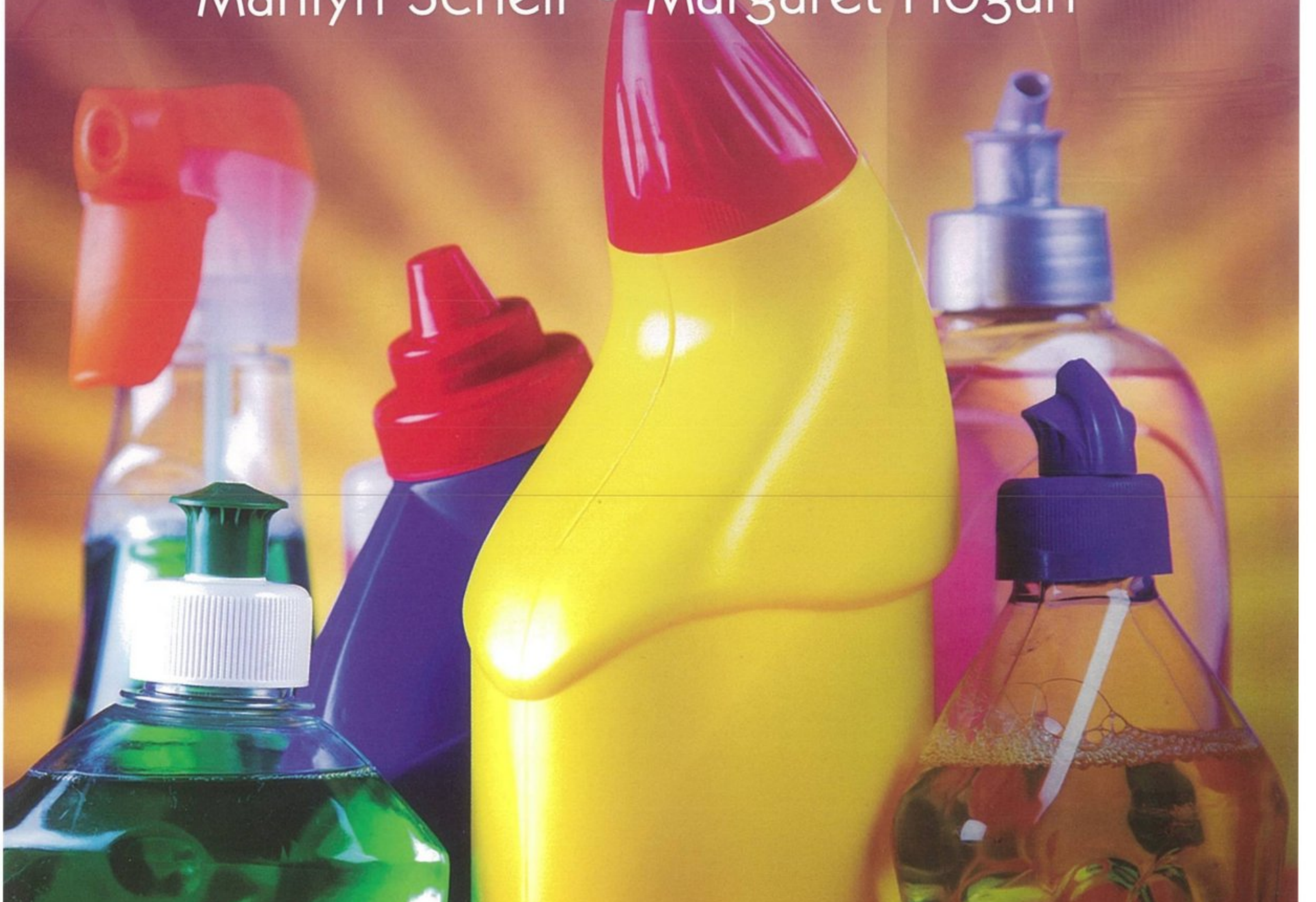
SURFING

# NSW CHEMISTRY 7&8

**Module 7** Organic Chemistry
**Module 8** Applying Chemical Ideas

Marilyn Schell • Margaret Hogan



S
Science Press

First published 2018

Science Press
Bag 7023 Marrickville NSW 1475 Australia
Tel: (02) 9516 1122 Fax: (02) 9550 1915
sales@sciencepress.com.au
www.sciencepress.com.au

# Contents

## Module 7 Organic Chemistry

### Nomenclature

**INQUIRY QUESTION**

How do we systematically name organic chemical compounds?

