Chapter 16 - Sulphur

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Sulphur – the element

Sulphur is a non-metallic element which has a very important role in the chemical industry. It is a yellow solid which is found in large quantities but in various forms throughout the world (Figure 16.1).

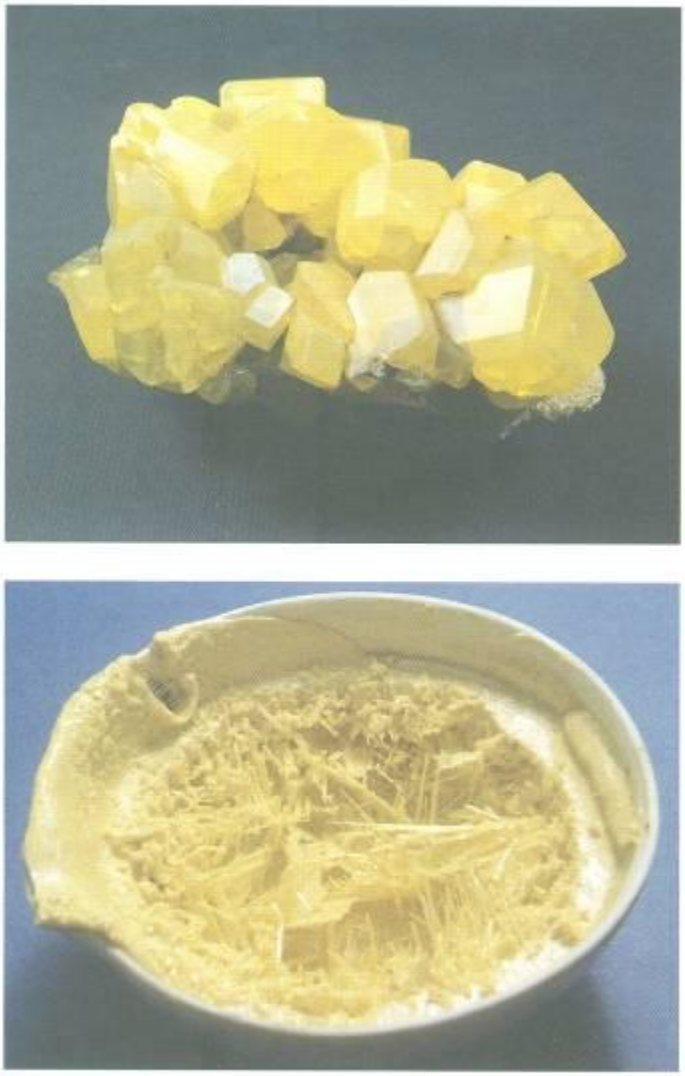


Figure 16.1 Sulphur – rhombic (top) and monoclinic.

It is found in metal ores such as copper pyrites ($CuFeS_2$) and zinc blende (ZnS) and in volcanic regions of the world. Natural gas and oil contain sulphur and its compounds, but the majority of this sulphur is removed as it would cause environmental problems. Sulphur obtained from these sources is known as 'recovered sulphur' and it is an important source of the element. It is also found as elemental sulphur in sulphur beds in Poland,

Russia and the US (Louisiana). These sulphur beds are typically 200 m below the ground. Sulphur from these beds is extracted using the **Frasch process**, named after its inventor Hermann Frasch.

The Frasch process

Superheated water at 170°C and hot compressed air are forced underground through pipes, forcing water and molten sulphur to the surface. Sulphur is insoluble in water and so the two substances emerging from the pipes are easily separated. The sulphur is kept molten and sold in this form. The sulphur obtained from this process is about 99.5% pure and can be used directly (Figure 16.2).

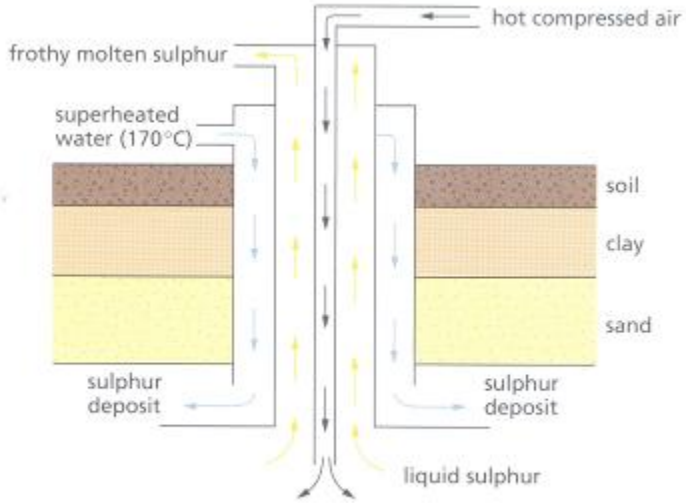


Figure 16.2 The Frasch process.

