

12. SULPHUR AND ITS COMPOUNDS

12.1 Introduction

Sulphur, like oxygen, is a group VI element. It has six electrons in its outermost shell, with the electronic configuration 2, 8, 6. Sulphur is a yellow solid. It occurs free in nature and in combination with other elements as in copper pyrites, CuS , iron pyrites, FeS , and in zinc blende, ZnS .

12.2 Extraction of Sulphur

The Frasch process is the most important method of extracting sulphur. It is used extensively in Texas, USA, where large deposits of sulphur occur about 200 metres below the surface of the earth. The quicksand above the sulphur deposits in this region make the normal mining process difficult.

In the Frasch process, three pipes arranged in a concentric form are sunk down to the sulphur deposits (Figure 12.1). Superheated water at 10 atmosphere pressure and about 180°C is pumped down to the sulphur deposits through the outermost pipe. This melts the sulphur underground (melting point of sulphur is 114°C). Hot compressed air is forced down to reach the molten sulphur through the innermost pipe. The pressure built up underground forces the molten sulphur up through the middle pipe. The hot water and hot air moving down the pipes ensure that the sulphur remains molten on its way up.

On reaching the surface, the molten sulphur is collected in tanks where it solidifies on cooling. It can be remelted and put into moulds where it forms roll sulphur. Sulphur obtained by the Frasch process is up to 99.5% pure, and needs no further purification for commercial use.

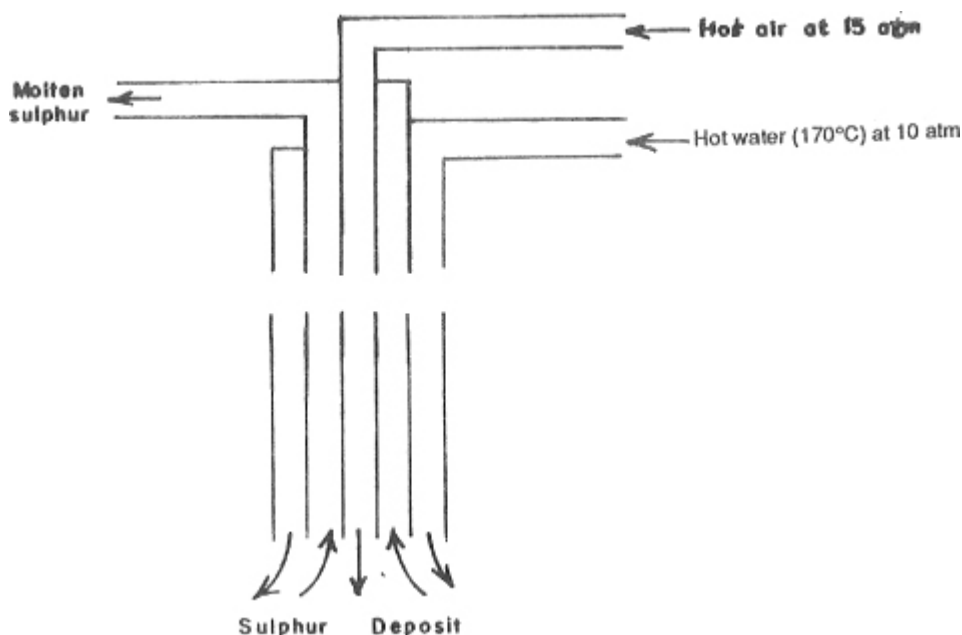


Figure 12.1 Frasch process for the extraction of sulphur

12.3 Allotropes of Sulphur

Experiment 12.1: Investigating Allotropy in Sulphur.

- Put some powdered sulphur into an evaporating dish. Add carbon(IV) sulphide, CS_2 , to it and stir to dissolve (Figure 12.2). Leave in the fume cupboard for sometime, then filter into a dry beaker. Cover the beaker with perforated filter paper to ensure slow evaporation of the solvent. When the carbon(IV) sulphide has evaporated, octahedral crystals, known as **rhombic ($\hat{I}\pm$) sulphur** are left.

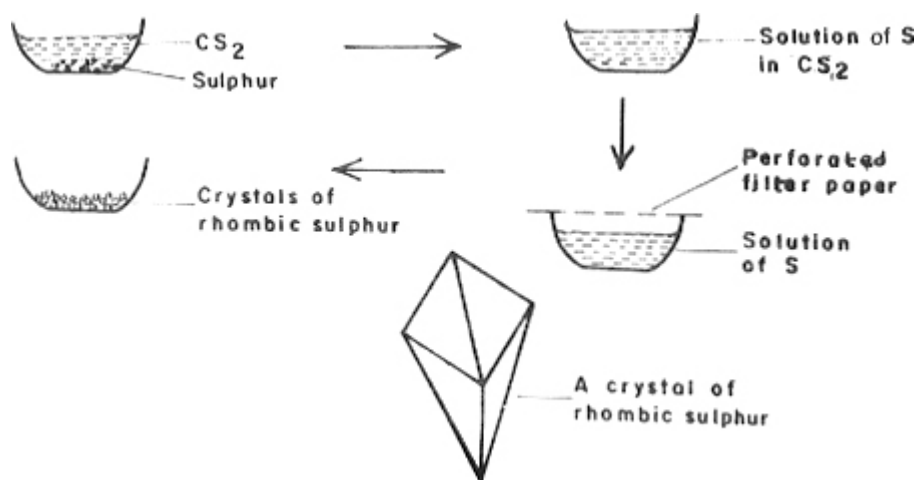


Figure 12.2 Rhombic sulphur

- Put about 6g of powdered sulphur into a crucible. Heat it slowly so that the sulphur does not ignite. Continue the heating until the sulphur melts, then leave to cool. After sometime, a crust forms on

the surface of the molten sulphur (Figure 12.3). Pierce the crust and pour off sulphur that is still in the liquid state, to obtain needles of **monoclinic (β) sulphur**.

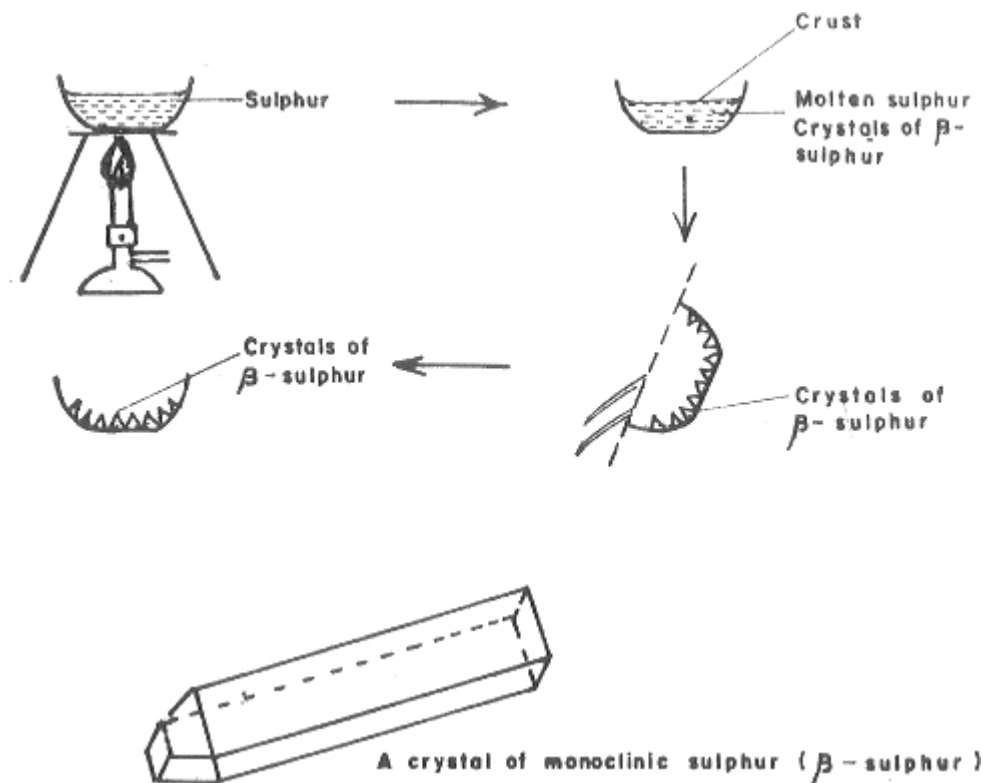


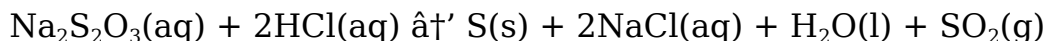
Figure 12.3 Monoclinic sulphur (β -sulphur)

Alternatively, monoclinic sulphur may be made by dissolving powdered sulphur in hot methylbenzene (toluene) in a water bath and cooling the solution slowly, to form the needle-like crystals.

Apart from these two crystalline forms, sulphur also exists in various non-crystalline forms.

Experiment 12.2: Investigating non-crystalline, forms of Sulphur.

1. Make a solution of sodium thiosulphate in a beaker of water. Add dilute hydrogen Chloride acid (hydrochloric acid) to it, a little at a time, until a white precipitate is formed. The white precipitate is **colloidal sulphur**.



2. Melt some sulphur in a test-tube, then pour it into cold water in a beaker (Figure 12.4). **Plastic sulphur**, an elastic form of sulphur, is formed.

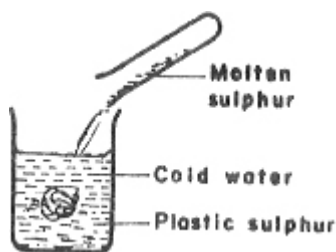


Figure 12.4 Plastic sulphur

3. Bubble hydrogen sulphide gas into distilled water in a beaker until it is saturated. Expose the solution to air for sometime. **Amorphous sulphur** is deposited as a white powder (Figure 12.5).

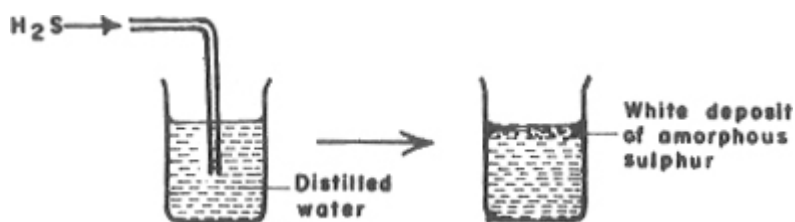


Figure 12.5 Amorphous sulphur

Rhombic (or $\hat{I}\pm$ -) sulphur, and monoclinic (or \hat{I}^2 -) sulphur, are the two crystalline forms of sulphur. They are allotropes of sulphur. Table 12.1 summarises the differences between the two allotropes.

TABLE 12.1 ALLOTROPES OF SULPHUR

Property	Rhombic ($\hat{I}\pm$)	Monoclinic (\hat{I}^2)
Colour	Yellow	Amber
Density	2.08 g cm ⁻³	1.98 g cm ⁻³
M.p. ($\hat{A}^\circ\text{C}$)	114	119
Stability	Stable below 96 $\hat{A}^\circ\text{C}$	Unstable below 96 $\hat{A}^\circ\text{C}$
Shape	Octahedral	Needle-shaped
Transmission of light	Transluscent	Transparent

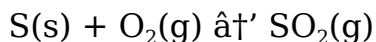
12.4 Reactions of Sulphur

Experiment 12.3: Investigating the properties of sulphur.

