pump.

Hot compressed air under a pressure of about 15 atmospheres is pumped down through the innermost tube. This keeps the sulphur in molten and forces the molten sulphur and water to the surface through the middle pipe. The molten sulphur is collected in setlling tanks where it solidifies into yellow solid sulphur. Water is evaporated off and almost 99% pure Sulphur is obtained.

1.4. Extraction of sulphur from natural gas

Natural gases obtained during the refining of petroleum contain hydrogen sulphide which is absorbed by special solvents. The gas is removed from the solvent and a small portion of the gas is burnt in air to form sulphur dioxide.

$2H_2S\ (g) + 3O_2\ (g) \rightarrow 2H_2O\ (l) + 2SO_2\ (g)$

The remaining portion of the gas is left to react with the sulphur dioxide to form sulphur and water. The water is evaporated off.

$2H_2S\ (g) + SO_2\ (g) \rightarrow 3S\ (s) + 2H_2O\ (l)$

1.5. ALLOTROPES OF SULPHUR

An allotrope is one of the different distinct forms of an element but existing in the same physical state. Allotropes are of the same element having different physical properties but similar chemical properties.

Sulphur like carbon also exists in many different structural forms but in the same physical states.

- Rhombic sulphur
- Monoclinic sulphur

NB: Amorphous sulphur and plastic sulphur are **non-crystalline** allotropes.

Plastic sulphur is formed when liquid sulphur is poured in cold water.

Amorphous sulphur is formed by oxidation of hydrogen sulphide by air.

$2H_2S\ (g) + O_2\ (g) \rightarrow 2S\ (s) + 2H_2O\ (l)$

1.5.1. Rhombic sulphur

Rhombic sulphur is also referred to as octahedral sulphur or α-sulphur.

Rhombic sulphur is stable at temperatures below 96^{o}C. If heated to temperatures above 96^{o}C, the rhombic sulphur changes shape to monoclinic sulphur. has an octahedral shape hence its name.

It has a melting point of 113 ^{o}C and has a density of 2.06g/cm^3

It is stable and exists below 96 ^{o}C

Preparation of rhombic or octahedral sulphur (alpha sulphur) in the laboratory

Rhombic sulphur is prepared by dissolving powdered sulphur in carbon disulphide (or methylbenzene) as solvent in a boiling tube. The carbon disulphide (or methylbenzene) is allowed to evaporate slowly below 96 ^{o}C. Large crystals of rhombic of sulphur having an octahedral shape form.

1.5.2. Monoclinic sulphur

Monoclinic sulphur is also referred to as prismatic sulphur or β-sulphur.

Monoclinic sulphur is stable only at temperatures above 96 ^{o}C, below 96 ^{o}C, it changes to rhombic sulphur.

Its crystals are needle shaped.

It has a melting point of 119 ^{o}C and has a density of 1.98 g/cm^3.

It exists only above 96 ^{o}C

96 ^{o}C is called the **transition temperature** of sulphur.

$$\text{Rhombic sulphur} \underset{\text{Below } 96\ ^{o}\text{C}}{\overset{\text{Above } 96\ ^{o}\text{C}}{\rightleftarrows}} \text{Monoclinic sulphur}$$

Preparation of monoclinic sulphur (Beta sulphur) in the laboratory

Monoclinic sulphur is prepared by heating Place powdered sulphur in a crucible up to its melting point and allowing the molten sulphur to slowly cool above 96 ^{o}C. A thin layer of sulphur is formed above the crucible, which is cracked off to obtain needle-like crystals of monoclinic sulphur.

Transition temperature

This is the temperature at which a change from one form of sulphur to another form takes place. It is 96^{o}C. Rhombic sulphur is stable below 96^{o}C. Above this temperature, it slowly changes to the monoclinic form. Monoclinic stable is stable above 96^{o}C and therefore below this temperature it slowly changes to the rhombic form.

Differences between rhombic sulphur and monoclinic sulphur

Rhombic sulphur consists of relatively large yellow, translucent, octahedral crystals with a melting point of 114^{o}C while monoclinic sulphur consists of needle shaped, pale yellow transparent crystals with a melting point of 119^{o}C.

Rhombic sulphur has a density of 2.06g/cm^3 while monoclinic sulphur has a density of 1.98 g/cm^3.

Crystals of rhombic sulphur are stable below 96^{o}C while monoclinic sulphur is stable above 96 ^{o}C.

