

MODULE 4

energy

Industrialised societies such as ours use energy not just for biological survival (food and shelter) but also for a variety of other purposes such as transport, lighting, heating and cooling, manufacturing and entertainment. We obtain this energy from many sources, but most importantly from the so-called fossil fuels (coal, crude oil and natural gas). We extract that energy mainly by burning the fuels.

There are problems with burning fossil fuels. It pollutes the air in the vicinity of the vehicle, home, power station or factory, and it releases enormous quantities of carbon dioxide into the atmosphere, causing global warming. Today localised pollution can be minimised and managed, but global warming appears to be an intractable problem.

Another problem is that fossil fuels are non-renewable resources (at least on human time-scales) and we are consuming them at alarming rates. Table 1 shows the way that energy consumption escalates as living standards rise.

To provide a background for discussing such problems, this module will look at the nature of fossil fuels and at combustion, the process by which we extract the energy.

We shall start in Chapter 9 with photosynthesis which is the origin of all our fossil fuels, then because fossil fuels consist predominantly of compounds of carbon, we will survey some of the simpler classes of carbon compounds so that we can identify the compounds present in fossil fuels.



**TABLE 1 Energy used per person per day by different groups of people**

Energy (in MJ per person per day)	
primitive humans	10 <sup>a</sup>
people in less developed countries (e.g. Asia, Africa, Central America)	20 to 100 (but likely to increase rapidly)
people in more developed countries (e.g. Australia, Europe, Japan)	400 to 500 <sup>b</sup>
people in the USA	800 to 1000

<sup>a</sup> Equivalent to 600 g sugar per day.

<sup>b</sup> Equivalent to 12 L petrol or 15 kg coal per day.

In Chapter 10 the focus will be on combustion. First we shall look at energy aspects of chemical reactions generally and of combustion reactions in particular. Then kinetic aspects will be considered; that is, the meaning of rate (speed) of reaction and the factors that affect it. This will involve a survey of what are called catalysts—substances that speed up a reaction without being consumed by it. Finally we will look at safety issues surrounding the storing of fossil fuels and compounds extracted or made from them.



## ENERGY IS A MAJOR CONSIDERATION IN OUR LIFESTYLE

We generate electricity from coal and extract crude oil for transport needs.  
And of course we use energy (from food) in personal exertion



# Energy and its traditional sources

## IN THIS CHAPTER

Why do we need energy and where do we get it from?

Photosynthesis

Fossil fuels

The element carbon

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Double and triple covalent bonds

Carbon–carbon bonds

Fractional distillation of crude oil

Alkanes

Alkenes

Functional groups

Composition of fossil fuels

Uses of hydrocarbons

Safety precautions

We saw in the preamble that people in industrialised societies use large amounts of energy and that most of it comes from the so-called fossil fuels (coal, crude oil and natural gas). This energy, along with all the other energy we use today, comes directly or indirectly from the sun via photosynthesis. In this chapter we shall discuss photosynthesis and examine some of the chemical compounds used to store energy. But first let us look at why and how we use energy and where we get it from.

## 9.1 WHY DO WE NEED ENERGY?

All forms of life, including humans, need energy to function and grow. Plants get their energy from the sun through photosynthesis (next section). Other living organisms obtain energy from their food (eating plants and other life forms). Primitive humans living as hunter–gatherer societies had fairly low energy requirements. They needed energy:

- to keep their bodies functioning (that is, they needed food)
- to obtain their food (collect fruits and nuts, dig up roots, and chase and kill animals)
- to build simple shelters and make basic clothing
- to make tools or weapons (to help obtain food and make shelters)
- to keep themselves warm and
- to move around (travel—walk or ride animals).

Modern industrialised humans need energy for those same functions but also for:

- more extensive travel and transport of goods (cars, trains, ships, planes)
- constructing buildings, cities, roads, railways, water supplies, waste treatment plants
- elaborate homes, appliances, furniture and furnishings, and more varied clothing
- books, newspapers, magazines, entertainment
- health facilities (hospitals and drugs)
- food processing and
- for commerce and industry generally.

It should be emphasised that we use energy not just for obvious activities such as operating motor cars, trains and planes, cooking, heating water, running electrical appliances and using electric lights but also when we buy consumer goods. Everything we buy, from motor cars to clothes, refrigerators, television sets, newspapers and furniture, has a very high energy content quite apart from the energy used in running them; that is, large amounts of energy were used to make them, and when we buy new ones we are really using up a lot of energy.

The amounts of energy used per person per day in different times or situations were shown in Table 1 of the preamble. These are the total amounts—bodily needs, home uses, transport and the averaged energy content of all goods and services used or owned.

Table 9.1 gives a breakdown of the non-food energy that we use.

**TABLE 9.1 How energy is used in Australia**

Activity	Percentage of total energy it uses
manufacturing (e.g. cars, building materials, appliances, furniture, clothing, electronic goods)	27
transport (cars, trucks, planes, trains) <sup>a</sup>	25
domestic (energy used directly in homes including electricity)	15
agriculture, mining and construction	7
electricity generation (excluding that used directly in homes) <sup>b</sup>	20
other	6

<sup>a</sup> Does not include electricity used for transport (such as city electric trains and battery based electric vehicles).

<sup>b</sup> This electricity is used for all other activities in the table except ‘domestic’.

## Where do we get our energy from?

Table 9.2 shows the relative amounts of non-food energy that we get from various sources. Energy from solar hot water heaters, windmills and solar cells is not included because of the difficulty in estimating it; such sources probably contribute less than 1% of the total energy included in the table.

## Fossil fuels

Coal, crude oil and natural gas are called *fossil fuels*.

**Fossil fuels** are substances that were formed by the action of high temperature and high pressure upon decaying plant and animal matter over millions of years.

**TABLE 9.2 Sources of (non-food) energy in Australia**

Source	Percentage of total energy provided
coal	40
crude oil	36
natural gas	18
wood and bagasse <sup>a</sup>	4
hydro-electricity	2 <sup>b</sup>

<sup>a</sup> Bagasse is the fibrous waste from sugar cane after the sugar has been extracted: it is used as fuel in sugar mills.

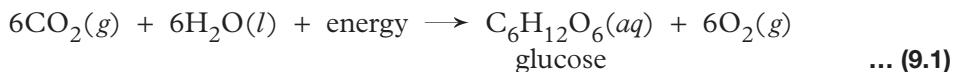
<sup>b</sup> 2% of total energy but 9% of total electricity generated.

The word ‘fossil’ is used because these substances were formed in essentially the same way and over similar time scales as normal geological fossils. Fossil fuels are basically stored solar energy that was initially ‘harvested’ by photosynthesis.

Let us then start our survey of energy with photosynthesis.

## 9.2 PHOTOSYNTHESIS

**Photosynthesis** is the process in which plants use solar energy to convert carbon dioxide from the air and water from the ground into carbohydrates such as glucose, sucrose, starch and cellulose. For example:



Photosynthesis is an *endothermic* reaction (Section 8.12), meaning that heat is *absorbed* as it occurs. When Reaction 9.1 occurs, 2830 kJ of energy is absorbed per mole of glucose formed.

**Carbohydrates** are compounds of carbon, hydrogen and oxygen. Common carbohydrates are glucose, fructose, sucrose, starch, glycogen and cellulose. The name arises because many (though not all) of them can be represented by the formula  $\text{C}_x(\text{H}_2\text{O})_y$ . For example glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$  is  $\text{C}_6(\text{H}_2\text{O})_6$ .

Photosynthesis is a complex multi-step reaction brought about by the green colouring matter (chlorophyll) in the leaves of plants. It is light energy from the sun, not heat energy, that chlorophyll collects. Solar energy is converted into chemical energy by photosynthesis. We say that energy has been *stored* in the glucose. Apart from direct absorption of heat by living organisms and their surroundings, photosynthesis is the only way in which the natural environment can absorb solar energy. The raw materials for photosynthesis are carbon dioxide from the atmosphere and water from the soil; light energy from the sun is used to bring about the reaction.

Carbohydrates in plants are the energy source (food) for animals, including humans. In cellular **respiration**, the stored chemical energy is made available to the animal:



The amount of energy released during respiration is the same as was absorbed during photosynthesis, namely 2830 kJ per mole of glucose used. Some

of this energy is used for the day-to-day functioning of the animal, while much is dissipated as heat. A small portion is transformed into protein and fat. The fat is again stored chemical energy—reserves the animal can call upon to supply energy if the daily food intake fails to meet body needs.

Carbohydrates are considered to be *high energy compounds* because when they react chemically as in respiration (above) or in combustion (next chapter), large amounts of energy are released.

## Energy flow through the environment

Growing crops such as wheat is the main way we collect solar energy today



Figure 9.1 shows a simplified food web. It shows the flow of energy through the environment from the sun to plants (the primary producers or autotrophs) to animals (herbivores, carnivores and omnivores), then after their death through decomposers and back to the environment. Only about 10 to 20% of the energy taken in at any point in the chain is actually used by the next consumer—the rest is released as heat.

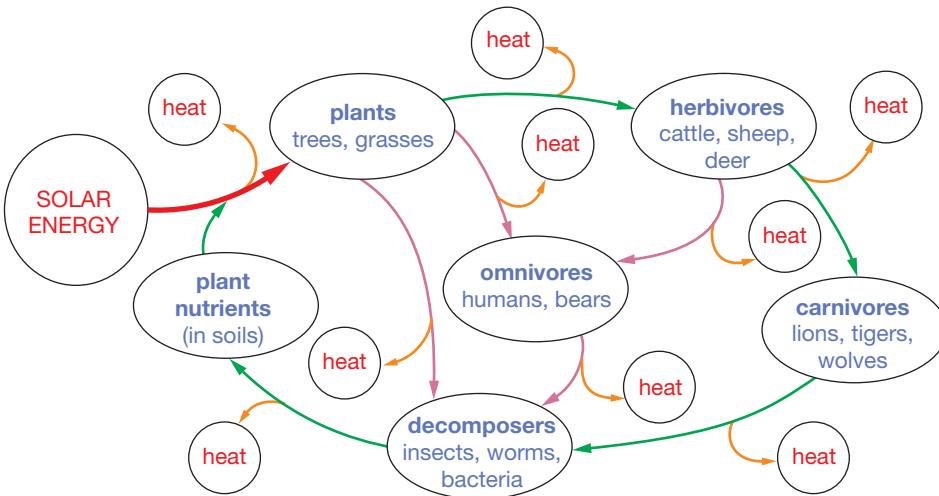
Two points warrant emphasis:

- 1 Virtually all the solar energy trapped by plants ends up as heat in the environment to be re-radiated into space as each life form completes its life cycle.
- 2 The longer the food chain, the more inefficient it is: gaining energy by eating meat effectively consumes far more solar energy than getting the same amount of energy from plant matter (grains, fruit and vegetables).

Figure 9.1 makes it clear that all forms of life on Earth are dependent upon sunlight for their supply of energy; without the sun there would be no life as we know it. Production of carbohydrates by photosynthesis is the main way in which solar energy is collected for use by plants and animals.

There is one important omission from Figure 9.1 and that is fossil fuels.

FIGURE 9.1  
The food web for life forms on Earth



## 9.3 FOSSIL FUELS

Plants ‘harvest’ solar energy to live and grow, and animals live by eating plants (or other animals which ate plants). Normally when plants and animals die, insects, fungi, worms and bacteria (decomposers) convert them back to carbon dioxide, water and nutrients and release the stored energy into the environment, so completing the materials and energy cycles that are part of the living world.

However in some locations and under certain conditions, over geological time scales the decay processes were interrupted. Instead of being fully decomposed to carbon dioxide and water, some plant and animal material was only partially decomposed and remained stored in the Earth as energy-rich compounds. We call these substances fossil fuels. The geological processes that led to their formation were mainly high temperatures and high pressures over millions of years.

**Energy-rich compounds** are ones that release large amounts of energy when they undergo chemical reactions such as combustion (burning in oxygen or air) or respiration. We say that energy is *stored* in these compounds and we call it **chemical energy**. When such compounds react they release their stored chemical energy, generally in the form of heat energy.

By mining fossil fuels from the Earth and burning them (to carbon dioxide and water), we are able to extract the stored energy. Fossil fuels are the world’s major source of energy today (Table 9.2), but supplies of them are finite so eventually we will use them up.

The common fossil fuels are:

- coal
  - crude oil
  - natural gas
  - oil shales (e.g. in Queensland at Rundle near Gladstone and Condor near Proserpine)
  - tar sands (not common in Australia)
- } in widespread use today: our major energy sources
- } not economic today, but in the future?

The major sources of fossil fuels in Australia are listed in Table 9.3. Australia has plenty of coal and adequate supplies of natural gas but very limited reserves of crude oil.

We saw in Chapter 1 that living matter is mainly made up of compounds of carbon (apart from water). Therefore fossil fuels were naturally synthesised by

**TABLE 9.3 Major sources of fossil fuels in Australia**

Fuel	Major Australian sources
black coal	Bowen Basin (Bowen to Gladstone) in Qld Sydney Basin (Newcastle to Wollongong) in NSW There is very little coal in the western half of the continent.
brown coal	Latrobe Valley in Vic.
natural gas	Gippsland Basin (Bass Strait) in Vic. Cooper Basin (north-east of SA) Carnarvon Basin (North-West Shelf of WA)
crude oil	Bass Strait in Vic. (expected to be exhausted within a couple of decades)

geological processes acting upon compounds of carbon. It is not surprising then that fossil fuels themselves are compounds of carbon. We shall look at the actual composition of the common fossil fuels in Section 9.12 after some of the main classes of carbon compounds have been introduced.

### Exercises

- \*1 What are the major activities in your home that use energy? What are the sources of this energy? Which of these are fossil fuels and which are not? Could you get any of the fossil-fuel sourced energy from a non-fossil fuel source? Explain how or why not. Suggest some ways of minimising household energy consumption without seriously degrading your quality of life.
- 2 The Earth absorbs a lot of solar energy by photosynthesis and by direct absorption of heat, yet the average global temperature of the Earth is approximately constant. Explain how this can happen.
- \*3 List several non-fossil-fuel sources of energy. Discuss the possibility of using these as total or partial substitutes for fossil fuels in Australia today.
- The following information may be needed in some of the following exercises: the energy absorbed when one mole of glucose is formed from carbon dioxide and water is 2830 kJ.*
- 4 Explain why burning wood (taken as pure cellulose,  $C_6H_{10}O_5$ ) and eating sugar (sucrose,  $C_{12}H_{22}O_{11}$ ) can be regarded as reversing photosynthesis. Write all relevant equations.
- 5 In photosynthesis, using orange light (wavelength 650 nm), it takes 8400 kJ of light energy to make 1 mole of glucose. Using blue light (450 nm) it takes 12 000 kJ of light energy to make 1 mole of glucose. Calculate the efficiency of photosynthesis for each colour of light; that is, express the energy stored in the glucose as a percentage of the energy used to make the glucose. What happens to the rest of the light energy absorbed by the plant?
- 6 a Fructose is a sugar,  $C_6H_{12}O_6$ , commonly found in grapes. Write an equation for the formation of fructose by photosynthesis. This reaction absorbs 2830 kJ per mole of fructose produced. When fructose is eaten by a person it is converted to carbon dioxide and water. Write an equation. How much energy is liberated or absorbed (state which) in the person's body when this occurs?  
b In winemaking, fructose is fermented to an equimolar mixture of ethanol ( $C_2H_5OH$ ) and carbon dioxide. Write an equation for this reaction.  
c When this reaction occurs, 110 kJ of energy is released per mole of fructose. What has happened to the rest of the energy involved in the formation of fructose by photosynthesis? Would it be possible to recover this 'missing' energy? Explain fully.

## 9.4 THE ELEMENT CARBON

The element carbon belongs to Group 4 of the Periodic Table. With atomic number 6, its electron configuration is 2, 4. This means that it has four valence electrons. We saw in Section 7.3 how carbon forms covalent bonds to each of four hydrogen atoms to form methane,  $\text{CH}_4$  (Figures 7.1 and 7.2). In addition, we saw in Section 2.23 how carbon formed the covalent network solid, diamond, by each carbon atom making covalent bonds to each of four other carbon atoms (Figure 2.15, which is reproduced here as Figure 9.2). Actually diamond is not the only form of the uncombined element carbon.

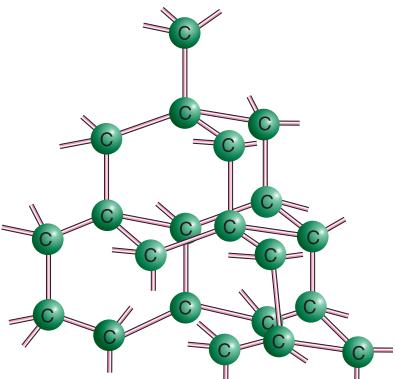


FIGURE 9.2  
The structure of diamond

## 9.5 ALLOTROPES OF CARBON

Sparkling colourless diamonds would seem to have little in common with dull, black graphite rods from inside torch batteries, yet both materials are pure forms of the same element, carbon. This existence of two or more physically distinct forms of the one element is called **allotropy**.

**Allotropes** are forms of the one element (in the same physical state) which have distinctly different physical properties (colour, density, hardness, electrical conductivity).

Diamond and graphite are allotropes of carbon. Other common elements displaying allotropy are phosphorus, sulfur, tin and oxygen.

The difference in physical properties between allotropes shows up most strikingly in the allotropes of carbon: diamond is colourless, extremely hard, and a non-conductor of electricity, while graphite is black, soft and slippery (used as a dry lubricant), and it conducts electricity.

The reason allotropes have different properties is that the atoms are joined or packed together in different ways to form molecules or crystals.

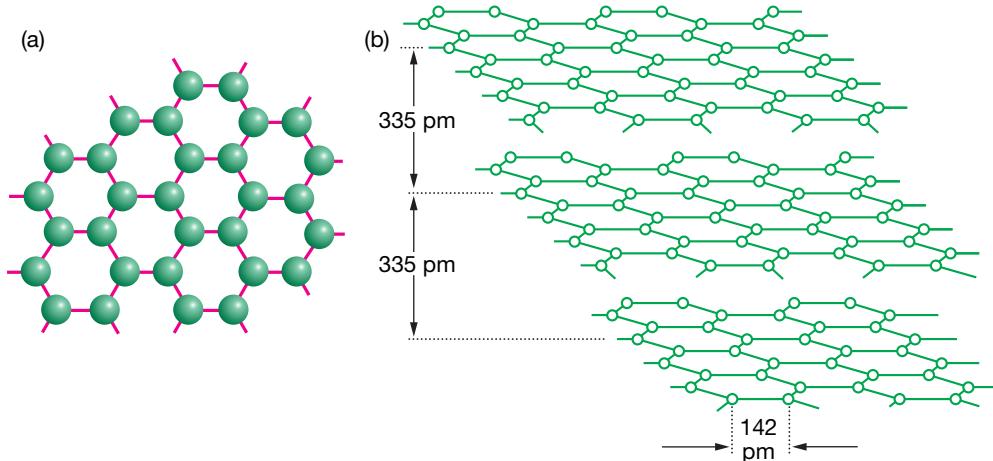
*Diamond* consists of carbon atoms each covalently bonded to four other carbon atoms as shown in Figure 9.2. We saw in Section 7.3 that the four bonds around the carbon atom in methane were tetrahedrally arranged. Similarly in diamond the shape around each carbon atom is tetrahedral. This means that diamond is a three-dimensional structure. In addition, note that the carbon atoms are actually arranged in six-membered rings; the rings are buckled not flat. This three-dimensional structure means that diamond is very hard. With all its valence electrons tied up in strong covalent bonds, diamond has no mobile electrons and so it does not conduct electricity. The orderly arrangement of atoms throughout the whole crystal also gives rise to its transparency and brilliance.

*Graphite* is also a covalent network solid (covalent lattice), but in this case each C atom is bonded to only *three* other C atoms to form a planar structure as shown in Figure 9.3(a). Notice that the structure consists of *flat* six-membered rings. Three bonds per C atom leaves each C atom with a free valence electron; these excess electrons form a delocalised electron cloud similar to that in metals (Section 2.24). It is the presence of these delocalised electrons which makes

graphite a conductor of electricity: the electron cloud can move under the influence of an applied voltage in the same way as in metals.

In a sample of graphite, these two-dimensional lattices are packed one upon the other as shown in Figure 9.3(b). Because there are only weak intermolecular forces between these layers, they can easily slide across one another; this explains the slipperiness of graphite and its good lubricating properties.

FIGURE 9.3  
The structure of graphite:  
(a) the structure of one  
graphite layer, (b) the  
arrangement of layers



## Other allotropes of carbon

In recent years, a third allotrope of carbon has been prepared called **buckminsterfullerene** (or **buckyball** for short). If an electric discharge is set up between graphite electrodes in a low pressure of helium, some of the graphite evaporates, then condenses as a soot. Some of this soot is soluble in benzene or toluene (normal soot is insoluble) and when separated out has a yellow-brown colour. Chemical analysis shows this to be a pure substance of formula  $C_{60}$  with a ‘soccer ball’ structure; the carbon atoms are arranged in five- and six-membered rings joined together as on a soccer ball, as illustrated in Figure 9.4. There are 20 hexagons and 12 pentagons joined together with a C atom at each apex. Each carbon atom is joined to three other carbon atoms (as in graphite) but the bonds are *not* planar: the structure resembles a spherical cage. There are some delocalised electrons but buckminsterfullerene is less reactive than graphite.

Substances with formulae  $C_{70}$  and  $C_{84}$  have also been prepared: they have similar structures to buckminsterfullerene but are more egg-shaped than spherical. This group of substances ( $C_{60}$ ,  $C_{70}$ ,  $C_{84}$ ) are called

**fullerenes**. The  $C_{60}$  fullerene is buckminsterfullerene, named after an architect, Buckminster Fuller, who specialised in geometric dome structures. Each of the fullerenes is an allotrope of carbon.



FIGURE 9.4  
Place a carbon atom  
at every one of the 60  
apexes of a soccer ball  
and you have the structure  
of buckminsterfullerene

## Uses of carbon allotropes

Diamonds are widely used as *jewellery*. This is because of their brilliant sparkle and hardness (they cannot be dulled by scratches as gold and platinum can).

However a larger proportion of the world's diamond production is used in industry for making *drills* and *cutting implements* (such as circular saw blades for cutting tiles, bricks and steel): again it is the hardness of diamond that makes it useful for these purposes.

Graphite, being an electrical conductor, is used as *electrodes* in ordinary and alkaline dry-cell batteries. It is similarly used as electrodes in extracting aluminium from alumina (Sections 4.14 and 4.15). Graphite is used as a *dry lubricant* (often on door catches in motor cars) and in the 'lead' of *lead pencils* (no lead content at all!). It is its slipperiness that makes it useful for these purposes (the planar layers slide over one another).

Although fullerenes are largely laboratory curiosities at the moment, there is growing evidence that they may become useful for making superconductors (zero electrical resistance), specialised polymers, drugs and high temperature lubricants.