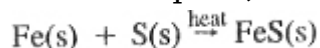
1. Shake some sulphur with water. Warm and stir. The sulphur does not dissolve. Sulphur is insoluble in water.
2. Place some powdered sulphur into a beaker. Add carbon(IV) sulphide, CS₂, to it. A clear solution is produced. Sulphur is soluble in organic solvents such as carbon(IV) sulphide and methylbenzene.
3. Heat a little sulphur in a long narrow test-tube to exclude air. It

melts at about 115°C to an amber-coloured mobile liquid, which pours out if the test-tube is inverted. As heating is continued, it becomes a darker coloured liquid, and at 160°C the liquid becomes very viscous. If the test-tube is now inverted, the molten sulphur does not pour out. As the temperature rises it becomes very dark reddish-brown and more mobile. Finally, at 444°C it boils, giving off a light-brown vapour.

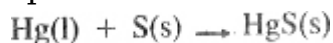
- Put some sulphur into a deflagrating spoon and ignite it. Lower the burning sulphur into a gas jar and test the gaseous product with wet blue litmus paper. The blue litmus paper turns red. The gaseous product is an acidic gas, sulphur(IV) oxide.



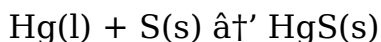
- Put equimolar quantities of sulphur and iron fillings into a crucible. Heat the mixture. The yellow specks of sulphur in the mixture are no longer visible in the product. A binary compound of iron and sulphur, iron(II) sulphide, is formed.



Repeat with copper turnings in place of iron fillings. Copper(II) sulphide is formed.

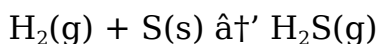


Mix sulphur and mercury without heating. A black solid, mercury(II) sulphide, is formed.

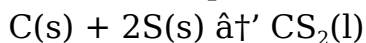


Sulphur is thus a reactive non-metal. It combines directly with a number of metals, forming their sulphides.

- Pass hydrogen gas into a test-tube of molten sulphur. Test the gas evolved with lead ethanoate paper. The paper is blackened by the gas which smells like rotten eggs. The gas is hydrogen sulphide.



Sulphur also combines with carbon when coke is heated with it to high temperatures. The product is a foul-smelling liquid, carbon(IV) sulphide.

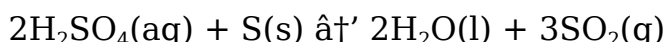


Thus sulphur also combines directly with some non-metals.

Put some sulphur powder into a test-tube. Add concentrated trioxonitrate(V) acid to it, then heat the mixture. Brown fumes of nitrogen(IV) oxide are evolved. Trioxonitrate(V) acid oxidises sulphur to tetraoxosulphate(VI) acid, becoming itself reduced to nitrogen(IV) oxide.



Repeat with concentrated tetraoxosulphate(VI) acid. Sulphur(IV) oxide is liberated.



Tetraoxosulphate(VI) acid acts as an oxidizing agent in this reaction.

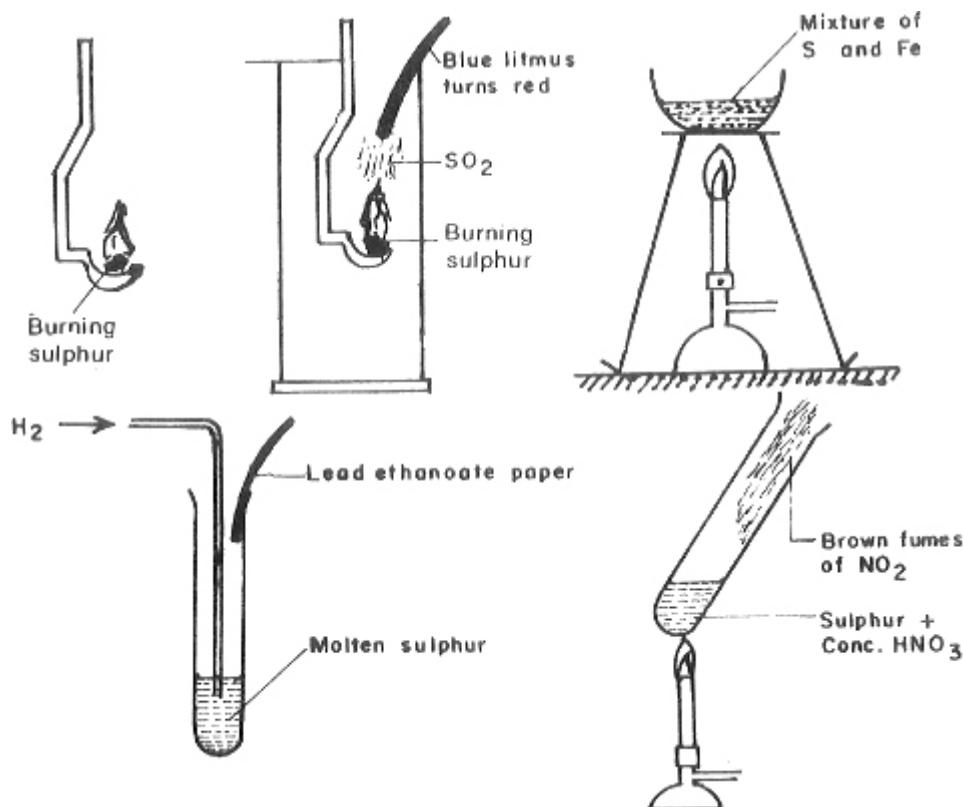


Figure 12.6 Properties of sulphur

12.5 Uses of Sulphur

Sulphur is used for the following purposes.

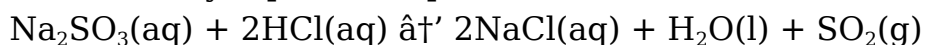
1. Manufacture of tetraoxosulphate(VI) acid.
2. Vulcanization of rubber to make it hard and tough for the manufacture of tyres.
3. Making matches and gun powder.
4. As a medicinal ointment for treating skin diseases.
5. Manufacture of CS_2 , an industrial solvent.

12.6 Oxides of Sulphur

Sulphur forms two compounds with oxygen: sulphur(IV) oxide, SO_2 , and sulphur(VI) oxide, SO_3 .

Experiment 12.4: Laboratory Preparation of Sulphur(IV) Oxide, SO_2 .

Put some sodium trioxosulphate(IV) crystals into a round-bottomed flask. Add dilute hydrogen chloride acid (hydrochloric acid) to it, through a thistle funnel (Figure 12.7). Pass the gas evolved through concentrated tetraoxosulphate(VI) acid to dry it. Collect the gas by downward delivery (upward displacement of air).



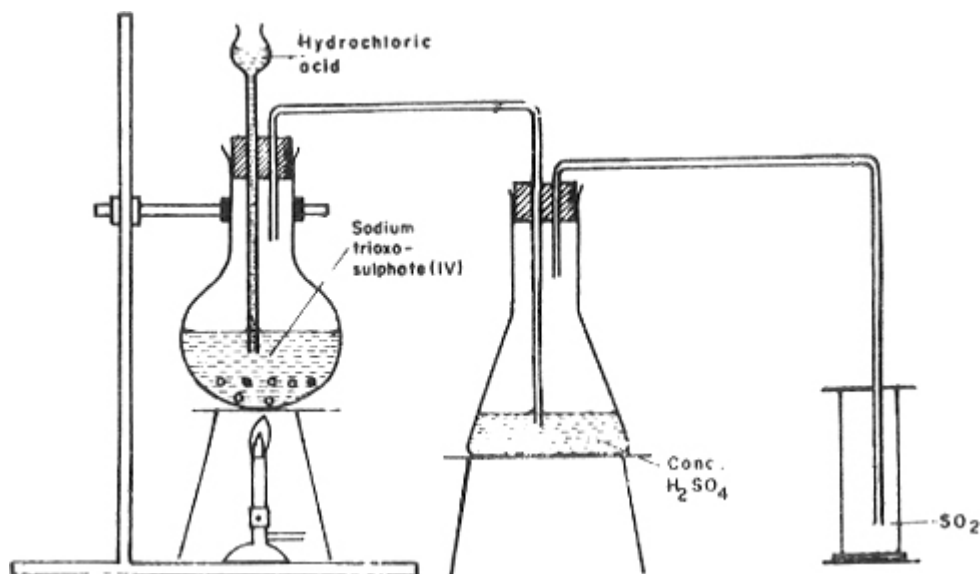
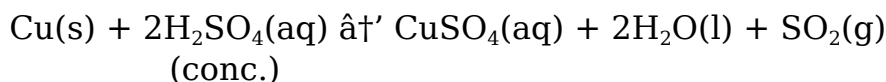


Figure 12.7 Preparation of sulphur(IV) oxide

Alternative reagents for the preparation:

Heating copper turnings with concentrated tetraoxosulphate(VI) acid.



Collect five gas jars for the following tests.

12.7 Properties of Sulphur(IV) Oxide.

Experiment 12.5: Investigating the Properties of Sulphur(IV) oxide.

1. Note the colour and odour of the gas. It is a colourless gas with a choking smell.
2. Introduce wet litmus into a gas jar of the gas. Blue litmus turns red, showing that the gas is acidic.
3. Bubble the gas into water in a beaker, then test the resulting solution with blue litmus paper. The blue litmus turns red showing that the gas dissolves in water to form an acidic solution.

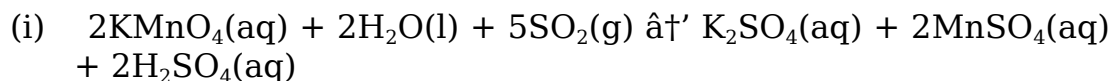
4. Reducing Reactions

- (i) Bubble the gas into potassium tetraoxomanganate(VII) solution in a test-tube. The purple colour of the manganate(VII) solution is decolourised.
- (ii) Bubble the gas into potassium heptaoxodichromate(VI) solution. The orange colour of that solution turns green.
- (iii) Pass the gas into a test-tube containing iron(III) chloride solution. The reddish-brown solution turns green.

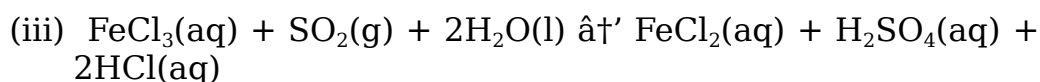
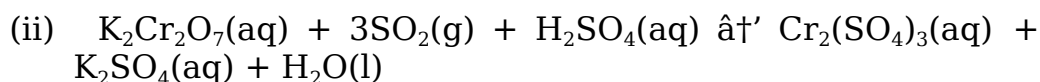
In these reactions sulphur(IV) oxide is acting as a reducing agent. It reduces manganese from oxidation state of +7 in MnO_4^- to +2 in MnSO_4 . It reduces chromium from oxidation

state of +6 in $\text{Cr}_2\text{O}_7^{2-}$ to +3 in $\text{Cr}_2(\text{SO}_4)_3$, which gives the green coloured solution. It also reduces iron from the +3 to the +2 oxidation state.

The equations for reactions are

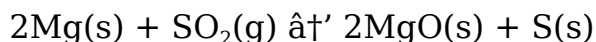


Sulphur(IV) oxide is oxidised to tetraoxosulphate(VI) acid.