Uses of sulphur

The vast majority of sulphur is used to produce perhaps the most important industrial chemical, sulphuric acid. Sulphur is also used to **vulcanise** rubber, a process which makes the rubber harder and increases its elasticity. Relatively small amounts are used in the manufacture of matches, fireworks and fungicides, as a sterilising agent and in medicines.

Allotropes of sulphur

Sulphur is one of the few non-metal elements which exist as allotropes (Chapter 4). The main allotropes are called rhombic sulphur and monoclinic

sulphur. Both of these solid forms of sulphur are made up of S_8 molecules (Figure 16.3).

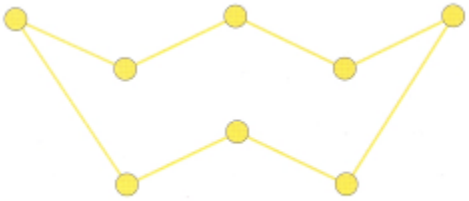
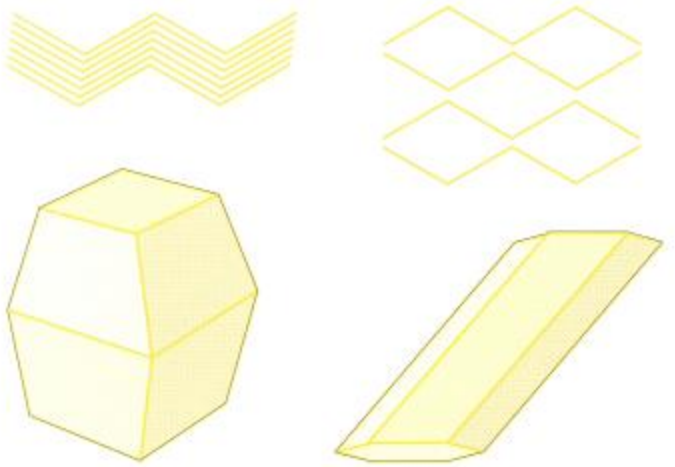


Figure 16.3 S_8 molecule.

The fact that there are two different allotropes of sulphur is due to the way in which these S_8 molecules pack together. In rhombic sulphur the molecules are packed more closely than in the monoclinic form (Figure 16.4).



a A rhombic crystal. b A monoclinic crystal of sulphur.

Figure 16.4 The packing of S_8 molecules

Although sulphur is insoluble in water, it will dissolve in an organic solvent such as methylbenzene. If a solution of sulphur in methylbenzene is heated and allowed to cool then crystals of monoclinic sulphur are produced. When the temperature of the solution falls below 96°C, rhombic sulphur crystals are produced. Rhombic sulphur is stable below 96°C and monoclinic sulphur is stable above 96°C. This temperature is called the **transition temperature**.

When solid sulphur is heated, it melts at 112°C and forms a runny (mobile) liquid. At this point the S_8 molecules are moving freely around each other,

as the weak attractive forces between them have been overcome (Figure 16.5).

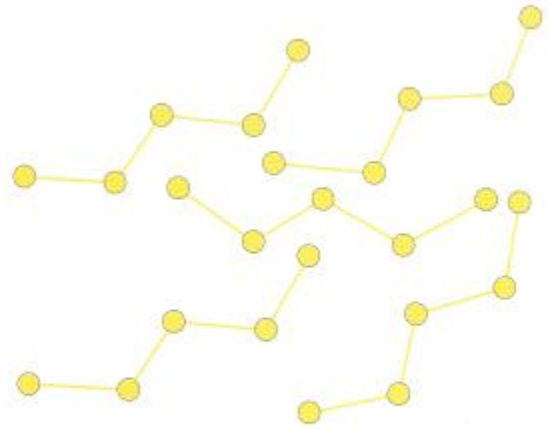


Figure 16.5 At the melting point S_8 rings move freely around one another.