## 9.6 DOUBLE AND TRIPLE COVALENT BONDS

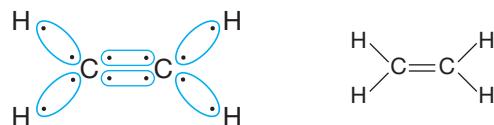
In all the examples of covalent bonding considered so far (Sections 2.17 and 7.3), just one pair of electrons has been shared between a particular pair of atoms. We call such bonds **single bonds**.

Sometimes, in order to attain noble gas electron configurations, it is necessary for pairs of atoms to share more than one pair of electrons. In order to form carbon dioxide, carbon (2, 4), which needs to gain four more electrons, and oxygen (2, 6), which needs to gain two more electrons, pair up their electrons as follows:



Between the carbon atom and each oxygen atom there are *two* shared pairs of electrons. In this way, carbon 'considers' that it has eight outer electrons (counting all of the shared electrons), and each oxygen atom 'considers' that it too has eight outer electrons. Because there are two shared pairs of electrons between carbon and each oxygen atom, we call these **double bonds**. Remember in Section 2.17 it was stated that a dash is used to represent a pair of bonding electrons. Because there are two shared pairs between C and each O, we draw two dashes as in the right-hand diagram above (called a structural formula).

Similarly for ethene,  $\text{C}_2\text{H}_4$ , there is a double bond between the carbon atoms (and single bonds between each carbon atom and the hydrogen atoms):



Nitrogen (2, 5) needs to gain three electrons to become like neon (2, 8). Hence to form nitrogen molecules, it is necessary for pairs of atoms to share *three* pairs of electrons to form what we call a **triple bond**:



Similarly in ethyne (acetylene),  $\text{C}_2\text{H}_2$ , a triple bond is formed between the carbon atoms in order to satisfy the bonding drives of all four atoms. Again three dashes are used to represent a triple bond (three shared pairs of electrons).



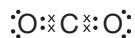
## Other ways of drawing electron-dot structures

While the type of electron-dot structure being drawn in this book makes it easy to see which electrons have been paired up, to check that each atom has the required number of valence electrons (2 or 8) and to count the number of covalent bonds, there are three other forms of electron-dot structure that are much more widely used. These just put the bonding electrons between the atoms they are joining without any loops or balloons; they represent the electrons in different ways:

- 1 dots are used for all electrons:



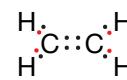
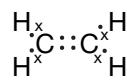
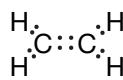
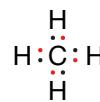
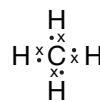
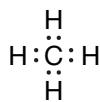
- 2 dots are used for the electrons from one atom with crosses for those from the other atom:



- 3 different coloured dots are used for the electrons from different atoms:



Electron-dot structures in these three styles for methane (compare with Figure 7.1 on page 187) and the three other molecules just discussed are:



These types of structures are often called **Lewis electron-dot structures** or just **Lewis structures** after the person who introduced them in the 1920s.

You should use whichever form of electron-dot structure you are most comfortable with—all are acceptable to HSC examiners. However if using dots only, make sure they are big enough to be clearly recognised and not mistaken for stray marks on the paper!

## Structural formulae

So far we have used two types of drawings to show chemical bonding:

- 1 *electron-dot structures*, which show valence electrons and how they combine to form chemical bonds, and
- 2 drawings in which dashes are used to indicate bonding pairs of electrons.

These diagrams are called **structural formulae**. They show the way atoms are held to one another in molecules. The structural formulae of the compounds discussed in Sections 2.17 and 7.3 are shown in Table 9.4 along with the corresponding molecular formulae. The diagrams to the right of the electron-

dot structures above for carbon dioxide, ethene, nitrogen and ethyne are structural formulae.

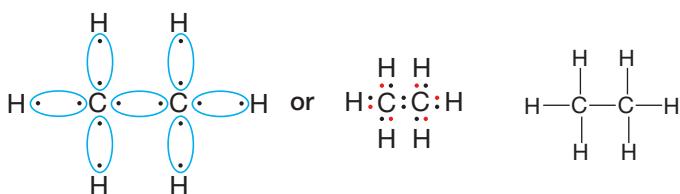
Structural formulae are sometimes drawn to show the geometrical arrangement of bonds (as was done in Figure 7.3) but are often drawn with all dashes at right angles for printing convenience (as in Table 9.4).

**TABLE 9.4 Structural and molecular formulae for compounds in Sections 2.17 and 7.3**

	Chlorine	Hydrogen chloride	Water	Ammonia	Methane	Hydrogen sulfide
structural formula	Cl—Cl	H—Cl	H—O—H	H—N—H   H	H—C—H   H	H—S—H
molecular formula	Cl <sub>2</sub>	HCl	H <sub>2</sub> O	NH <sub>3</sub>	CH <sub>4</sub>	H <sub>2</sub> S

## 9.7 CARBON-CARBON BONDS

We have just seen that carbon can form carbon–carbon double and triple bonds. As the structure of diamond shows, carbon can also form carbon–carbon single bonds—not just in diamond but in many compounds as well. The simplest compound containing a carbon–carbon single bond is ethane, C<sub>2</sub>H<sub>6</sub>. It has three hydrogen atoms attached to each carbon atom with the two carbon atoms joined together. Its electron-dot structure and structural formula are:



We often need to consider the shape of molecules, or in other words, the geometric arrangement of bonds around a central atom. For example, in Section 7.4 we saw that shape was an important factor in determining whether a molecule was polar or not. As mentioned in Section 7.3, when drawing electron-dot structures we do not attempt to include the shape of the molecule. With simple molecules as in Section 7.4, structural formulae can be drawn to show molecular shape. However, with more complicated molecules there is often difficulty in showing shape on such structures. What are more useful are different types of molecular models.

## Structural formulae and molecular models

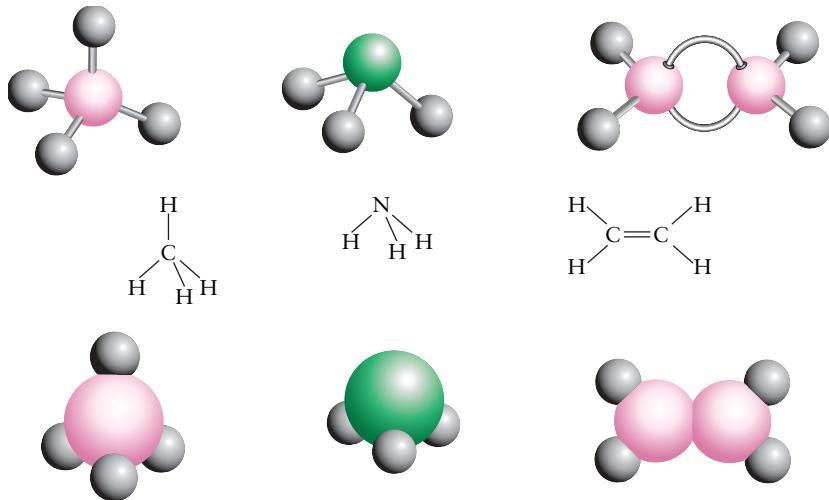
The best description of the *physical* appearance of molecules is given by so-called **space-filling models** as shown in Figures 2.2, 2.3, 2.4 and 2.7. However, these models do not show the nature of the chemical bonding very clearly, and therefore chemists often use **ball-and-stick models** which represent molecules as balls (atoms) held together by sticks (bonds).

A comparison of these two types of models with structural formulae is shown in Figure 9.5. In ball-and-stick models, the balls are best regarded as nuclei of atoms with the sticks merely indicating the type and geometry of the bonding;

such models are really ‘skeletons’. We have to imagine the electron clouds superimposed upon them to ‘flesh out’ the skeletons into real molecules: *the sticks have no physical reality*.

FIGURE 9.5

Ball-and-stick models, structural formulae and space-filling models of methane, ammonia and ethene

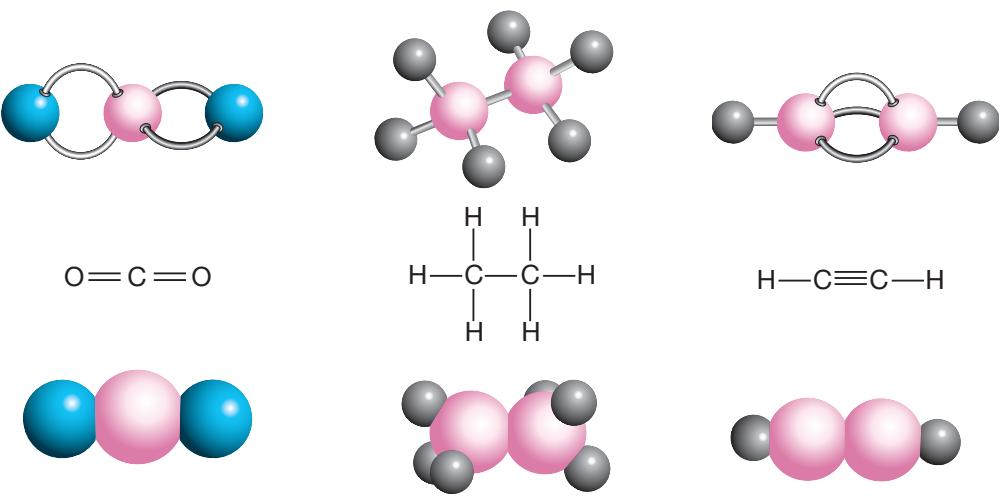


## Shapes of simple carbon molecules

We saw in Section 7.3 that the four single bonds in methane were tetrahedrally arranged about the carbon atom. This is true in all molecules in which carbon forms only single bonds. In ethane, the four bonds around each carbon atom are tetrahedrally arranged. This gives the molecule the shape shown in Figure 9.6. Note that it is the ball-and-stick model that shows the shape most clearly. When a carbon atom forms a double bond and two single bonds as in ethene, the atoms are planar. In ethene, all six atoms lie in the one plane as Figure 9.5 shows. When the carbon atom forms two double bonds as in carbon dioxide, the arrangement of atoms is linear (Fig. 9.6). These shapes are summarised in Table 9.5.

FIGURE 9.6

Ball-and-stick and space-filling models for carbon dioxide, ethane and ethyne



## The huge number of carbon compounds

Carbon forms a huge range of compounds. There are more compounds of carbon than of any other element, except hydrogen (but that is because carbon compounds almost always contain hydrogen). In fact the vast majority of compounds known to chemists are carbon compounds.

This is because:

- carbon readily forms carbon–carbon bonds
- these bonds can be single, double or triple, and
- carbon readily forms cyclic compounds (rings) as well as straight and branched chain compounds.

And in all of these carbon–carbon compounds *carbon always forms four covalent bonds* (4 single, 1 double plus 2 single, 2 double, or 1 triple plus 1 single as in Table 9.5).

**TABLE 9.5 Geometrical arrangement of bonds around carbon atoms**

Bonds around the C atom	Geometrical arrangement of the bonds	Example
four single bonds		tetrahedral methane (Fig. 9.5)
one double and two single		planar (angle between bonds 120°) ethene (Fig. 9.5)
two double bonds		linear carbon dioxide (Fig. 9.6)
one triple and one single		linear ethyne (Fig. 9.6)

Many of the compounds of carbon contain only carbon and hydrogen. These are called **hydrocarbons**. The range of hydrocarbons that exists can be illustrated by separating the compounds that occur in the naturally occurring mixture known as crude oil.

## Exercises

- 7 **a** Diamond and graphite have densities of 3.51 and 2.26 g/mL respectively. Offer an explanation for this difference in terms of their structures.  
**b** Based on structure, the density to buckminsterfullerene would be closer to that of which of the allotropes in (a)? Explain your choice.
- 8 Carbon disulfide has two sulfur atoms attached to a central carbon atom. Draw an electron-dot structure and structural formula for it. What shape do you expect for this molecule? Why? Do you expect carbon disulfide to be polar or non-polar? Explain why.
- 9 Draw electron-dot diagrams and structural formulae for:
  - a** formaldehyde (systematic name methanal), H<sub>2</sub>CO (H and O atoms all attached to the C atom)
  - b** nitrosyl chloride, ClNO (Cl and O atoms attached to a central N atom)
  - c** hydrogen cyanide, HCN (H and N atoms attached to a central C atom)
- 10 **a** What shape do you expect for the molecules of formaldehyde and hydrogen cyanide in Exercise 9?  
**b** Nitrosyl chloride has a bent shape. Which (if any) of the three molecules in Exercise 9 do you expect to be polar and which (if any) non-polar? Explain your reasoning.



## 9.8 FRACTIONAL DISTILLATION OF CRUDE OIL

Fractionating towers (columns) at an oil refinery



**Crude oil** is a complex mixture of hydrocarbons formed by geological action on decayed aquatic plant and animal matter over millions of years.

Oil accumulates under domes of impervious rock hundreds to thousands of metres below the Earth's surface. It has to be refined before use.

The first step in oil refining is **fractional distillation**, which was described in Section 1.10. For separating components of crude oil it is carried out in large steel towers up to 40 metres high. In this process, the components of oil are separated according to their boiling points. Since boiling point increases as molecular weight increases, the separation is roughly in order of increasing molecular weights (or increasing number of carbon atoms per molecule). The crude oil is vaporised by heating, then fed into the bottom of the fractionating column which contains a series of trays as shown in Figure 9.7.

The temperature falls as the vapour rises up through the column. The least volatile components (highest boiling points and hence highest molecular weights) condense near the bottom of the column while the most volatile ones do not condense until they reach the top of the column. Liquids are drawn off the column

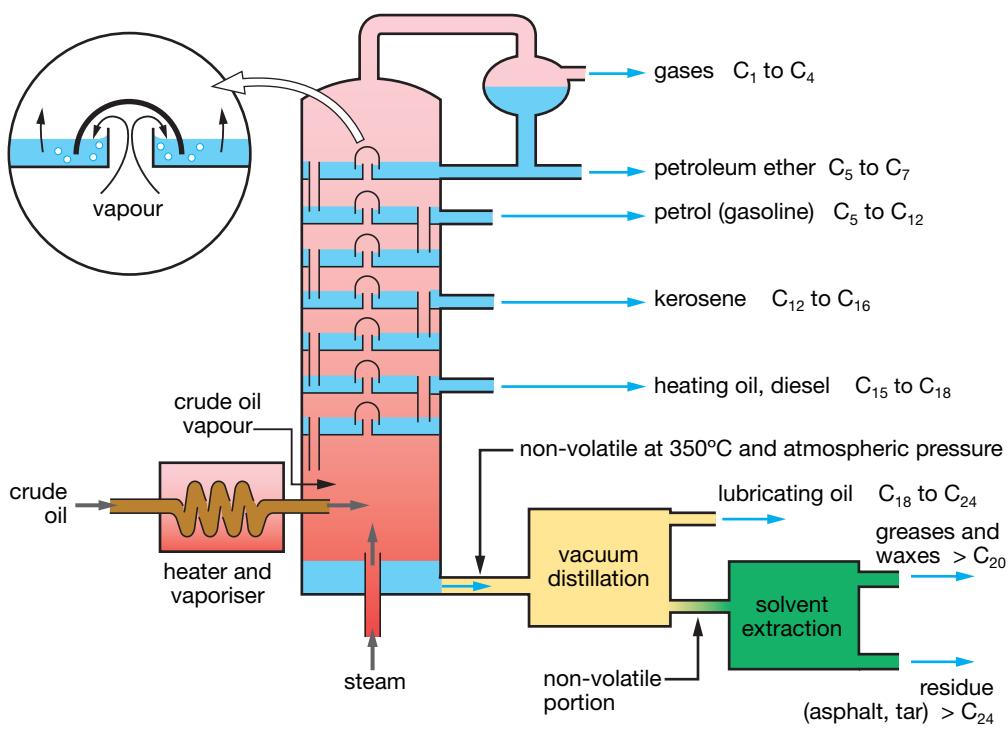


FIGURE 9.7  
The workings of a fractionating column for separating crude oil and the 'fractions' it produces. The processes for separating the non-volatile components are also shown

at various heights and these are the various ‘fractions’ which are collected. Lubricating oils are obtained from the least volatile fraction (Fig. 9.7) by distilling under vacuum (so they will boil off at lower temperatures than would be needed at atmospheric pressure). Greases are separated from the remaining non-volatile material by solvent extraction and the final residue is asphalt or tar, which is used for road-making.

Table 9.6 lists the fractions most commonly taken off, and gives the major use for each.

**TABLE 9.6 The various fractions from crude oil and their uses<sup>a</sup>**

Fraction	Boiling point range (°C)	Carbon atoms per molecule	Major uses
gases	less than 30	1 to 4	liquefied petroleum gas (LPG)
petroleum ether <sup>b</sup>	30–80	5 to 6	industrial solvents
gasoline	70–200	6 to 12	motor fuel
kerosene	175–250	12 to 16	jet fuel, domestic heating
gas oil (or fuel oil or heating oil)	250–350	15 to 18	diesel fuel, industrial and domestic heating
lubricating oil	} >350	18 to 25	motor oils
greases		>20	lubrication
asphalt and tar	residue	>25	road-making, roofing

<sup>a</sup> You may see similar tables in other books with different numbers for boiling point ranges and carbon atoms per molecule. This is because different crude oils have different compositions and different refineries use different operating conditions. In addition, petrol compositions are deliberately varied to suit the season of the year.

<sup>b</sup> A highly volatile liquid, not to be confused with ‘ordinary’ or ‘common’ ether,  $C_4H_{10}O$ , which was formerly used as an anaesthetic.

## Composition of crude oil

The composition of crude oil varies from one oil field to another. Light crudes are oils that have a high proportion of gasoline and kerosene. Heavy crudes have higher proportions of higher boiling point components. Australia’s Bass Strait crude is a light crude. Compositions of two typical crude oils are given in Table 9.7.

**TABLE 9.7 Typical % composition by mass of two crude oils**

	Bass Strait crude	Middle East crude
gases (used as LPG)	2	2
gasoline (straight run)	35	15
kerosene	15	15
gas oil (diesel and heating)	20	15
remainder (lubricating oil, wax, tar, asphalt)	25–30	50–55

The oil product in greatest demand is *gasoline* (petrol), which is the fuel for motor cars. However, the proportion of ‘straight-run’ gasoline obtained

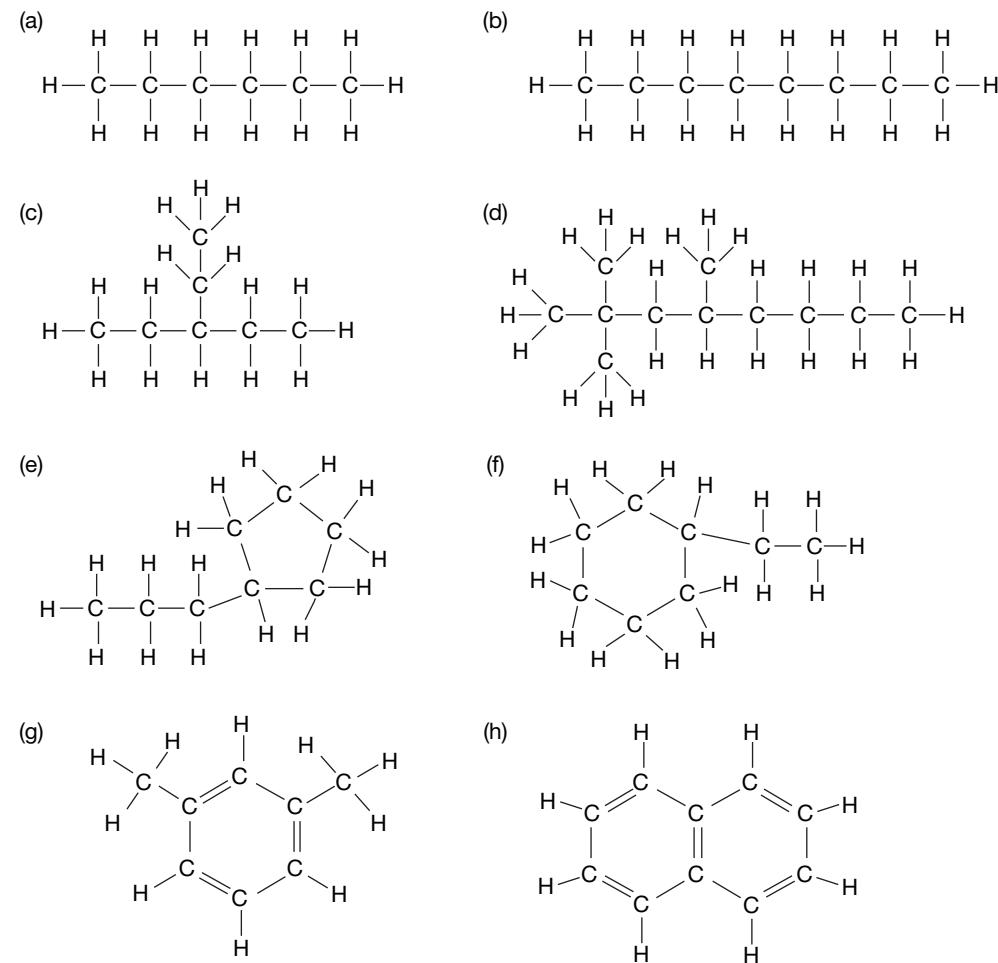
from fractional distillation (15 to 35% of crude oil) is not high enough to meet demand. Put another way, if sufficient oil were fractionated to meet the demand for gasoline, then there would be far more kerosene, fuel oil, lubricating oil and so on than there is demand for. So oil refineries increase the proportion of gasoline by converting some of the lower demand fractions into gasoline in a process called *catalytic cracking*. This will be described in CCHSC Chapter 1.

Oil refineries just separate crude oil into a few broad fractions of commercially useful substances—petrol, kerosene, diesel and the like; each of these substances is a mixture of many compounds. In the laboratory these mixtures can be further fractionated into individual compounds.

The vast majority of compounds in crude oil are hydrocarbons. They can be divided into four classes. Typical members of each class are shown in Figure 9.8. The four classes are:

- 1** *straight-chain hydrocarbons*, molecules with the carbon atoms strung together in a long chain: each C atom is joined to no more than two other C atoms (a and b in Fig. 9.8)
- 2** *branched chain hydrocarbons*, molecules with some carbon atoms joined to three or four other carbon atoms (c and d in Fig. 9.8)
- 3** *cyclic hydrocarbons*, molecules with some carbon atoms joined into rings of five or six carbon atoms with chains attached to the rings (e and f in Fig. 9.8)
- 4** *aromatic hydrocarbons*, molecules that contain some six-membered rings with bonds that are not just the simple single C—C bonds of the other three classes (g and h of Fig. 9.8).

**FIGURE 9.8**  
Typical hydrocarbons  
from crude oil: (a) and  
(b) straight chain, (c) and  
(d) branched chain, (e)  
and (f) cyclic, (g) and (h)  
aromatic



Let us now look more closely at some of these hydrocarbons.

## 9.9 ALKANES

Hydrocarbons in which all the bonds are single bonds are called **alkanes**.