5. Oxidizing Reactions

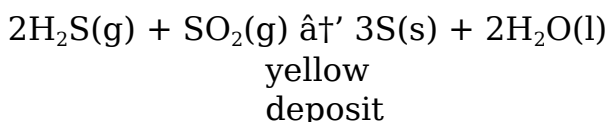
- (i) Lower a piece of burning magnesium into a gas jar of sulphur(IV) oxide. It continues to burn, producing white powder of magnesium oxide and a yellow deposit of sulphur.



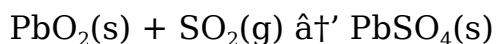
Sulphur(IV) oxide is acting as an oxidizing agent in this reaction, oxidising magnesium from oxidation number of 0 (elemental magnesium) to +2 in magnesium oxide.

- (ii) Invert a gas jar of sulphur(IV) oxide over that of hydrogen sulphide, then remove both gas jar covers for the gases to mix. A yellow deposit of sulphur is formed.

Sulphur(IV) oxide oxidises hydrogen sulphide to sulphur, and is itself reduced to sulphur.

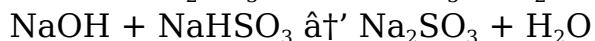
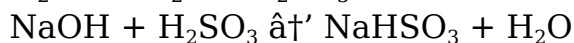
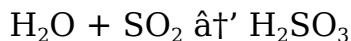


- (iii) Pass sulphur(IV) oxide over heated lead(IV) oxide in a combustion tube. White lead(II) tetraoxosulphate(VI) is formed.



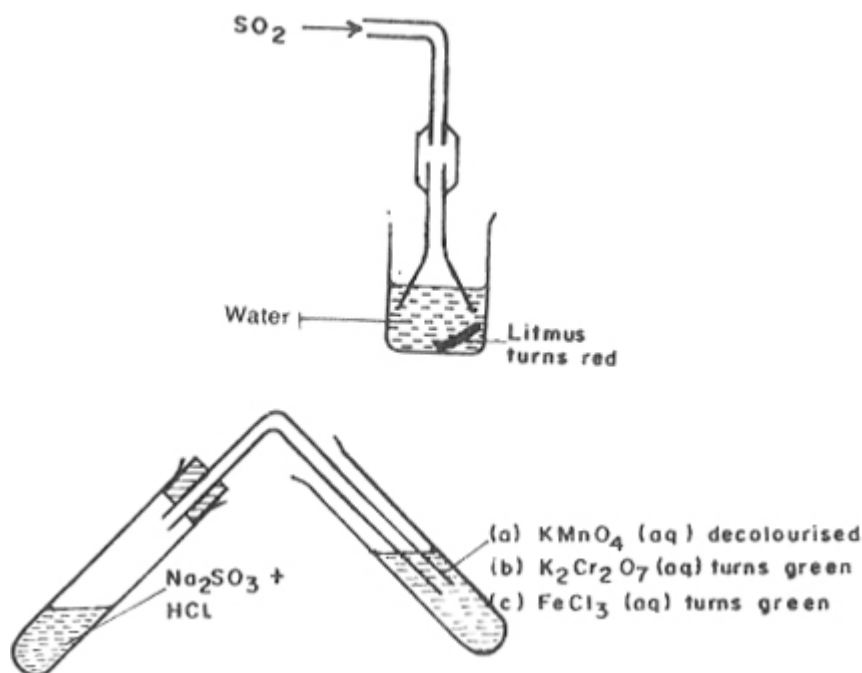
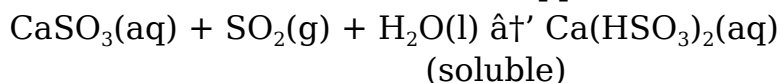
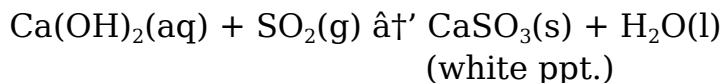
6. **Bleaching action of sulphur(IV) oxide:** Moisten some flowers and drop them into a gas jar of sulphur(IV) oxide. The flowers become bleached after sometime. **Sulphur(IV) oxide bleaches by** reduction. It takes up oxygen from coloured substances for its own oxidation to tetraoxosulphate(VI) acid, in the presence of water. The coloured substance thus becomes colourless. On standing in the atmosphere, however, the substance takes up oxygen to regain its original colour. Hence, the bleaching effect of sulphur(IV) oxide is temporary, unlike that of chlorine, which is permanent.

7. **Neutralization:** Pass sulphur(IV) oxide into dilute solution of sodium hydroxide in a conical flask into which a drop of methyl orange has been added. The yellow colour of the indicator becomes pink after sometime, as the acidic gas neutralises all the alkali.



8. **Action on lime water:** Bubble sulphur(IV) oxide into lime water in a test-tube. Continue to bubble the gas until no further change occurs. An initial milkiness clears when excess of the gas has passed into solution.

Sulphur(IV) oxide forms the insoluble salt, calcium trioxosulphate(IV), when the gas is passed into lime water. With excess of gas, calcium hydrogen trioxosulphate(IV), a soluble salt is formed.



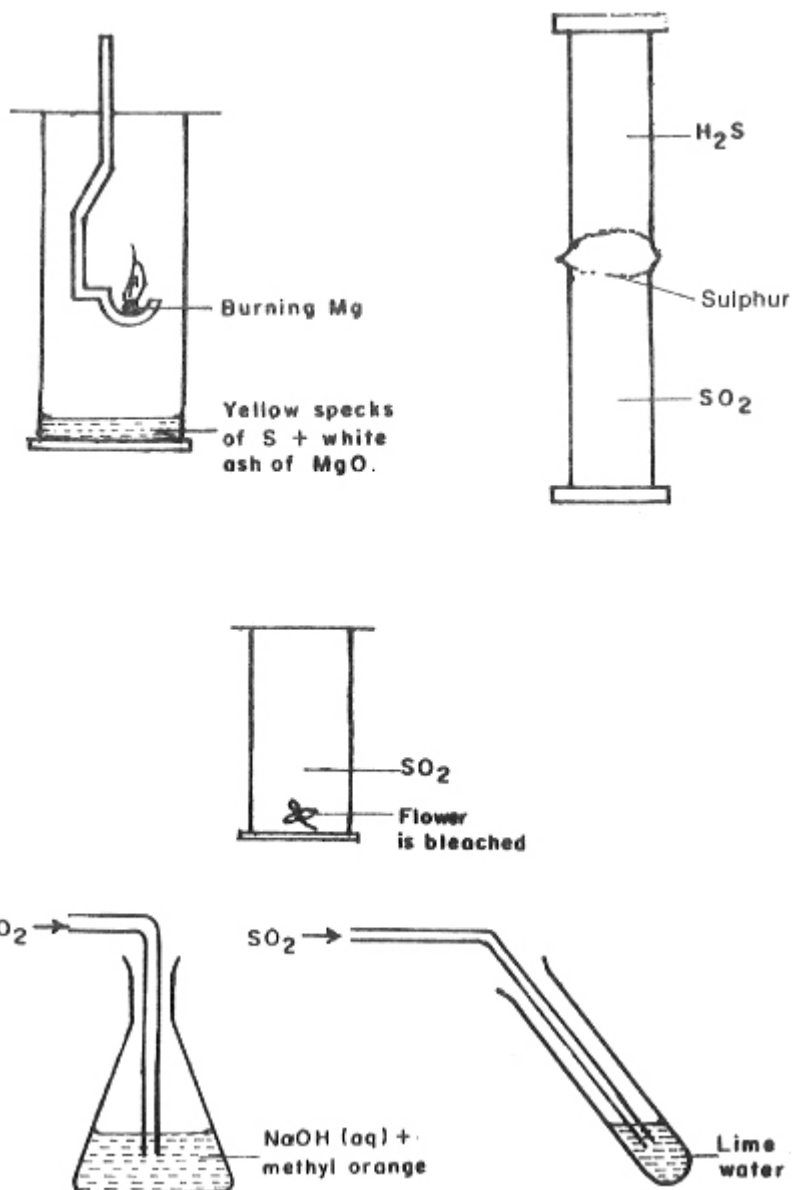


Figure 12.8 Reactions of sulphur(IV) oxide

12.8 Uses of Sulphur(IV) Oxide

Sulphur(IV) oxide is used

1. as a bleaching agent for bleaching straw and wood pulp.
2. for the manufacture of tetraoxosulphate(VI) acid, by oxidising it to sulphur(VI) oxide.
3. for preserving fruits and fruit juices by preventing oxidation.
4. as a refrigerant, as an alternative to ammonia or carbon(IV) oxide, because it is easily liquefied by slight increase in pressure.

12.9 Sulphur(VI) Oxide

Sulphur(VI) oxide can be prepared in the laboratory by passing dry sulphur(IV) oxide and oxygen over heated platinised asbestos, using the apparatus in Figure 12.9.

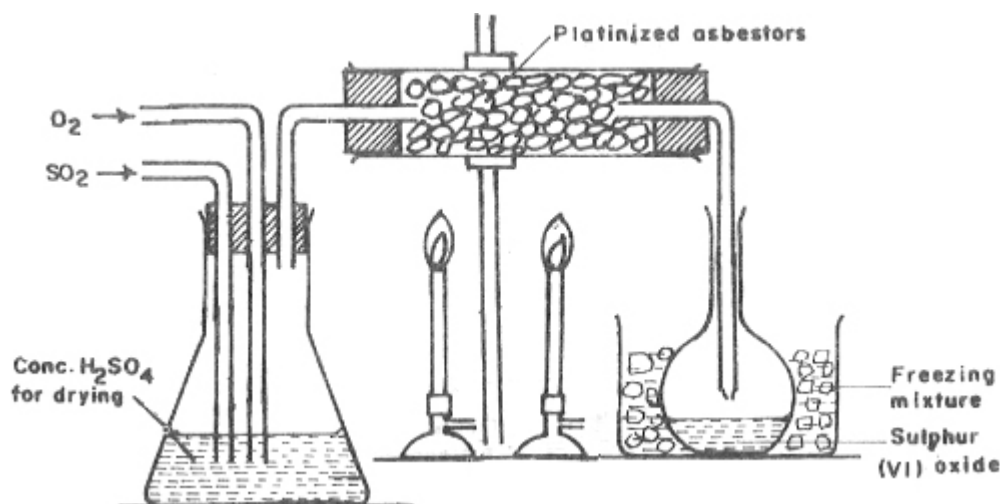
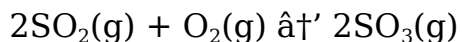
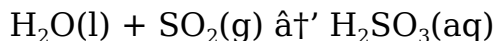


Figure 12.9 Preparation of sulphur(VI) oxide

12.10 Trioxosulphate(IV) Acid

A solution of sulphur(IV) oxide in water gives trioxosulphate(IV) acid.



Sulphur(IV) oxide is thus an acid anhydride. The dissolution of sulphur(IV) oxide in water is carried out through a glass funnel to avoid sucking back (Figure 12.10).

Since trioxosulphate(IV) acid is merely a solution of sulphur(IV) oxide in water, the acid has all the properties of sulphur(IV) oxide. It therefore decolourises potassium tetraoxomanganate(VII) solution, turns potassium heptaoxodichromate(VI) solution green, etc.

It forms two types of salts with aqueous alkali solutions, an acid salt and a normal salt.