1.5.3. Amorphous sulphur

Amorphous sulphur is formed by oxidation of hydrogen sulphide by air. When a saturated solution of hydrogen sulphide is left exposed to air for two days, a yellow powder of amorphous sulphur is formed.

$2H_2S(aq) + O_2(g) \rightarrow 2S(s) + 2H_2O(l)$

1.5.4. Plastic sulphur

When boiling sulphur is quickly cooled by pouring it into cold water, yellow/brown elastic solid called plastic sulphur is formed.

1.5.5. Colloidal sulphur

When dilute hydrochloric acid is added to dilute sodium thiosulphate, a yellow suspension of colloidal sulphur is formed

$Na_2S_2O_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + S(s) + SO_2(g)$

1.6. PROPERTIES OF SULPHUR

1.6.1. PHYSICAL PROPERTIES OF SULPHUR

- It is a yellow solid
- It is a non-metal.
- It is insoluble in water but soluble in organic solvents like carbon disulphide(CS_2), methylbenzene.
- Has a low melting point of 115^oC.
- It is a poor conductor of heat and electricity (an insulator).

1.6.2. CHEMICAL PROPERTIES OF SULPHUR

1. Action of heat on sulphur (in absence of air)

When a yellow solid of sulphur is heated, it melts at about 113^oC to a clear amber liquid which flows easily like water. Sulphur contains small rings of atoms, S_8; the liquid flows with ease because the rings have been separated. On further heating at about 160^oC, the sulphur becomes brown and viscous. It flows slowly because the small rings of 8 atoms break and longer chains are formed. These chains twist together and do not flow readily over one another.

On further heating, the liquid becomes very dark, reddish brown in colour and less viscous again. The chains break and become shorter which can flow more readily. Sulphur boils at 444^oC and forms a brown vapour. On cold surfaces, the vapour condenses directly into a yellow sublimate.

2. Combustion of sulphur (in a plentiful supply of air)

When burning sulphur is plunged into a gas-jar of air, the sulphur burns with a blue flame producing a colourless gas

$S(s) + O_2 (g) \rightarrow SO_2 (g)$

The sulphur dioxide gas is readily oxidized to sulphur trioxide, formed as **dense white fumes.**

$2SO_2 (g) + O_2 (g) \rightleftharpoons 2 SO_3 (g)$

3. Reaction with iron

When a mixture of iron filings and sulphur is heated, the mixture glows red and a **black solid** formed of iron (II) sulphide.

$Fe(s) + S(s) \rightarrow FeS(s)$

4. Reaction with copper

Sulphur reacts with copper when heated forming a **black solid**, copper (II) sulphide.

$2Cu(s) + S(s) \rightarrow CuS(s)$

5. Reaction with carbon

When heated, sulphur reacts with Carbon to form a liquid, carbon disulphide. Very high temperatures are required for this reaction to occur.

$C(s) + 2S(s) \rightarrow CS_2(l)$

6. Reaction of sulphur with acids

Sulphur does not react with dilute acids. Sulphur is oxidized by **hot concentrated** sulphuric acid forming sulphur dioxide and water.

$S(s) + 2H_2SO_4(l) \rightarrow 3SO_2(g) + 2H_2O(l)$

Sulphur is oxidized by **hot concentrated** nitric acid forming sulphuric acid and brown fumes of nitrogen(IV)oxide. Bromine is added to speed up the rate of reaction.

$S(s) + 6HNO_3(s) \rightarrow H_2SO_4(aq) + 6NO_2(g) + 2H_2O(l)$

COMPOUNDS OF SULPHUR

SULPHUR DIOXIDE GAS (SO_2)

Laboratory preparation of sulphur dioxide

Preparation of sulphur dioxide

Reagents: sodium sulphite and dilute sulphuric acid

Conditions for the reaction: The reaction takes place at room temperature.

However, the mixture is warmed gently to drive out the sulphur dioxide gas which would otherwise dissolve in cold water.

PROCEDURE

Solid sodium sulphate is placed into a flask fitted with cork, a delivery tube and a thistle funnel.

Dilute sulphuric acid being a liquid is added onto sodium sulphite through the thistle funnel.

The sodium sulphite dissolves with effervescence and bubbles of a colourless gas given out.

