Figure 5.7 Sapphires sparkle in the light when polished. They are cut by exerting a force on the cleavage planes between layers of ions in the crystal.

Metallic lattices

In Chapter 4, we learnt that a metallic lattice consists of ions surrounded by a sea of electrons. The ions are often packed in hexagonal layers or in a cubic arrangement. When a force is applied, the layers can slide over each other. But in a metallic bond, the attractive forces between the metal ions and the delocalised electrons act in all directions. So when the layers slide, new metallic bonds are easily re-formed between ions in new lattice positions and the delocalised electrons (Figure 5.8). The delocalised electrons continue to hold the ions in the lattice together. The metal now has a different shape. This explains why metals are malleable (they can be hammered into different shapes) and ductile (they can be drawn into wires). The high tensile strength and hardness of most metals is also due to the strong attractive forces between the metal ions and the delocalised electrons.

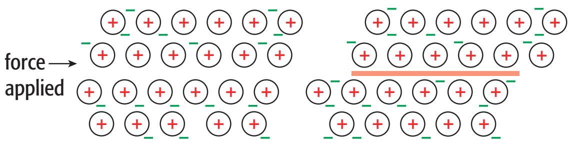


Figure 5.8 When a force is applied to a metallic structure, the layers slide over each other and re-form in new lattice positions.

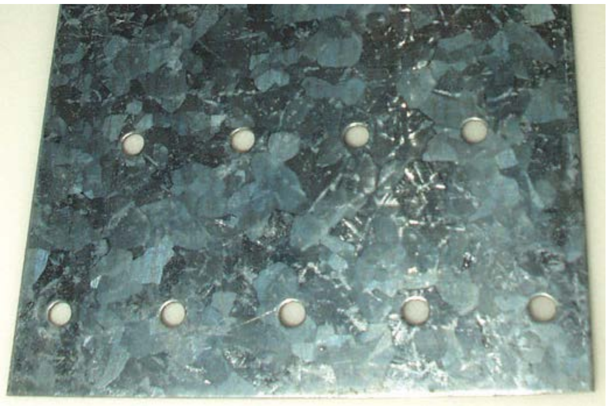


Figure 5.9 You can clearly see the metal crystals or 'grains' in this metal plate.

Alloys and their properties

An alloy is a mixture of two or more metals or a metal with a non-metal. The metal added to create the alloy becomes part of the crystal lattice of the other metal.

Brass is an alloy of copper (70%) with zinc (30%). It is stronger than copper but still malleable. For these reasons it is used for musical instruments, ornaments and household items such as door handles.

But why is brass stronger than pure copper?

Zinc ions are larger than copper ions. The presence of different-sized metal ions makes the arrangement of the lattice less regular. This stops the layers of ions from sliding over each other so easily when a force is applied (Figure 5.10).

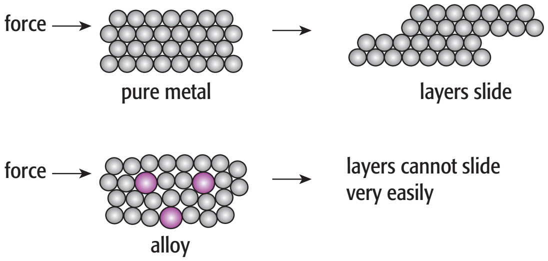


Figure 5.10 The layers of ions in an alloy slide less easily than in a pure metal because the structure of the lattice is less regular.

Pure aluminium is soft, ductile and has high electrical and thermal conductivity. Because of its low strength, pure aluminium is of little use in engineering. But its strength can be increased by addition of other elements such as copper, magnesium, silicon and manganese. Many alloys of aluminium are lightweight, strong and resistant to corrosion. These are used for the bodies of aircraft, for the cylinder blocks of car engines and for bicycle frames, all situations where low density combined with strength and corrosion resistance is important.

Bronze is an alloy of copper and tin. A 33-metre high bronze statue was built near the harbour in Rhodes (Greece) over 2000 years ago. The statue fell down after an earthquake and was eventually bought by a Syrian merchant. The bronze was recycled to make useful implements.

QUESTION

9 Explain the following:

- **a** why are most metals strong, but ionic solids are brittle?
- **b** why is an alloy of copper and tin stronger than either copper or tin alone?

Simple molecular lattices

Substances with a simple molecular structure, such as iodine, can also form crystals (Figure 5.11). This reflects the regular packing of the molecules in a lattice structure.

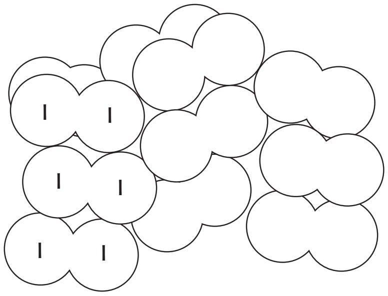


Figure 5.11 Iodine molecules are arranged in a lattice structure.