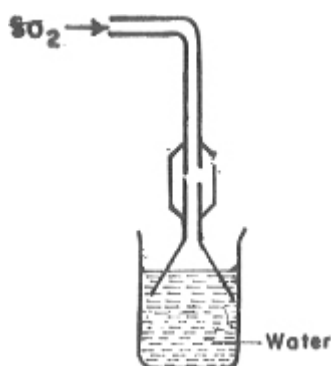
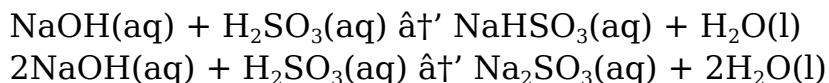


Figure 12.10 Dissolving SO₂ in water to make trioxosulphate(IV)

acid



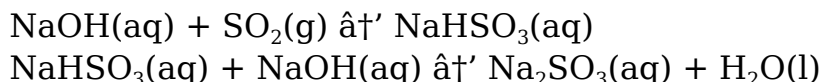
It is slowly oxidised to tetraoxosulphate(VI) acid by atmospheric oxygen.

12.11 Trioxosulphate(IV) Salts

Experiment 12.6: Preparation of Sodium Trioxosulphate(IV).

Transfer 25.0 cm³ of 2 M sodium hydroxide solution into a beaker. Saturate it with sulphur(IV) oxide gas. An acid salt, sodium hydrogen trioxosulphate(IV) is formed. Add another 25.0 cm³ of 2 M sodium hydroxide to the beaker and stir to mix well. The normal salt, sodium trioxosulphate(IV) is formed.

Concentrate the solution in the beaker by evaporation. Withdraw samples occasionally to test for saturation. When the test sample forms crystals, cool the rest of the solution to obtain crystals of sodium trioxosulphate(IV). Filter them off and dry in a desiccator.



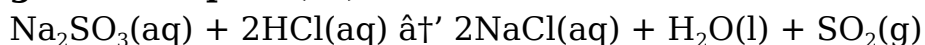
Potassium trioxosulphate(IV) can be similarly prepared. Trioxosulphates(IV) of other metals are, however, prepared by passing sulphur(IV) oxide into their salt solutions. For example, passing sulphur(IV) oxide into a solution of magnesium trioxonitrate(V) precipitates magnesium trioxosulphate(IV) as a white crystalline solid.



Experiment 12.7: Studying the Properties of Trioxosulphate(IV) Salts.

Carry out the following tests on several trioxosulphate(IV) salts such as sodium, potassium, calcium and magnesium trioxosulphates(IV).

1. Shake a little of each trioxosulphate(IV) salt with water in a test-tube. Trioxosulphates(IV) of sodium and potassium dissolve, others are insoluble.
2. Add dilute hydrogen chloride acid (hydrochloric acid) to a little of each trioxosulphate(IV) in a test-tube, and to a little of sodium or potassium hydrogen trioxosulphate(IV). Effervescence occurs in each case and a colourless choking gas is evolved. Warm, and then test the gas in each case with blue litmus paper. It turns wet blue litmus paper red. The gas is sulphur(IV) oxide. **All trioxosulphate(IV) and hydrogen trioxosulphate(IV) salts give off sulphur(IV) oxide with dilute acids.**



3. Make solutions of the trioxosulphate(IV) salts in water (for sodium and potassium trioxosulphates(IV)). Add barium chloride solution, or barium trioxonitrate(V) to each solution, then dilute hydrogen chloride acid (hydrochloric acid,) (or dilute trioxonitrate(V) acid). A white precipitate which is initially formed in each case, dissolves in the dilute acid added. This test can be used as a test for trioxosulphate(IV) ion. Tetraoxosulphate(VI) ion also forms a white precipitate with barium chloride solution, but the precipitate is insoluble in dilute hydrogen chloride acid (hydrochloric acid) or trioxonitrate(V) acid.

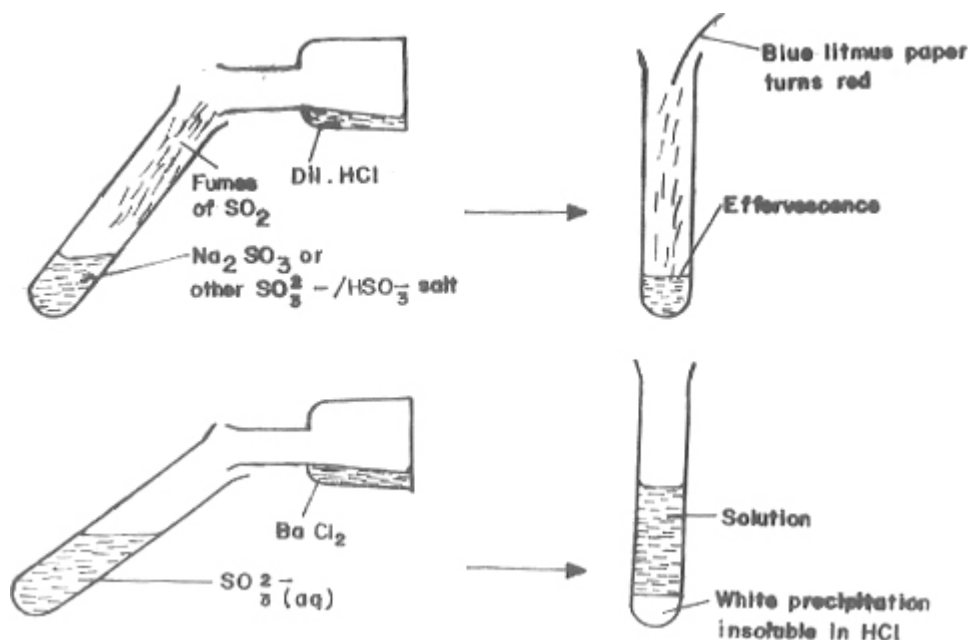
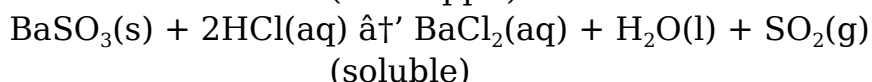
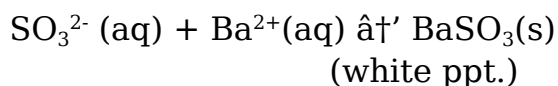


Figure 12.11: Properties of trioxosulphate(IV) salts

12.12 Uses of Trioxosulphate(IV) Salts

1. Calcium hydrogen trioxosulphate(IV) is used for the production of sulphur(IV) oxide needed for bleaching pulp and paper.
2. Disodium pentaoxodisulphate(IV) $\text{Na}_2\text{S}_2\text{O}_5$, and sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$, are used in photography. Sodium thiosulphate(IV) $\text{Na}_2\text{S}_2\text{O}_3$, is called hypo. Its action in photography is to remove excess halogen from the silver halide on the film or photographic plate. It is also used for the same purpose on bleached fabrics.

EXERCISE 12A

1. Name two allotropic forms of sulphur. Describe the changes which

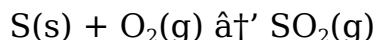
occur, and explain what happens when sulphur is heated without air.

2. What is the action of sulphur(IV) oxide on
 - (i) chlorine water,
 - (ii) iron(III) tetraoxosulphate(VI) solution,
 - (iii) hydrogen sulphide.

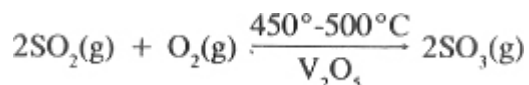
What type of reaction is taking place in each case?

12.13 Preparation of Tetraoxosulphate(VI) Acid by the Contact Process

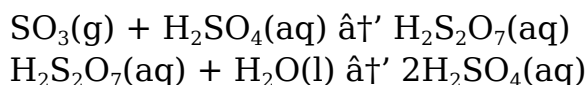
In the contact process for the manufacture of tetraoxosulphate(VI) acid, sulphur is burnt in air to produce sulphur(IV) oxide.



The sulphur(IV) oxide is mixed with air and passed over heated vanadium(V) oxide or platinum catalyst at a temperature of 450°C-500°C to form sulphur(VI) oxide.



The sulphur(VI) oxide is then dissolved in moderately concentrated tetraoxosulphate(VI) acid to form **oleum** (fuming tetraoxosulphate(VI) acid), which is diluted with water to obtain concentrated tetraoxosulphate(VI) acid (Figure 12.12).



The process is made up of the following stages:

1. Preparation of sulphur(IV) oxide

Sulphur(IV) oxide is obtained by

- (i) burning sulphur in air.

$$\text{S(s)} + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g})$$
- (ii) roasting iron pyrites in air.

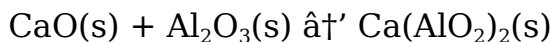
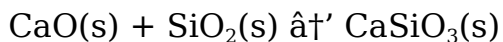
$$4\text{FeS(s)} + 7\text{O}_2(\text{g}) \rightarrow 2\text{Fe}_2\text{O}_3(\text{s}) + 4\text{SO}_2(\text{g})$$
- (iii) heating anhydrite, calcium tetraoxosulphate(VI), with carbon.

$$\text{CaSO}_4(\text{s}) + 2\text{C(s)} \rightarrow \text{CaS(s)} + 2\text{CO}_2(\text{g})$$

$$\text{CaS(s)} + 3\text{CaSO}_4(\text{s}) \rightleftharpoons 4\text{SO}_2(\text{g}) + 4\text{CaO(s)}$$

Silicon(IV) oxide and/or aluminium oxide are incorporated to remove calcium oxide, and hence shift the equilibrium of the

reaction to the right.

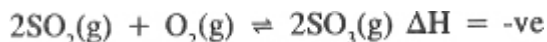


2. Purification of gases

The sulphur(IV) oxide and oxygen gases are purified (dust removed) before passing them to the catalyst chamber. Purification is necessary to avoid catalytic poisoning.

3. Oxidation of Sulphur(IV) oxide

The oxidation reaction is exothermic and reversible.



A total of three volumes of reactants yields only two volumes of product. Therefore, the gaseous reaction is favoured by high pressure. Being exothermic, it is also favoured by low temperature. But at low temperature the reaction is slow. A compromise temperature of 450°C to 500°C gives optimal yield. The catalyst employed is finely divided vanadium(V) oxide or platinum. Vanadium(V) oxide is preferred because it is cheaper and more resistant to poisoning.

4. Dissolution of sulphur (VI) oxide

Sulphur(VI) oxide is dissolved in moderately concentrated tetraoxosulphate(VI) acid to form oleum and not into water, because dissolution into water would send a mist of tetraoxosulphate(VI) acid droplets into the factory. The oleum is diluted with water to obtain the required acid.