### Hydrocarbons

**INQUIRY QUESTION**

How can hydrocarbons be classified based on their structure and reactivity?

### Products Of Reactions Involving Hydrocarbons

**INQUIRY QUESTION**

What are the products of reactions of hydrocarbons and how do they react?

### Alcohols

**INQUIRY QUESTION**

How can alcohols be produced and what are their properties?

### Reactions Of Organic Acids and Bases

**INQUIRY QUESTION**

What are the properties of organic acids and bases?

### Polymers

**INQUIRY QUESTION**

What are the properties and uses of polymers?

# Module 8 Applying Chemical Ideas

## Analysis Of Inorganic Substances

**INQUIRY QUESTION**

How are the ions present in the environment identified and measured?

## Analysis Of Organic Substances

**INQUIRY QUESTION**

How is information about the reactivity and structure of organic compounds obtained?

## Chemical Synthesis and Design

**INQUIRY QUESTION**

What are the implications for society of chemical synthesis and design?

# Introduction

This book covers the Chemistry content specified in the NSW Chemistry Stage 6 Syllabus. Sample data has been included for suggested experiments to give you practice to reinforce practical work in class.

Each book in the *Surfing* series contains a summary, with occasional more detailed sections, of all the mandatory parts of the syllabus, along with questions and answers.

All types of questions – multiple choice, short response, structured response and free response – are provided. Questions are written in exam style so that you will become familiar with the concepts of the topic and answering questions in the required way.

Answers to all questions are included.

A topic test at the end of the book contains an extensive set of summary questions. These cover every aspect of the topic, and are useful for revision and exam practice.