The simplest alkanes are methane, CH<sub>4</sub>, and ethane, C<sub>2</sub>H<sub>6</sub> (Figs 9.5 and 9.6). The next two alkanes are propane, C<sub>3</sub>H<sub>8</sub>, and butane, C<sub>4</sub>H<sub>10</sub>. Models and structural formulae are shown in Figure 9.9.

Although the structural formulae in Figures 9.5, 9.6 and 9.9 have been drawn flat and with bonds at right angles to one another, this is not the true shape of these molecules. *The four bonds around each carbon atom are tetrahedrally arranged, regardless of whether the bonds join to hydrogen atoms or to other carbon atoms.* The true shape of these molecules is best appreciated by examining models of the types depicted in Figures 9.5, 9.6 and 9.9.

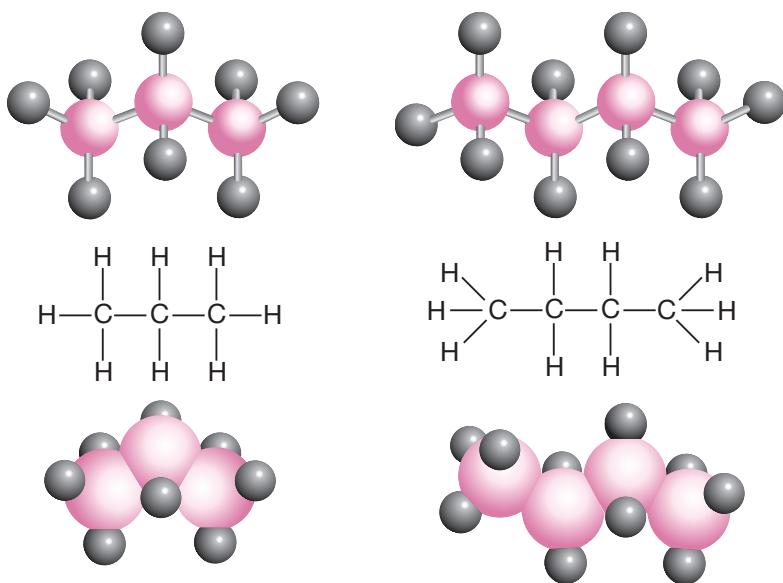


FIGURE 9.9  
Models and structural formulae for propane, C<sub>3</sub>H<sub>8</sub>, and butane, C<sub>4</sub>H<sub>10</sub>

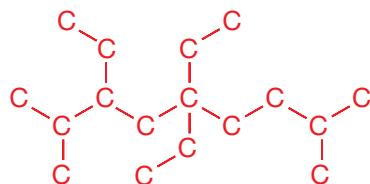
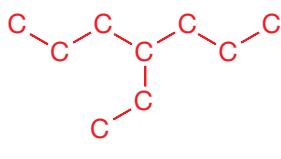
There is a whole family of alkanes made up of different numbers of carbon atoms joined together to form a single chain. They are called **straight-chain alkanes**, meaning that all the carbon atoms are joined in the one continuous string. Names and structures of the first eight straight-chain alkanes are given in Table 9.8. Straight-chain alkanes are a sub-group of straight-chain hydrocarbons: we will meet another sub-group in Section 9.10.

Although we call them ‘straight-chain’ alkanes, the chain is not really straight at all, but rather it is zig-zagged or twisted up, because the C—C—C angle is the normal tetrahedral angle of 109°.



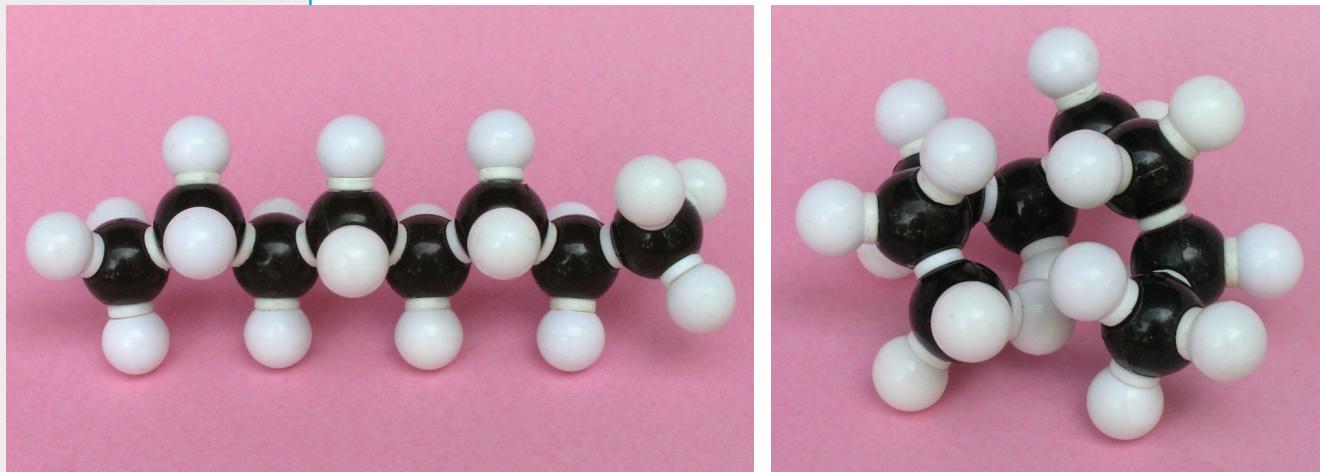
Figure 9.10 illustrates how a carbon chain can be roughly linear or all curled up into a ball. In both cases all the CCC, CCH and HCH angles are still 109°.

Straight-chain alkanes have all carbon atoms joined together in the one string so that no carbon atom is joined to more than two other carbon atoms. In addition there are **branched-chain alkanes** with carbon skeletons such as:



In branched-chain compounds, at least one carbon atom is attached to more than two other carbon atoms.

When drawing structures of actual molecules, we must *always include all the hydrogen atoms*. The H atoms have been left off the red structures above in order to show more clearly the nature of the carbon chains.



**FIGURE 9.10**  
Space-filling models of octane showing how the molecule can be stretched out or curled up while keeping all the bond angles at the tetrahedral value of  $109^\circ$

## Homologous series

The molecular formulae in Table 9.8 are all special cases of the general formula  $\text{C}_n\text{H}_{2n+2}$  where  $n$  can be 1, 2, 3, ... 8, ...

A family of compounds which can be represented by one general molecular formula is called an **homologous series**.

Table 9.8 presents the first eight members of the homologous series called *alkanes*. Alkanes have the general formula  $\text{C}_n\text{H}_{2n+2}$ . Alkanes having up to 30 and 40 carbon atoms per molecule are quite common. Alkanes are hydrocarbons in which all the carbon–carbon bonds are single ones; there are no double or triple bonds (Section 9.6).

In carbon chemistry there are many families of related compounds with very similar physical properties and reactions—that is, many homologous series. Hence the study of this branch of chemistry is the study of structure and properties of *families* of compounds rather than of individual substances.

## Naming alkanes

Because there are so many carbon compounds, we need a systematic method of naming them. With *systematic names*, the name allows us to work out the structure of the molecule, and the structure allows us to work out the name. This avoids having to memorise long lists of names and structures.

The name for a carbon compound consists of a *stem*, which tells us the length of the carbon chain, and a *suffix* (ending), which tells us the family the

**TABLE 9.8** The first eight straight-chain alkanes

Name	Molecular formula	Boiling point (°C) <sup>a</sup>	Physical state <sup>b</sup>	Structural formula
methane	CH <sub>4</sub>	-162	gas	<pre>       H         H-C-H               H     </pre>
ethane	C <sub>2</sub> H <sub>6</sub>	-89	gas	<pre>       H   H             H-C-C-H                   H   H     </pre>
propane	C <sub>3</sub> H <sub>8</sub>	-42	gas	<pre>       H   H   H                 H-C-C-C-H                   H   H   H     </pre>
butane	C <sub>4</sub> H <sub>10</sub>	-0.5	gas	<pre>       H   H   H   H                     H-C-C-C-C-H                   H   H   H   H     </pre>
pentane	C <sub>5</sub> H <sub>12</sub>	36	liquid	<pre>       H   H   H   H   H                     H-C-C-C-C-C-H                   H   H   H   H   H     </pre>
hexane	C <sub>6</sub> H <sub>14</sub>	69	liquid	<pre>       H   H   H   H   H   H                     H-C-C-C-C-C-C-H                   H   H   H   H   H   H     </pre>
heptane	C <sub>7</sub> H <sub>16</sub>	98	liquid	<pre>       H   H   H   H   H   H   H                     H-C-C-C-C-C-C-C-H                   H   H   H   H   H   H   H     </pre>
octane	C <sub>8</sub> H <sub>18</sub>	126	liquid	<pre>       H   H   H   H   H   H   H   H                     H-C-C-C-C-C-C-C-C-H                   H   H   H   H   H   H   H   H     </pre>

<sup>a</sup> at standard atmospheric pressure.

<sup>b</sup> at normal atmospheric pressures and temperatures.

compound belongs to; for example the alkanes have the ending *-ane*. The stems for the first eight members of the series are:

C <sub>1</sub>	meth-	C <sub>4</sub>	but-	C <sub>7</sub>	hept-
C <sub>2</sub>	eth-	C <sub>5</sub>	pent-	C <sub>8</sub>	oct-
C <sub>3</sub>	prop-	C <sub>6</sub>	hex-		

Combination of these stems with the suffix *-ane* leads to the names in Table 9.8. While it may seem difficult to have to memorise these eight stem names, it is essential because they keep recurring in all the families we shall be dealing with.

Systematic names are sometimes called **IUPAC nomenclature**, because IUPAC, the International Union of Pure and Applied Chemistry, is the body that

draws up the rules for systematic naming of compounds. Systematic naming was only introduced in the 1930s and the use of the pre-existing non-systematic names, called *trivial names*, was so entrenched in the chemical industry that many of them continue to be used and some of these are now the preferred IUPAC names. Examples are ethylene (for ethene) and acetic acid (for ethanoic acid). Trivial names such as the two just mentioned do not give any indication of the structure of the compound they refer to.

## Physical properties

As Table 9.8 shows, the simplest alkanes ( $C_1$  to  $C_4$ ) are gases at room temperature. Alkanes with 5 to about 18 carbon atoms per molecule are colourless liquids, while compounds with 20 or more carbon atoms per molecule are waxy solids. Paraffin wax and Vaseline are mixtures of alkanes with about 30 carbon atoms per molecule. In other words:

the melting and boiling points of alkanes increase as molecular weight increases (that is as the number of C atoms per molecule increases).

The *densities* of both liquid and solid alkanes are significantly less than that of water (1.00 g/mL). Alkanes are *insoluble in water* and, as expected for molecular compounds, they *do not conduct electricity*.

We can explain these properties in terms of molecular structure.

In Sections 7.3 and 7.4 we saw that C—H bonds were slightly polar (electronegativities of 2.20 for H and 2.55 for C), but that in symmetrical structures such as methane the small dipoles cancel out to produce non-polar molecules. Even though not all alkanes are strictly symmetrical, *alkanes are non-polar molecules*. This is because C—C bonds are non-polar, C—H bonds are only slightly polar, and the geometry usually cancels out much of this small polarity. This lack of polarity accounts for alkanes being insoluble in water (a polar solvent).

Being non-polar, the only intermolecular forces between alkane molecules are dispersion forces (Section 7.4). These are quite weak intermolecular forces so it is easy to separate alkane molecules from one another. This means that alkanes have relatively low boiling and melting points.

Dispersion forces arise from the attraction of the nuclei of one molecule for the electron cloud of a neighbouring molecule. This attraction is of course opposed by the repulsion between the electron clouds of the neighbouring molecules, so the force of attraction is quite small. However, dispersion forces do increase as the number of electrons in the electron cloud increases (which is also as the number of positive charges on the nuclei increases, because the molecules are electrically neutral). This means that:

dispersion forces increase as molecular weight increases.

This shows up most clearly in the molecular elements chlorine (gas, molecular weight 71), bromine (liquid, mol. wt 160) and iodine (solid, mol. wt 254). Dispersion forces are also the reason why boiling points of alkanes increase as molecular weight increases.

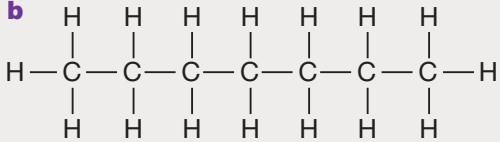
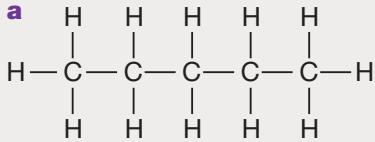
The **volatility** of a substance is the ease with which it can be converted to a vapour. Volatility increases as boiling point decreases. So for alkanes, volatility decreases as molecular weight increases.

## Exercises



- 11 Write molecular formulae for the compounds shown in Figure 9.8.
- 12 What would be the molecular formula and molecular weight of the alkane containing:
- a 9                    b 13                    c 24 carbon atoms?

- 13 Give the name and molecular formula for each of the following compounds:



- 14 Write the structural and molecular formulae for:

- a hexane                    b octane

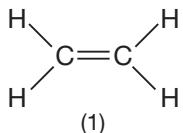
- 15 Upon analysis a hydrocarbon was found to contain 82.6% carbon and 17.4% hydrogen. Calculate its empirical formula. Could this compound be an alkane? If so, suggest a molecular formula for it and draw its structural formula.

- \*16 For the alkanes in Table 9.8 (except for methane) plot boiling point against number of carbon atoms in the molecule. Draw a suitable curve through the points and summarise how boiling point depends upon number of carbon atoms in the molecule. Keep this graph for Exercise 27 below.

## 9.10 ALKENES

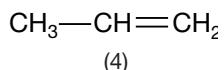
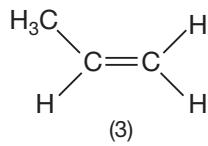
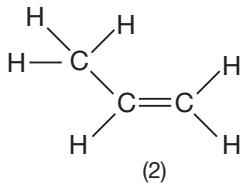
Hydrocarbons which contain a double bond between a pair of carbon atoms are called **alkenes**.

The simplest alkene is ethene, C<sub>2</sub>H<sub>4</sub>:



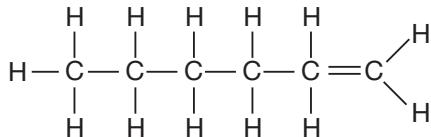
Its structure was discussed in Section 9.6. You will recall that a double bond consists of two pairs of electrons being shared by the two carbon atoms. A consequence of this is that the molecule is planar (Section 9.7): each H—C—H and H—C=C angle is 120°. Models of ethene were shown in Figure 9.5.

There is a whole family or *homologous series* of alkenes with general formula, C<sub>n</sub>H<sub>2n</sub>, with n > 1. The first three members are ethene (above), propene, C<sub>3</sub>H<sub>6</sub>, and butene, C<sub>4</sub>H<sub>8</sub>.



Structures (2), (3) and (4) are different ways of representing propene. (2) tries to show the planar geometry about the double bond, and the tetrahedral arrangement about the other carbon atom. (3) shows the geometry about the double bond but leaves it to the reader to infer the tetrahedral shape about the H<sub>3</sub>C carbon. (4) is the simplest way of writing propene: it makes no attempt to show geometry. (2) is a full structural formula. (4) is called a *condensed structural formula*, while (3) is an intermediate type.

A **condensed structural formula** is a ‘cross’ between a molecular formula and a full structural formula. It provides enough detail for a full structural formula to be written if required, but writes common groups of atoms (for which the reader can be assumed to know the full structural arrangement) in molecular formula form. The formulae shown in Table 9.9 are condensed structural formulae. For comparison the full structural formula of 1-hexene is:



As you gain proficiency in carbon chemistry you will find yourself using condensed structural formulae more frequently, although at this stage it is probably best to stick with full structural formulae or perhaps the intermediate type such as (3) above.

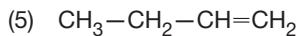
Names, structures and boiling points for seven members of the homologous series of alkenes are shown in Table 9.9.

**TABLE 9.9 Formulae and boiling points of common alkenes**

Name	Formula	Boiling point (°C)
ethene	$\text{CH}_2=\text{CH}_2$	-103.7
propene	$\text{CH}_3-\text{CH}=\text{CH}_2$	-47.7
1-butene	$\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$	-6.3
1-pentene	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$	30.0
1-hexene	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$	63.5
1-heptene	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$	93.6
1-octene	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$	121.3

## Isomers

For the straight-chain alkene with four carbon atoms there are two possible structures:



Structure (5) has the double bond between the first and second carbon atoms (counting from the right end) while (6) has it between the second and third carbon atoms. Both of these structures exist. They are quite distinct compounds with different boiling points and densities.

	Boiling point (°C)	Density (g/mL)
$\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$	-6.3	0.589
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3^{\dagger}$	+3.7	0.615

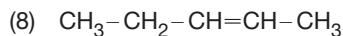
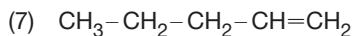
These two compounds are called *isomers*.

† There are actually two compounds with this structure. The other one has a boiling point of 0.9°C and a density of 0.598 g/mL. Can you work out the structural difference between them? (Not required for NSW HSC.)

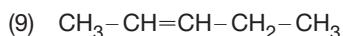
**Isomers** are sets of different compounds that have the same molecular formula (but different structural formulae).

The two compounds in the above table have different structural formulae (double bond in different places) but are both C<sub>4</sub>H<sub>8</sub>.

Similarly, a straight-chain compound with five carbon atoms and one double bond gives rise to two isomers of C<sub>5</sub>H<sub>10</sub>:



At first sight structure (9)



looks to be another isomer. However it is actually just (8) written the other way round: the double bond is still between the second and third carbon atoms along the chain. The best way to convince yourself that (8) and (9) are identical is to build models and compare them.

This existence of isomers raises the question of how to name these compounds.

## Naming alkenes

To name straight-chain alkenes:

- take the usual stem name (but-, pent- hex-, etc) to denote the number of carbon atoms in the chain, then add the ending, *-ene*, to denote a compound containing a double bond
- then show the location of the double bond by putting in front of the name the number of the carbon atom at which the double bond starts
- begin the numbering of the carbon chain from the end of the molecule *that minimises the number for the double bond*.

Compound (5) above is 1-butene (not 3- or 4-butene), while (6) is 2-butene (not 3-butene). Compound (7) is 1-pentene while (8) and (9) are different ways of writing 2-pentene (not 3-pentene).

C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> are called ethene and propene: no 1- is used with these compounds, because no isomers are possible.

## Physical properties

The straight-chain alkenes have similar physical properties to the alkanes. The C<sub>2</sub> to C<sub>4</sub> alkenes are gases while the C<sub>5</sub> to C<sub>17</sub> ones are liquids with boiling point increasing as molecular weight increases. Boiling points of alkenes are slightly lower than those of corresponding alkanes (compare Tables 9.8 and 9.9). Densities are similar to those of corresponding alkanes. Alkenes are insoluble in water and do not conduct electricity.

These properties arise because alkenes contain only C—C and C=C bonds which are non-polar, and C—H bonds which are just slightly polar. This means that *alkene molecules, like alkanes, are non-polar* so that the only intermolecular forces are weak dispersion forces. This explains their low boiling points and their insolubility in water.



## Exercises

- 17** Write the molecular formulae for the alkenes in Table 9.9.
- 18 a** Draw a complete structural formula for 1-pentene.  
**b** Draw condensed structural formulae for heptane and 3-heptene.
- 19** What are the molecular formulae for alkenes containing:  
**a** 9                   **b** 13                   **c** 18 carbon atoms?
- 20** Do 1-butene and 3-hexene belong to the same homologous series? Justify your answer.
- 21** Name the following compounds and give their molecular weights:  
**a**  $\text{CH}_3\text{--CH}_2\text{--CH=CH--CH}_2\text{--CH}_3$   
**b**  $\text{CH}_3\text{--CH=CH--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_3$
- 22** Draw the structural formula for and name an isomer of each of the compounds (a) and (b) in Exercise 21.
- 23** Draw structural formulae for:  
**a** 2-hexene                   **b** 3-heptene
- 24** What is wrong about the following names? Give the correct names.  
**a** 5-octene                   **b** 3-pentene                   **c** 1-propene
- 25** Which of the following compounds are pairs or sets of isomers? Which (if any) are structures that represent the same compound?  
**a**  $\text{CH}_3\text{--CH=CH--CH}_2\text{--CH}_3$   
**b**  $\text{CH}_2\text{=CH--CH}_2\text{--CH}_3$   
**c**  $\begin{matrix} \text{CH}_3 & \text{C}=\text{C} & \text{CH}_3 \\ | & & | \\ \text{H} & & \text{H} \end{matrix}$   
**d**  $\begin{matrix} & \text{H} & & \text{H} \\ & | & & | \\ \text{CH}_3 & -\text{C} & -\text{C}=\text{C} & -\text{CH}_3 \\ & | & & | \\ & \text{H} & & \text{H} \end{matrix}$   
**e**  $\text{CH}_3\text{--CH}_2\text{--CH=CH--CH}_2\text{--CH}_3$   
**f**  $\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH=CH--CH}_3$   
**g**  $\begin{matrix} \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\ | & & | & & | \\ \text{H} & -\text{C} & -\text{C}=\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{H} \\ | & & | & & | & & | \\ \text{H} & & \text{H} & & \text{H} & & \text{H} \end{matrix}$
- 26** Name the compounds in Exercise 25 and give their molecular formulae.
- 27** On the same graph you used in Exercise 16, plot boiling points of the alkenes in Table 9.9 against number of carbon atoms in the molecule. Use a different symbol for these points so they are clearly distinguishable from the alkane points. Draw a suitable line through the points and summarise the way that boiling points of alkenes depend upon number of carbon atoms. In addition, what can you say about boiling points of alkenes compared with those of alkanes?
- 28** Explain what is meant by the statement that straight-chain alkanes are a sub-group of compounds called straight-chain hydrocarbons. Use a specific example to illustrate.

## 9.11 FUNCTIONAL GROUPS

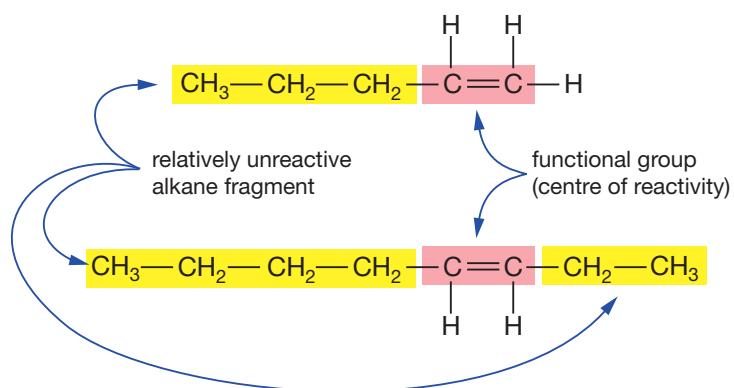
Compared with other carbon compounds, alkanes are relatively unreactive. When a double bond is introduced, the molecule becomes much more reactive,

but the reactivity is associated with the double bond, not with the rest of the molecule. Similarly, when a halogen atom, OH group or  $\text{NH}_2$  group replaces a hydrogen atom in an alkane, the molecule becomes much more reactive, again with the reactivity centred around the halogen atom, the OH group or the  $\text{NH}_2$  group. Hence we use the term **functional group**, to describe the *centre of reactivity* in a carbon compound. In alkenes, the functional group is the double bond. The functional group is ‘where the action is’.