However, if the sulphur is heated further the liquid becomes thicker (viscous). This is because the S_8 rings have been broken by the energy given to the sulphur and they bond together, forming long chains of sulphur atoms which become tangled, making the liquid viscous (Figure 16.6). Continued heating, to 444°C, makes the liquid more mobile once again as the long chains are broken down into smaller ones which move around one another freely.

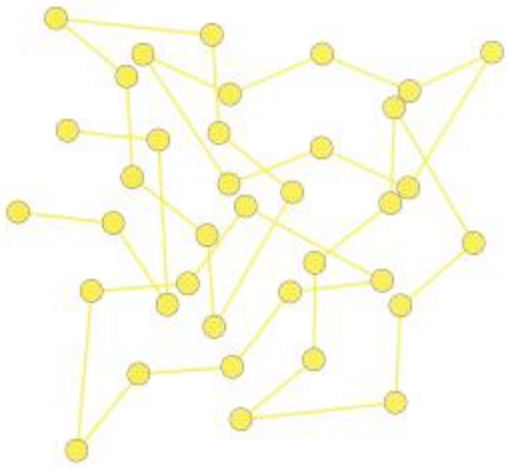


Figure 16.6 A viscous liquid is produced as long chains of sulphur atoms are formed and get tangled together.

If this liquid is poured into a beaker of cold water, a substance called **plastic sulphur** is formed. This is an elastic, rubber-like substance. In plastic sulphur, the sulphur atoms remain bonded together in the form of chains, very similar to chains of carbon atoms in plastics such as polythene. After a few hours, however, the plastic sulphur loses its elasticity and once again becomes solid as the Ss molecular rings re-form.

Properties of sulphur

Sulphur:

- is a yellow, brittle solid at room temperature
- does not conduct electricity
- is insoluble in water.

Sulphur will react with both metals and non-metals.

- It reacts with magnesium metal to form magnesium sulphide.

$$\text{magnesium + sulphur} \rightarrow \text{magnesium sulphide}$$

$$Mg(s) + S(s) \rightarrow MgS(s)$$

- It reacts with oxygen to produce sulphur dioxide gas.

$$\text{sulphur + oxygen} \rightarrow \text{sulphur dioxide}$$

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

Sulphur dioxide

Sulphur dioxide is a colourless gas produced when sulphur or substances containing sulphur, for example crude oil or natural gas, are burned in oxygen gas. It has a choking smell and is extremely posionous. The gas dissolves in water to produce an acidic solution of sulphurous acid.

$$\text{sulphur dioxide + water} \leftrightarrow \text{sulphurous acid}$$

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

It is one of the major pollutant gases and is the gas principally responsible for **acid rain**. However, it does have some uses: as a bleaching agent, in fumigants and in the preservation of food by killing bacteria.

Questions

1. What is meant by the term 'allotrope'?

2. 'Sulphur is a non-metallic element.' Discuss this statement, giving physical and chemical reasons to support your answer.

Acid rain

Rainwater is naturally acidic since it dissolves carbon dioxide gas from the atmosphere as it falls. Natural rainwater has a pH of about 5.7. In recent years, especially in central Europe, the pH of rainwater has fallen to between pH 3 and pH 4.8. This increase in acidity has led to extensive damage to forests (Figure 16.7), lakes and marine life.

Figure 16.7 This forest has been devastated by acid rain.

The amount of sulphur dioxide in the atmosphere has increased dramatically over recent years. There has always been some sulphur dioxide in the atmosphere, from natural processes such as volcanoes and rotting vegetation. Over Europe, however, around 80% of the sulphur dioxide in the atmosphere is formed from the combustion of fuels containing sulphur (Figure 16.8). After dissolving in rain to produce sulphurous acid, it further reacts with oxygen to form sulphuric acid.

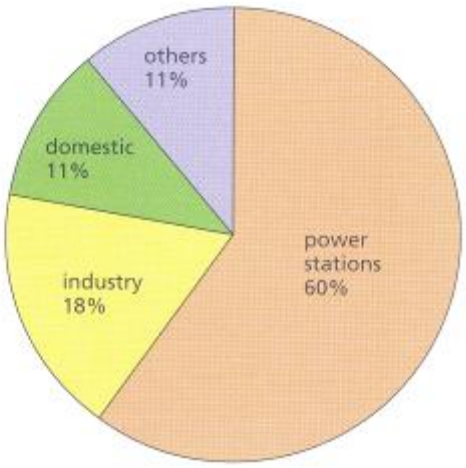


Figure 16.8 Sources of sulphur dioxide.