Ice also forms a crystalline lattice. Ice and water have peculiar properties because of hydrogen bonding (see page 66).

The distance between the nuclei of neighbouring iodine molecules is greater than the distance between the nuclei within the iodine molecule. This is because the forces between the molecules are weak van der Waals' forces whereas the forces between the atoms within the molecule are strong covalent bonds. Very little energy is needed to overcome the weak van der Waals' forces between the molecules. The lattice is easily broken down when iodine crystals are heated; iodine has a low melting point.

QUESTION

10 The table shows some properties of four elements. Use the data to answer the following questions. (Assume that steel has similar properties to iron.)

Element	Density / g cm^{-3}	Tensile strength / 10^{10} Pa	Electrical conductivity / 10^{8} S m^{-1}
aluminium	2.70	7.0	0.38
iron	7.86	21.1	0.10
copper	8.92	13.0	0.59
sulfur	2.07	breaks easily	1×10^{-23}

- **a** Why is aluminium with a steel core used for overhead electricity cables in preference to copper?
- **b** Suggest why many car engine blocks are made from aluminium alloys rather than from steel.
- **c** Explain the differences in tensile strength and electrical conductivity of iron and sulfur.

Giant molecular structures

Some covalently bonded structures have a three-dimensional network of covalent bonds throughout the whole structure. We call these structures giant molecular structures or giant covalent structures. They have high melting and boiling points because of the large number of strong covalent bonds linking the whole structure. Both elements, such as carbon (graphite and diamond), and compounds, such as silicon dioxide, can be giant molecular structures. Carbon and graphite are different forms of the same element. Different crystalline or molecular forms of the same element are called allotropes.

Graphite

In graphite, the carbon atoms are arranged in planar layers. Within the layers, the carbon atoms are arranged in hexagons. Each carbon atom is joined to three other carbon atoms by strong covalent bonds (Figure 5.12). The fourth electron of each carbon atom occupies a p orbital. These p orbitals on every carbon atom in each planar layer overlap sideways. A cloud of delocalised electrons is formed above and below the plane of the carbon rings. These electron clouds join up to form extended delocalised rings of electrons.

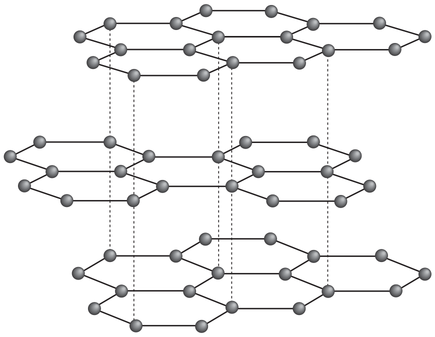


Figure 5.12 The structure of graphite.

The layers of carbon atoms are kept next to each other by weak van der Waals' forces.

The properties of graphite are related to its structure.

- High melting and boiling points: there is strong covalent bonding throughout the layers of carbon atoms. A lot of energy is needed to overcome these strong bonds.
- Softness: graphite is easily scratched. The forces between the layers of carbon atoms are weak. The layers of graphite can slide over each other when a force is applied. The layers readily flake off. This 'flakiness' is why graphite is used in pencil 'leads' and feels slippery.
- Good conductor of electricity: when a voltage is applied, the delocalised electrons (mobile electrons) can move along the layers.

Diamond

In diamond, each carbon atom forms four covalent bonds with other carbon atoms (Figure 5.13). The carbon atoms are tetrahedrally arranged around each other. The network of carbon atoms extends almost unbroken throughout the whole structure. The regular arrangement of the atoms gives diamond a crystalline structure.

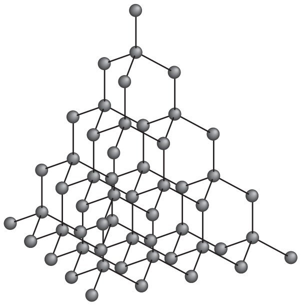


Figure 5.13 The structure of diamond.

The properties of diamond are related to its structure.

- High melting and boiling points: there is strong covalent bonding throughout the whole structure. A lot of energy is needed to break these strong bonds and separate the atoms.
- Hardness: diamond cannot be scratched easily because it is difficult to break the three-dimensional network of strong covalent bonds.
- Does not conduct electricity or heat: each of the four outer electrons on every carbon atom is involved in covalent bonding. This means that there are no free electrons available to carry the electric current.