# Words To Watch

**account, account for** State reasons for, report on, give an account of, narrate a series of events or transactions.

**analyse** Interpret data to reach conclusions.

**annotate** Add brief notes to a diagram or graph.

**apply** Put to use in a particular situation.

**assess** Make a judgement about the value of something.

**calculate** Find a numerical answer.

**clarify** Make clear or plain.

**classify** Arrange into classes, groups or categories.

**comment** Give a judgement based on a given statement or result of a calculation.

**compare** Estimate, measure or note how things are similar or different.

**construct** Represent or develop in graphical form.

**contrast** Show how things are different or opposite.

**create** Originate or bring into existence.

**deduce** Reach a conclusion from given information.

**define** Give the precise meaning of a word, phrase or physical quantity.

**demonstrate** Show by example.

**derive** Manipulate a mathematical relationship(s) to give a new equation or relationship.

**describe** Give a detailed account.

**design** Produce a plan, simulation or model.

**determine** Find the only possible answer.

**discuss** Talk or write about a topic, taking into account different issues or ideas.

**distinguish** Give differences between two or more different items.

**draw** Represent by means of pencil lines.

**estimate** Find an approximate value for an unknown quantity.

**evaluate** Assess the implications and limitations.

**examine** Inquire into.

**explain** Make something clear or easy to understand.

**extract** Choose relevant and/or appropriate details.

**extrapolate** Infer from what is known.

**hypothesise** Suggest an explanation for a group of facts or phenomena.

**identify** Recognise and name.

**interpret** Draw meaning from.

**investigate** Plan, inquire into and draw conclusions about.

**justify** Support an argument or conclusion.

**label** Add labels to a diagram.

**list** Give a sequence of names or other brief answers.

**measure** Find a value for a quantity.

**outline** Give a brief account or summary.

**plan** Use strategies to develop a series of steps or processes.

**predict** Give an expected result.

**propose** Put forward a plan or suggestion for consideration or action.

**recall** Present remembered ideas, facts or experiences.

**relate** Tell or report about happenings, events or circumstances.

**represent** Use words, images or symbols to convey meaning.

**select** Choose in preference to another or others.

**sequence** Arrange in order.

**show** Give the steps in a calculation or derivation.

**sketch** Make a quick, rough drawing of something.

**solve** Work out the answer to a problem.

**state** Give a specific name, value or other brief answer.

**suggest** Put forward an idea for consideration.

**summarise** Give a brief statement of the main points.

**synthesise** Combine various elements to make a whole.

SURFING

# NSW CHEMISTRY 7&8

## Module 7

# ORGANIC CHEMISTRY

## CONTENT FOCUS

In this module you will:

- Focus on the principles and applications of chemical synthesis in organic chemistry, including pharmaceuticals, fuels and polymers.
- Investigate the naming, structure and classification of organic chemicals.
- Investigate the characteristic chemical properties and reactions of classes of organic compounds based on their functional groups.
- Consider the primary, secondary and tertiary structures of organic materials and how this affects properties such as strength, density and biodegradability of proteins, carbohydrates and synthetic polymers.

# 1 The Element Carbon

Carbon is a non-metal element. Its atomic number is 6 because it contains 6 positively charged protons in the nucleus of each atom. There are also 6 negatively charged electrons orbiting the nucleus, with two electrons in the first shell and four electrons in the outer shell. So the electron configuration of carbon is 2.4 and it has a valency of 4.

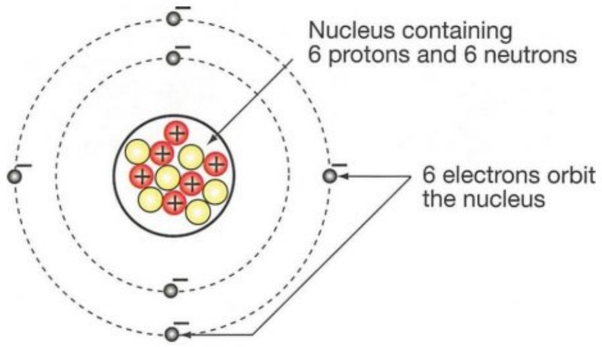


**Figure 1.1** Atom of carbon-12.

Carbon is a special element because of the millions of compounds it can form and because carbon compounds are important constituents of living as well as non-living things.

The huge number of carbon compounds in existence is due largely to its ability to form strong bonds with other carbon atoms, making **chains and rings**, and also the stable bonds it can form with other elements.

## Bonding of carbon atoms

Carbon atoms bond to each other by **sharing electrons**, forming strong covalent **carbon-carbon bonds**. You saw this last year when you studied carbon allotropes – diamond, graphite and fullerenes.

You will recall that carbon-carbon bonds can be single, double or triple bonds. Single bonds are the most common.

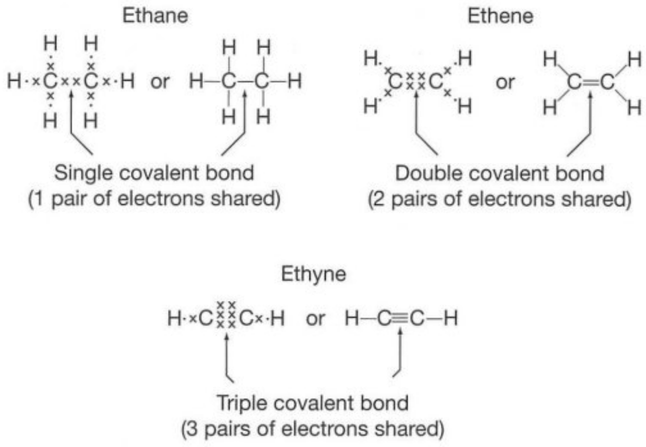


**Figure 1.2** Single, double and triple C–C bonds.

*Note*: Although the electrons in all atoms are identical, they are sometimes illustrated as crosses and dots as in Figure 1.2 to show that the two electrons in a bond come from different atoms.