Questions

1. How could the amount of sulphur dioxide being produced by the above sources be reduced?

2. Devise an experiment which you could carry out in the school laboratory to determine the amount of sulphur in two different types of coal.

Industrial manufacture of sulphuric acid – the Contact process

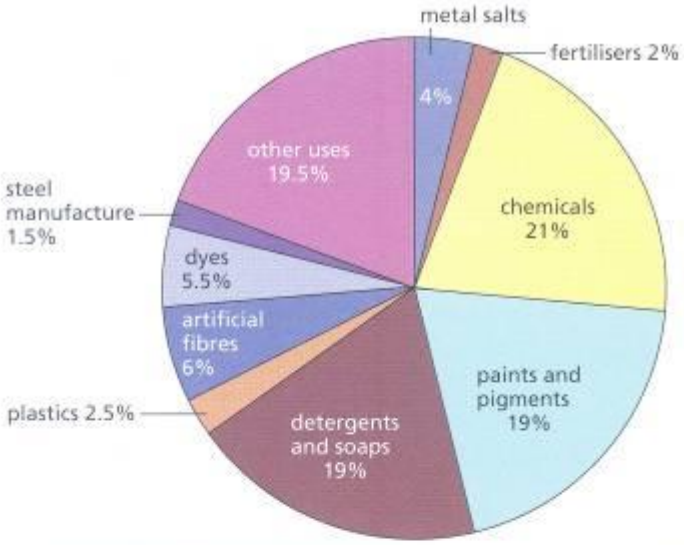


Figure 16.9 Products made from sulphuric acid include fertilisers, paints and pigments.

The major use of sulphur is in the production of sulphuric acid. This is probably the most important industrial chemical, and the quantity of it produced by a country has been linked with the economic stability of the country. Many millions of tonnes of sulphuric acid are produced in the UK each year. It is used mainly as the raw material for the production of many substances (Figure 16.9).

The process by which sulphuric acid is produced is known as the **Contact process** (Figure 16.10).

Figure 16.10 A Contact process plant used for making sulphuric acid

The process has the following stages.

- Sulphur dioxide is first produced, primarily by the reaction of sulphur with air.

$$\text{sulphur} + \text{oxygen} \rightarrow \text{sulphur dioxide}$$

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

- Any dust and impurities are removed from the sulphur dioxide produced, as well as any unreacted oxygen. These 'clean' gases are heated to a temperature of approximately 450°C and fed into a reaction vessel, where they are passed over a catalyst of vanadium (v) oxide (V_2O_5). This catalyses the reaction between sulphur dioxide and oxygen to produce sulphur trioxide (sulphur (VI) oxide, SO_3).

$$\text{sulphur dioxide} + \text{oxygen} \leftrightarrow \text{sulphur trioxide}$$

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

$$\Delta H = -197 \text{ kJ mol}^{-1}$$

  This reaction is reversible and so the ideas of Le Chatelier (Chapter 15) can be used to increase the proportion of sulphur trioxide in the equilibrium mixture. The forward reaction is exothermic and so would be favoured by low temperatures. The temperature of 450°C used is an optimum temperature which produces sufficient sulphur trioxide at an economical rate. Since the reaction from left to right is also accompanied by a decrease in the number of molecules of gas, it will be favoured by a high pressure. In reality, the process is run at atmospheric pressure. Under these conditions, about 96% of the sulphur dioxide and oxygen are converted into sulphur trioxide. The heat produced by this reaction is used to heat the incoming gases, thereby saving money.

- If this sulphur trioxide is added directly to water, sulphuric acid is produced. This reaction, however, is very violent and a thick mist is produced.

sulphur trioxide + water → sulphuric acid

$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$

This acid mist is very difficult to deal with and so a different route to sulphuric acid is employed. Instead, the sulphur trioxide is dissolved in concentrated sulphuric acid (98%) to give a substance called **oleum**.

sulphuric acid + sulphur trioxide → oleum

$H_2SO_4(aq) + SO_3(g) \rightarrow H_2S_2O_7(i)$

The oleum formed is then added to the correct amount of water to produce sulphuric acid of the required concentration.

oleum + water → sulphuric acid

$H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l)$

Question

1. Produce a flow diagram to show the different processes which occur during the production of sulphuric acid by the Contact process. Write balanced chemical equations showing the processes which occur at the different stages, giving the essential raw materials and conditions used.