Most of the diamonds used around the world have been mined from the Earth's crust. However, artificial diamonds can be made by heating other forms of carbon under high pressure. Artificial diamonds are too small to be used for jewellery but they can be used for drill tips.

Silicon(IV) oxide

There are several forms of silicon(IV) oxide. The silicon(IV) oxide found in the mineral quartz (Figure 5.14) has a structure similar to diamond (Figure 5.15).

Figure 5.14 The shape of these quartz crystals reflects the regular arrangement of the silicon and oxygen atoms.

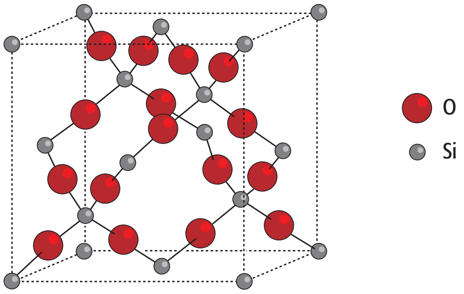


Figure 5.15 The structure of silicon(IV) oxide.

Each silicon atom is bonded to four oxygen atoms but each oxygen atom is bonded to only two silicon atoms. So the formula for silicon(IV) oxide is SiO_2. Silicon dioxide has properties similar to that of diamond. It forms hard, colourless crystals with high melting and boiling points and it does not conduct electricity.

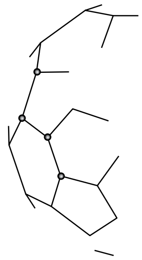
Sand is largely silicon(IV)oxide.

Carbon nanoparticles

Graphite and diamond are not the only allotropes of carbon. In recent years, substances called fullerenes have been made. The structure of many fullerenes is based on rings of carbon atoms, as is the structure of graphite. But many fullerenes exhibit properties unlike those of graphite. The individual particles in fullerenes may have one of their dimensions between 0.1 and 100 nanometres (1 nanometre = 10^{-9} m). Particles of this size are called nanoparticles. Another form of carbon, graphene, can be regarded as a single layer of graphite.

Fullerenes

Fullerenes are allotropes of carbon in the form of hollow spheres or tubes. They are similar in structure to graphite, in that each carbon atom is bonded to three other carbon atoms. They contain rings of carbon atoms arranged in hexagons and in addition many contain rings of carbon atoms arranged in pentagons. The first fullerene discovered was called **buckminsterfullerene**, C_{60} (Figure 5.16). The C_{60} molecule has the shape of a football (soccer ball). The carbon atoms are arranged at the corners of 20 hexagons and 12 pentagons. The bonds where two hexagons join are shorter than the bonds between the hexagons and the pentagons. As in graphite, some of the electrons in C_{60} are delocalised, but to a lesser extent than in graphite. Since the discovery of the C_{60} molecule, many types of buckminsterfullerene have been discovered. Some are ball-shaped molecules that are multiples of C_{60}, e.g. C_{120}. Other fullerene molecules include C_{20}, C_{70} and C_{72}.



high electron density in certain parts of the molecule (see electrophilic addition on page 209).

A second type of fullerene is a class of molecules described as **nanotubes**. Nanotubes are fullerenes of hexagonally arranged carbon atoms like a single layer of graphite bent into the form of a cylinder (Figure 5.17). The first nanotubes to be made were one layer of carbon atoms in thickness. More recently nanotubes have behave been made with thicker walls with several tubes inside one another. Although the diameter of a nanotube is very small, it can be made relatively long. The length of the nanotube cylinder can be a million times greater than its diameter.

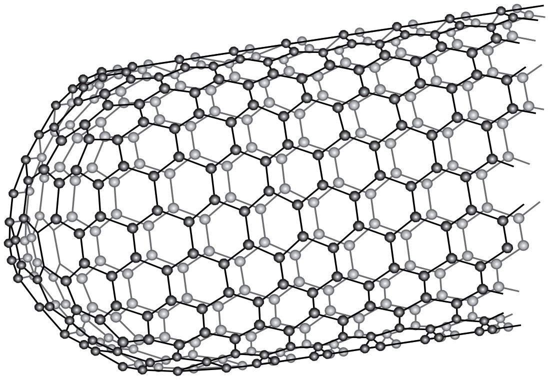


Figure 5.17 Part of the structure of a nanotube. The ends of the cylinder are often closed.

Nanotubes have characteristic properties:

- They have high electrical conductivity along the long axis of the cylinder. This is because, like graphite, some of the electrons are delocalised and are able to move along the cylinder when a voltage is applied.
- They have a very high tensile strength when a force is applied along the long axis of the cylinder. They can be up to 100 times stronger than steel of the same thickness.
- They have very high melting points (typically about 3500 °C). This is because there is strong covalent bonding throughout the structure.