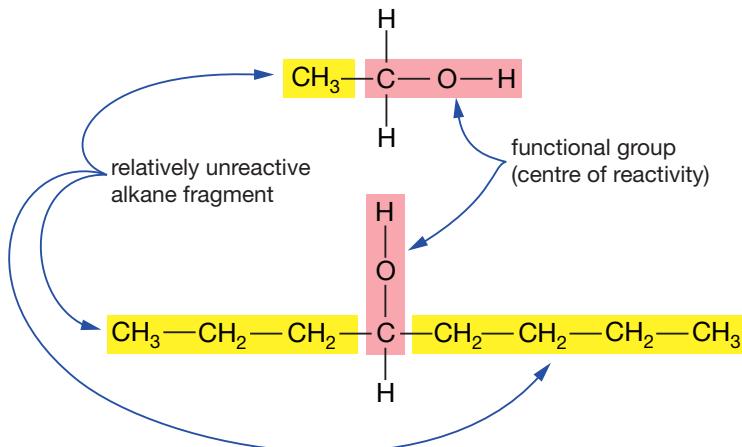
Carbon compounds may be considered as relatively unreactive alkane fragments (alkane minus an end H atom), called **alkyl groups**, attached to functional groups which are the reactive centres of the molecules. Figure 9.11(a) shows two alkenes with the functional group and the alkane fragments (alkyl groups) identified.

Another family of carbon compounds is the alkanols of which ethanol (common alcohol) is the best known member. Alkanols contain the functional group C—O—H called the alcohol functional group (or hydroxyl group). Figure 9.11(b) shows two alkanols with the functional group and the alkane fragments (alkyl groups) identified.

(a)



(b)



**FIGURE 9.11**  
Functional groups  
and unreactive alkane  
fragments (alkyl groups)  
(a) for two alkenes (b) for  
two alkanols (with the  
alcohol functional group)

All molecules with a particular functional group react very similarly, regardless of which carbon, hydrogen chain(s) is(are) attached. Therefore the study of carbon compounds is really the study of the reactions of the various functional groups.

Functional groups are used for naming compounds. Each functional group has its own particular ending (suffix) which is added to the usual stem. Compounds containing the double bond functional group have names ending in *-ene* (butene, hexene, etc). The alcohol group gives rise to the ending *-ol* as in ethanol, butanol, etc. We will meet other functional groups later.

In Section 9.9 we defined a homologous series as a group of compounds that could be represented by the one general formula. It follows that all the compounds in a homologous series will have the same functional group (except for the alkanes where there is no functional group). The alkenes contain the C=C functional group.

Having surveyed some types of hydrocarbons, let us now return to the fossil fuels and look at which compounds they are comprised of.

## 9.12 COMPOSITION OF FOSSIL FUELS

We looked at the composition of crude oil in Section 9.8 where we saw that it was a mixture of hydrocarbons. Most of those hydrocarbons are alkanes from C<sub>1</sub> to about C<sub>30</sub>. Crude oil is able to contain the gaseous hydrocarbons, methane to butane, because they are dissolved in the liquid ones; the gaseous ones only vaporise out when the liquid is heated (distilled). The gasoline fraction from distillation is mainly *straight-chain alkanes*, though it is further processed before sale as petrol. The kerosene and gas oil (heating oil) fractions again contain mainly alkanes, but in these fractions there are large proportions of branched-chain alkanes.

### Natural gas

Natural gas is a mixture of methane (75–90%), ethane (5–10%), propane and butane (3–6%) and smaller amounts of other alkanes, along with a few per cent of nitrogen and/or carbon dioxide gases and some water vapour. It was formed in a similar fashion to oil by geological degradation of decaying plant and animal matter over long periods of time, and became trapped beneath impervious domes of rock. Natural gas is often, though not always, found together with crude oil.

Natural gas often contains traces of hydrogen sulfide which must be removed before use because it is poisonous, it corrodes pipes and is converted to polluting sulfur dioxide during combustion. The propane and butane are also condensed out and used as LPG (liquefied petroleum gas).

Purified natural gas is basically a mixture of methane and ethane. It is piped to various industrial and commercial users and to homes. It is an extremely clean and efficient source of heat and its combustion products produce virtually no pollution. It is the ‘town gas’ used in all major Australian cities today.

Unfortunately, natural gas cannot be liquefied at room temperature, which makes it difficult to transport other than by pipeline. This is the reason why it is not widely used as a fuel for motor cars.

### Coal

Coal is a brown to black rock-like substance that was formed by the action of heat and pressure on decayed plant matter over millions of years. Coals vary greatly in their composition and properties, depending upon the geological treatment received.



### FOR INVESTIGATION

For one of the fossil fuels, coal, crude oil, natural gas, search out and present in a systematic way the range of compounds found in it and list the locations of deposits of it in Australia.

Coals range from *anthracite* (hard coal) through *bituminous coal* to *brown coal* (lignite).

Anthracite is about 90% carbon combined with hydrogen, oxygen, nitrogen and sulfur.

Brown coal is only about 50% carbon; it contains significant amounts of water and non-volatile matter (dirt!).

The compounds that make up coal are very complex. They typically have molecular weights of several hundred, and generally have many six-membered rings of carbon atoms fused together as in (h) of Figure 9.8. Most of the compounds have some oxygen and nitrogen incorporated into their structure, and some also include sulfur. Despite its black colour, there is virtually no uncombined carbon in coal.

When coal is heated to about 1000°C in the absence of air, it decomposes to form a mixture of gases and vapours, leaving behind a porous solid called  *coke*. Coke is nearly-pure carbon. When the gaseous mixture is cooled, much of it condenses to a liquid called *coal tar*. This is a source of many carbon compounds such as the so-called coal-tar dyes. The non-condensable portion of the gas consists mainly of carbon monoxide and hydrogen. Before natural gas was discovered in Australia, this was used as town gas; now it is used mainly as a raw material in industry.



Natural gas is exported from Australia's North West Shelf in ships specially fitted out with vacuum jacketed containers to maintain the required very low temperatures needed to be able to store and transport natural gas as a liquid

## 9.13 USES OF HYDROCARBONS

The major uses of hydrocarbons are as *fuels*, such as:

- natural gas for domestic cooking and heating and in industry
- LPG for caravans and barbecues (and some cars)
- petrol and diesel for cars, trucks, vans and trains
- kerosene for jet aircraft.

Higher molecular weight hydrocarbons are used as  *lubricating oils* and  *greases*. Vaseline is a highly purified hydrocarbon grease, which has a variety of medicinal and domestic uses. Paraffin wax is a mixture of high molecular weight alkanes and is widely used in candle making and as a sealant.

Low molecular weight hydrocarbons are used as *propellants in aerosol sprays* (and hence the warning to keep them away from flames).

Many hydrocarbons are used as *solvents*:

- *Petroleum ether*<sup>†</sup>, a lower boiling point fraction than petrol, is widely used as an industrial solvent for degreasing metals and other materials before applying coatings or paint; and as a household dry-cleaning fluid.

† See footnote b to Table 9.6 on page 257.

Everyday products that are or contain predominantly hydrocarbons. In the three aerosol sprays on the right hydrocarbons are the solvent but not the active ingredient



- Mineral turpentine ('turps') is a mixture of higher molecular weight hydrocarbons, including some alkenes; it is used as a solvent for oil-based paints
- Other mixtures of hydrocarbons are used as solvents for insecticides in household and garden sprays.

Two by-products from oil refining are ethene and propene; these form the basis of a very extensive *petrochemical industry*. They are used to make plastics (CCHSC Chapter 1). Ethene is also used to prepare ethanol, ethylene glycol (motor car anti-freeze) and acetic acid. Propene is used to prepare glycerine (for cosmetics and sweets) and nitroglycerine (a common explosive and constituent of dynamite).

## 9.14 SAFETY PRECAUTIONS FOR STORING ALKANES

Alkanes, particularly the low molecular weight ones such as C<sub>1</sub> to C<sub>8</sub>, are *extremely flammable*. In addition at high concentrations they can be *toxic* (poisonous). Therefore we need to be careful in storing them. An added hazard is the high volatility (low boiling points) of the liquid ones, which means that if a container is left open to the atmosphere, the liquid quickly evaporates and forms a flammable or explosive mixture with air. Remember (from Section 9.9) that their high volatility arises because the only intermolecular forces present in alkanes are weak dispersion forces.

### Some important safety precautions

- Use well-maintained cylinders and fittings for gaseous hydrocarbons.

Methane and ethane (and natural gas) are non-condensable gases at room temperature and are therefore stored and transported in high-pressure cylinders, which need regular testing and checking. They must be used with proper valves and regulators and stored in well-ventilated places. Any pipe work used for transporting them from cylinder or gas main to the place of use (such as cook top or hot water heater) must be carefully checked to eliminate leaks at installation and periodically thereafter.

Propane and butane are condensable with moderate pressures at ambient temperatures and are sold as LPG, liquefied petroleum gas. Cylinders for their storage and transport need not be so sturdy but still need to be handled with care, and checked regularly. Because of the flammability of the gases, the cylinders should be stored outdoors or on the outside of caravans and campervans.

■ **Add odours for early detection of leaks.**

Because these gases are so flammable and form explosive mixtures with air, the commercial products, natural gas and LPG, are dosed with a nasty-smelling substance so that leaks can be detected before explosive mixtures develop.

■ **Use sturdy containers for liquids.**

Liquid alkane mixtures such as petroleum ether, petrol and kerosene are quite volatile and highly flammable. Hence they need to be stored in sturdy containers (metal rather than plastic) with narrow mouths (to restrict evaporation).

■ **Minimise the quantities in everyday use.**

Only the minimum quantities for immediate needs should be stored in laboratories, homes or other enclosed places. Bulk quantities of such liquids should be stored out of the sun (to avoid overheating) but in places which are well ventilated.

■ **Keep alkanes away from naked flames or sparks.**

Store alkanes in places where there is little or no likelihood of naked flames or hot filaments ever being present. In addition, ensure that any electrical switches and motors (including refrigerators) are ones that have been designed to operate without creating sparks. And ban cigarette smoking in the vicinity.

■ **Erect warning signs.**

In places where alkanes (gases or liquids) are being stored, erect signs prohibiting cigarette smoking, naked flames or the use of ordinary electrical equipment.

■ **Do not handle these liquids in confined spaces.**

Explosive mixtures with air can easily build up if these liquids are poured from one container to others in confined spaces. They should be handled outdoors whenever possible. When filling small storage containers from large ones, do so in an open, well-ventilated place.

## In motor cars and vehicles for transporting fuels

- The fuel tank is located at the end remote from the hot engine and is outside the main shell of the vehicle.
- The fuel tank has narrow inlet and outlet pipes, which are both at the top of the tank to minimise chances of leakage during accidents; fuel has to be pumped from the tank by the engine, so that in most cars even a fuel line rupture will not cause rapid leakage of petrol.
- When petrol is transported by road or rail, heavy steel tanks are used; these can be well sealed and are designed to withstand most collisions or overturnings without rupture of the tank or of the inlet or outlet valves, and therefore without spillage.
- Features are built into petrol tankers to dissipate any static electricity which could cause sparks during filling and emptying.
- As a further safety precaution, some commonly used fuels are coloured with added dyes for easy identification (alkanes are colourless). Unleaded petrol is coloured yellow and kerosene blue.



## Exercises

- 29** Using Tables 9.6 and 9.8, in which fractions from the distillation of crude oil would you expect to find each of the various straight chain alkanes (up to C<sub>8</sub>)?
- \*30** Name substances that you have at home which contain hydrocarbons. (This may require you to read contents lists on many containers.) Where possible, state whether they are alkanes or alkenes.
- \*31** List the safety precautions that are built into the design of an automobile service station. Include features that apply to handling LPG.
- \*32 a** Suppose you have a caravan with an LPG stove and refrigerator. What precautions would you take to ensure the safety of the caravan and its occupants?
- b** Suppose you own a cabin cruiser (boat) with an in-board engine. What precautions would you take to avoid explosions or fires in the engine compartment?
- c** What safety advantage does a boat with an outboard motor have over one with a motor inside the boat?

## Important new terms

You should know the meaning of the following terms:

alkanes (p. 259)  
alkenes (p. 263)  
alkyl group (p. 267)  
allotropes (p. 249)  
allotropy (p. 249)  
ball-and-stick models (p. 253)  
branched-chain alkanes (p. 259)  
buckminsterfullerene (p. 250)  
buckyball (p. 250)  
carbohydrates (p. 245)  
chemical energy (p. 247)  
condensed structural formula (p. 264)  
crude oil (p. 256)  
double bond (p. 251)  
energy-rich compounds (p. 247)  
fossil fuel (p. 244)

fractional distillation (p. 256)  
fullerenes (p. 250)  
functional group (p. 267)  
homologous series (p. 260)  
hydrocarbons (p. 255)  
isomers (p. 265)  
IUPAC nomenclature (p. 261)  
Lewis electron-dot structures (Lewis structures) (p. 252)  
photosynthesis (p. 245)  
respiration (p. 245)  
single bond (p. 251)  
space-filling models (p. 253)  
straight-chain alkanes (p. 259)  
structural formula (p. 252)  
triple bond (p. 251)  
volatility (p. 262)

## CHAPTER 9

## Test yourself

- 1 Explain the meaning of each of the items in the ‘Important new terms’ section above.
- 2 Write a chemical equation for the photosynthesis of glucose. Explain how this reaction traps solar energy. How do we recover this energy?
- 3 Name and give molecular formulae for three carbohydrates. What is the origin of the name *carbohydrate*?
- 4 Explain how humans derive energy from the sun.
- 5 Why is eating meat a less efficient way of absorbing solar energy than eating grains, fruit or vegetables?

- 6** Name three common fossil fuels. Why are they called *fossil fuels*?
- 7** List the major sources of fossil fuels in Australia.
- 8** Name three elements that have allotropes.
- 9** Describe the structure of diamond and graphite and show how they explain the different properties of these two forms of carbon.
- 10** Describe the structure of buckminsterfullerene. Why is it an allotrope of carbon?
- 11** Draw electron-dot structures for a carbon atom, carbon dioxide, ethene, nitrogen gas and ethyne (acetylene).
- 12** Sketch space-filling and ball-and-stick models of ethene.
- 13** Describe the composition of crude oil in a couple of sentences.
- 14** List the five major fractions obtained from distillation of crude oil and give the major use for each.
- 15** Write the molecular and structural formulae for methane. State clearly the spatial arrangement of the bonds in the molecule.
- 16** Name two homologous series of hydrocarbons.
- 17** Name the first eight alkanes and give their molecular formulae.
- 18** What is the general formula for the alkanes?
- 19** Give the structural and condensed structural formulae for hexane.
- 20** For straight-chain alkanes, how does boiling point vary with the number of carbon atoms in the molecule? How does volatility vary?
- 21** Give the name and molecular and structural formulae of the simplest alkene, and describe the shape of the molecule.
- 22** Name the first seven straight-chain alkenes and give their molecular formulae.
- 23** Give the general formula for the alkenes.
- 24** Give an example of isomerism in straight-chain alkenes. Name the compounds used.
- 25** Draw structural formulae for the three straight-chain isomers of  $C_6H_{12}$  and name them.
- 26** How do the boiling points of alkenes compare with those of alkanes (with the same numbers of carbon atoms per molecule)?
- 27** What are the functional groups (if any) in propene and propane?
- 28** What are the major and minor constituents of natural gas?
- 29** Describe the composition of coal (in chemical terms).
- 30** List three non-fuel uses of hydrocarbons.
- 31** List the safety precautions that you would take in storing  
**(a)** LPG   **(b)** petrol.
- 32** What design features are built into motor cars to ensure safe handling of the fuel?

# CHAPTER 10

# Combustion

## IN THIS CHAPTER

Exothermic and endothermic reactions  
Enthalpy—its meaning and use  
Measuring enthalpy changes for reactions  
Heat of combustion  
Explaining chemical energy changes  
Activation energy  
Ignition temperature  
Pollution from burning fossil fuels

Greenhouse effect  
Rates of combustion reactions  
Meaning of rate of reaction  
Factors influencing rate of reaction  
Temperature effect and activation energy  
Catalysis  
Explosions and small particles

In the previous chapter we saw that our main sources of energy today are fossil fuels. We obtain energy from these fuels by burning them—in a process called *combustion*.

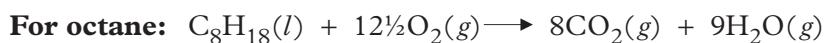
**Combustion** is a process in which a self-sustaining chemical reaction occurs at temperatures above those of the surroundings. More simply, combustion is burning. Explosions are also forms of combustion.

Some common combustion reactions are the burning of coke (carbon), petrol (for example, octane) and natural gas (methane). The reactants are oxygen from the air and the greyish-black solid (coke), the colourless liquid (octane) and the colourless gas (methane). Each of these burns with a bluish flame to form colourless carbon dioxide gas and colourless water vapour. The presence of water vapour in the products of these reactions can be demonstrated by holding a test tube filled with water above the flame: drops of colourless liquid (water) condense on the outside of the test tube. The presence of carbon dioxide can be shown by using a simple suction device to draw some of the gaseous product of the reaction through a solution of calcium hydroxide (limewater): carbon dioxide turns this colourless solution milky because it forms insoluble calcium carbonate with it.

In terms of the criteria of Section 3.1, chemical reactions have occurred here (rather than just physical changes) because:

- light and much heat have been emitted
- completely new substances have been formed ( $\text{CO}_2$  and  $\text{H}_2\text{O}$ )
- the processes cannot easily be reversed.

The chemical equations for the combustion reactions just described are:



The amounts of heat released in the above reactions are 393 kJ/mol for coke, 890 kJ/mol for methane and 5460 kJ/mol for octane.

All combustion reactions liberate large amounts of heat. They are what we call *exothermic reactions*.

## 10.1 EXOTHERMIC AND ENDOTHERMIC REACTIONS

As we saw in Chapter 3, in most chemical reactions significant amounts of energy are either released or absorbed. We use special terms to describe this release or absorption of energy:

Reactions that release heat are called **exothermic reactions**.

Reactions that absorb heat are called **endothermic reactions**.

We previously used these terms exothermic and endothermic in connection with the dissolution of substances in water in Section 8.12.

**Examples of exothermic chemical reactions (apart from combustion) are:**

- the direct combination reactions of Section 3.3  
(Mg + O<sub>2</sub>, Cu + S, H<sub>2</sub> + Cl<sub>2</sub>, P + Cl<sub>2</sub>)
- reactions of metals with water and acids  
(Section 4.9, Na + H<sub>2</sub>O, Mg + HCl)
- reactions of acids with bases  
(HCl + NaOH, H<sub>2</sub>SO<sub>4</sub> + CuO, HNO<sub>3</sub> + NH<sub>3</sub>)

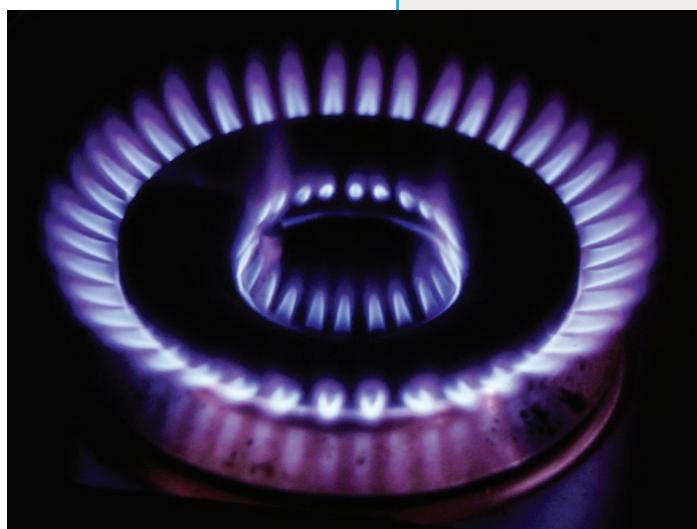
**Examples of endothermic chemical reactions are:**

- the decomposition reactions discussed in Section 3.2 (Cu(NO<sub>3</sub>)<sub>2</sub>, CaCO<sub>3</sub>)
- photosynthesis (Section 9.2)
- some precipitation reactions such as MgCl<sub>2</sub> + Na<sub>2</sub>CO<sub>3</sub>
- formation of synthesis gas (CO + H<sub>2</sub>) for industry by reacting CH<sub>4</sub> or C with steam.

There are far more exothermic reactions than endothermic ones.

When we carry out an exothermic reaction in a test tube, the test tube gets hot. This is because as the reaction occurs there is a decrease in chemical energy and the 'lost' chemical energy is released as heat, which warms up the test tube and its contents. When an endothermic reaction occurs, the test tube gets cold. This is because the reaction as it occurs needs to take in heat (to convert to chemical energy). The only place the reaction can get this heat is from the test tube and its contents and so they get cold.

Combustion of methane (natural gas) is an exothermic reaction that is widely used for cooking in homes



Unfortunately the heat released or absorbed during a reaction depends to some extent on the conditions under which the reaction is carried out, in particular upon whether it is performed at constant volume (in a closed vessel) or at constant pressure (in a container open to the atmosphere). This is particularly true for reactions involving gases. When we compare heats from different reactions, we should do so using constant conditions. Hence we introduce a new term called enthalpy.

## 10.2 ENTHALPY<sup>†</sup>

**Enthalpy** is a measure of the total energy possessed by a substance or group of substances. We can think of enthalpy as being mainly the chemical energy stored in a substance. Unfortunately we cannot measure this total energy or enthalpy of a substance; all we can do is measure *changes* in it.

The **change in enthalpy** for a chemical reaction,  $\Delta H$ , is defined as the heat absorbed (per mole of specified reactant or product) when the reaction occurs at constant pressure.

Since most experiments we shall be dealing with occur at constant pressure (open to the atmosphere), the heat absorbed or released will be a direct measure of  $\Delta H$ .