These are all strong covalent bonds and they increase in strength from single C–C bonds to double C=C bonds, with the shortest and strongest being triple C≡C bonds.

**Table 1.1** Bond energies between carbon atoms.

| Bond | Bond energy (kJ $mol^{-1}$) |
|---|---|
| Single bond: C–C | 348 |
| Double bond: C=C | 614 |
| Triple bond: C≡C | 839 |

Carbon also bonds with other elements. It forms strong **covalent bonds with hydrogen atoms**. These are considered to be non-polar bonds as the electronegativity difference between the atoms involved is very small.

Carbon also forms stable **polar bonds with oxygen, nitrogen, phosphorus and the halogens**.

You already know that the strength of these bonds varies with such factors as length of bonds (strength increases as length decreases) and differences in electronegativity (strength increases as electronegativity difference increases). For example, bond energy between carbon and the halogens decreases down the halogen group.

**Table 1.2** Bond energies between carbon and some other atoms. (These vary slightly in different sources.)

| Bond | Bond energy (kJ $mol^{-1}$) |
|---|---|
| C–H | 414 |
| C–O | 358 |
| C–N | 305 |
| C–F | 485 |
| C–Cl | 339 |
| C–I | 238 |

## QUESTIONS

1. (a) Outline the position of carbon on the periodic table and state its electron configuration.
   (b) How many valence electrons are present in each atom of carbon?
2. List four factors that contribute to the huge number of carbon compounds that exist.
3. (a) Describe the type of bonding that occurs between carbon atoms.
   (b) Distinguish between single, double and triple carbon-carbon bonds.
4. (a) Name three other elements that bond to carbon atoms.
   (b) Identify two factors than can determine the strength of the bonds between atoms of carbon and other elements.

# 2 Organic Chemistry

**Organic chemistry** is the chemistry of carbon and its compounds. Carbon compounds are involved in our everyday life – the food we eat, fuels we burn, our own structure, and the polymers that we use to make everything from clothing to cars – all of these are carbon compounds.

**Figure 2.1** Carbon fibre is used in car bodies.

Organic compounds make up over 80% of all known compounds and this does not include compounds such as carbon oxides and carbonates. Organic chemicals include the homologous series of alkanes and alkenes that you learned about in year 11 as well as many other groups of carbon compounds which are involved in everyday life such as alcohols, proteins, fats, carbohydrates, polymers and many more.

You will recall that alkanes and alkenes have functional groups (C–C for alkanes, C=C for alkenes). In this section you will be looking at more series of organic molecules that have other functional groups attached – the alcohols, carboxylic acids, esters, amines and amides. You will be seeing how the molecular structure of organic compounds and also the presence of functional groups are related to their properties. Later you will be looking at structures of proteins, carbohydrates and polymers.

The two scientists most influential in the initial development of carbon chemistry were a German chemist **August Kekulé** (1829-1896) and a Scottish chemist **Archibald Scott Couper** (1831-1892). Based on their observations of reactions, these two chemists independently developed a theory of how carbon formed bonds. They proposed that carbon was tetravalent (valency of 4) and described carbon atoms linking to each other, as well as to other atoms, and forming chains and rings.