Fullerenes have a large range of potential uses. Reactive groups can be attached to their surfaces and metal complexes (see page 371) can also be formed. Small molecules or atoms can be trapped in the cage of buckminsterfullerenes. Possible medical uses include delivering drugs to specific places in the body. Nanotubes are used in tiny electrical circuits as 'wires' and as electrodes in paper-thin batteries. They can be incorporated into clothing and sports equipment for added strength. They have also been used in the treatment of certain types of cancer.

Graphene

Graphene is a single isolated layer of graphite (Figure 5.18). The hexagonally arranged sheet of carbon atoms is not completely rigid and it can be distorted.

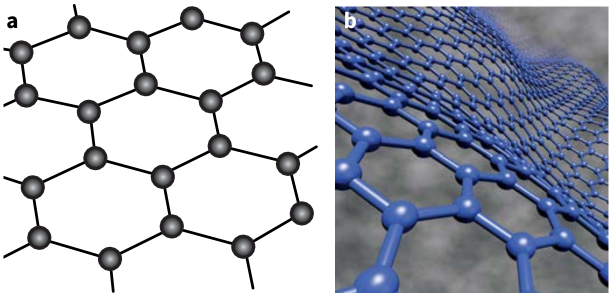


Figure 5.18 **a** Part of a graphene sheet. **b** 'Waves' in a sheet of graphene.

Graphene has some of the properties of graphite, but they are more exaggerated. For example:

- Graphene is the most chemically reactive form of carbon. Single sheets of graphene burn at very low temperatures and are much more reactive than graphite.
- Graphene is extremely strong for its mass.
- For a given amount of material, graphene conducts electricity and heat much better than graphite.

It has been said that 'a one square metre hammock made of graphene could support a 4 kg cat but would weigh only as much as the cat's whisker'. Potential applications of graphene include use in tiny electrical circuits and for tiny transistors, touchscreens, solar cells and other energy storage devices.

QUESTION

13 Suggest, using ideas of structure and bonding, why:

- **a** buckminsterfullerene, C_{60}, is converted from a solid to a gas at a relatively low temperature
- **b** graphene is a good conductor of electricity
- **c** nanotubes conduct electricity better along the long axis of the tube than across the tube
- **d** buckminsterfullerene, C_{60}, is relatively soft.

Conserving materials

Why conserve materials?

There is only a limited supply of metal ores in the Earth. If we use them all up, they cannot be replaced. The things we make from metals and other materials from the

Earth's crust are often thrown away. This leads to huge waste dumps and landfill sites scarring the landscape and problems with litter. Extracting metals from their ores requires a lot of energy. Energy resources are also limited and we need to conserve these as well. One way to help conserve materials and energy is to recycle metals (Figure 5.19).

Figure 5.19 Remember to recycle your cans. As well as aluminium cans, we can also save energy and resources by recycling steel cans.

Recycling materials

Large amounts of energy are needed to extract and purify metals. It is often cheaper to collect used metals and recycle them rather than extract them from their ores.

Recycling has several advantages:

- it saves energy (this helps tackle global warming, as we burn less fossil fuel)
- it conserves supplies of the ore
- landfill sites do not get filled up as fast and there is less waste
- it is cheaper than extracting the metal from the ore.

It is not always easy to recycle metals. They have to be collected and sorted and then transported to the recycling plant. This takes energy and money. It may be difficult to separate individual metals. For example 'tin' cans are made from steel coated with tin. The two metals have to be separated before they can be used again. Two metals that can be recycled easily are copper and aluminium.

Copper

Most copper ores remaining in the Earth contain less than 1% copper. Recycling copper is important because:

- less energy is needed to recycle copper than is needed to transport copper ore to the smelting plant and extract copper from it
- less energy is needed to extract and refine the recycled copper so that it is pure enough to be electrolysed.

The copper used for water pipes and cooking utensils does not have to be very pure, so little purification of recycled copper is needed for these uses. The copper used for electrical wiring has to be 99.99% pure. This has to be purified by electrolysis.

Aluminium

Purifying and remoulding aluminium is much cheaper than extracting aluminium from bauxite ore. Savings are made because:

- it is not necessary to extract the aluminium ore from the ground or to transport it to the smelting plant; these processes require energy
- the treatment of bauxite to make pure aluminium oxide for electrolysis does not need to be carried out
- the aluminium scrap needs less energy to melt it, compared with melting aluminium oxide
- the expensive electrolysis of aluminium oxide does not need to be carried out .

There is a 95% saving in energy if we recycle aluminium rather than extract it from its ore.