By ‘change in enthalpy’ we mean the increase in enthalpy in going from reactants to products:

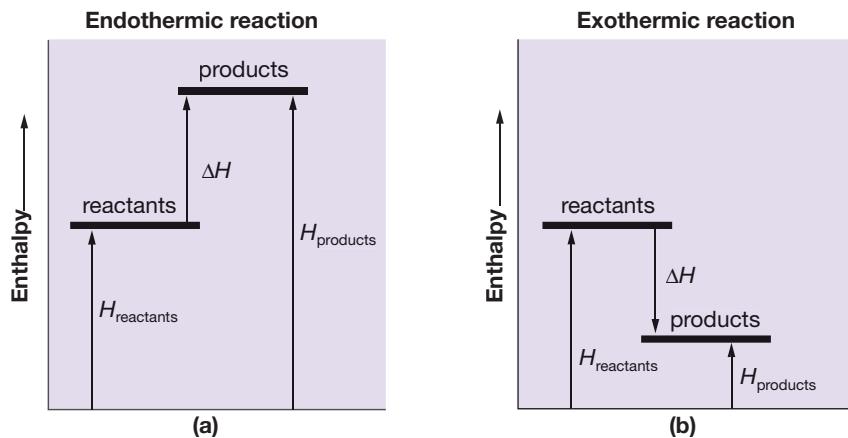
$$\Delta H = \text{enthalpy of products} - \text{enthalpy of reactants} \quad \dots (10.1)$$

$\Delta$  in front of a symbol means ‘change in’, and it always means final state minus initial state—always products minus reactants. Since  $\Delta H$  is defined as heat absorbed in going from reactants to products:

for endothermic reactions,  $\Delta H$  is positive  
for exothermic reactions,  $\Delta H$  is negative

Figure 10.1 shows graphically the relation between enthalpies of products and reactants, and  $\Delta H$  for endothermic and exothermic reactions.

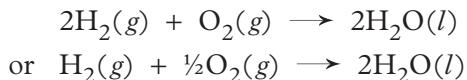
FIGURE 10.1  
Graphical representation  
of enthalpy changes



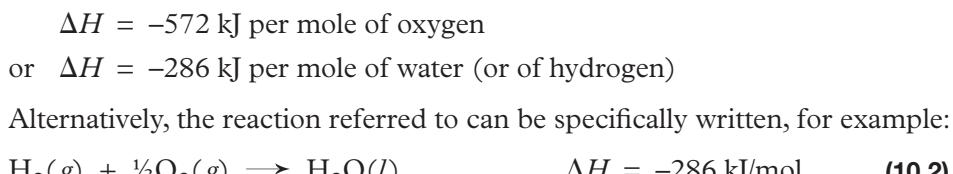
The definition of  $\Delta H$  above includes the term *per mole of specified reactant or product*, because it is often possible to write the reaction in more than one way.

<sup>†</sup> Enthalpy is not specifically mentioned in the Preliminary Course syllabus. However, it is such a basic concept in accounts of energy aspects of chemical reactions that its inclusion is warranted.

For example, the statement that  $\Delta H$  for the formation of water from hydrogen and oxygen is  $-572 \text{ kJ}$  is ambiguous because it does not make clear whether the reaction concerned is:



Ambiguity is removed by saying:



Here, ‘per mole’ means *per mole of the reaction as written*, in this case per mole of hydrogen or per mole of water.

We put ‘per mole’ in the units of  $\Delta H$  to show that the value is not a ‘per molecule’ one, because as we saw in Section 5.9 equations can be read in terms of molecules or moles.

$\Delta H$  depends upon the physical state (solid, liquid, gas or solution) of the reactants and products, and therefore *in chemical energy contexts, we always indicate the physical state of the substances involved in chemical equations*.

Equation 10.2 is the usual way of writing the enthalpy change for a chemical reaction: we write the equation in the normal way, then put a  $\Delta H =$  expression after it. For the combustion of methane:



$\Delta H$  is sometimes loosely referred to as the **heat of reaction**.

Examples will illustrate ways that enthalpy changes are determined and used.

### Example 1

When 3.4 g ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , was burnt in excess oxygen, 101 kJ of heat was released. Write the equation for the reaction and calculate the molar enthalpy change,  $\Delta H$ , for it.

The equation is



We need to calculate the heat released per mole of ethanol used.

$$\begin{aligned} \text{Molar mass of ethanol} &= 2 \times 12.01 + 6 \times 1.01 + 16.0 \\ &= 46.1 \text{ g/mol} \end{aligned}$$

$$\begin{aligned} \text{Number of moles of ethanol burnt} &= \frac{3.4}{46.1} \\ &= 0.074 \text{ mol} \end{aligned}$$

$$\text{Heat released by } 0.074 \text{ mol} = 101 \text{ kJ}$$

$$\begin{aligned} \text{Heat released per mole} &= \frac{101}{0.074} \\ &= 1370 \text{ kJ/mol} \end{aligned}$$

When a reaction releases heat (as here), we say that the heat *absorbed* is *minus* the quantity of heat released (in this case,  $-1370 \text{ kJ/mol}$ ). Because  $\Delta H$  is defined as heat absorbed,

$$\Delta H = -1370 \text{ kJ/mol}$$





### Example 2

The molar enthalpy change for the reaction of butane,  $C_4H_{10}$ , with oxygen is  $-2880 \text{ kJ/mol}$ . How much heat is absorbed or released (state which) when 1.5 g butane is burnt in excess oxygen?

$$\begin{aligned}\text{Molar mass of butane} &= 4 \times 12.01 + 10 \times 1.01 \\ &= 58.1 \text{ g/mol}\end{aligned}$$

$$\begin{aligned}\text{Number of moles of butane used} &= \frac{1.5}{58.1} \\ &= 0.026 \text{ mol}\end{aligned}$$

$\Delta H$  is negative so heat is *released* when butane burns.

$$\begin{aligned}\text{Heat released by } 0.026 \text{ mol} &= 0.026 \times 2880 \\ &= 74 \text{ kJ}\end{aligned}$$

## 10.3 MEASURING ENTHALPY CHANGES FOR REACTIONS<sup>†</sup>

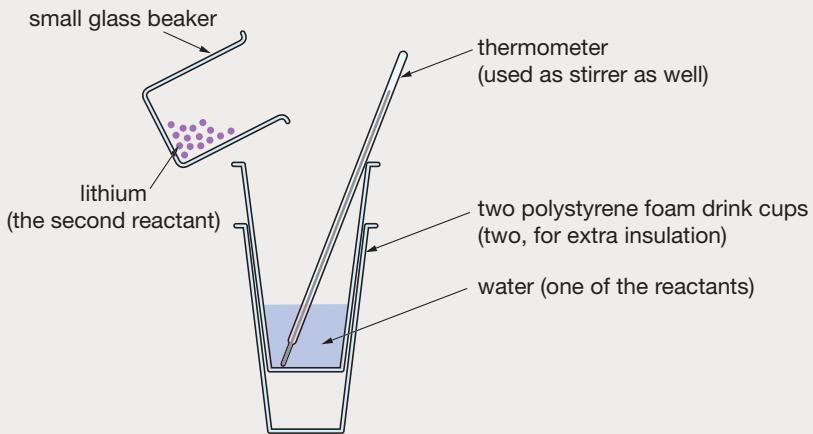
Enthalpy changes for many chemical reactions can be measured in a similar way to that used for measuring heats of solution in Section 8.12. Reactants (pure or in solution) at the same known temperature are mixed in a well-insulated container of low heat capacity and the temperature after complete reaction is noted. An example will illustrate.

<sup>†</sup> Not required by the Preliminary Course syllabus, but more difficult measurements of heats of reaction (for combustion) are required in Module 1 of the HSC Course, so this simple introduction is included here.



### Example 3

1.62 g lithium was added to 150 g water at  $17.4^\circ\text{C}$  in a well-insulated beaker of very low heat capacity (disposable polystyrene coffee cup) as shown in the diagram. The mixture was stirred with the thermometer until all the lithium had reacted. The final temperature was  $37.2^\circ\text{C}$ . Write a balanced chemical equation for the reaction and calculate the molar enthalpy change for it. Take the specific heat capacity of the final solution as that of water, namely  $4.2 \text{ J K}^{-1} \text{ g}^{-1}$ .



The reaction is one discussed in Section 4.9. The equation is:



We use Equation 8.11 to calculate the amount of heat released:

$$q = m C \Delta T \quad \dots (8.11)$$

$m$  is  $150 + 1.62 = 152$  g,  $C$  is  $4.2 \text{ J K}^{-1} \text{ g}^{-1}$  and  $\Delta T$  is  $37.2 - 17.4 = 19.8^\circ\text{C}$ . Therefore:

$$\begin{aligned}\text{heat released} &= 152 \times 4.2 \times 19.8 \\ &= 1.26 \times 10^4 \text{ J}\end{aligned}$$

This heat was released by the reaction of 1.62 g lithium. Because of the equation we have written, we want the heat released by two moles of lithium.

Molar mass of lithium = 6.9 g/mol

$$\begin{aligned}\text{number of moles of lithium used} &= \frac{1.62}{6.9} \\ &= 0.235 \text{ mol} \\ \text{Heat released by 2 moles of lithium} &= \frac{2 \times 1.26 \times 10^4}{0.235} \\ &= 107 \text{ kJ/mol}\end{aligned}$$

Hence we can say heat *absorbed* =  $-107 \text{ kJ/mol}$

and because  $\Delta H$  is heat absorbed,

for the reaction written  $\Delta H = -107 \text{ kJ/mol}$

The general procedure for calculating molar enthalpy changes from experimental data is summarised in Box 10.1.

#### BOX 10.1 TO CALCULATE $\Delta H$ FOR A REACTION

- Calculate the amount of heat released or absorbed, generally by using

$$q = m C \Delta T$$

- Calculate the number of moles that reacted from

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}}$$

- Calculate heat released or absorbed per mole from

$$\frac{\text{total heat released or absorbed}}{\text{number of moles that reacted}}$$

- $\Delta H$  is *plus* the heat absorbed or *minus* the heat released.

## Exercises

- Which of the following reactions are exothermic and which are endothermic?

a	$2\text{SO}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{SO}_3\text{(g)}$	$\Delta H = -198 \text{ kJ/mol}$
b	$\text{CH}_4\text{(g)} + \text{H}_2\text{O(g)} \rightarrow \text{CO(g)} + 3\text{H}_2\text{(g)}$	$\Delta H = +206 \text{ kJ/mol}$
c	$\text{NH}_3\text{(aq)} + \text{HCl(aq)} \rightarrow \text{NH}_4^+\text{(aq)} + \text{Cl}^-\text{(aq)}$	$\Delta H = -52 \text{ kJ/mol}$
d	$\text{Ag}^+\text{(aq)} + \text{I}^-\text{(aq)} \rightarrow \text{Agl(s)}$	$\Delta H = -112 \text{ kJ/mol}$
e	$\text{NiCl}_2\text{(aq)} + \text{Na}_2\text{CO}_3\text{(aq)} \rightarrow \text{NiCO}_3\text{(s)} + 2\text{NaCl(aq)}$	$\Delta H = +59 \text{ kJ/mol}$

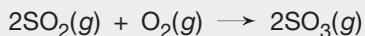
If reactions (c), (d) and (e) were carried out in thermally insulated containers, for which ones would the temperature increase as reaction proceeded and for which would it decrease?



- 2** When ammonia and hydrochloric acid solutions are mixed in a test tube, the tube gets warm. When solutions of potassium carbonate and nickel sulfate are mixed in a test tube, a precipitate forms and the tube gets cold. Write equations for the reactions that occur. Which reaction (if either) is endothermic and which (if either) is exothermic? Explain how you decided this from the information given.
- 3** Write the chemical equation and calculate  $\Delta H$  for the reaction that occurs in each of the following:
- when 0.50 g magnesium is burned in air, 12.4 kJ of heat is released
  - when 1.1 g zinc is dissolved in excess hydrochloric acid, 2.6 kJ of heat is liberated
  - when an aqueous solution containing 18.0 g magnesium chloride is added to an excess of sodium carbonate solution, 9.2 kJ of heat is absorbed (temperature falls)
- 4** Given the  $\Delta H$  values in Exercise 1, calculate the amount of heat released or absorbed (stating whether released or absorbed) when:
- 5.0 g sulfur dioxide reacts with excess oxygen
  - 5.0 g nickel chloride is added to excess sodium carbonate solution
  - 25 mL 0.20 mol/L HCl is added to 50 mL of a solution containing excess ammonia

In Exercises 5 and 6, make the approximations:

- the heat capacity of all solutions is that of water ( $4.2 \text{ J K}^{-1} \text{ g}^{-1}$ )
  - the heat capacity of the calorimeter (beaker) is negligible
  - there are negligible heat losses to the surroundings
  - the density of all solutions is 1.0 g/mL
- 5** When 25 mL 0.20 mol/L sodium hydroxide solution at  $23.2^\circ\text{C}$  was added to excess hydrochloric acid present in 50 mL of solution at the same temperature in a light plastic beaker, the temperature of the mixture rose to  $24.1^\circ\text{C}$ . Calculate the heat released and hence the enthalpy change for the reaction.
- 6** 50 mL 0.20 mol/L lead nitrate solution is added to excess potassium iodide contained in 30 mL of solution. Both solutions are initially at  $19.6^\circ\text{C}$ . After mixing, the temperature rose to  $22.2^\circ\text{C}$ . Calculate the enthalpy change (per mole of  $\text{Pb}^{2+}$ ) for the reaction.
- 7** For the reaction



$$\Delta H = -198 \text{ kJ/mol}$$

What is  $\Delta H$  for each of the reactions below?

- $\text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{SO}_3(g)$
- $2\text{SO}_3(g) \rightarrow 2\text{SO}_2(g) + \text{O}_2(g)$

## 10.4 HEAT OF COMBUSTION<sup>†</sup>

Our main concern in this module is energy and extracting it from fuels by combustion. A useful quantity in this context is the heat of combustion, or more precisely the molar heat of combustion.

The **molar heat of combustion** of a substance is the heat liberated when 1 mole of the substance undergoes complete combustion with oxygen at standard atmospheric pressure with the final products being carbon dioxide gas and liquid water.

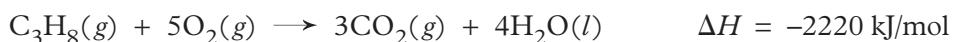
<sup>†</sup> Not required for the Preliminary Course but is required for Module 1 of the HSC Course and this is a good place to introduce the concept.

As thus defined, the molar heat of combustion is minus the enthalpy change for the combustion process because  $\Delta H$  is defined as heat gained.

Combustion (or burning) is always exothermic. This means that heat is always given out, so  $\Delta H$  for combustion processes is always negative. This difference in sign—using a positive value for heat of combustion while the enthalpy change for the reaction is negative—can be a trap when working problems. Remembering that combustion reactions are always exothermic, regardless of the sign of the value given, helps avoid any confusion. Enthalpy change for combustion is sometimes abbreviated to *enthalpy of combustion*. In summary:

molar heat of combustion	(= heat released) is positive
enthalpy change for a combustion process }	(= heat absorbed) is negative
enthalpy of combustion	

The molar heat of combustion of propane (a major constituent of liquefied petroleum gas, LPG) is 2220 kJ/mol. This means that for the reaction:



Some other heats of combustion are shown in Table 10.1.

**TABLE 10.1 Molar heats of combustion<sup>a</sup> for some common substances**

Substance	Molar heat of combustion (kJ/mol)	Substance	Molar heat of combustion (kJ/mol)
hydrogen, H <sub>2</sub>	285	ethyne, C <sub>2</sub> H <sub>2</sub>	1300
carbon, C	393	octane, C <sub>8</sub> H <sub>18</sub>	5460
carbon monoxide, CO	280	toluene, C <sub>7</sub> H <sub>8</sub>	3910
methane, CH <sub>4</sub>	890	dodecane, C <sub>12</sub> H <sub>26</sub>	8080
ethane, C <sub>2</sub> H <sub>6</sub>	1560	ethanol, C <sub>2</sub> H <sub>5</sub> OH	1360
propane, C <sub>3</sub> H <sub>8</sub>	2220	sucrose, C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	5650

<sup>a</sup> Molar heat of combustion is minus the enthalpy change for the combustion process with CO<sub>2</sub>(g) and H<sub>2</sub>O(l) being the final products

## Exercises

- 8** The heat of combustion of hexane is 4160 kJ/mol. What is  $\Delta H$  for the reaction? Draw an enthalpy diagram similar to Figure 10.1 showing reactants and products and  $\Delta H$ . Let the ‘up the page’ direction be positive.
- 9** **a** Calculate the heat released per gram from the combustion of each of the following fuels (heats of combustion in kJ/mol are given in brackets):
- |   |  |
|---|--|
| <b>i</b> hydrogen (285)   | <b>iv</b> propane (2220)   |
| <b>ii</b> ethanol, C <sub>2</sub> H <sub>5</sub> OH (1360)          | <b>v</b> sucrose, C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> (5650) |
| <b>iii</b> ethyne (acetylene), C <sub>2</sub> H <sub>2</sub> (1300) | <b>vi</b> octane (5460)  |
- b** Arrange these fuels in decreasing order of heat released per gram. What can you say about the heat released per gram for hydrocarbons? What is the effect of having oxygen in the fuel molecule?



- 10 a** Using data in Exercise 9, calculate the amount of heat released by 1.0 L petrol (taken as pure octane with a density of 0.70 g/mL). Do the same calculation for LPG (taken as pure liquid propane with a density of 0.49 g/mL).
- b** If petrol sells at 95 cents per litre, what would the price of LPG need to be for it to have an equivalent price in cents per kilojoule as petrol?

The question of why there are energy changes when chemical reactions occur warrants consideration.

## 10.5 EXPLAINING CHEMICAL ENERGY CHANGES

We saw in Section 3.4 that the reason why decomposition reactions required an input of energy was because energy is needed to break chemical bonds. Conversely, energy was liberated when atoms formed molecules because making chemical bonds releases energy. That is:

Energy must be supplied to break chemical bonds.  
Making chemical bonds releases energy.

In other words, breaking bonds is endothermic while making bonds is exothermic.

In many chemical reactions, some bonds (in reactant molecules) are broken and new bonds are formed to make the product molecules. Two examples are:

- When hydrogen burns in oxygen to form water, effectively H—H bonds in hydrogen gas and O—O bonds in oxygen gas break and H—O bonds form to make water. The reaction does not actually occur by each reactant breaking up completely into atoms with the atoms then recombining to form product molecules, but that is the net effect.
- When methane burns in oxygen to form carbon dioxide and water, C—H bonds in methane and O—O bonds in oxygen gas are broken and C—O and H—O bonds are formed to make carbon dioxide and water respectively.

The enthalpy change for a reaction,  $\Delta H$ , will be the energy required to break the necessary bonds in reactant molecules minus the energy released when the new bonds are formed:

$$\Delta H = \left\{ \begin{array}{l} \text{energy to break} \\ \text{bonds in reactants} \end{array} \right\} - \left\{ \begin{array}{l} \text{energy to make} \\ \text{bonds for products} \end{array} \right\} \quad \dots (10.3)$$

This equation is illustrated in Figure 10.2 for the two reactions:

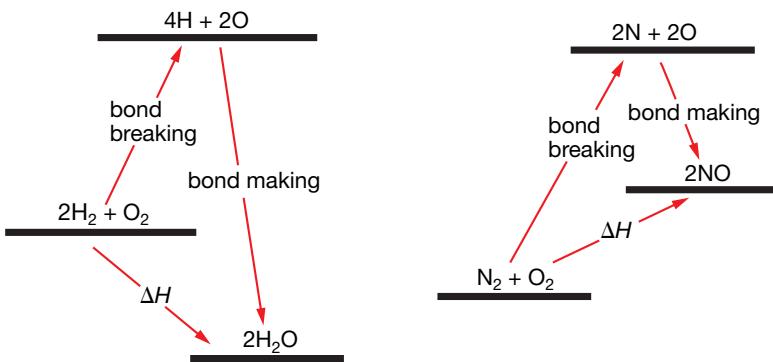


FIGURE 10.2  
Energy diagrams for forming  $\text{H}_2\text{O}$  and  $\text{NO}$   
(Equations 10.4 and 10.5)

For Reaction 10.4, the energy required to break the H—H and O—O bonds is less than the energy released when H—O bonds form, so the reaction is exothermic ( $\Delta H$  negative). On the other hand, for Reaction 10.5 the energy required to break N—N and O—O bonds is greater than the energy released when N—O bonds form, so the reaction is endothermic ( $\Delta H$  positive).

## Exercises

- 11 Ammonia is made from nitrogen and hydrogen gases. Write an equation for the reaction. It is an exothermic reaction. What bonds have to be broken and what bonds made for the reaction to occur? Draw a diagram similar to those in Figure 10.2 for this reaction.
- 12 a Hydrazine,  $\text{H}_2\text{N}-\text{NH}_2$ , burns in oxygen to form nitrogen gas and water. Write an equation for the reaction. The reaction is exothermic. Draw an energy diagram showing the reaction as occurring by breaking hydrazine and oxygen into atoms and then the atoms forming products.  
b The energies required to break all the bonds in hydrazine, oxygen, nitrogen gas and water are 1722, 498, 945 and 926 kJ/mol respectively. Use these data with your energy diagram from (a) to calculate  $\Delta H$  for the reaction.



A convenient property of common fuels is that they do not react with oxygen at room temperature. They react only if we ignite them; that is, ‘set fire’ to them. A heap of coal does not spontaneously burst into flames. We can expose petrol to the air without any reaction occurring, and natural gas flows out of an open tap without burning. We need to heat the coal in a flame, strike a match near the petrol or apply a heated electrical filament to the natural gas to get them all to burn (react with oxygen). Let us look for a reason for this.

## 10.6 ACTIVATION ENERGY

The reason why many reactions do not occur spontaneously, but need some sort of a ‘prod’ to get them going, is that there is often an energy barrier between reactants and products. We therefore have to give the reactant molecules sufficient energy to scale this energy barrier. Once an exothermic reaction gets going, it releases sufficient energy to activate further reactant molecules and so the reaction becomes self-sustaining. We call this energy barrier an *activation energy*.

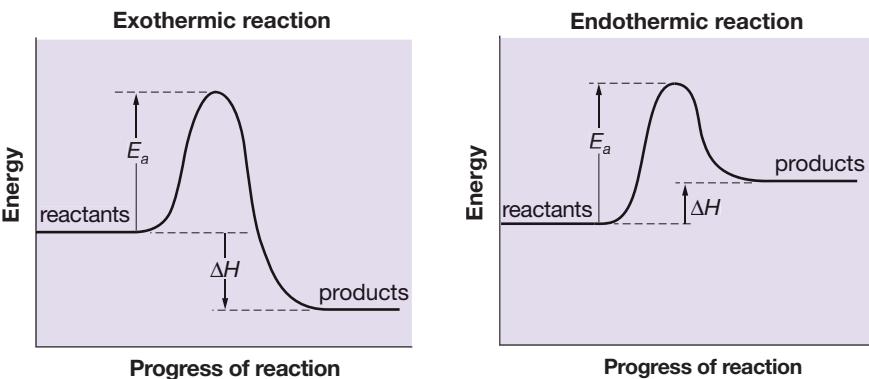
The **activation energy**,  $E_a$ , of a reaction is the minimum amount of energy reactant molecules must possess in order to form products.

It is generally expressed in kilojoules per mole, kJ/mol. This energy barrier exists for both exothermic and endothermic reactions as Figure 10.3 shows.