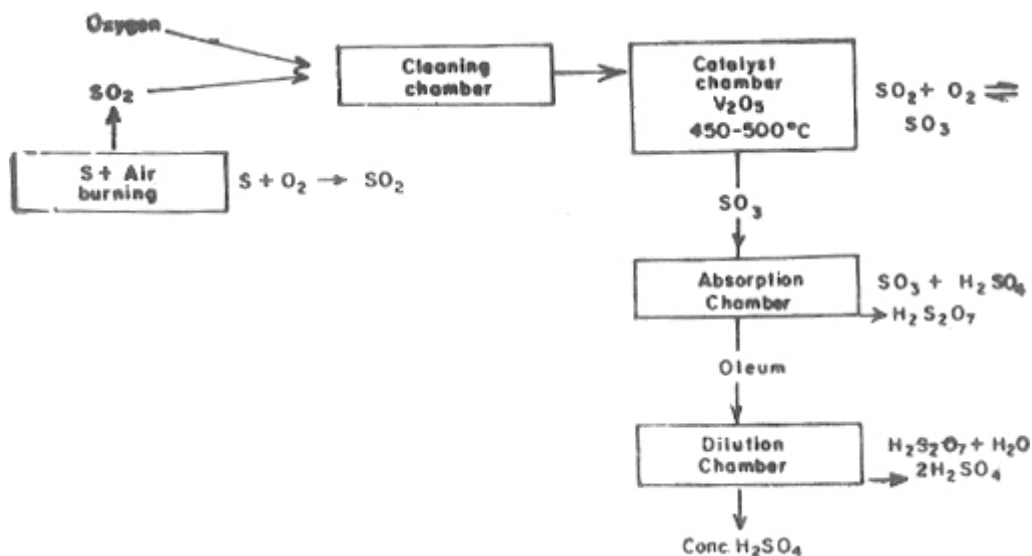


Figure 12.12 The contact process

12.14 Properties of Tetraoxosulphate(VI)

Acid

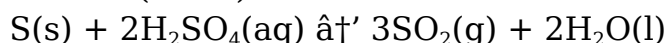
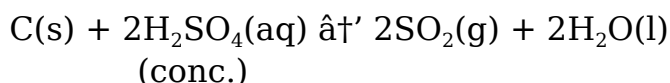
Experiment 12.8: Investigating the properties of tetraoxosulphate(VI) acid.

1. **Observe the acid:** It is a colourless, viscous liquid of density 1.84 g cm^{-3} .
Add a few drops of it to water in a beaker. It dissolves with evolution of a large amount of heat. **The acid is always added to water, and not water to concentrated tetraoxosulphate(VI) acid** when diluting it, to avoid explosive reaction.
2. **Reactions as an acid:** Dilute tetraoxosulphate (VI) acid shows all the reactions of strong acids, e.g, it is neutralised by bases, liberates hydrogen from metals, liberates carbon(IV) oxide from trioxocarbonates(IV) and hydrogen trioxocarbonates(IV), and turns blue litmus paper red. It is a strong dibasic acid from which both acidic and normal salts can be prepared.
3. **Oxidation reactions:** Add the concentrated acid to copper turnings and heat. A colourless pungent acidic gas, sulphur(IV) oxide, is liberated. Test the gas with acidified heptaoxodichromate(VI) solution. It turns the orange solution green. The gas is sulphur(IV) oxide.



Copper has been oxidised to Cu^{2+} , and tetraoxosulphate(VI) acid reduced to sulphur(IV) oxide.

The concentrated acid also oxidises carbon to carbon(IV) oxide, and sulphur to sulphur(IV) oxide.

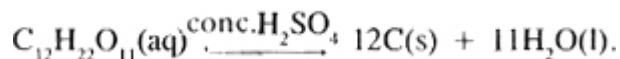


The hot concentrated tetraoxosulphate(VI) acid is a powerful oxidizing agent.

4. **Dehydration Reactions:**

- (i) Add some concentrated tetraoxosulphate(VI) acid to (a) some sugar, (b) a piece of paper, (c) a piece of cloth. These substances become charred.

Concentrated tetraoxosulphate(VI) acid removes the elements of water from carbohydrates, including cellulose, dehydrating them to a mass of carbon.



- (ii) Add concentrated tetraoxosulphate(VI) acid to some hydrated copper(II) tetraoxosulphate(VI) in an evaporating dish. The blue crystals become white as the concentrated acid removes

$$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s}) \xrightarrow{\text{conc. H}_2\text{SO}_4} \text{CuSO}_4(\text{s}) + 5\text{H}_2\text{O}(\text{l})$$

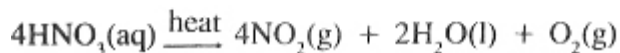
(blue) (white)

- $$\text{HOOC.COOH(s)} \xrightarrow{\text{conc. H}_2\text{SO}_4} \text{CO}_2(\text{g}) + \text{CO(g)} + \text{H}_2\text{O(l)}$$

- ### 5. Reaction with metallic chlorides and trioxonitrates(V):

- $$\text{NaCl(aq)} + \text{H}_2\text{SO}_4 \xrightarrow[\text{(conc.)}]{\text{heat}} \text{NaHSO}_4\text{(aq)} + \text{HCl(g)}$$

- $$\text{NaNO}_3(\text{s}) + \text{H}_2\text{SO}_4(\text{aq}) \xrightarrow{\text{heat}} \text{NaHSO}_4(\text{aq}) + \text{HNO}_3(\text{aq})$$
- (conc.)



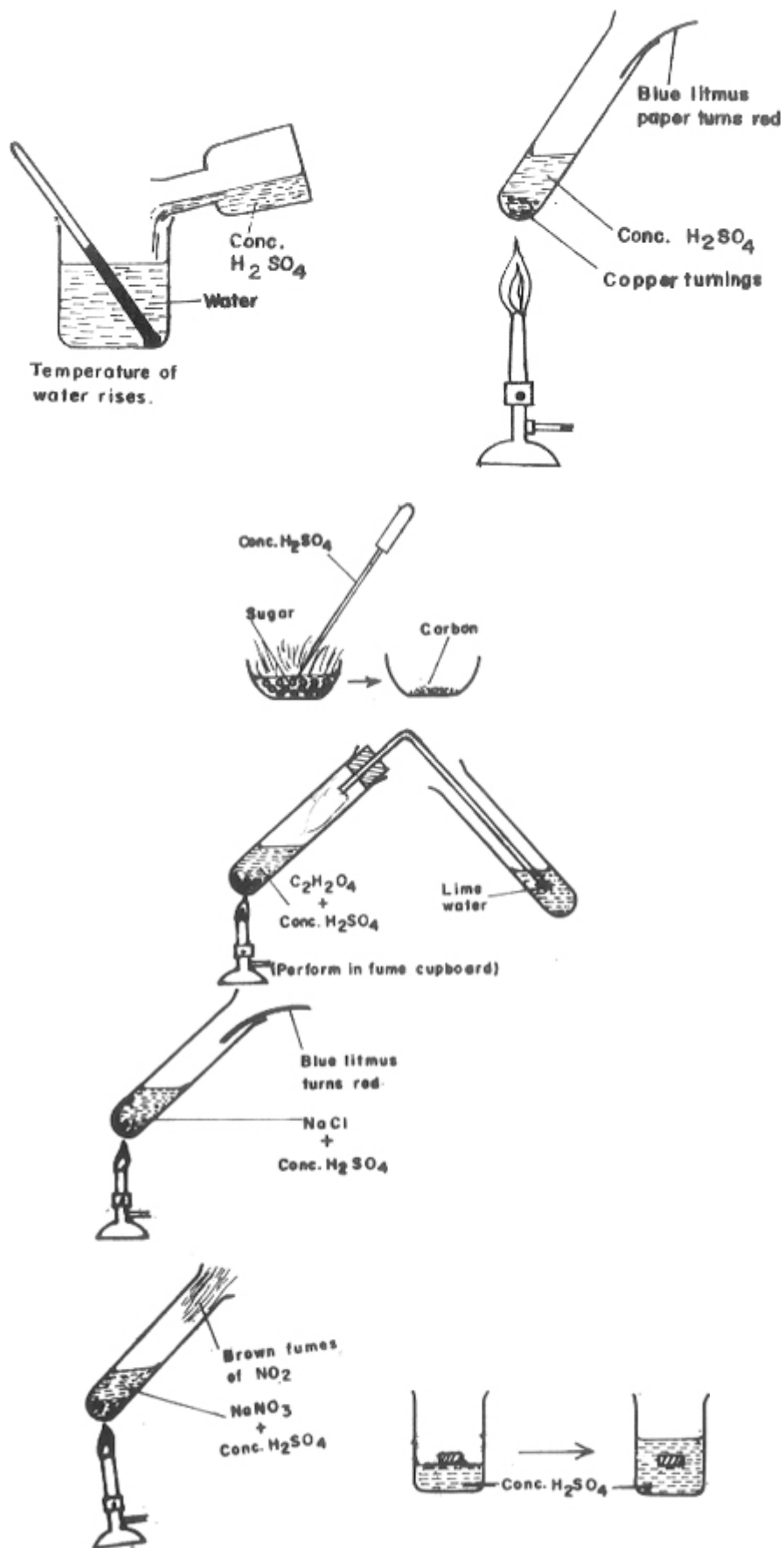


Figure 12.13 Properties of concentrated tetraoxosulphate(VI) acid.

12.15 Uses of Tetraoxosulphate(VI) Acid

Tetraoxosulphate(VI) acid is needed in most chemical industries. So much of it is used, that a nation's stage of industrialisation can be measured by the quantity of tetraoxosulphate(VI) acid used up in its chemical industries annually. The acid is used:

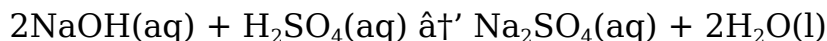
1. in the manufacture of paints.
2. in the manufacture of detergents.
3. in the production of other chemicals.
4. in lead accumulator batteries.
5. in the manufacture of fertilizers such as ammonium tetraoxosulphate(VI).
6. for desulphurisation (removal of sulphur and sulphur compounds in petroleum).

12.16 Tetraoxosulphate(VI) Salts, and Hydrogen Tetraoxosulphates(VI)

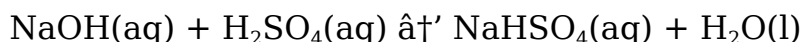
Soluble tetraoxosulphate(VI) salts can be made by neutralisation reactions.

Experiment 12.9: Preparation of Sodium Tetraoxosulphate(VI) and Sodium Hydrogen Tetraoxosulphate (VI).

Transfer 25.0 cm³ 2 mol dm⁻³ sodium hydroxide solution into a conical flask (Figure 12.14). Add two drops of methyl orange to it. Run 2 M tetraoxosulphate(VI) acid into it from a burette, shaking the flask continuously until a colour change from yellow to pink is observed. Note the volume of acid added. To another portion of 25.0 cm³ of 2 mol dm⁻³ sodium hydroxide in a beaker, add just that volume of 2 mol dm⁻³ tetraoxosulphate(VI) acid which was needed to produce the colour change. Heat the solution to concentrate it. Occasionally test for saturation by cooling small test-portions under a water tap. Cool the whole solution, when saturated. Filter off the crystals formed, and dry in a desiccator. These are crystals of sodium tetraoxosulphate(VI).



Add double the volume of 2 mol dm⁻³ tetraoxosulphate(VI) acid that was needed for neutralisation, to another 25.0 cm³ portion of the alkali, and boil to concentrate the solution to saturation. Cool to crystallise out the acid salt. Filter off and dry the crystals between filter papers.