Properties of sulphuric acid

Dilute sulphuric acid

Dilute sulphuric acid is a typical strong **dibasic** acid. A dibasic acid is one with two replaceable hydrogen atoms which may produce two series of salts — normal and acid salts (Chapter 7).

It will react with bases such as sodium hydroxide and copper (II) oxide to produce normal salts, called **sulphates**, and water.

- With sodium hydroxide:

  sodium hydroxide + sulphuric acid → sodium sulphate + water

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

- With copper (II) oxide:

  copper (II) oxide + sulphuric acid → copper (II) sulphate + water

  $$CuO(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2O(l)$$

It also reacts with carbonates to give normal salts, carbon dioxide and water, and with reactive metals to give a normal salt and hydrogen gas. The reaction between zinc and sulphuric acid is often used to pre-pare hydrogen gas in the laboratory (Figure 16.11).

zinc + sulphuric acid → zinc sulphate + hydrogen

$$Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$$

The preparation of the acid salt with sodium hydroxide requires twice the volume of acid as that used in the preparation of the normal salt. Therefore, if 25 cm^3 of dilute sulphuric acid were required to form the normal salt from a given volume of alkali of the same concentration then 50 cm^3 of the same acid solution would be required to produce the acid salt, sodium hydrogensulphate, from the same volume of alkali.

sodium hydroxide + sulphuric acid → sodium hydrogensulphate + water

$$NaOH(aq) + H_2SO_4(aq) \rightarrow NaHSO_4(aq) + H_2O(l)$$

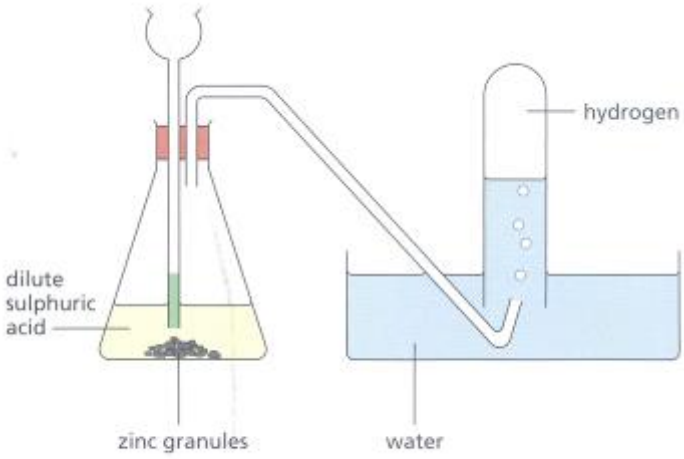


Figure 16.11 The laboratory preparation of hydrogen gas.

Sulphates

The salts of sulphuric acid, sulphates, can be identified by a simple test-tube reaction. To test for a sulphate, add a few drops of dilute hydrochloric acid to your unknown followed by a few drops of barium chloride. If a sulphate is present, a white precipitate of barium sulphate is produced.

barium ions + sulphate ions → barium sulphate

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

Many sulphates have very important uses, as can be seen from Table 16.1.

Table 16.1 Uses of some metal sulphates.

Salt	**Formula**	**Use**
Ammonium sulphate	$(NH_4)_2SO_4$	Fertiliser
Barium sulphate	$BaSO_4$	'Barium meal' used in diagnostic medical X-ray studies
Calcium sulphate	$CaSO_4.2H_2O$	'Plaster of Paris' used to set bones
Magnesium sulphate	$MgSO_4$	In medicine it is used as a laxative

Concentrated sulphuric acid

Concentrated sulphuric acid is a powerful **dehydrating agent**. This means it will take water from a variety of substances. One such substance is cane sugar, or sucrose (Figure 16.12).

$$\text{sucrose (sugar)} \xrightarrow{\text{conc } H_2SO_4} \text{carbon + water}$$

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

Concentrated sulphuric acid will also take water from hydrated copper (II) sulphate crystals, leaving only anhydrous copper (II) sulphate. If a few drops of concentrated sulphuric acid are added to some blue hydrated copper (II) sulphate crystals, they slowly turn white as the water of crystallisation is removed by the acid. Eventually, only a white powder — anhydrous copper (II) sulphate — remains.

$$\text{hydrated copper (II) sulphate} \xrightarrow{\text{conc } H_2SO_4} \text{anhydrous copper (II) sulphate} + \text{water}$$

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

Concentrated sulphuric acid should be treated very carefully, because it will also remove water from flesh! It is a very corrosive substance and should always be handled with care.