Summary

- The kinetic theory of gases states that gas particles are always in constant random motion at a variety of speeds.
- The volume of a gas increases when the temperature increases and decreases when the pressure increases.
- The volume of a gas under different conditions of temperature and pressure can be calculated using the ideal gas equation $pV = nRT$.
- The ideal gas equation can be used to determine the relative molecular mass of simple molecules.
- Gases do not obey the ideal gas equation at low temperatures and high pressures.
- The kinetic-molecular model can be used to describe the states of matter in terms of proximity and motion of the particles, and to describe changes of state and vapour pressure.
- Ionic compounds such as sodium chloride and magnesium oxide form a giant three-dimensional lattice structure containing ions in a regularly repeating pattern.
- The strong ionic forces acting in all directions between the ions in the lattice cause ionic substances to have high melting and boiling points.
- Simple molecular solids with low melting points such as iodine have a regular arrangement of molecules; they are crystalline. There are weak intermolecular forces between the molecules.
- Giant covalent (giant molecular) structures such as diamond have a large number of covalent bonds arranged in a regularly repeating pattern.
- Fullerenes are allotropes of carbon in the shape of hollow spheres (buckminsterfullerene) or tubes (nanotubes).
- Graphene is composed of a single flat sheet of hexagonally-arranged carbon atoms.
- The strong covalent bonds between the atoms in giant molecular structures cause these substances to have high melting and boiling points.
- In metals, the atoms are closely packed in a giant lattice in which the outer electrons are free to move.
- Metals such as aluminium and copper and their alloys have a variety of uses, which can be related to their physical properties, e.g. density, malleability, conductivity, hardness.
- Physical data can be used to suggest the type of structure and bonding present in a substance.
- Recycling plays an important part in conserving finite resources such as metals.

End-of-chapter questions

1 Four types of structure are:

giant molecular
giant ionic
giant metallic
simple molecular

a Give two examples of a giant ionic structure and two examples of a simple molecular structure. [4]

b Explain why substances with giant ionic structures are often brittle but metallic structures are malleable. [6]

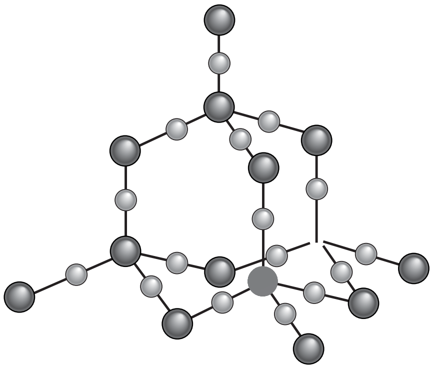
c Explain why giant molecular structures have higher melting points than simple molecular structures. [6]

d Diamond and graphite are two forms of carbon with giant molecular structures. Explain why graphite conducts electricity but diamond does not. [5]

Total = 21

2 The structures of carbon dioxide and silicon dioxide are shown in the diagram below.

$O{=}C{=}O$



5 The table gives data on the physical properties of five substances, **A** to **E**.

a Copy the table and fill in the gaps. [7]

Substance	Melting point	Electrical conductivity		Type of structure
		as a solid	as a liquid	
A	high	poor	good	**i**
B	low	**ii**	**iii**	**iv**
C	high	poor	poor	**v**
D	high	good	**vi**	giant metallic
E	high	poor	**vii**	giant covalent

b Explain the melting point and electrical conductivity of substance **A**. [6]

c Explain the melting point and electrical conductivity of substance **B**. [5]

Total = 18

6 The uses of metals are often related to their properties.

a Describe the structure of a typical metal. [2]

b Explain why metals are malleable. [4]

c Use the information in the table below to answer the questions that follow.

Element	Density / g cm^{-3}	Tensile strength / 10^{10} Pa	Electrical conductivity / 10^{8} S m^{-1}
aluminium	2.70	7.0	0.38
copper	8.92	13.0	0.59
steel	7.86	21.1	0.10

i Why is aluminium more suitable than steel for building aeroplane bodies? [1]

ii Explain why overhead electricity cables are made from aluminium with a steel core rather than just from copper. [5]

d The effect of alloying copper with zinc on the strength of the alloy is shown in the table below.