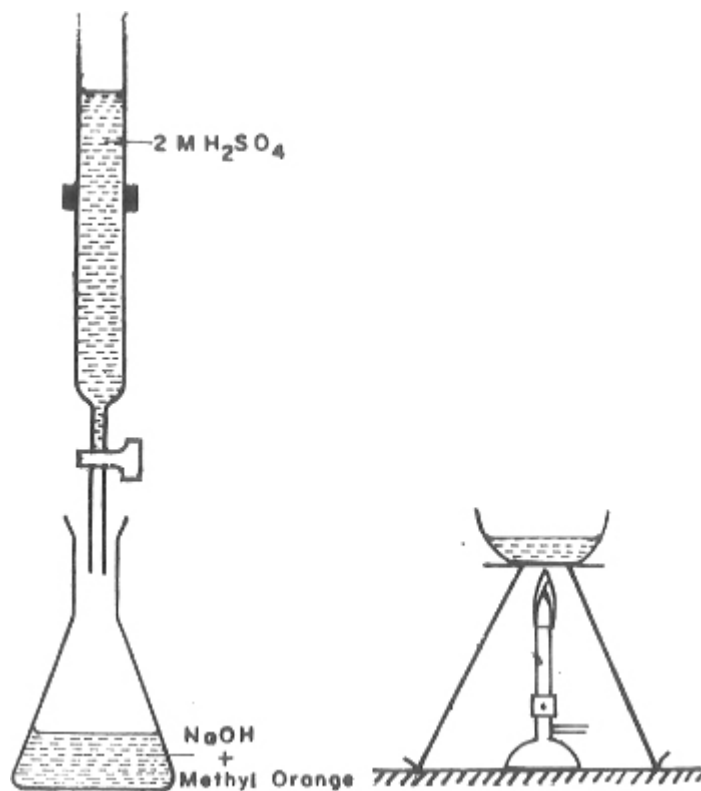
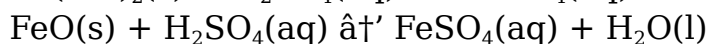
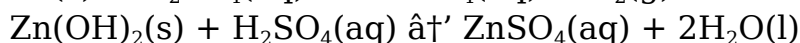
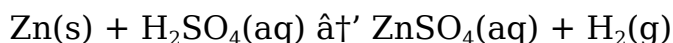


Figure 12.14 Preparation of sodium tetraoxosulphate(VI)

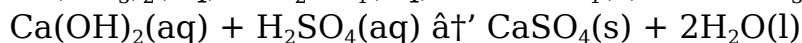
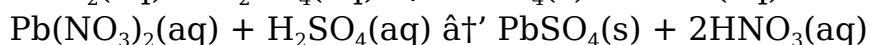
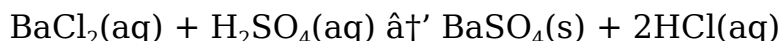
Potassium tetraoxosulphate(VI) and potassium hydrogen tetraoxosulphate(VI) can be prepared by similar methods.

The tetraoxosulphates(VI) of iron, magnesium, and zinc can be prepared by adding dilute tetraoxosulphate(VI) acid to their hydroxides, oxides or to the metals.



The crystals are similarly obtained by crystallisation from concentrated solutions.

Insoluble tetraoxosulphate(VI) salts such as calcium tetraoxosulphate(VI) (sparingly soluble), lead tetraoxosulphate(VI) and barium tetraoxosulphate(VI), are prepared by double decomposition. This involves adding tetraoxosulphate(VI) acid to solutions of the soluble salt of the metals.



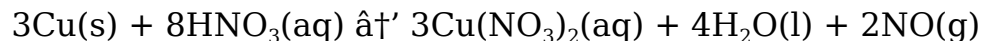
The precipitated insoluble tetraoxosulphates(VI) are filtered off and dried.

Copper(II) tetraoxosulphate(VI) can be prepared from copper metal by reacting it with concentrated tetraoxosulphate(VI) acid or by the

indirect method described below.

Experiment 12.10: Preparation of Copper (II) tetraoxosulphate(VI) from copper turnings.

Add dilute trioxonitrate(V) acid to copper turnings in a beaker, and heat the mixture in a fume cupboard, till the evolution of brown fumes ceases.



Filter off any undissolved copper. Add dilute tetraoxosulphate(VI) acid to the filtrate, then concentrate the solution to saturation. Cool the solution. Copper(II) tetraoxosulphate(VI) crystallises out as the pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Filter off the crystals, and dry in an oven.

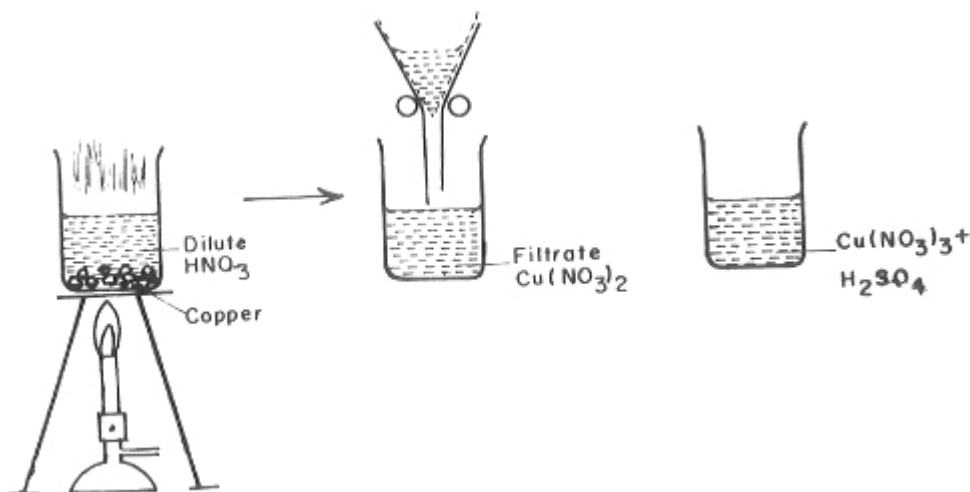
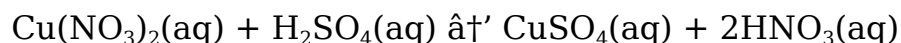


Figure 12.15 Preparation of Copper(II) tetraoxosulphate(VI) pentahydrate.

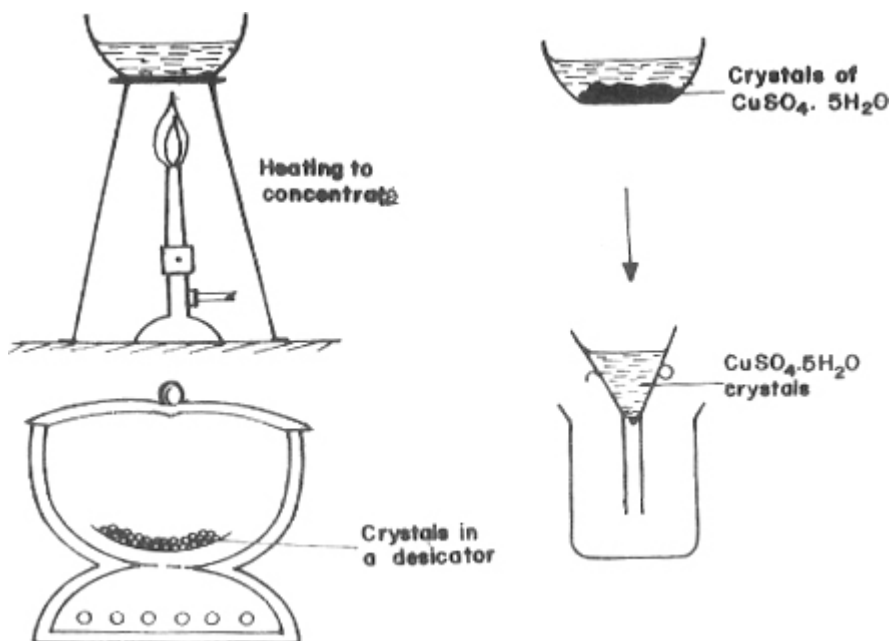


Figure 12.15 Preparation of copper(II) tetraoxosulphate(VI) pentahydrate

12.17 Alums

Alums are double salts of aluminium, iron(III) or chromium(III) tetraoxosulphate(VI), and tetraoxosulphates(VI) of sodium, potassium or ammonium ion. They have the general formula:



where X is either Na^+ , K^+ or NH_4^+ , and Y is either Al^{3+} , Cr^{3+} or Fe^{3+}

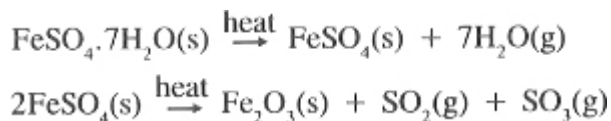
Experiment 12.11: Preparation of Potassium Alum.

Mix equimolar proportions of potassium tetraoxosulphate(VI) and aluminium tetraoxosulphate(VI) together, and dissolve the mixture in water. Heat the solution to concentrate it. When saturated, cool it to obtain crystals of potash alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$.

Experiment 12.12: Investigating the Reactions of Tetraoxosulphate(VI) Salts.

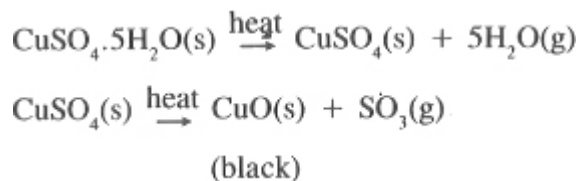
Carry out the following tests on the named tetraoxosulphate(VI) salts.

1. Heat some crystals of iron(II) tetraoxosulphate(VI) heptahydrate, $FeSO_4 \cdot 7H_2O$, in a test-tube, gently at first, then more strongly. Water vapour condenses near the mouth of the test-tube on gentle heating. On heating strongly, white fumes of sulphur(IV) oxide and sulphur(VI) oxide are evolved. Both gases turn blue litmus red and turn orange solution of potassium heptaoxodichromate(VI), green.

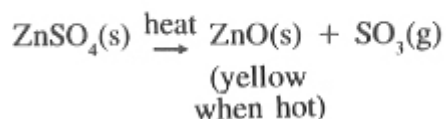
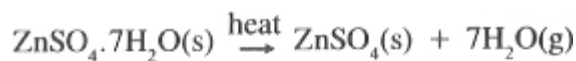


The residue in the test-tube, iron (III) oxide, is reddish-brown.

On heating, blue copper(II) tetraoxosulphate(VI), it first loses its water of crystallisation, then gives off sulphur(VI) oxide (but no sulphur(IV) oxide) to form a black oxide residue.

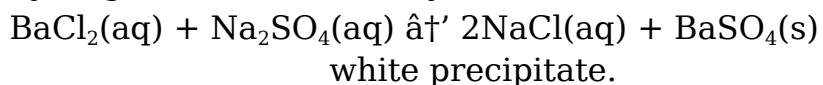


White zinc tetraoxosulphate(VI) crystals behave similarly.



The residual zinc oxide is yellow when hot, but white when cold.

2. Dissolve some sodium tetraoxosulphate(VI) crystals in water. Acidify the solution with dilute hydrogen chloride acid (hydrochloric acid), then add barium chloride solution to it. A white precipitate of barium tetraoxosulphate(VI) is formed. **This is the test for the tetraoxosulphate(VI) ion in solution.** Trioxosulphate(IV) ion which also forms a white precipitate with barium chloride solution does not do so in the presence of hydrogen chloride acid (hydrochloric acid).