For exothermic reactions (such as combustion of common fuels), once we get them going they generate enough energy to become self-sustaining. However, for endothermic reactions we have to supply energy continuously. For example, the reaction between nitrogen and oxygen (Equation 10.5) occurs only at temperatures above about  $1000^\circ\text{C}$  and only while we supply energy to maintain that temperature. If we stop supplying energy, the reaction stops (which is just as well, otherwise we would lose our precious atmosphere!).

We shall see in Section 10.14 that there are many reactions that occur at room temperature even though they have a significant activation energy.

**FIGURE 10.3**  
Energy diagrams showing activation energy  $E_a$  and enthalpy change  $\Delta H$  for both exothermic and endothermic reactions



However, the reactions of our common fuels with oxygen have much higher activation energies and so there is no significant reaction at room temperature: we have to ignite them. This gives rise to the idea of an ignition temperature.

## 10.7 IGNITION TEMPERATURE

Some fuels are easier to ignite (set fire to) than others. A measure of the ease of ignition is the *ignition temperature*.

The **ignition temperature** of a fuel–air mixture is the minimum temperature to which the mixture (or portion of it) must be heated in order for combustion to occur.

There are several ways of reaching the ignition temperature as the following examples illustrate.

- 1 Matches and their striking surfaces contain fuel and an oxygen source of such low ignition temperature that the frictional heat generated by rubbing the match head over the rough surface is sufficient to reach the ignition temperature. Hence the chemicals in the match head start to burn. In so doing, the temperature of the wood of the matchstick is brought to the ignition temperature for wood and oxygen. The matchstick then burns freely.
- 2 If a fine wire filament is heated to red heat in a mixture of hydrogen and oxygen, it will heat the gas mixture in its vicinity to the ignition temperature. This starts the combustion reaction, which will then propagate rapidly through the whole mixture. This happens so quickly that an explosion results.
- 3 If a spark is fired through a mixture of petrol and air in the cylinder of a motor car engine, it will cause the ignition temperature of the petrol–air mixture to be exceeded near the spark. This will set off the combustion reaction, which again will propagate rapidly through the whole mixture and release the energy needed to push down the piston and propel the car.
- 4 If diesel fuel is injected into a sample of air which has been heated by compression to above the ignition temperature of that fuel–air mixture, then the fuel will ignite. The combustion will spread through the whole combustion chamber (cylinder). This is how diesel engines operate.

Note that it is not necessary to heat *all* of the fuel–air mixture to the ignition temperature; it is often sufficient to heat just a small portion to the required temperature. This is because the combustion reaction, being exothermic, once started at one spot, soon spreads throughout the whole mixture.

Ignition temperatures are of particular importance in choosing fuels for engines. However, the ignition temperature depends upon the ratio of fuel to

air and upon the size, shape and material of the apparatus used to measure it. Consequently there are different ways of measuring ignition temperatures for different situations (e.g. for petrol or diesel engines).

Fuels have ignition temperatures well above room temperature because their combustion reactions have quite high activation energies. In general:

The greater the activation energy, the higher is the ignition temperature.

An advantage of a fuel having an ignition temperature well above room temperature is that we can leave the fuel in contact with air at room temperature without causing any spontaneous reaction.

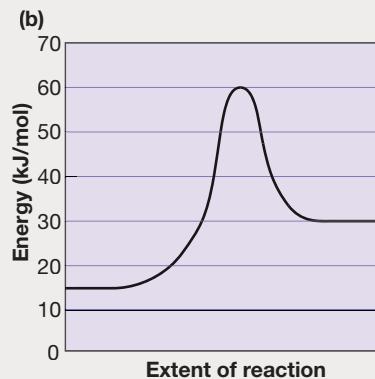
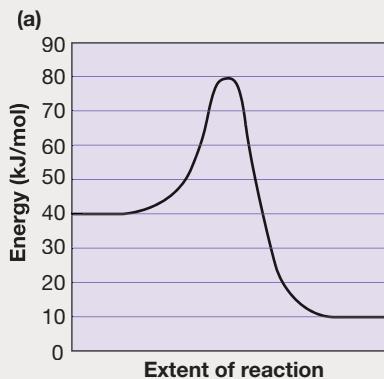
## Exercises

**13 \*a** Sketch energy diagrams for reactions having:

- i  $\Delta H = -80 \text{ kJ/mol}$  and  $E_a = 40 \text{ kJ/mol}$
- ii  $\Delta H = -30 \text{ kJ/mol}$  and  $E_a = 120 \text{ kJ/mol}$

b Which reaction would you expect to have the lower ignition temperature?

**14** The diagrams below show energy profiles for two reactions. What is the activation energy and the enthalpy change for each of these reactions?



**15** For the combustion reactions of two fuels, A and B, enthalpy changes and activation energies are:

Fuel A:  $\Delta H = -200 \text{ kJ/mol}$ ,  $E_a = 100 \text{ kJ/mol}$

Fuel B:  $\Delta H = -70 \text{ kJ/mol}$ ,  $E_a = 250 \text{ kJ/mol}$

Draw energy profiles for these reactions on the one set of axes, clearly identifying each reaction. Use the same energy position for both sets of reactants.

In terms of heat released per mole, which of A or B would be the better fuel? Which fuel-air mixture would have the lower ignition temperature?

**16** With air, octane has a higher ignition temperature and a greater heat of combustion than does pentane. On the one sketch draw an energy profile for the combustion of each substance. Draw the profiles so that they reflect these facts.



## 10.8 POLLUTION FROM BURNING FOSSIL FUELS

Burning fossil fuels in motor vehicles, power stations, factories and homes is the main source of pollution in the world today.

The major types of pollution produced by burning fossil fuels are:

- carbon monoxide and/or soot (carbon) from incomplete combustion of the fuel
- sulfur dioxide from impurities in the fuel
- oxides of nitrogen from some reaction between oxygen and nitrogen from air at the high temperatures of the combustion process
- particulates (very small particles of solid or droplets of liquid) especially from coal.

### Carbon monoxide and soot

If insufficient air is available for the complete combustion of a fuel (to carbon dioxide and water), then some carbon monoxide and/or soot (carbon) is formed. For example when pentane is burnt in a plentiful supply of air, the reaction is:



If insufficient air (oxygen) is available, one possible reaction is:



Depending on conditions the number of molecules of CO formed per molecule of pentane could range from zero to 5. If even less oxygen was available, the reaction could produce carbon:

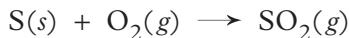


Formation of carbon monoxide is common in petrol engines where the air-to-fuel ratio is close to the stoichiometric value (only a very small excess of oxygen (as air) is present). Diesel engines and electricity generating stations use a much higher air-to-fuel ratio (that is, they use excess air (oxygen)) and so produce very little carbon monoxide. Badly maintained diesel engines can produce a lot of soot under certain conditions.

The way to minimise production of carbon monoxide and soot is to use excess air; that is, to keep the air-to-fuel ratio high. This is not possible in petrol engines (ignition becomes too difficult) so emission of carbon monoxide from cars is minimised by using a catalyst in the exhaust (Section 10.15) to convert any CO formed to  $\text{CO}_2$ .

### Sulfur dioxide

Sulfur dioxide is produced from impurities in the fuel—most commonly from coal. Coal normally contains from 0.5 to 5% sulfur, though Australian coals generally have lower amounts—0.5 to 2%. When coal burns this sulfur is converted to sulfur dioxide, a pungent gas which causes breathing difficulties at quite low concentrations:



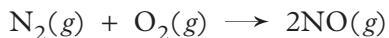
Removing sulfur from coal is difficult, so power stations try to use low-sulfur coals whenever possible (which is why there is high demand for Australian

coals). Alternatively sulfur dioxide has to be removed from the effluent gas at power stations but this is expensive.

When crude oil and natural gas are processed for use, virtually all of the sulfur-containing compounds are removed.

## Oxides of nitrogen

Nitrogen and oxygen gases do not normally react with each other. However, at high temperatures (above about 1000°C) they combine to form nitric oxide:



Nitric oxide reacts slowly with oxygen to form nitrogen dioxide:



These reactions occur in petrol and diesel engines and in power stations. Consequently motor vehicles and power stations emit small concentrations of both of these gases. The term *oxides of nitrogen* is commonly used to describe this mixture. Sometimes the abbreviation NO<sub>x</sub> or NO<sub>x</sub> is used for this mixture.

Nitrogen dioxide causes respiratory difficulties and damages organ tissue. However, the main concern with nitrogen dioxide is that under the influence of sunlight it leads to the production of ozone, a far more dangerous substance, in what is called *photochemical smog*.

Today most new cars use a catalyst (Section 10.15) to remove nitric oxide by speeding up the reaction:



Diesel engines produce more oxides of nitrogen than do petrol engines. To minimise pollution from motor vehicles there are laws that limit the amount of CO and NO<sub>x</sub> that vehicles can emit.

Until recently emissions of oxides of nitrogen from power stations have been tolerated by locating power stations away from population centres. However there is a growing trend towards using catalysts to remove oxides of nitrogen from the gas effluents from power stations.

## Particulates

As mentioned above **particulates** are very small particles of solids and/or droplets of liquid. The particles or droplets are so small that they do not easily settle out of the air. They are the most obvious form of air pollution because they affect visibility as Figure 10.4 shows. They frequently contribute to respiratory problems for aged and frail people and for asthma sufferers.

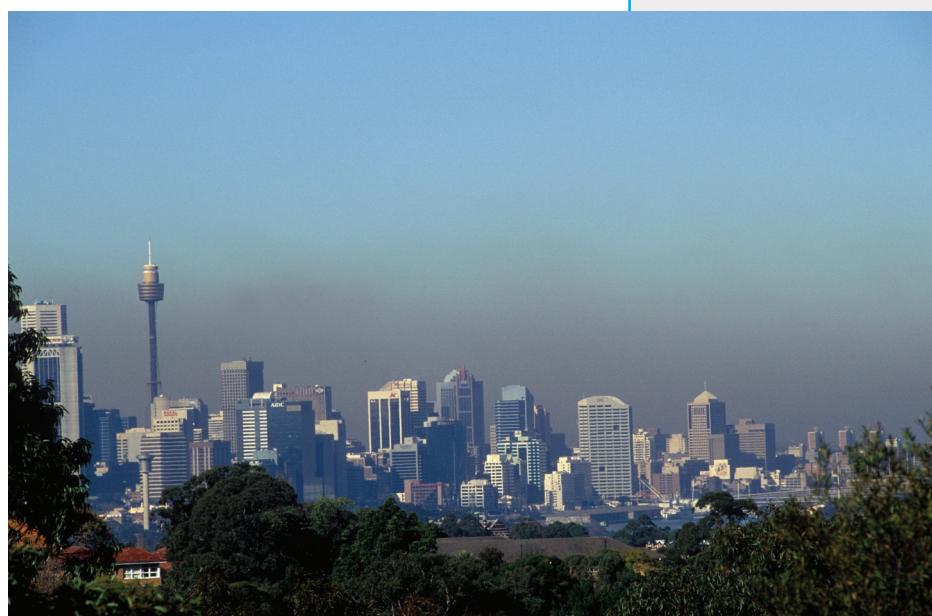


FIGURE 10.4  
High concentrations of particulates spoil visibility

Although vehicles produce some particulates, the major sources are from industry and power generation, in particular from burning coal and the higher boiling point fractions of crude oil (gas oil or heating oil). From coal and oil, particulates arise from the incomplete combustion of the fuel (as soot did). From coal they also form from the incombustible inorganic matter present in coal to a small extent.

Emission of particulates from stationary sources (power stations and industries) is generally minimised by using *electrostatic precipitators*. These are devices that use a high voltage to cause small particles to combine into big ones that can be filtered out of the exhaust gas.

## 10.9 THE GREENHOUSE EFFECT<sup>†</sup>

Carbon dioxide is not normally considered a pollutant: it has no detrimental effects on humans or other living matter and does not spoil the appearance or our enjoyment of the environment. However its release to the atmosphere does have a very serious effect—it contributes to global warming or, as it is commonly called, the **greenhouse effect**.

Increasing atmospheric concentrations of carbon dioxide and some other gases such as methane result in more of the heat that Earth is radiating into space being trapped by the atmosphere. Consequently average global temperatures are increasing. This is expected to cause detrimental climate changes and rising sea levels.

Burning fossil fuels is the major contributor to global warming.

It is impractical to remove carbon dioxide from the atmosphere or from the emissions of power stations, factories or vehicles. Therefore our only method of combating global warming is to use less fossil fuel. This means developing more efficient cars and appliances so that the same useful work can be obtained from less energy, developing alternative sources of energy, and modifying our lifestyles to lower our overall energy demands.

<sup>†</sup> Not required for the Preliminary Course but no discussion of fossil fuels would be complete without some mention of it.



### FOR INVESTIGATION

Light a candle, then describe in detail the processes that are occurring as the candle burns. Pay close attention to the changes of state that are occurring.



## Exercises



17 Write balanced chemical equations for the reaction of heptane, C<sub>7</sub>H<sub>16</sub>, with oxygen when the carbon products are:

- a all carbon dioxide
- b carbon dioxide and carbon monoxide in the ratio of 3:4
- c carbon dioxide and carbon monoxide in the ratio of 1:6
- d carbon and carbon monoxide in the ratio of 1:6
- e carbon and carbon monoxide in the ratio of 5:2
- f all carbon

What do these equations tell you about the nature of the products of this combustion as the ratio of oxygen to hydrocarbon decreases?

18 The heats of combustion of octane and carbon monoxide are 5460 kJ/mol and 280 kJ/mol respectively. Calculate how much heat is ‘lost’ (per mole) when octane is incompletely burnt to CO instead of to CO<sub>2</sub>. What percentage of the theoretical energy available has been lost?

## 10.10 RATES OF COMBUSTION REACTIONS

The combustion reactions we use in everyday life proceed at very different rates. We have:

- *slow combustion* as in slow combustion stoves where large lumps of fuel (coal, coke or wood) take many hours to burn
- *fast combustion* such as burning methane, LPG, kerosene or heating oil in stoves or heating appliances or of powdered coal in power stations, and
- *explosive combustion* as in the cylinders of petrol and diesel engines in vehicles.

All of the chemical reactions involved in these combustion processes are **spontaneous reactions**. This means that once started (ignited) they proceed without further assistance and continue to go until all of the fuel is used up.

Slow combustion occurs when we use big lumps of fuel and limit the supply of air. This means that burning occurs only on the surface of the big lumps and its speed is controlled by the limited supply of air.

For fast combustion in power stations, coal is ground into very small particles that are sprayed into a plentiful supply of air. There is a large surface area of fuel exposed to an excess of oxygen and there is good mixing to stop oxygen concentrations becoming depleted near the surface of the particles. In other fast combustion appliances, gaseous fuel or vaporised liquid fuel is mixed with excess air: the gaseous nature of the mixture and the high temperature ensure that fuel is always in contact with oxygen and so combustion proceeds rapidly.

In petrol engines a spark is used to ignite a heated mixture of petrol and air. In diesel engines liquid fuel is injected and vaporised into an excess amount of heated air. In both cases the conditions used are such as to promote very rapid reaction. An explosion is just an extremely rapid reaction—one that goes to completion within a few microseconds.

Changes in conditions lead to changes in the rates of the reactions. Let us then look at what we mean by rate of a reaction and at the factors that affect reaction rates.

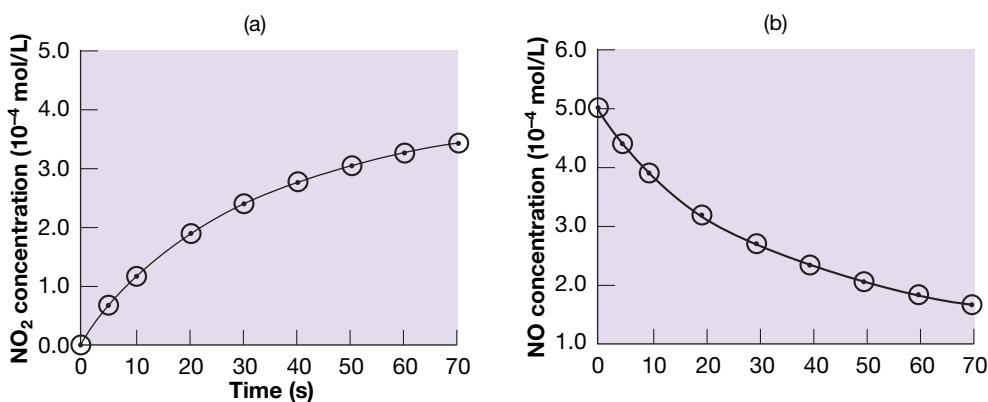
## 10.11 MEANING OF RATE OF REACTION

By ‘rate of reaction’ we mean the rate at which reactants disappear or, alternatively, the rate at which products form. A specific example will illustrate. As explained in Section 10.8, nitric oxide reacts with oxygen to form nitrogen dioxide:



Nitric oxide is colourless whereas nitrogen dioxide is brown. We can follow the progress of this reaction by measuring the increasing intensity of the brown colour. This allows us to construct a graph of concentration of nitrogen dioxide as a function of time after mixing oxygen and nitric oxide; this is shown in Figure 10.5(a).

FIGURE 10.5  
Concentrations of (a) nitrogen dioxide and (b) nitric oxide as functions of time after mixing nitric oxide and oxygen. Initial concentrations were  $4.1 \times 10^{-3}$  mol/L for  $\text{O}_2$  and  $5.0 \times 10^{-4}$  mol/L for NO.



The **rate of reaction** is the rate of change of concentration with time.  
Alternatively the **average rate of reaction** over a small time interval is *the change in concentration divided by the time taken for the change to occur*.

$$\text{Average rate} = \frac{\text{change in concentration}}{\text{time taken}}$$

If the concentration is  $c_1$  at time  $t_1$  and  $c_2$  at  $t_2$  a short time later, then

$$\text{Average rate} = \frac{c_2 - c_1}{t_2 - t_1}$$

Or if we use  $\Delta$  for *change in*,

$$\text{Average rate} = \frac{\Delta c}{\Delta t}$$

where  $\Delta c = c_2 - c_1$  and  $\Delta t = t_2 - t_1$ .

In terms of a concentration versus time graph, the rate of reaction at any particular time is the slope (gradient) of the curve at that time.

In Figure 10.5(a) we see that as the reaction proceeds, the slope of the curve decreases (curve gets less steep). This means that the rate of reaction is decreasing as the reaction proceeds.

Figure 10.5(a) presented the concentration of  $\text{NO}_2$ , the reaction product, as a function of time. Alternatively we could plot the concentration of NO, the reactant, as a function of time, as in Figure 10.5(b). The rate of reaction is

now the rate of change in concentration of NO. It is still the slope (gradient) of the curve except that we always take the rate of reaction as positive, so in Figure 10.5(b) the rate of the reaction is the *magnitude* of the slope (i.e. *minus* the actual slope because that slope is negative).

In Figure 10.5(b) the magnitude of the slope decreases as reaction proceeds, so the rate of reaction is still decreasing as reaction proceeds (as we expect from Figure 10.5(a)).

The shapes of the curves (a) and (b) in Figure 10.5 are typical for products and reactants respectively. These curves show that:

Reaction rate decreases as reaction proceeds.

This is by far the most usual situation. An explanation will emerge in the next section.

The key point from this discussion is that:

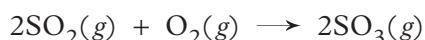
the rate of a reaction is the magnitude of the slope (gradient) of the concentration versus time curve.

## 10.12 FACTORS INFLUENCING THE RATE OF REACTION

Experimentally, we find that *increasing the concentration of a reactant generally increases the rate of the reaction*. This explains the shape of the concentration versus time curves in Figures 10.5(a) and (b). As reaction proceeds, the concentrations of the reactants decrease and so the rate of reaction continuously decreases; that is, the magnitude of the slope decreases as time increases.

For most reactions, *the rate increases as the temperature is increased*. This increase is often quite marked: for some reactions a 10°C increase can double the rate of reaction.

Sometimes the rate of a reaction is increased by the presence of a substance which is not even involved in the stoichiometric equation for the reaction. For example, the reaction of sulfur dioxide with oxygen to form sulfur trioxide:

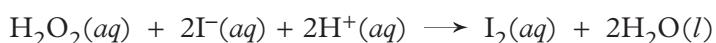


is quite slow. However if some nitrogen dioxide is added to the reaction mixture, reaction proceeds much more rapidly.

Substances that increase the rate of a reaction without undergoing permanent chemical change in the reaction are called **catalysts**.

Nitrogen dioxide is a catalyst for the  $\text{SO}_2 + \text{O}_2$  reaction.

The two reactions which we have been considering so far in this section,  $\text{NO} + \text{O}_2$  and  $\text{SO}_2 + \text{O}_2$ , involve species that are all in the gas phase, and the reaction occurs uniformly throughout the whole gaseous mixture. Such reactions are called **homogeneous reactions**. Reactions that occur uniformly throughout a solution are also homogeneous reactions. An example is the reaction between colourless hydrogen peroxide and acidic iodide solutions to form brown iodine solution:



In summary:

**FACTORS INFLUENCING THE RATE OF HOMOGENEOUS REACTIONS ARE:**

- 1 concentration of reactants (in solution or in the gas phase)
- 2 nature and concentration of any catalyst present
- 3 temperature

There are many reactions, some extremely important industrially, that occur at the interface between two phases; such reactions are called **heterogeneous reactions**. Some common examples are:

- reaction of zinc metal with hydrochloric acid (to form hydrogen gas and zinc chloride)
- decomposition of hydrogen peroxide in solution (to form oxygen and water) occurring on the surface of various solids such as manganese dioxide
- hydrogenation of alkenes and vegetable oils (to form alkanes and margarine, respectively) on the surface of finely divided nickel metal
- cracking of high molecular weight compounds from crude oil (gas oil fraction) to lower molecular weight ones (for use as gasoline).