$Na_2SO_3 (s) + H_2SO_4 (aq) \rightarrow Na_2SO_4 (aq) + H_2O (l) + SO_2 (g)$

The mixture is warmed gently to drive out the sulphur dioxide gas which would otherwise dissolve in the cold water.

The gas is passed through concentrated sulphuric acid to dry the gas and since the gas is acidic, it does not react with sulphuric acid.

The gas is then collected by downward delivery because it is denser than air.

TEST FOR SULPHUR DIOXIDE GAS

1. <u>Using Acidified potassium dichromate(VI) solution</u>

When sulphur dioxide gas is bubbled through acidified potassium dichromate(VI) solution.

Observation: The gas turns acidified potassium dichromate(VI) solution from **orange** to **green**.

Equation of reaction:

$3SO_2\ (g) + K_2Cr_2O_7\ (aq) + H_2SO4(aq) \rightarrow K_2SO_4(aq) + Cr_2(SO4)_3(aq) + H_2O\ (l)$

OR

$3SO_2\ (g) + Cr_2O_7^{2-}\ (aq) + 2H^+\ (aq) \rightarrow 3SO_4^{2-}\ (aq) + 2Cr^{3+}(aq) + H_2O\ (l)$

Reason:

In acidic medium, sulphur dioxide reduces the dichromate(VI) ions (**orange**) to chromium(III) ions (**green**).

This is a characteristic test for Sulphur dioxide

2. <u>Using Acidified potassium manganite(VII) solution</u>

When sulphur dioxide gas is bubbled through acidified potassium manganate (VII) solution.

Observation: The gas turns acidified potassium manganate (VII) solution from **purple** to **colourless**.

Equation of reaction:

$2KMnO_4(aq) + 5SO_2(aq) + 2H_2O(l) \rightarrow 2MnSO4(aq) + 5K_2SO4(aq) + 2H_2SO4(aq)$

OR

$2MnO_4^{2-}(aq) + 5SO_2(aq) + 2H_2O(l) \rightarrow 2Mn^{2+}(aq) + 5SO4^{2-}(aq) + 4H^+(aq)$

PROPERTIES OF SULPHUR DIOXIDE GAS

(a) <u>PHYSICAL PROPERTIES</u>

1. It is a colourless gas with an irritating smell
2. It is denser than air
3. It is very soluble in water
4. It is fairly poisonous
5. It turns damp blue litmus paper red because it is an acidic gas

   $SO_2(g) + H_2O\ (l) \rightarrow H_2SO_3(aq)$

(b) CHEMICAL PROPERTIES

1. **Reaction with alkalis**

Sulphur dioxide gas reacts with sodium hydroxide to form sodium sulphite and water.

$NaOH(aq) + SO_2(g) \rightarrow Na_2SO3(aq) + H_2O(l)$

If excess sulphur dioxide gas is bubbled through, it forms sodium hydrogen sulphite.

$Na_2SO3(aq) + H_2O(l) + SO_2(g) \rightarrow 2NaHSO3(aq)$

2. **Reaction with iron (III) sulphate solution**

When sulphur dioxide gas is bubbled through a solution of iron (III) sulphate.

Observation: The **brown solution** of iron (III) sulphate turns **pale green.**

Reason: This is because sulphur dioxide gas reduces iron (III) sulphate (**brown**) to iron (II) sulphate (**green**).

Equation of reaction:

$2Fe_2(SO4)_3(aq) + SO_2(g) + 2H_2O(l) \rightarrow 2FeSO4(aq) + 2H_2SO4(aq)$

OR

$2Fe^{3+}(aq) + SO_2(g) + 2H_2O(l) \rightarrow 2Fe^{2+}(aq) + 4H^{+}(aq) + SO_4^{2-}(aq)$

NB: In this reaction, sulphur dioxide acts as a powerful reducing agent

3. **Reaction with nitric acid.**

Sulphur dioxide reduces concentrated nitric acid to nitrogen dioxide(brown fumes), the sulphur dioxide itself oxidized to sulphuric acid. Brown fumes are observed

$SO_2 (g) + 2HNO_3 (l) \rightarrow H_2SO_4 (aq) + 2NO_2 (g)$

4. **Reaction with chlorine**

In the presence of water, sulphur dioxide gas reduces chlorine gas to hydrochloric acid.