% copper	% zinc	Tensile strength / 10^{8} Pa
100	0	2.3
80	20	3.0
60	40	3.6
0	100	1.4

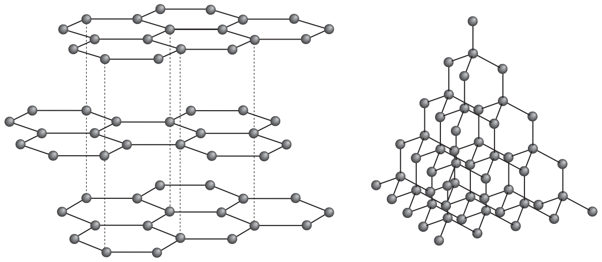
i Describe and explain the change in tensile strength as the percentage of zinc increases from 0% to 40%. [5]

ii State the name of the alloy of copper with zinc. [1]

e Many metals, such aluminium, can be recycled. Give three reasons why about 90% of aluminium is made by recycling rather than extracting it from its ore. [3]

Total = 21

7 The diagram shows the structures of graphite and diamond.



Use the diagrams and your knowledge of structure and bonding to answer the following questions.

a Explain why both diamond and graphite have high melting points. [2]

b **i** Why is graphite used in making handles for tennis racquets? [3]

ii Explain why graphite is used in pencil 'leads' for writing. [4]

c Explain why diamond is used on the tips of high-speed drills. [5]

Total = 14

8 Crystals of sodium chloride have a lattice structure.

a Describe a sodium chloride lattice. [3]

b Explain the following properties of sodium chloride.

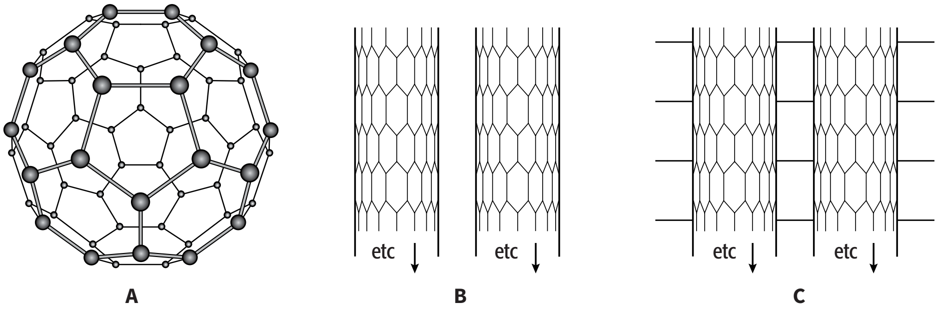
i Sodium chloride has a high melting point. [3]

ii Sodium chloride conducts electricity when molten but not when solid. [3]

iii Sodium chloride is hard but brittle. [5]

Total = 14

9 The diagram shows some allotropes of carbon.



a Give the name of allotrope **A**, which has the formula C_{60}. [1]

b Explain in terms of structure and bonding why structure **A** is gaseous at 800 °C but diamond is not. [6]

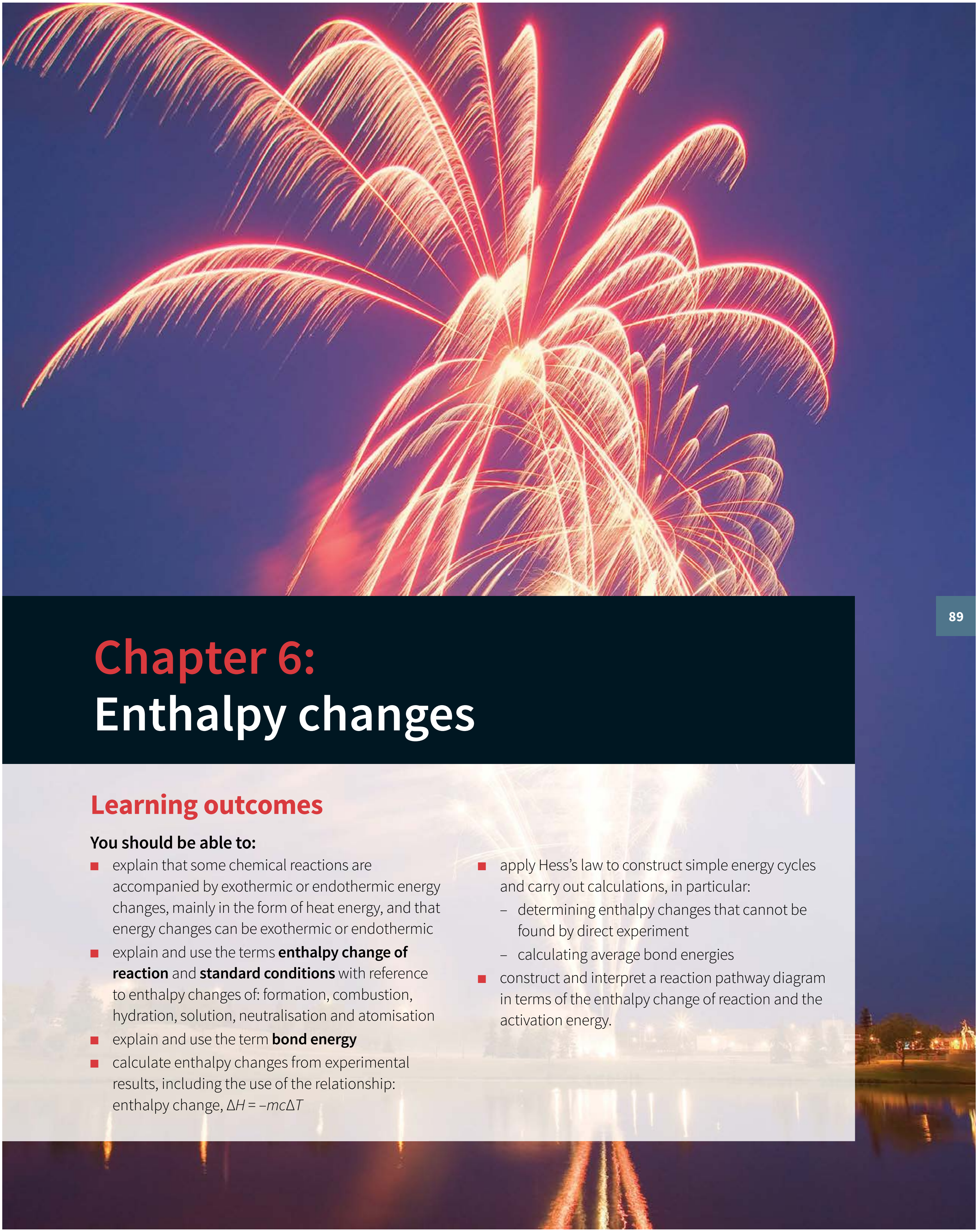
c Structure **B** shows an allotrope of carbon in the form of tubes.