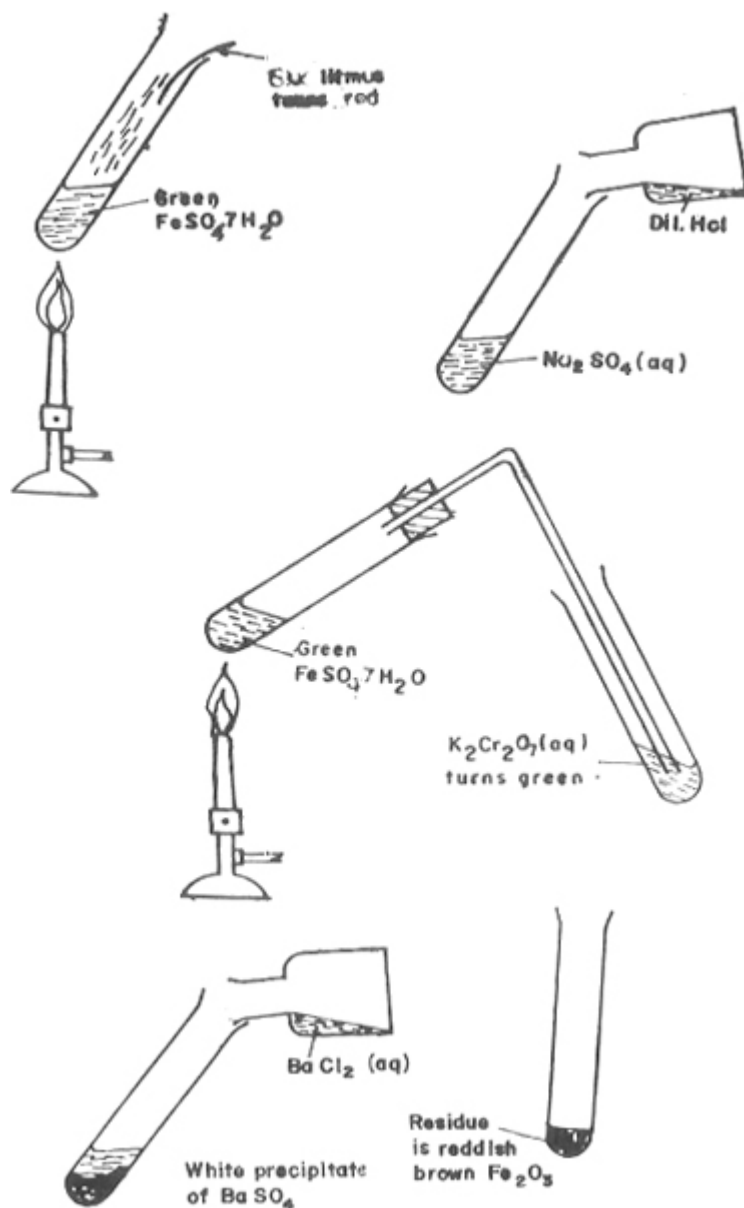


Figure 12.16 Reactions of tetraoxosulphate(VI) salts

TABLE 12.2 SUMMARY OF THE PROPERTIES OF TETRAOXOSULPHATE(VI) SALTS

Salt	Solubility in water	Action of heat
Na_2SO_4	soluble	Not decomposed
K_2SO_4	soluble	Not decomposed
MgSO_4	soluble	Not decomposed
CaSO_4	sparingly soluble	Not decomposed
CuSO_4	soluble	Decomposed to $\text{CuO} + \text{SO}_3$
ZnSO_4	soluble	Decomposed to $\text{ZnO} + \text{SO}_3$
FeSO_4	soluble	Decomposed to $\text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$

BaSO ₄	insoluble	Not decomposed
PbSO ₄	insoluble	Not decomposed

12.18 Uses of Tetraoxosulphate(VI) Salts

1. Ammonium tetraoxosulphate(VI) is used as a fertilizer.
2. Calcium tetraoxosulphate(VI) is used to make plaster casts as (CaSO₄)₂.H₂O (Plaster of Paris). The anhydrite, CaSO₄, is used as a source of sulphur(IV) oxide for the manufacture of tetraoxosulphate(VI) acid.
3. Barium tetraoxosulphate(VI) is used as a white pigment in paints.
4. Alums, especially potash alum, K₂SO₄.Al₂(SO₄)₃.24H₂O, are used as mordants in dyeing, and in water treatment for coagulation of fine particles. Chrome alum, K₂SO₄.Cr₂(SO₄)₃.24H₂O, is used in the tanning of leather.
5. Iron(II) tetraoxosulphate(VI) is used in making ink, the pigment 'Venetian Red' (Fe₂O₃), and drugs such as iron tonics.
6. Sodium tetraoxosulphate(VI) is used for treating wood pulp, and as Glauber's salt, Na₂SO₄.10H₂O, which is a purgative.
7. Copper(II) tetraoxosulphate(VI) is used as a fungicide, and as electrolyte in electroplating or purification of copper.
8. Aluminium tetraoxosulphate(VI) is used in the purification of sewage, to precipitate proteins.

EXERCISE 12B

In the manufacture of matches, the prepared sticks are soaked in 10% copper(II) tetraoxosulphate(VI) for a day, then dried and soaked in liquid paraffin before putting on the head. What is the function of copper(II) tetraoxosulphate(VI) in that process?

12.19 Hydrogen Sulphide

Experiment 12.13: Preparation of hydrogen sulphide.

Put some iron(II) sulphide into a flat-bottomed flask (Figure 12.17). Add 50% hydrogen chloride acid (hydrochloric acid) to it through a thistle funnel. Pass the gas evolved through fused calcium chloride in a U-tube to dry the gas, then collect it by downward delivery into several gas jars.

Note: Since the gas has a foul odour and is poisonous, carry out the preparation in a fume cupboard.

Alternatively we may use the **Kipp's apparatus** to prepare the hydrogen sulphide. The Kipp's apparatus is shown in Figure 12.18.

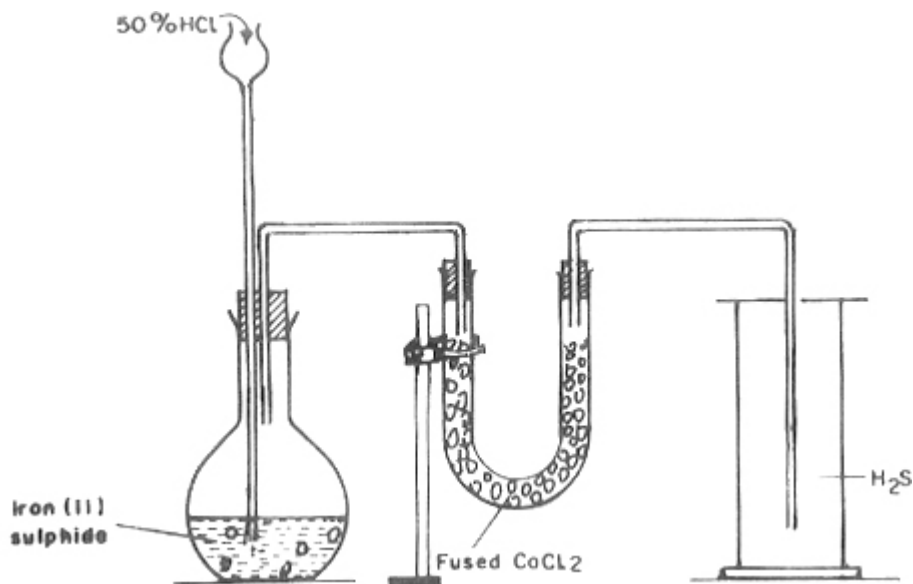


Figure 12.17 Preparation of hydrogen sulphide

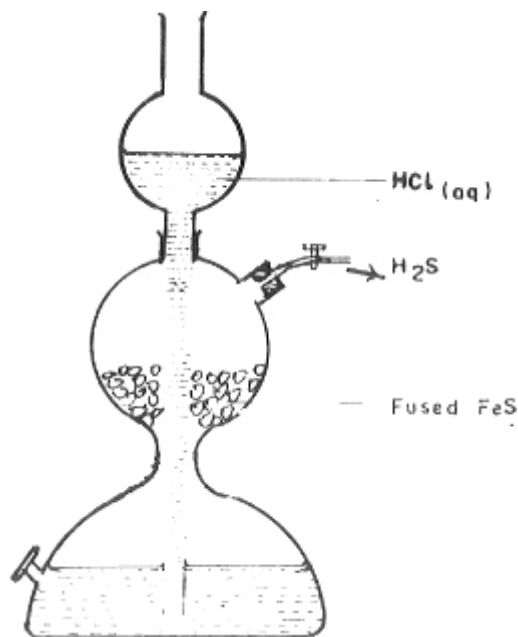
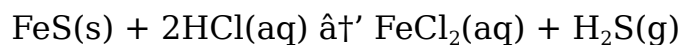


Figure 12.18 Kipp's apparatus

When the tap of the Kipp's apparatus is closed, the pressure of the gas pushes the acid down so that it no longer comes in contact with iron(II) sulphide. When the tap is opened, the acid level rises, and it reacts with iron(II) sulphide, liberating hydrogen sulphide.

12.20 Properties of Hydrogen Sulphide.

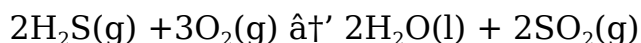
The following experiments illustrate the properties of hydrogen sulphide.

Experiment 12.14: Investigating the properties of hydrogen sulphide.

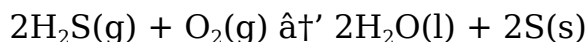
Carry out the following tests with hydrogen sulphide gas.

1. Note the colour and odour of the gas. It is a colourless gas, with the smell of a rotten egg.
2. Dip a moist blue litmus paper into a gas jar of the gas. The gas turns blue litmus paper pinkish red. This shows that it is a weak acid.
3. It is denser than air, hence it can be collected by downward delivery (upward displacement of air).
4. Light the gas issuing from a delivery tube in a gas jar. Test the gaseous product by shaking it with potassium heptaoxodichromate(VI) solution.

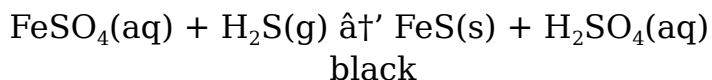
Hydrogen sulphide burns with a blue flame producing water and sulphur(IV) oxide. The sulphur(IV) oxide turns potassium heptaoxodichromate(VI) solution green.



If burning takes place in limited supply of oxygen, sulphur is produced.

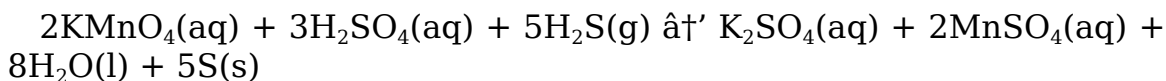


5. (i) Pass hydrogen sulphide into iron(III) chloride solution. The reddish-brown solution turns green, showing reduction of Fe^{3+} to Fe^{2+} . This indicates that **hydrogen sulphide is a reducing agent**, with excess hydrogen sulphide the green solution first formed darkens as iron(II) sulphide is precipitated.