$SO_2(g) + Cl_2(g) + 2H_2O(l) \rightarrow H_2SO_4 (aq) + HCl(g)$

5. When sulphur dioxide is dissolved in water, it forms sulphurous acid which is a **bleaching agent.** Sulphurous acid takes up oxygen from the dye to form sulphuric acid. The removal of oxygen from a dye converts the dye to a colourless compound. This is essentially a different reaction from that of other bleaching agents, which oxidize the dye to a colourless compound.

$SO_2 (g) + 2H_2O (l) + Dye \rightarrow H_2SO_4 (aq) + (Dye + 2H)$

Qn: 1.**State what is observed and explain the reaction which takes place when sulphur dioxide gas is bubbled through a solution containing a green dye.**

NB: Sulphur dioxide bleaches coloured dyes e.g if flowers are dipped in a jar full of sulphur dioxide, the coloured flowers turn colourless.

6. **Reaction with hydrogen sulphide**

Sulphur dioxide reacts with hydrogen sulphide to form a **yellow deposit** of sulphur. Sulphur dioxide oxidizes hydrogen sulphide to water by supplying oxygen and itself reduced to sulphur

$2H_2S\ (g)\ +\ SO_2\ (g)\ \rightarrow\ 2H_2O\ (l)\ +\ 3S\ (s)$

7. Reaction with magnesium

Burning magnesium continues to burn with a bright white flame in sulphur dioxide for sometime forming a **white powder** of magnesium oxide and a **yellow solid** of sulphur.

$2Mg\ (s)\ +\ SO_2\ (g)\ \rightarrow\ 2MgO\ (s)\ +\ S\ (s)$

USES OF SULPHUR DIOXIDE

1. It is used in the manufacture of sulphuric acid in the contact process
2. It is used as a bleaching agent in paper industry and also to bleach wool, silk and sponges
3. It is used as a preservative of foods e.g. orange juice and fruits where it reacts with oxygen and prevents oxidation
4. It is used for fumigation of houses since it is poisonous and kills microorganisms
5. As a cooling agent in refrigerators

SULPHUR TRIOXIDE GAS (SO_3)

Laboratory preparation of sulphur trioxide

Sulphur dioxide gas from a siphon and excess oxygen from a gas cylinder are dried by passing the gases through concentrated sulphuric acid.

The dried gases are passed over heated vanadium (V) oxide (or platinum asbestos) at 450 ^{o}C to form sulphur trioxide gas seen as dense white fumes.

The dense white fumes are condensed to white needles of sulphur trioxide in an ice-salt freezing mixture of ice and sodium chloride.

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

6.1 SULPHURIC ACID(H_2SO_4)

Sulphuric acid is a dibasic mineral acid.

Industrial manufacture of sulphuric acid by the contact process

The raw materials are **sulphur dioxide**, **oxygen** and water.

Stage 1: preparation of sulphur dioxide

Sulphur dioxide is obtained by burning Sulphur/sulphide ores.

$S(s) + O_2(g) \rightarrow SO_2(g)$

Or: $Zn(s) + O_2(g) \rightarrow ZnO(s) + SO_2(g)$

Stage II: purification

Sulphur dioxide and oxygen gases are purified by passing through electrostatic purifiers to remove dust which would poison the catalyst.

Stage III: Conversion of Sulphur dioxide to Sulphur trioxide

A mixture of Sulphur dioxide and excess oxygen is then passed over heated vanadium pentoxide (V_2O_5) catalyst at low temperature of 450 – 500^{o}C under high pressure of 200 atmospheres to obtain Sulphur trioxide.

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

NB: Vanadium(V) oxide is preferred as a catalyst because it is cheap and cannot be easily poisoned.

Stage IV: Absorption

Sulphur trioxide formed is absorbed into concentrated sulphuric acid forming fuming liquid called **oleum**.

$SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$

Stage IV: Dilution

The oleum is then diluted with a correct amount of water to form 98% pure sulphuric acid.

$H_2S_2O_7$ (l) + H_2O (l) → $2H_2SO_4$(l)

Note: Sulphur trioxide is not dissolved in water directly because the reaction is too exothermic and the heat produced from the reaction vaporizes the acid forming only tiny droplets of the acid leading to a spray of sulphuric acid which would affect the workers in the factory.

The following flow chat shows summarizes the steps involved in the manufacture of sulphuric acid by contact process.

PROPERTIES OF SULPHURIC ACID

PHYSICAL PROPERTIES

- It is a colourless and odourless oily liquid
- Has a high affinity for water (hygroscopic) and that is why it is used as a drying agent
- It has a density of 1.86g/cc and boils at $338^{o}C$
- It does not show any acidic properties unless water is present.