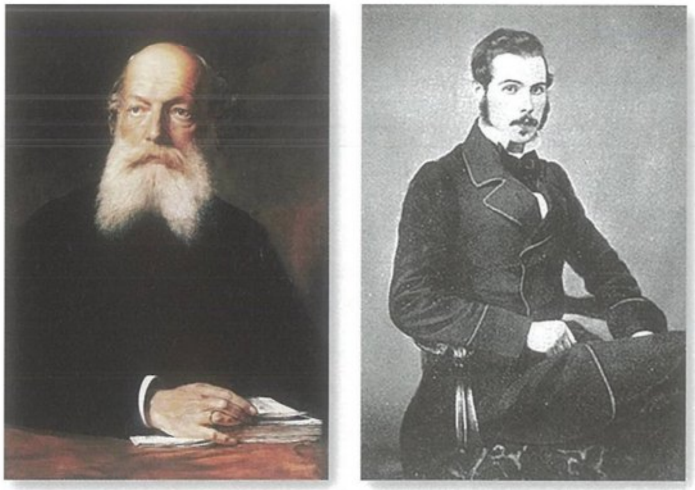


**Figure 2.2** August Kekulé and Archibald Couper.

Their work represents the beginning of the concept of bonds between the elements in a compound, and they developed their ideas before anything was known about the attractions between atoms forming bonds.

Today the atomic model and models of bonding are used to explain the structure and properties of both elements and compounds. Models and theories of the structure of molecules have developed using evidence from a range of sources. And they can be used to explain and predict the properties of substances.

Data from analytical techniques such as mass spectrometry and crystallography have given us a deeper understanding of bonding and the chemical structure of carbon compounds and we classify organic molecules according to the functional groups that they contain. Conversely, if we know the formula of an organic compound then we can predict its chemical behaviour based on what we know about the behaviour of the functional groups it contains.

## Functional groups

A **functional group** is a specific group of atoms, within a molecule, that is responsible for the chemical reactions of that molecule.

Functional groups are attached to the hydrocarbon 'backbone' of organic molecules. Figure 2.3 gives some examples of functional groups in organic compounds. You need to learn these.

The hydrocarbon backbone of organic compounds is represented by R in general formulas. An R can be added to the functional groups to indicate the position of any attached hydrocarbon chain. If there is more than one hydrocarbon chain, the chains are shown as $R^1$, $R^2$, $R^3$. Alternatively dashes may be used, e.g. $R'$, $R''$, $R'''$.

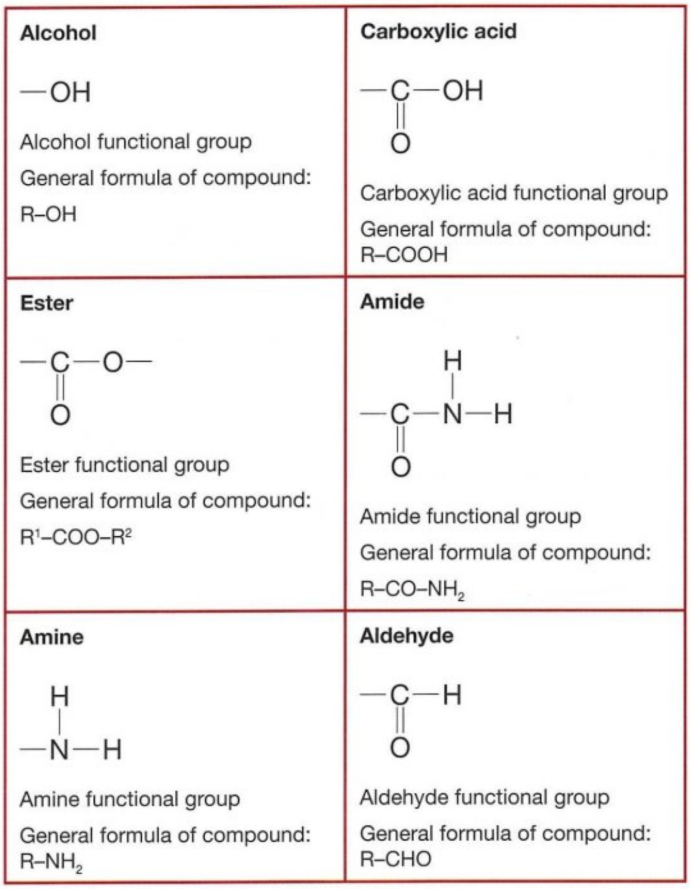


**Figure 2.3** Functional groups.

## Homologous series

Organic compounds containing only carbon and hydrogen atoms are called **hydrocarbons**. Each family of hydrocarbons is called an **homologous series**.