i Give the name of this allotrope of carbon. [1]

ii Describe the similarities and differences between structure **B** and graphite. [4]

d Structure **C** is stronger than structure **B** when a force is applied in the same direction as the long axis of the tube. Explain why structure **C** is stronger. [5]

Total = 17



Chapter 6:
Enthalpy changes

Learning outcomes

You should be able to:

- explain that some chemical reactions are accompanied by exothermic or endothermic energy changes, mainly in the form of heat energy, and that energy changes can be exothermic or endothermic
- explain and use the terms **enthalpy change of reaction** and **standard conditions** with reference to enthalpy changes of: formation, combustion, hydration, solution, neutralisation and atomisation
- explain and use the term **bond energy**
- calculate enthalpy changes from experimental results, including the use of the relationship: enthalpy change, $\Delta H = -mc\Delta T$
- apply Hess's law to construct simple energy cycles and carry out calculations, in particular:
  - determining enthalpy changes that cannot be found by direct experiment
  - calculating average bond energies
- construct and interpret a reaction pathway diagram in terms of the enthalpy change of reaction and the activation energy.

Introduction

When chemical reactions take place there is an energy change. Energy can take many forms, including heat, light, sound and electrical energy. The chemical energy in the atoms and bonds of a substance is also very important. One of the most obvious energy transfers in chemical reactions is the transfer of heat (Figure 6.1). A car engine gets hot when the energy is transferred from the burning fuel. Fireworks release a lot of energy as heat (as well as light and sound) when they explode. Our bodies keep warm because of the continuous oxidation of the food we eat.

Figure 6.1 The chemical reactions in this fire are releasing large quantities of energy.

What are enthalpy changes?

Exothermic or endothermic?

Chemical reactions that release energy to the surroundings are described as **exothermic**. In an exothermic reaction the temperature of the surroundings increases. For example, when magnesium reacts with sulfuric acid in a test tube, the energy released is transferred to the surroundings and the temperature of the reaction mixture in the tube increases.

$$Mg(s) + H_2SO_4(aq) \longrightarrow MgSO_4(aq) + H_2(g) \quad \text{(energy released)}$$

The **surroundings** include:

- the solvent (in this case water)
- the air around the test tube
- the test tube itself
- anything dipping into the test tube (e.g. a thermometer).

Other examples of exothermic reactions include:

- the combustion of fuels
- the oxidation of carbohydrates in the bodies of animals and plants (respiration)
- the reaction of water with quicklime (calcium oxide) (see page 166).

Chemical reactions that absorb energy from the surroundings are described as **endothermic**. In an endothermic reaction the temperature of the surroundings decreases (Figure 6.2). For example, when sodium hydrogencarbonate reacts with an aqueous solution of citric acid in a test tube the temperature of the reaction mixture in the tube decreases. The citric acid and sodium hydrogencarbonate are absorbing the heat energy from the solvent, the test tube and the air.