Note: Sulphuric acid has a high affinity for water. Never add water to the concentrated acid because it can explode. It is therefore advisable to add the acid to water rather than water to acid.

CHEMICAL PROPERTIES

1) **As an acid**

a) **Condition**: The acid Should be **dilute**
Sulphuric acid behaves as a **strong acid** in dilute or aqueous solution.
Is a strong acid, thus ionizes completely when in aqueous solution or dilute.

$H_2SO_4(aq) \rightarrow 2H^+(aq) + SO4^{2-}(aq)$

b) Reacts with metals to produce hydrogen gas
$Zn (s) + H_2SO_4(aq) \rightarrow ZnSO_4 (aq) + H_2 (g)$

c) Reacts with bases to form salt and water only
$CuO(s) + H_2SO_4 (aq) \rightarrow CuSO_4 (aq) + H_2O (l)$

d) It neutralises alkalis like sodium hydroxide solution to form a **salt** and **water** only

$2NaOH(aq) + H_2SO_4 (aq) \rightarrow Na_2SO_4 (aq) + 2H_2O (l)$

e) It reacts with carbonates and hydrogen carbonates liberating carbon dioxide
$Na_2CO_3(s) + H_2SO_4 (aq) \rightarrow Na_2SO_4 (aq) + H_2O (l) + CO_2(g)$

$2NaHCO_3(s) + H_2SO_4 (aq) \rightarrow Na_2SO_4 (aq) + H_2O (l) + 2CO_2(g)$

2) **As an oxidizing agent**

Condition: The acid should be **hot** and **dilute**.
When **concentrated** and **hot**, it acts as an oxidizing agent to both metals and non-metals and itself is reduced to sulphur dioxide. It accepts electrons or supplies oxygen in its reaction.

a) When **hot** and **concentrated** sulphuric acid is added to Copper, the copper dissolves with effervescence and a **blue solution** of copper(II)sulphate is formed.

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

b) It oxidizes hydrogen sulphide to sulphur forming a **yellow deposit**.

$H_2S (g) + H_2SO_4 (l) \rightarrow S (s) + 2H_2O(l) + SO_2(g)$

c) It oxidizes sulphur and carbon to their respective oxides.

$3S(s) + 2H_2SO_4(l) \rightarrow 2H_2O(l) + 3SO_2(g)$

$C(s) + 2H_2SO_4(l) \rightarrow CO_2 (g) + 2SO_2(g) + 2H_2O(l)$

3) **As a dehydrating agent.**

Condition: The acid must be **concentrated**
Sulphuric acid has a very high affinity for water and can remove it from substances including air, therefore, it is hygroscopic. It can be used as a **drying agent** for most gases.

a) **Reaction with cane sugar**

When concentrated sulphuric acid is poured onto sugar crystals (sucrose) in a beaker, the white crystals of sugar turn yellow then dark brown, swell up forming a **black (**spongy/porous) **mass**. Steam is given off and the whole mass becomes very hot. The acid takes out the elements of water from sugar leaving a black mass of carbon.

$C_{12}H_{22}O_{11}(s) \rightarrow 12C(s) + 11H_2O(l)$

Similar reactions take place when other carbohydrates like glucose are used

$C_6H_{12}O_6(s) \rightarrow 6C(s) + 6H_2O(l)$

The same observations would occur if cotton (cellulose) was used

$C_6H_{10}O_5(s) \rightarrow 6C(s) + 6H_2O(l)$

b) When concentrated sulphuric acid is added to blue crystals of copper (II) sulphate (hydrated) and warmed, they change to a white solid of anhydrous copper (II) sulphate as water of crystallisation is removed by concentrated sulphuric acid.

$CuSO_4.5H_2O(s) \rightarrow CuSO_4(s) + 5H_2O(l)$

c) Other substances which are dehydrated by concentrated sulphuric acid include ethanol, methanoic acid and oxalic aid

$C_2H_5OH(l) \rightarrow C_2H_4(g) + H_2O(l)$

Ethanol

$HCOOH(l) \rightarrow CO(g) + H_2O(l)$

Methanoic acid

$H_2C_2O_4(s) \rightarrow CO(g) + CO_2(g) + H_2O(l)$

Oxalic acid

4) Action of concentrated sulphuric on nitrates and chlorides

Concentrated sulphuric acid displaces hydrochloric acid from metallic chlorides and nitric acid from nitrates e.g. it reacts with sodium chloride when heated forming white fumes of hydrogen chloride gas which dissolves in water forming hydrochloric acid.