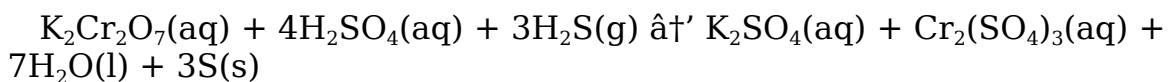


Other reducing reactions include:

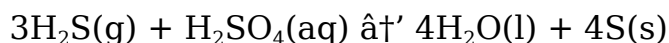
- (ii) decolourisation of the purple colour of potassium tetraoxomanganate(VII);



- (iii) turning of orange colour potassium heptaoxodichromate(VI) solution to green.



- (iv) reduction of concentrated tetraoxosulphate(VI) acid to water with a deposit of sulphur, and the oxidation of hydrogen sulphide by the concentrated acid.



(v) reduction of concentrated trioxonitrate(V) acid to brown fumes of nitrogen(IV) oxide.

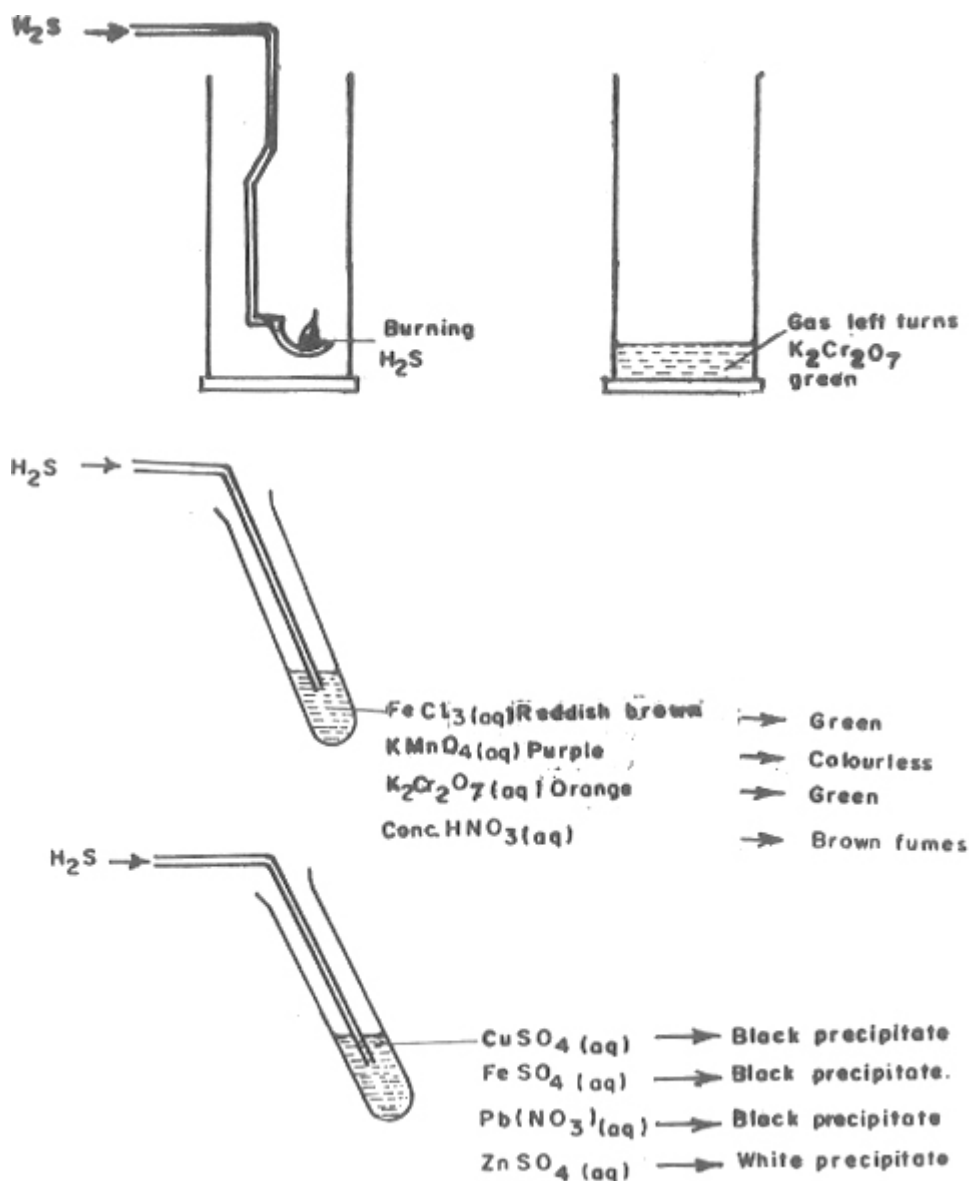
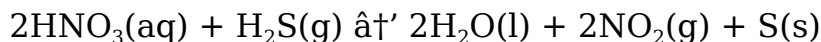
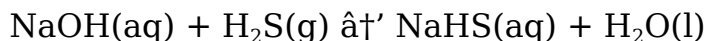
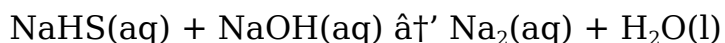


Figure 12.19 Properties of hydrogen sulphide.

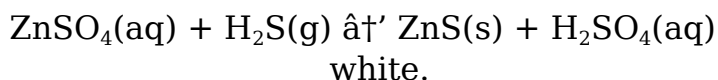
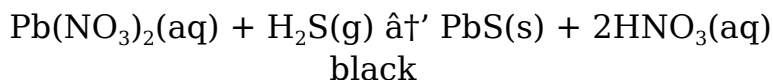
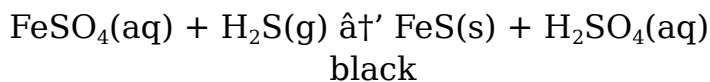
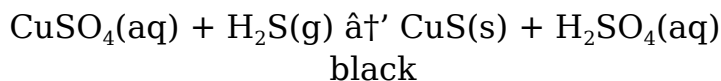
- Bubble hydrogen sulphide in to 25.0 cm³ of a 2 mol dm⁻³ sodium hydroxide solution until the solution smells of the gas. The acid salt, sodium hydrogen sulphide is formed. Add another 25.0 cm³ of 2 mol dm⁻³ sodium hydroxide to it and shake. Concentrate the solution by evaporation, and crystallise the sodium sulphide formed. With excess hydrogen sulphide the acid salt is formed.



With excess sodium hydroxide the normal salt is formed.



7. Pass hydrogen sulphide into solutions of copper(II) tetraoxosulphate(VI), iron(II) tetraoxosulphate(VI), lead(II) trioxonitrate(V) and zinc tetraoxosulphate(VI). A precipitate of the insoluble sulphide of the metallic ion is formed in each case. Most metallic sulphides are black, but zinc sulphide is white.



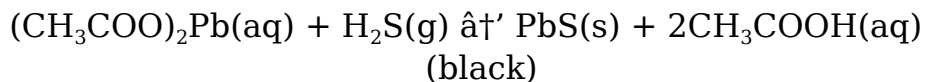
Summary of the properties of hydrogen sulphide

Hydrogen sulphide is a colourless gas with the odour of rotten eggs. It is denser than air and soluble in water. It is acidic. With alkalis, it forms two types of salts, an acidic salt and a normal salt.

It is a powerful reducing agent. It reduces even sulphur(IV) oxide which is itself a reducing agent. Its most important use in qualitative analysis is as a precipitating agent for the sulphides of many metallic ions in solution.

Test for hydrogen sulphide

If hydrogen sulphide is bubbled into lead ethanoate solution, a black precipitate is formed. If the delivery tube is directed on a lead ethanoate paper, the paper becomes blackened. This is used as a test for the gas.



Chapter Summary

1. Sulphur occurs free in nature and as sulphides of copper, iron and zinc.
2. Extraction of sulphur is by the Frasch method.
3. It exists in two crystalline forms, rhombic or α -sulphur, and monoclinic or β -sulphur.
4. There are two oxides of sulphur, both of which are acidic.
 - (i) Sulphur(IV) oxide is the anhydride of trioxosulphate(IV) acid. It bleaches by reduction.

- (ii) Sulphur(VI) oxide is the anhydride of tetraoxosulphate(VI) acid.
- 5. Tetraoxosulphate(VI) acid is manufactured by the Contact process which involves
 - (i) preparation of SO_2 .
 - (ii) purification of SO_2 .
 - (iii) oxidation of SO_2 to SO_3 using V_2O_5 catalyst.
 - (iv) dissolution of SO_3 in concentrated H_2SO_4 .Hot concentrated tetraoxosulphate(VI) acid has oxidising properties.
- 6. Test for SO_4^{2-} ion is by the precipitation of barium tetraoxosulphate(VI) with barium chloride solution in the presence of hydrochloric acid. Hydrogen tetraoxosulphate(VI) salts of metals are soluble in water.
- 7. Hydrogen sulphide is an acidic foul-smelling gas. It reduces even sulphur(IV) oxide, which is a reducing agent. It is used in qualitative analysis to precipitate the sulphides of many cations.

Assessment

1. (a) How is concentrated tetraoxosulphate(VI) acid prepared industrially, starting from sulphur?
(b) What happens when concentrated tetraoxosulphate(VI) acid is reacted with
 - (i) copper;
 - (ii) hydrogen sulphide?State the conditions of reaction in each case.
2. (a) Describe with the aid of a labelled diagram, the laboratory preparation of sulphur(IV) oxide.
(b) Describe what is observed and explain what happens when sulphur(IV) oxide is
 - (i) passed into iron(III)chloride solution,
 - (ii) mixed with hydrogen sulphide gas.(c) List five uses of sulphur(IV) oxide.
3. Explain what happens when
 - (i) sulphur(IV) oxide, and
 - (ii) hydrogen sulphide are bubbled separately into the following solutions:
 - (a) iron(III) tetraoxosulphate(VI),
 - (b) potassium tetraoxomanganate(VII),
 - (c) chlorine water.
4. Given dilute tetraoxosulphate(VI) acid, name other reagents you would need to prepare the following:

- (i) sulphur(IV) oxide,
- (ii) sodium hydrogen tetraoxosulphate(VI),
- (iii) copper(II) tetraoxosulphate(VI).

Write equations for the reactions.

Give details of the preparation of one of the salts.

5. How would you prepare and collect a few gas jars of hydrogen sulphide? Describe a chemical test for the gas. Write two equations to show the reducing action of hydrogen sulphide, and two equations to show its action as a precipitating agent.
6. (a) What is the source of sulphur(IV) oxide for the reaction

$$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$$

In which industrial process is this reaction involved? What are the conditions for the reaction?

How is this intermediate product converted to the final product of the named industrial process?

- (b) If air is 21 % oxygen by volume, what volume of air is consumed when 32g of sulphur(IV) oxide is oxidised to sulphur(VI) oxide?
7. Give two reactions in which tetraoxosulphate(VI) acid behaves as an oxidising agent, and two reactions in which it behaves as a dehydrating agent.
 Write an equation to show the action of concentrated tetraoxosulphate(VI) acid on calcium trioxonitrate(V).
 Describe the test for the tetraoxosulphate(VI) ion.
8. (a) Starting with sodium trioxosulphate(IV), how would you prepare and collect a dry sample of sulphur(IV) oxide gas?
- (b) What do you observe when sulphur(IV) oxide is passed into:
 - (i) an acidified solution of potassium heptaoxodichromate(VI),
 - (ii) dilute iron(III) tetraoxosulphate(VI) solution,
 - (c) What role does sulphur(IV) oxide play in each of the above reactions?
 - (d) Give two large scale uses of sulphur(IV) oxide.

(WAEC)