Homologous means that all members of a series have something in common – they share a **general formula** and a special feature or **functional group** (a grouping of atoms that is common to all members of that series).

There are three homologous series of hydrocarbons:

- Alkanes have only single –C–C– bonds.
- Alkenes contain at least one double –C=C– bond.
- Alkynes contain one or more triple –C≡C– bond.

**Table 2.1** Three homologous series.

| Homologous series | General formula | Functional group |
|---|---|---|
| Alkane | $C_nH_{2n+2}$ | –C–C–<br>Single bonded carbon atoms |
| Alkene | $C_nH_{2n}$ | –C=C–<br>Double bonded carbon atoms |
| Alkyne | $C_nH_{2n-2}$ | –C≡C–<br>Triple bonded carbon atoms |

## Alkyl group

Another term you should recall is an **alkyl group**. This refers to a hydrocarbon chain with the general formula $C_nH_{2n+1}$. An example is a methyl group (–$CH_3$). This is a fragment of a methane molecule ($CH_4$). Alkyl groups do not exist on their own, they are branches of carbon molecules.

**Table 2.2** Alkyl groups.

| Alkane | Formula | Alkyl group | Formula |
|---|---|---|---|
| Methane | $CH_4$ | Methyl group | $-CH_3$ |
| Ethane | $CH_3CH_3$ | Ethyl group | $-CH_2CH_3$ |
| Propane | $CH_3CH_2CH_3$ | Propyl group | $-CH_2CH_2CH_3$<br>or $-C_3H_7$ |

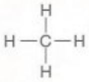
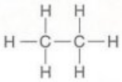
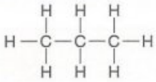
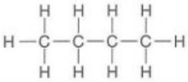
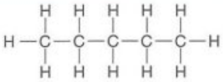
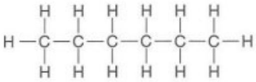
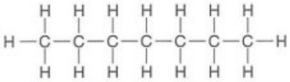
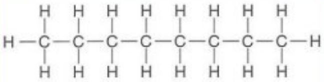
## QUESTIONS

1. (a) Define organic chemistry.
   (b) Name five examples of organic compounds.
2. Identify two chemists influential in the initial development of carbon chemistry.
3. (a) Define a functional group.
   (b) Recall the functional group for an alkene, an alcohol and a carboxylic acid.
4. What does IUPAC stand for?
5. (a) What is meant by a general formula?
   (b) Distinguish between the general formula for an alkane and an alkene.
6. What is meant by an homologous series? Include an example in your answer.
7. (a) What is meant by an alkyl group?
   (b) Distinguish between butane and butyl.
8. Check your knowledge with this quick quiz.
   (a) Hydrocarbons with single C–C bonds are called (alkanes/alkenes).
   (b) The stem (prefix) of a carbon compound with four carbon atoms would be named .......................... .
   (c) The carbon atom attached to a functional group is numbered so that it has the (lowest/highest) possible number.
   (d) State the general formula for an alkane.
   (e) The symbol R–OH is the general formula for an .......................... .
   (f) Which part of the name of a compound tells you the functional group present?
   (g) What is the stem (prefix) of an alkane with two carbon atoms present?

# 3 Hydrocarbons – Alkanes

The following table shows the first eight alkanes.