$2NaCl(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2HCl(g)$ (With heating)

$NaCl(s) + H_2SO_4(aq) \rightarrow NaHSO_4(aq) + HCl(g)$ (Without heating)

It also reacts with potassium nitrate to form nitric acid

$KNO_3(s) + H_2SO_4(aq) \rightarrow KHSO_4(aq) + HNO_3(aq)$

6.1.1. Uses of sulphuric acid

- It is used in the manufacture of detergents
- It is used in car batteries and accumulators as an electrolyte
- It is used in manufacture of fertilizers such as ammonium sulphate

$NH_3(g) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(s)$

- Used in extraction of metals and also cleaning them prior to plating
- Used in manufacture of paints, dyes and explosives

HYDROGEN SULPHIDE GAS (H_2S)

Laboratory preparation of hydrogen sulphide gas

Dilute hydrochloric acid beng a liquid is added to a flat bottomed flask containing clumps of iron (II) sulphide through a thistle funnel. Heating is not required.

Effervescence occurs and the hydrogen sulphide formed is passed through hot water to remove fumes of hydrogen chloride and then dried by passing it through a U-tube containing **anhydrous calcium chloride.**

The dry gas is then collected by **downward delivery** since it is denser than air.

$FeS(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2S(g)$

Dilute sulphuric acid may be used

$FeS(s) + H_2SO_4(aq) \rightarrow FeSO_4(aq) + H_2S(g)$

To prepare hydrogen sulphide from sulphur, iron (II) sulphide is first prepared by heating the mixture of iron and sulphur.

$Fe(s) + S(s) \rightarrow FeS(s)$

Concentrated Sulphuric acid is **not** used to dry the gas because it reacts with hydrogen sulphide forming a **yellow precipitate** of sulphur.

$H_2SO_4(aq) + 3H_2S(g) \rightarrow 4H_2O(l) + 4S(s)$

Testing for hydrogen sulphide

A strip of filter paper is soaked in lead (II) ethanoate (lead (II) acetate) solution and dropped into a gas jar of hydrogen sulphide. The paper turns black. This colour change is caused by precipitation of black lead (II) sulphide.

$(CH_3COO)_2Pb(aq) + H_2S(g) \rightarrow PbS(s) + 2CH_3COOH(aq)$

Black

PROPERTIES OF HYDROGEN SULPHIDE

PHYSICAL PROPERTIES

- The gas is colourless
- It has a repulsive smell similar like rotten eggs.
- It is also fairly soluble in cold water forming a weak acidic solution
- It is denser than air
- The gas is extremely poisonous

CHEMICAL PROPERTIES

1. Hydrogen sulphide is a powerful reducing agent

   It reduces reducing agents and itself oxidized to sulphur which appears as a pale yellow precipitate

   a. Hydrogen sulphide reduces iron (III) chloride to iron (II) chloride. When hydrogen sulphide is passed through iron (III) chloride solution (yellow solution) a yellow precipitate of sulphur appears. On filtering, a green solution of iron (II) chloride appears as the filtrate

   $H_2S(g) + 2FeCl_3(aq) \rightarrow 2FeCl_2(aq) + 2HCl(aq) + S(s)$

   b. Hydrogen sulphide reacts with concentrated nitric acid to form brown fumes of nitrogen dioxide and a yellow deposit of sulphur. Also the mixture becomes hot. The hydrogen sulphide reduces the nitric acid to nitrogen dioxide.

   $2HNO_3(l) + H_2S(g) \rightarrow 2H_2O(l) + 2NO_2(g) + S(s)$

2. Combustion of hydrogen sulphide

   a. With plentiful supply of air

Hydrogen sulphide burns with a blue flame forming water and sulphur dioxide.

$2H_2S(g) + 3O_2(g) \rightarrow 2SO_2(g) + 2H_2O(l)$

b. *With a limited supply of air*

When hydrogen sulphide is burnt in a limited supply of air, a yellow deposit of sulphur is formed. The oxygen supply cannot oxidize the gas completely and therefore free sulphur is deposited.