Diluting concentrated sulphuric acid must be done with great care because of its affinity for water. The concentrated sulphuric acid should always be added to the water, not the other way around.

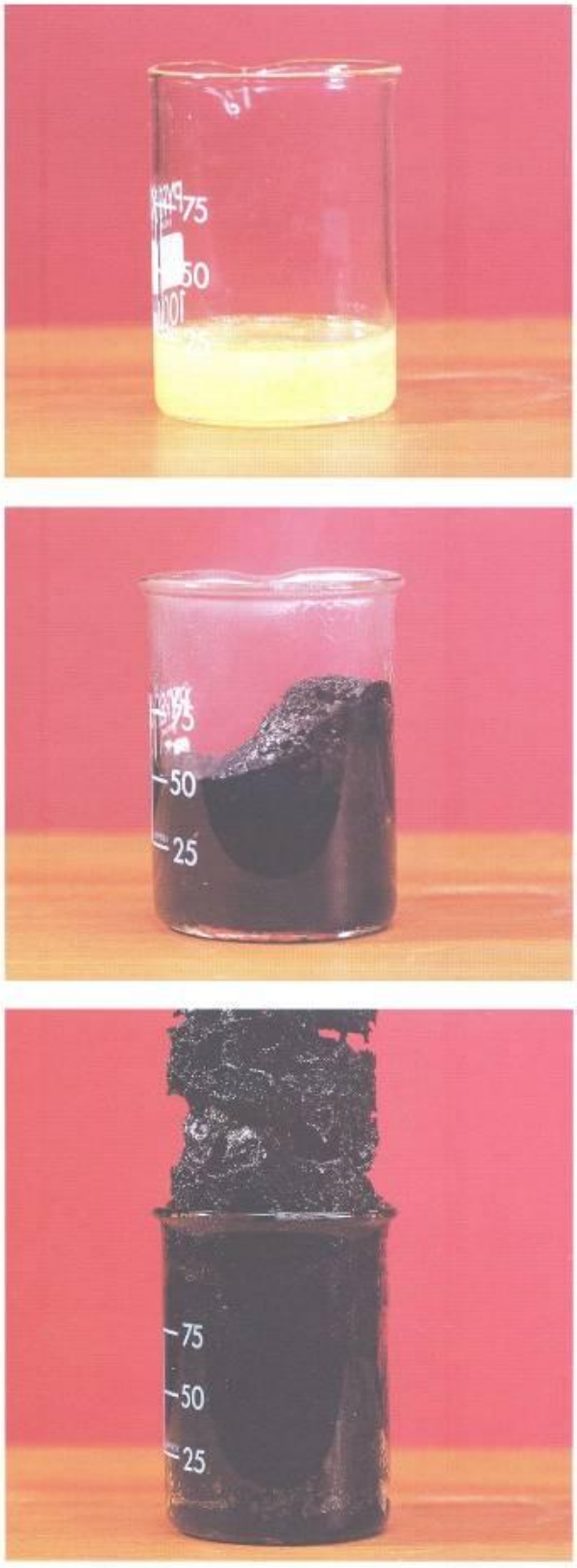


Figure 16.12 The concentrated sulphuric acid has removed the elements of water from the sugar, leaving black carbon.

Questions

1. If you were given an unlabelled bottle which was thought to be dilute sulphuric acid, how would you show that the solution contained sulphate ions (SO_4^{2-}(aq)), how would you show that it was an acid and how would you determine the concentration of the acid?

2. Write balanced chemical equations for the reactions between dilute sulphuric acid and:

a. zinc oxide
b. potassium carbonate
c. aluminium.

Manufacture of a soapless detergent

A more recent use of sulphuric acid is in the production of soapless detergents. These are detergents that can be used more effectively than soap in hard water areas, are fairly cheap to make and are gradually replacing soaps (Chapter 14).