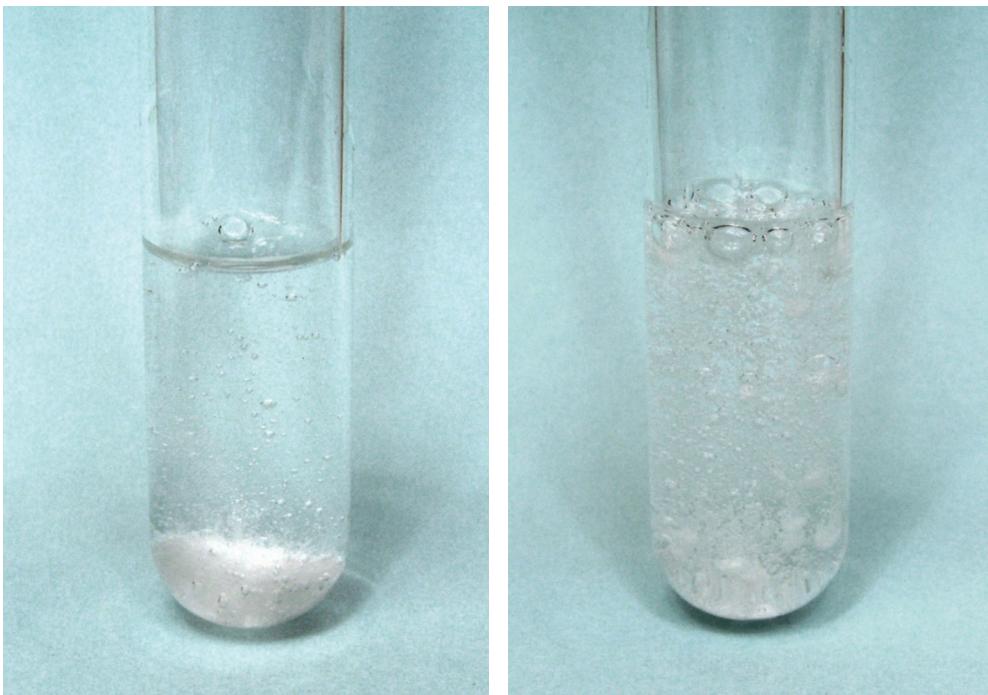
The rates of heterogeneous reactions, as well as depending upon the three factors listed above, also depend upon two other factors:

**EXTRA FACTORS INFLUENCING THE RATE OF HETEROGENEOUS REACTIONS ARE:**

- 4 the state of division of the solid
- 5 the rate of stirring which is used

For example, 1 g of finely crushed limestone,  $\text{CaCO}_3$ , added to 1 L hydrochloric acid solution causes carbon dioxide to be produced at a much greater rate than does one solid lump of the same mass added to a similar hydrochloric acid solution. Also, the reaction will be faster if the mixture is stirred continuously to keep the crushed limestone dispersed throughout the solution instead of letting it settle to the bottom of the flask. Both these effects are due to the fact that reaction is occurring on the surface of the solid.

A large lump of calcium carbonate reacts with a solution of hydrochloric acid more slowly (left test tube) than the same mass crushed into small pieces (right test tube)



For some reactions, the rate depends upon the intensity (brightness) of visible or ultraviolet light shining upon the reactants.

Ozone,  $\text{O}_3$ , is decomposed by ultraviolet light:



This reaction occurs in the stratosphere and filters out the harmful ultraviolet radiation from sunlight.

## Exercises

- 19** In order to determine whether or not the concentration of hydrochloric acid affected the rate of the reaction between magnesium and dilute hydrochloric acid, a chemist reacted 5.0 cm lengths of cleaned magnesium ribbon with 50 mL portions of hydrochloric acid solution and collected the hydrogen formed by displacement of water in an inverted burette. The volume of hydrogen was recorded at various times after the start of the reaction. Results are given in the following table.



### Experiment A (0.20 mol/L HCl)

Time (s)	0	40	70	100	140
Volume of $\text{H}_2$ (mL)	0	11	19.5	28	39

### Experiment B (0.60 mol/L HCl)

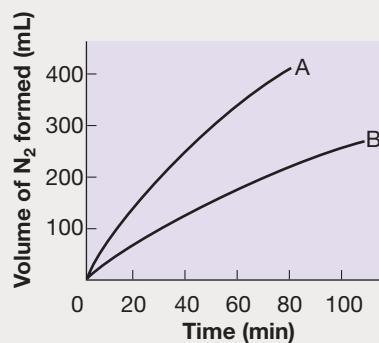
Time (s)	0	20	35	50
Volume of $\text{H}_2$ (mL)	0	16.5	29	41

- a On the one piece of graph paper plot volume of hydrogen versus time for each experiment and draw smooth lines through the points for each experiment.
  - b Which experiment has the greater rate of reaction? Explain how you decided this.
  - c In what way, if any, is the rate of this reaction affected by concentration of hydrochloric acid?
- 20** For Exercise 19 calculate the average rate of reaction (in mL  $\text{H}_2$  per s) over the first 40 s for Experiment A and over the first 20 s for Experiment B.

- 21** Aqueous ammonium nitrite solutions decompose to form nitrogen gas:



In two separate experiments, using different initial concentrations of reactant, the volume of nitrogen formed (at 25°C and standard atmospheric pressure) was measured as a function of time. The results are plotted in the graph.



- a Which experiment, A or B, has the greater initial rate of reaction? Give your reasoning.
- b Which experiment would you expect to correspond to the higher initial reactant concentration? Justify your choice.

- 22** Which of the following reactions are homogeneous and which are heterogeneous?

- a  $\text{Ca}(\text{OH})_2(\text{aq}) + 2\text{HNO}_3(\text{aq}) \rightarrow \text{Ca}(\text{NO}_3)_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$
- b  $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$
- c  $\text{BaO}(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{BaCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$

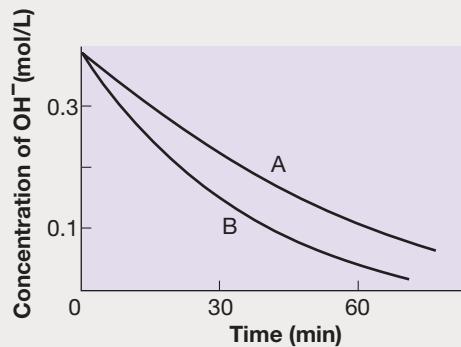
- d**  $\text{NO}(g) + \text{O}_3(g) \rightarrow \text{NO}_2(g) + \text{O}_2(g)$   
**e**  $2\text{NaOH(aq)} + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + 2\text{H}_2\text{O(l)}$   
**f**  $\text{Zn(s)} + \text{CuSO}_4(\text{aq}) \rightarrow \text{Cu(s)} + \text{ZnSO}_4(\text{aq})$

**23** In the reaction of bromoethane with aqueous sodium hydroxide solution to form ethanol:



the concentration of hydroxide was measured as a function of time in two experiments at different temperatures. The same reactant concentrations were used in both experiments. The results are shown in the accompanying graph.

- a** In which experiment, A or B, is the rate of reaction greater? Why?
- b** Which experiment was performed at the higher temperature? Explain your reasoning.
- \*c** Copy the graph on to your work pad and sketch on it the curve you would expect for an experiment using double the reactant concentrations at the higher temperature. Label this curve clearly and explain why it has the shape you have given it.



## 10.13 EXPLANATIONS

For a reaction to occur the reactant particles (atoms, molecules or ions) must collide.

Anything that increases the rate at which collisions occur will increase the rate of reaction. Increasing the concentration of reactants, state of division of a solid reactant, or rate of stirring increases the rate of collision and so the rate of reaction. The explanations are as follows:

- Concentration measures the number of particles of the particular substance per unit volume. Increasing the concentration puts more particles in unit volume and so increases the chance of collision between particles of one reactant and those of another reactant, which increases the reaction rate.
- Breaking big lumps of solid into smaller pieces increases the surface area of the solid (Exercise 24 below). In a reaction between a solute in solution and a suspended solid or between a gas and a solid, the reaction rate depends upon the rate of collision between the solute or gas particles and the solid. The greater the area of the solid, the more collisions that can occur in a given time, so reaction rate increases.
- Stirring has two effects. First it keeps the solid suspended in the solution or gas and so exposes the maximum surface area of the solid to the solute or gas. Secondly for reactions in solution, stirring quickly replaces solution in which the reactant has been used up with fresh solution, so ensuring that there is always plenty of solute for the solid to react with. In these two ways stirring increases the rate of collision between reactant particles and so increases the rate of reaction.

## 10.14 TEMPERATURE EFFECT AND ACTIVATION ENERGY

As temperature increases, the average kinetic energy (and so the speed) of particles increases. This means that the rate of collision will increase, which will cause an increase in reaction rate. However, this effect alone does not explain the very rapid increase in rate that we observe when temperature increases. There is another more important factor involved.

We saw in Section 10.6 that there is an energy barrier separating reactants from products: we call this the activation energy. Although our common fuels need to be heated above room temperature before they will start to react with oxygen (Sections 10.6 and 10.7), there are many reactions with significant activation energies which proceed at appreciable rates at room temperature. These get faster as the temperature rises. This is due to the activation energy. The explanation is as follows.

In order for a reaction to proceed, it is necessary not only for the reactant molecules to collide, but also for the colliding molecules to possess a certain minimum amount of kinetic energy so that they can reach the top of the energy barrier. Once they reach the top they easily ‘roll down the other side of the hill’ and fall apart to products (Figure 10.3). If the colliding molecules have insufficient energy, they just bounce apart and stay as reactants. Kinetic energy is energy of motion: the faster particles are moving, the higher is their kinetic energy.

In a sample of reactant molecules at room temperature, the average kinetic energy possessed by the molecules may be relatively low. However, a small fraction of the molecules will have kinetic energies very much higher than this average and some, in fact, may have enough to reach the top of the energy barrier and so these molecules will react. Because this fraction of the molecules having enough kinetic energy is small, the reaction rate is low (but still significant). If the sample is heated, not only is the average kinetic energy of the molecules increased, but also the fraction of the molecules having more than enough kinetic energy to scale the energy barrier is quite markedly increased, so that the reaction rate increases.

Figure 10.6 shows the distribution of kinetic energy for a sample of gas molecules at 300 K and at 500 K. At 300 K only a very small fraction of the molecules in the sample has kinetic energy greater than the activation energy,  $E'$  (the darker shaded area in the figure). Therefore the reaction rate is quite small. At 500 K a much greater fraction of the molecules (both shaded areas) has kinetic energy greater than  $E'$ . This means that the reaction rate increases quite markedly.

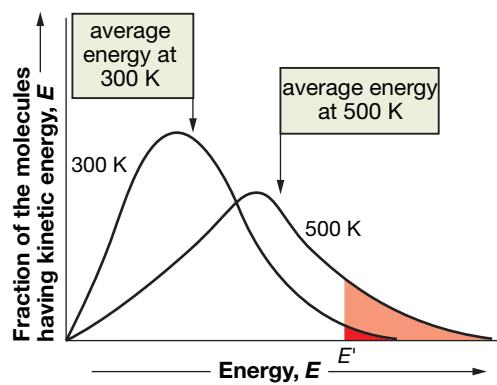


FIGURE 10.6  
Distribution of kinetic energy for particles in a gas at 300 K and at 500 K

If we compare two different reactions at the one temperature, then generally speaking the one with the greater activation energy will have the smaller reaction rate. In addition the higher the activation energy, the more rapidly the reaction rate increases as temperature increases.

Many reactions have quite small activation energies and so proceed quite rapidly at room temperature.



## Exercises

24 What is the surface area of a cube with a side of 1 cm? Suppose this was cut into 1000 cubes each with a side of 0.1 cm. What would be the total surface area of the solid now? This illustrates how crushing a lump of solid into small pieces increases the surface area.

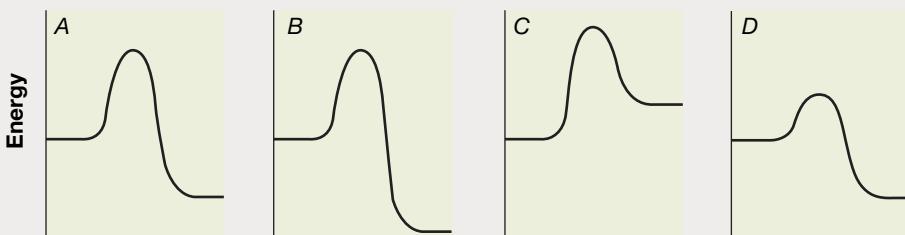
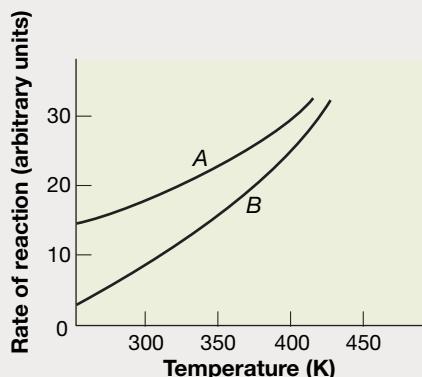
25 The diagram opposite shows how the rates of two reactions increase as temperature is increased. Which reaction, A or B:

- a has the higher rate at room temperature
- b has the higher activation energy?

Give your reasoning.

26 Energy profiles for four reactions are shown below.

- a Which reactions are endothermic and which exothermic?
- b Which reaction has the greatest activation energy and which the least?
- c Which reaction would you expect to show the greatest percentage increase in rate for a 30 K increase in temperature, and which the least? Give your reasoning.

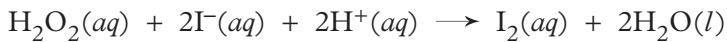


## 10.15 CATALYSIS

As was shown in Section 10.12, for many reactions the rate can be increased by using a catalyst. Catalysts may be *homogeneous* or *heterogeneous*.

### Homogeneous catalysts

**Homogeneous catalysts** work throughout the bulk of the reaction mixture (gas or solution). As mentioned above, nitrogen dioxide is a homogeneous catalyst for the reaction between sulfur dioxide and oxygen. As another example, hydrogen peroxide reacts fairly slowly with acidic iodide in aqueous solution to form iodine:



Adding about  $10^{-4}$  mol/L sodium molybdate to the reaction mixture makes the reaction very fast (complete in a few seconds). The molybdate ion,  $\text{MoO}_4^-$ , is a homogeneous catalyst for this reaction.

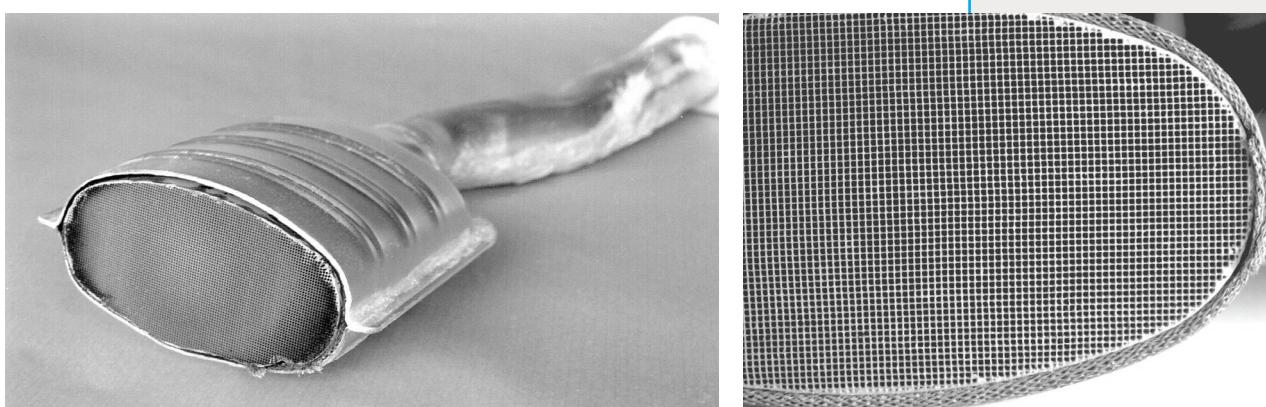
## Heterogeneous catalysts

A **heterogeneous catalyst** provides a surface on which the reaction occurs more rapidly than it does in the bulk of the reaction mixture. Finely divided nickel catalyses the reaction between alkenes and hydrogen to form alkanes (for example  $\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$ ). The nickel is a heterogeneous catalyst. The reaction occurs between gaseous hydrogen and liquid or gaseous alkene on the surface of the solid nickel particles.

Heterogeneous catalysts are of tremendous practical importance. Some examples of their use are:

- synthesis of ammonia for fertiliser from  $\text{N}_2$  and  $\text{H}_2$  (using an iron catalyst)
- sulfuric acid synthesis (using a vanadium pentoxide catalyst for the  $\text{SO}_2 + \text{O}_2$  step;  $\text{NO}_2$  is no longer used industrially)
- hydrogenation of liquid vegetable oils into semi-solid fats for use in margarine (using a nickel catalyst); the reaction adds hydrogen across some or all of the double bonds in the oil to form single bonds (the alkene  $\rightarrow$  alkane reaction mentioned above)
- catalytic cracking of hydrocarbons in oil refining to convert higher boiling point fractions into petrol (using zeolites—compounds of silicon, aluminium, oxygen and some cations)
- catalytic reforming of gasoline (using a platinum catalyst) to improve its octane rating and so eliminate the need to add lead compounds
- in catalytic converters in motor cars to remove nitric oxide, carbon monoxide and unburnt hydrocarbons from the exhaust gases (using a mixture of rhodium and platinum catalysts coated on the surface of a ceramic honeycomb block—Figure 10.7).

FIGURE 10.7  
A catalytic converter from a motor car cut open with a close-up of the ceramic honeycomb block



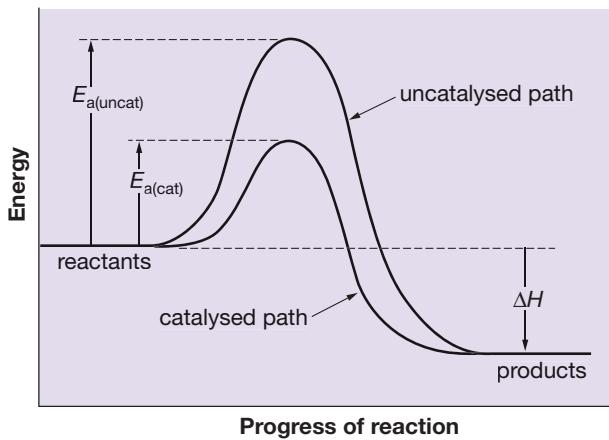
## How catalysts work

Catalysts are particularly useful when the uncatalysed reaction has a very high activation energy (and is therefore very slow). *The catalyst usually provides a pathway of lower activation energy*; this is shown schematically in Figure 10.8.

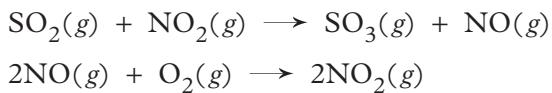
For example the direct reaction:



FIGURE 10.8  
Energy profiles for catalysed and uncatalysed paths of the one reaction



is extremely slow (very high activation energy). However, in the presence of  $\text{NO}_2$  the following two reactions occur fairly rapidly (both have relatively low activation energies):



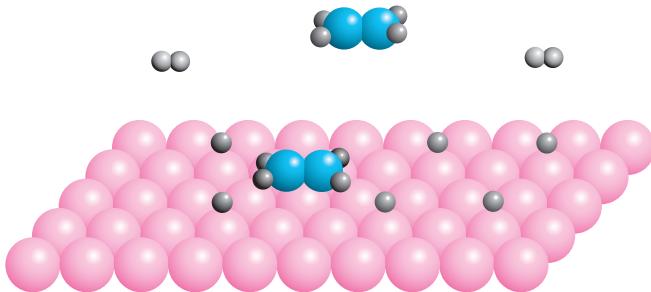
A combination of these two reactions (twice the first reaction added to the second) is effectively Reaction 10.7, and the combination occurs much more rapidly than the direct reaction. Note that there is no net consumption of  $\text{NO}_2$ .

Although catalysts decrease the activation energy of reactions, they have absolutely no effect upon  $\Delta H$ , the enthalpy change for the reaction.

Figure 10.8 shows this. The reason for this is that the reactants and products are exactly the same for both the catalysed and the uncatalysed reactions.

The way that heterogeneous catalysts work is as follows. Reactant particles (molecules or ions) **adsorb** (stick) onto the surface of the catalyst; in doing this some chemical bonds are broken or at least considerably weakened. In some reactions, gaseous or solute particles collide with these adsorbed particles with broken or weakened bonds, and so reaction occurs, with product particles desorbing (coming off) from the catalyst surface. For other reactions both reactants are adsorbed, and reaction occurs between neighbouring adsorbed reactant particles (Fig. 10.9).

FIGURE 10.9  
The reaction between ethene and hydrogen to form ethane occurring on the surface of nickel. Hydrogen adsorbs as atoms which then react with adsorbed ethene molecules.



## Biological catalysts—enzymes

Catalysis is extremely important in biological systems. **Enzymes** are biological catalysts. They are proteins that bring about important reactions in living plant and animal cells. Living organisms contain many enzymes; each catalyses one particular reaction. Amylase is a common enzyme in saliva and catalyses

the breakdown of starch to glucose. Lipase, in the stomach, catalyses the decomposition of fats to glycerol and fatty acids. A whole set of enzymes is involved in the reaction between glucose and oxygen to release the energy that cells and organisms need.

Without its particular enzyme, each of these biological reactions would proceed very slowly, if at all. Enzymes are extremely efficient catalysts in that quite small concentrations can accelerate reaction rates by factors of  $10^3$  to  $10^6$ .

## 10.16 EXPLOSIONS AND SMALL PARTICLES

Explosions occur when reactions become extremely rapid. This usually happens when there is good contact between reactant particles and when the reaction is highly exothermic with a high activation energy.

Once the reaction is initiated, it liberates energy, which heats up the reaction mixture. This makes the reaction go faster, releasing energy more quickly, so there is an extremely rapid escalation in temperature and reaction rate, causing an explosion. In order for the rate to increase in this way, there must be a good supply of oxygen available to the fuel, otherwise the fall in concentration of one reactant (oxygen) will slow down the reaction.

Large lumps of fuel such as coal rarely explode because they rapidly use up the oxygen available at their surfaces. However, very small particles of flammable material dispersed through a volume of air have great potential for causing explosions. The total surface area of the particles is large and each particle has a ready supply of oxygen available.

Consequently, one aspect of providing safe working conditions in situations where fine particles are formed is ensuring that there can be no build-up of concentrations of flammable particles. Formation of flammable dust should be minimised, and what does form must be efficiently removed from the air. It is not just dust from obvious fuels such as coal that provides a risk; it is also dust from anything that can burn—dust from handling grain such as wheat, or from processing fibres and textiles such as paper and cotton.

### Exercises

- \*27 Copy the diagram for Reaction A in Exercise 26 onto your work paper. A good catalyst is available for this reaction. Sketch the energy profile you would expect for the catalysed reaction. Clearly label the original and catalysed reactions.
- 28 A certain chemical reaction used in industry has the same rate at room temperature using a catalyst as it has at  $75^\circ\text{C}$  without a catalyst. Why is it more efficient energy-wise to carry out the reaction using the catalyst?
- \*29 a Sulfur dioxide and oxygen molecules react very slowly in the gas phase. However, solid vanadium pentoxide is a very effective heterogeneous catalyst for the reaction. Suggest a way that this reaction could be brought about by using the surface of the solid.  
b Nitrogen and hydrogen molecules do not react in the gas phase. However, they do react (to form ammonia) on an iron surface. Suggest how this reaction could be brought about by the surface.
- 30 Hydrogen peroxide decomposes to oxygen gas quite slowly at room temperature. However the reaction proceeds rapidly when finely divided solid manganese dioxide is added to the solution. How would you determine that the manganese dioxide was catalysing the reaction and not undergoing a separate reaction to produce oxygen gas?