Other examples of endothermic reactions include:

- the decomposition of limestone by heating (all thermal decomposition reactions are endothermic)
- photosynthesis (in which the energy is supplied by sunlight)
- dissolving certain ammonium salts in water

$$\underset{\text{ammonium chloride}}{NH_4Cl(s)} + \underset{\text{water}}{aq} \longrightarrow \underset{\text{ammonium ions}}{NH_4^+(aq)} + \underset{\text{chloride ions}}{Cl^-(aq)}$$

Figure 6.2 Using a cooling pack to treat a sports injury. When the pack is kneaded, water and ammonium chloride crystals mix. As the crystals dissolve, energy is transferred from the surroundings, cooling the injury.

QUESTION

1 Classify each process as exothermic or endothermic:
  - **a** the burning of magnesium in air
  - **b** the crystallisation of copper(II) sulfate from a saturated solution
  - **c** the thermal decomposition of magnesium nitrate
  - **d** the fermentation of glucose by yeast
  - **e** the evaporation of sea water.

Enthalpy changes and enthalpy profile diagrams

We call the energy exchange between a chemical reaction and its surroundings at constant pressure the **enthalpy change**. Enthalpy is the total energy associated with the materials that react. The symbol for enthalpy is H. We cannot measure enthalpy, but we can measure an enthalpy change when heat energy is exchanged with the surroundings. We can write this as:

$$\underset{\text{enthalpy change}}{\Delta H} = \underset{\text{enthalpy of products}}{H_{\text{products}}} - \underset{\text{enthalpy of reactants}}{H_{\text{reactants}}}$$

The symbol Δ is the upper case Greek letter 'delta'. This symbol is often used to mean a change in a quantity. For example, ΔT means a change in temperature and ΔH means the enthalpy change.

The units of enthalpy change are kilojoules per mole (kJ mol^{-1}).

We can draw **enthalpy profile diagrams** (also known as reaction pathway diagrams) to show enthalpy changes. The enthalpy of the reactants and products is shown on the y-axis. The x-axis shows the reaction pathway, with reactants on the left and products on the right. For an exothermic reaction, energy is released to the surroundings. So the enthalpy of the reactants must be greater than the enthalpy of the products. We can see from the enthalpy profile diagram for the combustion of methane (Figure 6.3) that $H_{\text{products}} - H_{\text{reactants}}$ is negative.

We can include this information in the equation for the reaction:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = -890.3\ \text{kJ mol}^{-1}$$

The negative sign shows that the reaction is exothermic.

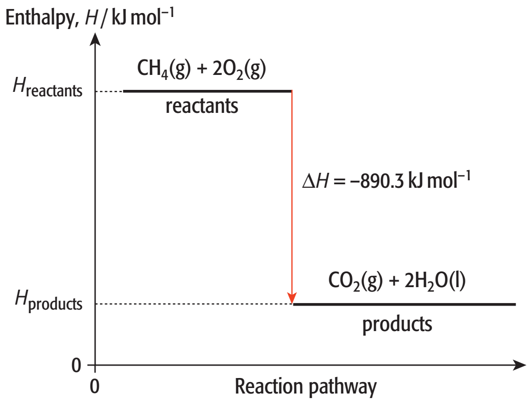


Figure 6.3 Enthalpy profile diagram for the combustion of methane.

For an endothermic reaction, energy is absorbed from the surroundings by the chemicals in the reaction. So the enthalpy of the products must be greater than the enthalpy of the reactants. We can see from the enthalpy profile diagram for the thermal decomposition of calcium carbonate (Figure 6.4) that $H_{\text{products}} - H_{\text{reactants}}$ is positive.

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g) \qquad \Delta H = +572\ \text{kJ mol}^{-1}$$

The positive sign shows that the reaction is endothermic.

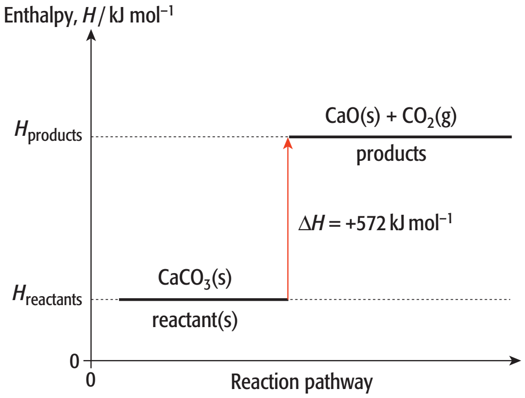


Figure 6.4 Enthalpy profile diagram for the decomposition of calcium carbonate.

QUESTION

2 Draw enthalpy profile diagrams for:
  - **a** the combustion of sulfur to form sulfur dioxide
  - **b** the endothermic reaction

    $H_2O(g) + C(s) \longrightarrow H_2(g) + CO(g)$