$2H_2S(g) + O_2(g) \rightarrow 2H_2O(l) + 2S(s)$

3. Reacting with salts of metals

   Hydrogen sulphide can precipitate insoluble sulphides of copper and lead only by reacting with solutions of their salts. A dark brown precipitate of copper (II) sulphide and a black precipitate of lead (II) sulphide are formed

$CuSO_4(aq) + H_2S(g) \rightarrow CuS(s) + H_2SO_4(aq)$

$Pb(NO_3)_2(aq) + H_2S(g) \rightarrow PbS(s) + 2HNO_3(aq)$

$Pb(NO_3)_2(aq) + H_2S(g) \rightarrow PbS(s) + 2HNO_3(aq)$

TEST FOR SULPHATE IONS (SO_4^{2-})

Action of heat on sulphates (SO_4^{2-})

Most sulphates are hydrated and when heated, they lose their water of crystallisation to form anhydrous salts which are resistant to further heating and therefore do not decompose. Therefore hydrated sulphates do not decompose on heating e.g.

$MgSO_4.7\,H_2O(s) \rightarrow MgSO_4(s) + 7\,H_2O(l)$

$Na_2SO_4.10H_2O(s) \rightarrow Na_2SO_4(s) + 10H_2O(l)$

When a blue solid of hydrated copper (II) sulphate is heated, water vapour is given off as water of crystallisation is lost, giving a white solid (residue). On further heating, it decomposes to form white fumes of sulphur trioxide and a black residue of copper (II) oxide.

$CuSO_4.5\,H_2O(s) \rightarrow CuSO_4(s) + 5H_2O(l)$

Blue White

$CuSO_4(s) \rightarrow CuO(s) + SO_3\,(g)$

Overall equation:

$CuSO_4.5H_2O \rightarrow CuO(s) + SO_3\,(g) + 5H_2O(l)$

On heating hydrated iron (II) sulphate (green), it loses its water of crystallisation

$FeSO_4.7\,H_2O(s) \rightarrow FeSO_4(s) + 7\,H_2O(l)$

On further heating, the anhydrous iron (II) sulphate formed decomposes to give white fumes of sulphur trioxide together with sulphur dioxide and leaves a brown residue of iron (III) oxide

$FeSO_4(s) \rightarrow Fe_2O_3(s) + SO_2(g) + SO_3(g)$

When ammonium sulphate is heated it decomposes to give ammonia, sulphur trioxide and water

$(NH_4)_2SO_4(s) \rightarrow NH_3(g) + SO_3(g) + H_2O(l)$

Testing for soluble sulphate (SO_4^{2-})

a. Using dilute hydrochloric acid and barium chloride solution.

To the solution add dilute hydrochloric acid followed by barium chloride solution.

A white precipitate of barium sulphate is formed

$BaCl_2(aq) \quad + \quad Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$

b. Using dilute nitric acid and barium nitrate solution.

To the solution add dilute nitric acid and barium nitrate solution. A white precipitate is formed.

$Ba(NO_3)_2(aq) \quad + \quad Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaNO_3(aq)$

Ionic equation

$Ba^{2+}(aq) \quad + \quad SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

Note: Carbonate ions (CO_3^{2-}) and sulphite ions (SO_3^{2-}) are precipitated as barium carbonate and barium sulphite respectively, if carbonate and sulphite ions are present in solution.

$Ba^{2+}(aq) \quad + \quad CO_3^{2-}(aq) \rightarrow BaCO_3(s)$

$Ba^{2+}(aq) \quad + \quad SO_3^{2-}(aq) \rightarrow BaSO_3(s)$

The purpose of adding dilute nitric acid or hydrochloric acid is to remove the carbonate ion and sulphite ions if they are present in solution.

$2H^+(aq) \quad + \quad CO_3^{2-}(aq) \quad \rightarrow \quad H_2O(l) + \quad CO_2(g)$

$2H^+(aq) \quad + \quad SO_3^{2-}(aq) \quad \rightarrow \quad H_2O(l) + \quad SO_2(g)$

The sulphite ions (SO_4^{2-}) remain in solution because they do not react with dilute hydrochloric acid acid or nitric acid.

c. Using lead (II) nitrate solution

Also lead (II) nitrate solution forms a white precipitate of lead (II) sulphate with a sulphate.

$Pb^{2+}(aq) \quad + \quad SO_4^{2-}(aq) \rightarrow PbSO_4(s)$