The general process involves the reaction of a long, straight-chain alkene, such as dodecene, with benzene.

$$\text{benzene} + \text{dodecene} \rightarrow \text{dodecylbenzene}$$

$$C_6H_6(l) + CH_3(CH_2)_9CH = CH_2(l) \rightarrow C_6H_5(CH_2)_{11}CH_3(l)$$

The molecular formula of dodecylbenzene is $C_{18}H_{30}$. This compound is then reacted with concentrated sulphuric acid to give a compound that is known as a sulphonic acid.

$$\text{dodecylbenzene} + \text{sulphuric acid} \rightarrow \text{dodecylbenzene sulphonic acid} + \text{water}$$

$$C_{18}H_{30}(l) + H_2SO_4(l) \rightarrow C_{18}H_{29}SO_3H(aq) + H_2O(l)$$

Finally, this is reacted with the alkali sodium hydroxide, NaOH.

$$\begin{matrix}\text{dodecylbenzene} \\ \text{sulphonic acid}\end{matrix} + \begin{matrix}\text{sodium} \\ \text{hydroxide}\end{matrix} \rightarrow \begin{matrix}\text{sodium dodecylbenzen} \\ \text{sulphonate}\end{matrix} + \text{water}$$

$$C_{18}H_{29}SO_3H(aq) + NaOH(aq) \rightarrow \underset{\text{(soapless detergent)}}{C_{18}H_{29}SO_3^-Na^-(aq)} + H_2O(l)$$

Soapless detergents such as this are to be found in most washing powders.

Checklist

After studying Chapter 16 you should know and understand the following terms.

Allotropes Different structural forms of the same element having the same physical state. For example, carbon exists as the allotropes diamond, graphite and buckminsterfullerene, and sulphur as rhombic and monoclinic sulphur.

Contact process The industrial manufacture of sulphuric acid using the raw materials sulphur and air.

Dibasic acid An acid which contains two replaceable hydrogen atoms per molecule of the acid, for example sulphuric acid, H_2SO_4.

Frasch process The process of obtaining sulphur from sulphur beds below the Earth's surface. Superheated water is pumped down a shaft to liquefy the sulphur, which is then brought back to the surface.

Soapless detergents Substances which are more effective than soap at producing lathers, especially in hard water areas. They are large organic molecules, produced using sulphuric acid.

Sulphate A salt of sulphuric acid formed by the reaction of the acid with carbonates, bases and some metals. It is possible to test for the presence of a sulphate by the addition of dilute hydrochloric acid and some barium chloride solution. A white precipitate of barium sulphate is formed if a sulphate is present.

Transition temperature The temperature boundary at which one allotropic form of an element is converted into another allotropic form.

Sulphur

Additional questions

1. What do you understand by the following terms?

a. Dehydrating agent.
b. Oxidising agent.
c. Optimum temperature.
d. Acid rain.

2. Explain the following.

a. Chemical plants that produce sulphuric acid are often located on the coast.

b. Even though more sulphuric acid could be produced using high pressures, normal atmospheric pressure is used.

c. Natural rubber cannot be used to produce car tyres but vulcanised rubber can.

d. Sulphur dioxide gas is regarded as a pollutant.

e. Coal-fired and oil-fired power stations produce sulphur dioxide. Some of them are being fitted with flue gas desulphurisation (FGD) units.

3. A type of coal contains 0.5% of sulphur by mass.

a. Write an equation for the formation of sulphur dioxide gas when this coal is burned.

b. If 1500 tonnes of coal was burned, what mass of sulphur would it contain?

c. What mass of sulphur dioxide gas would be formed if 1500 tonnes of coal were burned?

d. What volume would this mass of sulphur dioxide gas occupy, measured at room temperature and pressure (rtp)? (A_r: O = 16; S = 32. One mole of a gas occupies 24 dm^3 at rtp.)

4. Fossil fuels, such as oil, coal and natural gas, all contain some sulphur. When these fuels are burned they produce many different gases. Concern has grown in recent years about the effects of one of these gases, sulphur dioxide. When sulphur dioxide dissolves in rainwater it forms an acidic solution which has become known as acid rain.

Money has been made available to solve the problem of acid rain. Attempts are being made to clean gases being released from power stations and to look into ways in which the effects of acid rain can be reversed.

The table below and Figure 16.8 give some data about the emission of sulphur dioxide.

	Million tonnes per year
USA	26
Russia/Ukraine	18
Germany	7
UK	5
Canada	5
France	3
Poland	3
Italy	3
Other countries	30

a. Using the figures in the table, produce a bar chart to show the amount of sulphur dioxide produced by each of the countries listed.

b. What percentage of the world's sulphur dioxide is produced in:

(i) the UK?
(ii) North America?