## Important new terms

You should know the meaning of the following terms:

activation energy (p. 283)  
adsorb (p. 298)  
average rate of reaction (p. 290)  
catalyst (p. 291)  
change in enthalpy (p. 276)  
combustion (p. 274)  
endothermic reaction (p. 275)  
enthalpy (p. 276)  
enzymes (p. 298)  
exothermic reaction (p. 275)

greenhouse effect (p. 288)  
heat of reaction (p. 277)  
heterogeneous catalyst (p. 297)  
heterogeneous reaction (p. 291)  
homogeneous catalyst (p. 296)  
homogeneous reaction (p. 292)  
ignition temperature (p. 284)  
molar heat of combustion (p. 280)  
particulates (p. 287)  
rate of reaction (p. 290)  
spontaneous reactions (p. 289)

## Test yourself

- 1 Explain the meaning of each of the items in the ‘Important new terms’ section above.
- 2 Write equations for three combustion reactions.
- 3 What is the sign of the enthalpy change,  $\Delta H$ , for exothermic and endothermic reactions?
- 4 If a reaction is carried out in a test tube and the tube gets cold, is the reaction exothermic or endothermic? Explain.
- 5 What are the units for  $\Delta H$  for a chemical reaction?
- 6 In chemical energy contexts, why must we always specify the physical states of reactants and products in chemical equations?
- 7 How is  $\Delta H$  for a combustion process related to the heat of combustion?
- 8 Explain in terms of structure of molecules why energy is released in some reactions. Use a diagram for a specific reaction to illustrate your explanation.
- 9 Draw energy profiles for an exothermic and an endothermic reaction clearly labelling the activation energy and the enthalpy change for the reaction.
- 10 How does ignition temperature depend upon activation energy?
- 11 Describe four ways of igniting a fuel–air mixture.
- 12 Give an explanation of the fact that fuel–air mixtures do not react at appreciable rates at ambient temperatures.
- 13 What are the normal combustion products of hydrocarbon fuels? What undesirable products can be formed if insufficient air is used? Why are these products undesirable?
- 14 Why do we prefer fuels with low sulfur contents?
- 15 What are the three major air pollutants produced by coal burning? How do we minimise their production?

- 16** What pollutants are produced by motor-car engines? Why are they considered harmful?
- 17** Sketch the most usual type of curve for the dependence of concentration of a reactant upon time of reaction. Sketch the corresponding curve for concentration of a product.
- 18** For most reactions, does the rate increase, decrease or remain the same as reaction proceeds? Explain why.
- 19** Name two homogeneous and two heterogeneous reactions.
- 20** List three factors which influence the rate of homogeneous reactions.
- 21** Give two additional factors which affect the rate of heterogeneous reactions.
- 22** Explain why some molecules in a reactant sample can undergo reaction even though the average energy of reactant molecules is much less than the activation energy.
- 23** Explain how increasing the temperature causes reaction rate to increase.
- 24** Explain the difference between a *homogeneous catalyst* and a *heterogeneous catalyst*. Give an example of each.
- 25** In what way, if any, does a catalyst affect the activation energy and the enthalpy change for a reaction?
- 26** Why can mixtures of very small particles with air be explosive? What safety precautions are needed to avoid an explosion?

# EXTENDED RESPONSE EXAM-STYLE QUESTIONS FOR MODULE 4

For explanations about these New South Wales HSC exam-style questions, see page 84.

**MARKS**

- 1 **Explain** how photosynthesis converts solar energy into chemical energy and **evaluate** the importance of photosynthesis to life on Earth. **5**
- 2 **Discuss** the statement that fossil fuels are just stored solar energy. **4**
- 3 **Outline** the nature of single, double and triple carbon–carbon bonds: illustrate with specific examples. **6**
- 4 **Explain** why there are more compounds of carbon than of any other element (with the possible exception of hydrogen). **3**
- 5 **Describe** the structure of fullerenes and **explain** why they are considered allotropes of carbon. **4**
- 6 List common uses for diamond and graphite and relate these uses to the physical properties of the two substances. **5**
- 7 **Explain** what fractional distillation is and **outline** its use in refining crude oil. **5**
- 8 **Describe** an experiment you have performed to illustrate fractional distillation. How could this experiment be modified or extended to illustrate the process more effectively? **5**
- 9 **Explain** how certain physical properties of alkanes and alkenes arise from the nature of the intermolecular forces in these substances. **5**
- 10 **Discuss** the usefulness of IUPAC nomenclature. **3**
- 11 **Evaluate** the usefulness of the concept of functional groups. **4**
- 12 **Assess** the effectiveness of three safety precautions that are commonly used when storing liquid alkanes. **6**
- 13 **Justify** the procedures you would use for the safe storage of gaseous alkanes. **4**
- 14 **Interpret** the enthalpy change for a chemical reaction (heat of reaction) in terms of breaking and making chemical bonds. **3**
- 15 **Account** for the fact that many exothermic reactions (such as alkanes with oxygen) do not occur spontaneously at room temperature but do occur vigorously and in a self-sustaining manner at elevated temperatures. **4**
- 16 **Evaluate** the procedures that are commonly used to minimise pollution from combustion of fossil fuels. **7**
- 17 **Demonstrate** the fact that combustion reactions can be slow, rapid or explosive and **outline** conditions that favour each of these types of combustion. **6**
- 18 **Outline** an experiment you performed to **investigate** the effect of three reaction variables upon the rates of chemical reactions and **summarise** your results. **6**

- 19** Identify the factors that increase the rate of collision between reacting particles and explain how this increases the reaction rate. **5**
- 20** Assess the effectiveness of two methods that are commonly used to reduce the risk of explosions in places where fine particles tend to form and mix with air. **4**

## REVISION TEST FOR MODULE 4

MODULE  
**4**

**Total marks: 50 Suggested time: 90 minutes**

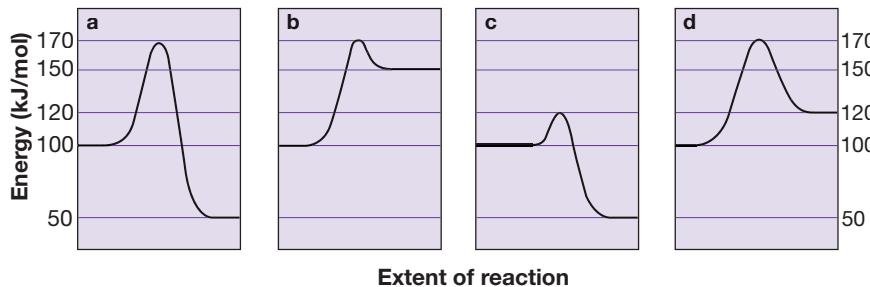
### MULTIPLE CHOICE QUESTIONS

Select the alternative **a**, **b**, **c**, or **d** which best answers the question.

- For the reaction of octane ( $\text{C}_8\text{H}_{18}$ , molecular weight 114.2) with oxygen,  $\Delta H$  is  $-5.5 \times 10^3 \text{ kJ mol}^{-1}$ . When 5.00 g octane is burnt in a plentiful supply of air (oxygen):
  - $5.5 \times 10^3 \text{ kJ}$  heat is absorbed from the surroundings
  - $2.8 \times 10^4 \text{ kJ}$  heat is released to the surroundings
  - $2.4 \times 10^2 \text{ kJ}$  heat is released to the surroundings
  - $2.4 \times 10^2 \text{ kJ}$  heat is absorbed from the surroundings
- Of the compounds below, the pair that are isomers is:
 

(W)	$\text{CH}_3\text{—CH}_2\text{—CH=CH—CH}_3$
(X)	$\text{CH}_3\text{—CH=CH—CH}_2\text{—CH}_3$
(Y)	$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_3$
(Z)	$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH=CH}_2$

  - W and X
  - X and Z
  - W and Y
  - Y and Z
- A particular chemical reaction has an enthalpy change of +50 kJ/mol and an activation energy of +70 kJ/mol. The correct energy profile for this reaction is:



- The main constituents of natural gas are:
 

<b>a</b> propane and butane	<b>c</b> propane and methane
<b>b</b> propene and hydrogen	<b>d</b> methane and ethane

- For the reaction



This means that for the reaction



a +114 kJ/mol

b -57 kJ/mol

c +57 kJ/mol

d +228 kJ/mol

- 6 Factors affecting the rate of the reaction of zinc with dilute hydrochloric acid were studied by dipping identical pieces of zinc into acid solutions of different concentrations and measuring the time required to collect particular volumes of hydrogen gas at the same temperature and pressure. The experiment with the greatest rate is the one in which:

- a 15 mL of gas was collected in 155 s  
b 10 mL of gas was collected in 270 s  
c 25 mL of gas was collected in 225 s  
d 7.5 mL of gas was collected in 180 s

- 7 A compound with the molecular formula C<sub>7</sub>H<sub>14</sub> could be:

- a an alkene      c 2-hexene  
b an alkane      d heptane

- 8 The only correct statement in the following set is:

- a Photosynthesis is an exothermic process.  
b Photosynthesis is the way that animals directly collect solar energy.  
c Photosynthesis was the original source of the energy stored in fossil fuels.  
d Photosynthesis releases large amounts of energy to plants.

- 9 The list containing substances in order of *increasing* volatility is:

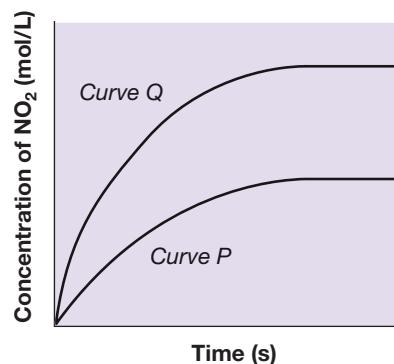
- a ethene, 2-hexene, ethane      c ethane, water, ethanol  
b butane, hexane, heptane      d octane, hexane, pentane

- 10 Dinitrogen pentoxide in carbon tetrachloride solution decomposes to form nitrogen dioxide and oxygen:



Curve P shows the production of oxygen in an experiment using a 0.50 mol/L solution of N<sub>2</sub>O<sub>5</sub> at 20°C. The results from a second experiment are shown in Curve Q. The difference between the two experiments is that in the second experiment:

- a a higher temperature was used  
b a catalyst was used  
c the reaction mixture was stirred rapidly  
d a higher concentration of N<sub>2</sub>O<sub>5</sub> was used

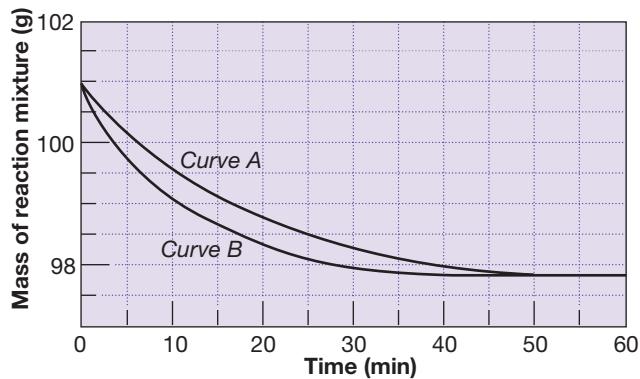


## SHORT ANSWER AND EXTENDED RESPONSE QUESTIONS

The number of marks for each part of each question is shown at the right-hand end of the question. Marks allocated are based on the HSC scale of 1 mark per 1.8 minutes.

- |   | MARKS |
|---|-------|
| <b>11 a</b> Draw the structural formula for an isomer of 2-hexene.  | 1     |
| <b>b</b> Draw the structural formula for a compound that is <i>not</i> an isomer of 2-hexene, but which contains the same functional group as 2-hexene.                                   | 1     |
| <b>c</b> Draw the structural formula and name a compound which has molecules that contain the same number of carbon atoms as 2-hexene but which belongs to a different homologous series. | 1     |

- 12** The rate of decomposition of hydrogen peroxide (to form oxygen) in the presence of manganese dioxide was studied by measuring the mass of the reaction mixture at various times after mixing the peroxide solution with the powdered  $\text{MnO}_2$  in an open beaker. In the graph below *Curve A* was obtained when 0.5 g  $\text{MnO}_2$  was added to 100 mL 2.0 mol/L hydrogen peroxide solution. In a second experiment 1.0 g  $\text{MnO}_2$  was added to a fresh 100 mL sample of the same peroxide solution and *Curve B* was obtained. In the figure, *Curve B* has been displaced 0.5 g downwards (to make it start at the same point as *Curve A*).



- a** Explain why at long reaction times there is the same loss of mass in both experiments despite the amounts of manganese dioxide being different.
- b** What do the two curves tell you about the relative rates of the reaction in the two experiments? Offer an explanation for this difference in rates.
- 13** Compare and contrast the structures of diamond and graphite and explain how the structures lead to the different physical properties of the two substances.
- 14 a** Why do we consider that there is energy stored in glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ ?
- b** How did this energy get there?

Include at least one chemical equation in your answer to this question.

- 15** Explain what is meant by *fractional distillation* of crude oil. A diagram may help. What are the major products from this process? How do they differ from one another? Give a major use for each of these products.
- 16** Disposable cigarette lighters generally contain butane,  $\text{C}_4\text{H}_{10}$ , as their fuel. One particular type contains 3.0 g butane. For butane the enthalpy change for the combustion reaction is  $-2.87 \times 10^3 \text{ kJ mol}^{-1}$ .
- a** Write an equation for the combustion of butane.
- b** If this lighter is used to heat 1.00 kg water at  $20.0^\circ\text{C}$  until all the butane has been used up, what will be the final temperature of the water? Assume that the container for the water has negligible heat capacity and that there are no heat losses. The specific heat capacity of water is  $4.2 \text{ J K}^{-1} \text{ g}^{-1}$ .
- 17 a** List two major types of pollution arising from burning fossil fuels.

**MODULE  
4**

- |   |   |
|---|---|
| Explain how or why each of these form.  | 2 |
| <b>b</b> For the pollutants listed in (a) explain how their production or release to the atmosphere can be minimised.   | 2 |
| <b>18</b> Describe an experiment that you have performed to determine whether particular reactions are exothermic or endothermic. Include equations for two of the reactions studied. | 5 |
| <b>19 a</b> For many chemical reactions the rate of reaction increases very rapidly as temperature increases. Interpret this rapid rise in terms of the energy of reactant particles. | 3 |
| <b>b</b> Explain how catalysts increase the rates of chemical reactions.  | 2 |

## MODULE 4 AND THE NEW SOUTH WALES HSC SYLLABUS

This section allows you to check that *Conquering Chemistry* has covered all necessary material for Module 4 of the New South Wales HSC Preliminary Course syllabus.

### Syllabus content

The following table lists (for Module 4) the items from the *students learn to* column of the HSC syllabus and shows where they are treated in *Conquering Chemistry Preliminary Course (CCPC)*.

Location of HSC syllabus Preliminary Course material in *Conquering Chemistry* for Module 4

Syllabus reference	Sections where found in CCPC
Students learn to:	
<b>8.5.1 Living organisms make compounds which are important sources of energy</b>	
■ outline the role of photosynthesis in transforming light energy to chemical energy and recall the raw materials for this process	9.2
■ outline the role of the production of high energy carbohydrates from carbon dioxide as the important step in the stabilisation of the sun's energy in a form that can be used by animals as well as plants	9.2
■ identify the photosynthetic origins of the chemical energy in coal, petroleum and natural gas	9.3
<b>8.5.2 There is a wide variety of carbon compounds</b>	
■ identify the position of carbon in the Periodic Table and describe its electron configuration	9.4
■ describe the structure of the diamond and graphite allotropes and account for their physical properties in terms of bonding	9.5
■ identify that carbon can form single, double or triple covalent bonds with other carbon atoms	9.6, 9.7

Syllabus reference	Sections where found in CCPC
Students learn to:	
<ul style="list-style-type: none"> <li>■ explain the relationship between carbon's combining power and ability to form a variety of bonds and the existence of a large number of carbon compounds</li> </ul>	9.7
<b>8.5.3 A variety of carbon compounds are extracted from organic sources</b>	
<ul style="list-style-type: none"> <li>■ describe the use of fractional distillation to separate the components of petroleum and identify the uses of each fraction obtained</li> </ul>	9.8
<ul style="list-style-type: none"> <li>■ identify and use the IUPAC nomenclature for describing straight-chained alkanes and alkenes from C<sub>1</sub> to C<sub>8</sub></li> </ul>	9.9, 9.10
<ul style="list-style-type: none"> <li>■ compare and contrast the properties of alkanes and alkenes C<sub>1</sub> to C<sub>8</sub> and use the term 'homologous series' to describe a series with the same functional group</li> </ul>	9.9, 9.10, 9.11
<ul style="list-style-type: none"> <li>■ explain the relationship between the melting point, boiling point and volatility of the above hydrocarbons, and their non-polar nature and intermolecular forces (dispersion forces)</li> </ul>	9.9, 9.10
<ul style="list-style-type: none"> <li>■ assess the safety issues associated with the storage of alkanes C<sub>1</sub> to C<sub>8</sub> in view of their weak intermolecular forces (dispersion forces)</li> </ul>	9.14
<b>8.5.4 Combustion provides another opportunity to examine the conditions under which chemical reactions occur</b>	
<ul style="list-style-type: none"> <li>■ describe the indicators of chemical reactions</li> </ul>	3.1 and introduction to Chapter 10
<ul style="list-style-type: none"> <li>■ identify combustion as an exothermic chemical reaction</li> </ul>	Introduction to Chapter 10, 10.1
<ul style="list-style-type: none"> <li>■ outline the changes in molecules during chemical reactions in terms of bond-breaking and bond-making</li> </ul>	10.5
<ul style="list-style-type: none"> <li>■ explain that energy is required to break bonds and energy is released when bonds are formed</li> </ul>	10.5
<ul style="list-style-type: none"> <li>■ describe the energy needed to begin a chemical reaction as activation energy</li> </ul>	10.6
<ul style="list-style-type: none"> <li>■ describe the energy profile diagram for both endothermic and exothermic reactions</li> </ul>	10.6
<ul style="list-style-type: none"> <li>■ explain the relationship between ignition temperature and activation energy</li> </ul>	10.7
<ul style="list-style-type: none"> <li>■ identify the sources of pollution which accompany the combustion of organic compounds and explain how these can be avoided</li> </ul>	10.8
<ul style="list-style-type: none"> <li>■ describe chemical reactions by using full balanced chemical equations to summarise examples of complete and incomplete combustion</li> </ul>	10.8
<b>8.5.5 The rate of energy release is affected by factors such as types of reactants</b>	
<ul style="list-style-type: none"> <li>■ describe combustion in terms of slow, spontaneous and explosive reactions and explain the conditions under which these occur</li> </ul>	10.10

Syllabus reference	Sections where found in CCPC
Students learn to:	
■ explain the importance of collisions between reacting particles as a criterion for determining reaction rates	10.13
■ explain the relationship between temperature and the kinetic energy of particles	10.14
■ describe the role of catalysts in chemical reactions, using a named industrial catalyst as an example	10.15
■ explain the role of catalysts in changing the activation energy and hence the rate of chemical reaction	10.15

## Compulsory experiments

The table below lists the compulsory experiments for Module 4 (from the right-hand column of the syllabus), along with places where you can find procedures for performing them (in *CCPC BLM*) and the location of relevant information in *CCPC*.

*CCPC* is an abbreviation for this book *Conquering Chemistry Preliminary Course*.

*CCPC BLM* is *Conquering Chemistry Preliminary Course Blackline Masters* by Debra Smith, McGraw-Hill, Sydney, 2003.

### Information about compulsory experiments for Module 4

Experiment	Location in CCPC BLM	Related material in CCPC
1 Build models to show differences in the arrangement of atoms in diamond, graphite and fullerenes	Module 4 Worksheet 2 (page 164)	Sections 9.4 and 9.5
2 Use fractional distillation to separate the components of a mixture	Module 4 Worksheet 4 (page 170) <sup>†</sup>	Sections 1.10 (including Figure 1.6) and 9.8
3 Measure the change in mass when wood is burned in an open container	Module 4 Worksheet 8 (page 189)	
4 Observe and describe examples of endothermic and exothermic reactions	Module 4 Worksheet 12 (page 199)	Section 10.1 Revision test question 18
5 Determine the effects upon reaction rate of changing temperature, concentration and size of solid particles and of adding a catalyst	Module 4 Worksheet 14, 15, 16 (pages 206, 210, 214)	Section 10.12 Exam-style question 18
<sup>†</sup> Not directly fractional distillation, but can easily be modified to illustrate fractional distillation by doing three successive distillations, collecting 40, 20 and 10 mL of distillate.		

### Other items in the student activity (right-hand) column

The table below lists (in abbreviated form) the non-experimental items in the student activity (right-hand) column of the syllabus and indicates where in *Conquering Chemistry* relevant information is located.

## Location of material for other Module 4 activities

Syllabus item	Relevant material in CCPC
<b>8.5.1</b>	■ process and present information ... on the range of compounds found in either coal, petroleum or natural gas and on the location of deposits of the selected fossil fuel in Australia For investigation box on page 268
<b>8.5.2</b>	<ul style="list-style-type: none"> <li>■ Experiment 1 (see above)</li> <li>■ process ... uses of diamond and graphite and relate their uses to their physical properties</li> </ul> Sections 9.4 and 9.5 Exam-style question 6
	<ul style="list-style-type: none"> <li>■ identify data, and choose resources ... to model the formation of single, double and triple bonds in simple carbon compounds</li> </ul> Sections 9.6 and 9.7, particularly Table 9.5
<b>8.5.3</b>	<ul style="list-style-type: none"> <li>■ Experiment 2 (see above)</li> <li>■ plan... model the structure of alkanes and alkenes ...</li> </ul> Figures 9.5 and 9.6 and the photos in Figure 9.10 may help
	<ul style="list-style-type: none"> <li>■ process... to identify safety issues associated with the storage of alkanes</li> </ul> Section 9.14
<b>8.5.4</b>	<ul style="list-style-type: none"> <li>■ Experiment 3 (see above)</li> <li>■ analyse a burning candle to identify the changes of state involved in combustion</li> </ul> Photograph and For Investigation box on page 288
	<ul style="list-style-type: none"> <li>■ Experiment 4 (see above)</li> </ul>
<b>8.5.5</b>	<ul style="list-style-type: none"> <li>■ Experiment 5 (see above)</li> <li>■ process ... investigate the conditions under which explosions occur and relate these to the importance of collisions ...</li> </ul> Section 10.16
	<ul style="list-style-type: none"> <li>■ analyse ...to relate the conditions under which explosions occur to the need for safety in work environments where fine particles mix with air</li> </ul> Section 10.16
	<ul style="list-style-type: none"> <li>■ analyse information ... to develop models to simulate the role of catalysts in changing the rate ...</li> </ul> Section 10.15, particularly Figure 10.10

## Prescribed focus areas

The five prescribed focus areas of the syllabus are listed on page 94.

The material of Module 4 (in this book and in the syllabus) relates predominantly to Areas 2 and 3, the nature and practice of chemistry and applications and uses of chemistry. There is some scope for discussing implications for society and the environment (Area 4) in treating pollution from burning fossil fuels and the likelihood of running out of fossil fuels and possible alternative sources of energy, though the latter topics are not really in the syllabus. There is very little scope in this module for discussing the history of chemistry (Area 1) and, apart from the production and possible uses of the fullerenes, very limited opportunities to discuss current issues, research and development.