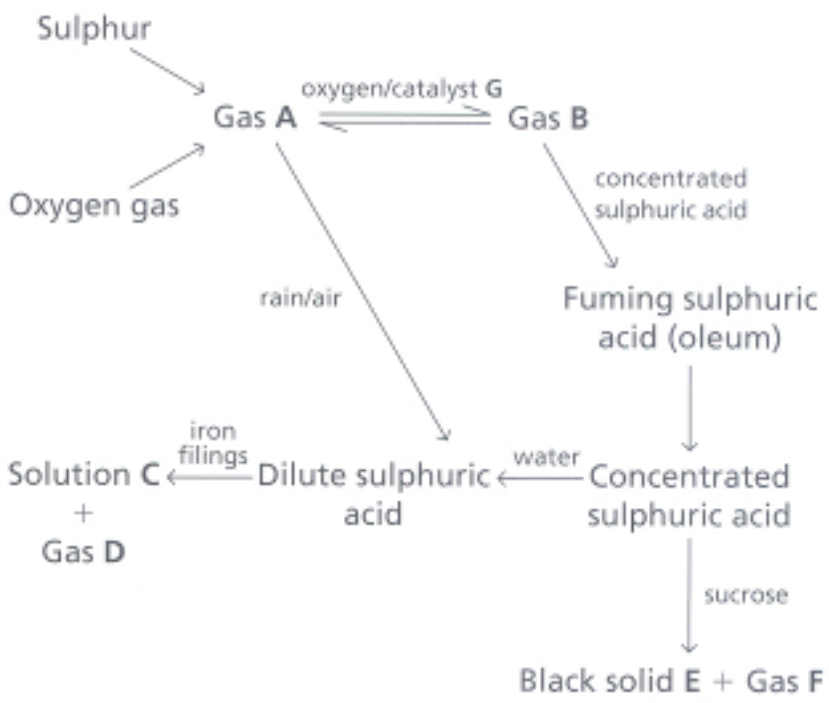
c. Using the information above, explain why countries such as the US, Russia and Germany are at the top of the list of sulphur dioxide producers.

d. If the total amount of sulphur dioxide produced by the UK is 5 million tonnes per year, what amount is produced by:

(i) power stations?

(ii) domestic users?
(iii) industry?

5. Study the following reaction scheme:



a. Identify the substances A to H by giving their names and formulae.

b. Write a balanced chemical equation for the formation of gas B.

c. (i) Describe a chemical test, and give the positive result of it, to identify gas D.

(ii) Describe a chemical test, and give the positive result of it, to identify gas F.

d. How would you obtain solid C from the solution C?

e. Which pathway shows the formation of acid rain?

f. In which way is the concentrated sulphuric acid acting in its reaction with sucrose?

g. Where does the oxygen gas come from to form gas A?

6. In a neutralisation experiment, 25 cm^3 of dilute sulphuric acid was required to react completely with 40 cm^3 of a solution of 0.25 mol dm^{-3} potassium hydroxide.

a. Write a balanced chemical equation for the reaction between dilute sulphuric acid and potassium hydroxide.

b. Calculate the number of moles of potassium hydroxide solution used in the reaction.

c. How many moles of dilute sulphuric acid would this number of moles of potassium hydroxide react with?

d. Calculate the concentration of the dilute sulphuric acid.

e. Which indicator could have been used to determine when neutralisation had just occurred?

7 Describe how you would prepare some crystals of hydrated copper (II) sulphate from copper (II) oxide and dilute sulphuric acid. Draw a diagram of the apparatus you would use and write a balanced chemical equation for the reaction.

8. When sulphur is extracted from sulphur beds below the Earth's surface, superheated water is pumped down a shaft into the beds to melt the solid sulphur.

a. What is meant by superheated water?

b. Why does the water have to be superheated? Why would boiling water not work?

c. (i) When the molten sulphur is pumped to the surface it solidifies. Which allotrope of sulphur forms first?

(ii) What eventually happens to this allotrope as the temperature falls?

Most sulphur obtained from these sulphur beds, in countries such as Poland and France, is exported.

d. In which form do you think the sulphur is loaded on to sulphur tankers? Explain your answer.

e. What hazards do you think are faced by people working in industries that use sulphur? Give reasons for your answer.