**Table 3.1** Alkanes.

| Name of alkane | Molecular formula | Structural formula |
|---|---|---|
| Methane | $CH_4$ |  |
| Ethane | $C_2H_6$ |  |
| Propane | $C_3H_8$ |  |
| Butane | $C_4H_{10}$ |  |
| Pentane | $C_5H_{12}$ |  |
| Hexane | $C_6H_{14}$ |  |
| Heptane | $C_7H_{16}$ |  |
| Octane | $C_8H_{18}$ |  |

- Molecules increase in size by a $CH_2$ grouping each step down a series. General formula $C_nH_{2n+2}$.
- Alkanes are saturated hydrocarbons – they contain only single carbon-carbon bonds.
- Alkanes are described as non-polar as there is no net charge on each molecule.
- Intramolecular bonds (within the molecule) are strong covalent bonds.
- Intermolecular bonds (between molecules) are weak dispersion forces. These are broken when the alkane changes state (melts or boils). C1 to C4 have the lowest boiling points. Larger molecules have higher boiling points because dispersion forces increase as the mass of the molecule increases.
- At 25°C and 100 kPa pressure, alkanes from C1 to C4 are gases, C5 to C20 are liquids and those with larger molecules are soft solids.

## Naming alkanes

Carbon compounds are named systematically using IUPAC naming. IUPAC stands for the International Union of Pure and Applied Chemistry.

- The prefix or stem of the name indicates the number of carbon atoms that form the longest continuous chain. For example, meth– $C_1$, eth– $C_2$, prop– $C_3$, but– $C_4$, pent– $C_5$, hex– $C_6$, hept– $C_7$, oct– $C_8$.
- The **end of the name (suffix)** indicates the series to which the compound belongs. For example, ... ane indicates an alkane with single C–C bonds.

## Cyclohexane

Some carbon compounds exist as ring structures. An example is cyclohexane, which is a cycloalkane with molecular formula $C_6H_{12}$.

**Cyclohexane** is a clear, colourless, flammable liquid which is used as a solvent and in the manufacture of nylon.

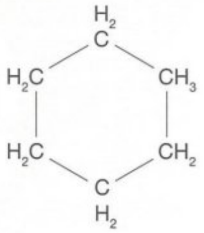


**Figure 3.1** Cyclohexane.

## Alkanes as fuels

The most common **fuels** are alkanes, derived from petroleum and summarised below.

**Table 3.2** Alkanes as fuels.

| | |
|---|---|
| Natural gas<br> | Mostly methane (75% to 90%), with small amounts of ethane (5% to 10%), propane (2% to 7%) and butane (3% to 6%). It can also contain nitrogen, water vapour, carbon dioxide and sometimes hydrogen sulfide. |
| LPG<br> | LPG is liquefied petroleum gas and it contains propane and/or butane. LPG is used as a fuel in heating appliances, cooking and in vehicles. It is also used as an aerosol propellant. LPG is heavier than air, so leaks will flow along the floor and settle in low spots. |
| Petrol, kerosene and diesel<br> | Used in industry and for transport. These are mixtures of carbon compounds, mostly alkanes. The composition varies, but petrol for cars is made mostly of alkanes from about C4 to C12, kerosene and aviation fuel from C9 to C18. |
| Liquefied butane<br> | Used for cigarette lighters and camp stoves and as a propellant and refrigerant. It is a gas at room temperature but is easily liquefied under pressure. |

## Safety issues associated with the storage of alkanes

The **weak intermolecular forces between molecules** of alkanes means that they have **low boiling points**. This makes them volatile.

**Volatile** substances turn to a gas easily and tend to have a high pressure of vapour above their liquid surface. Often their flash points are low, sometimes even lower than room temperature. A low flash point means they can be ignited by a flame at a low temperature. Because they are easily ignited, they often form explosive mixtures with air or oxygen.

These fuels must be **handled, transported and stored with care**, taking precautions such as the following.

- Store at low temperatures.
- Store in well-ventilated areas to prevent explosive fumes building up.
- Keep naked flames and sparks away.
- Have suitable fire extinguishers available.
- Use sturdy containers and check regularly for leaks in cylinders, pipes and valves.
- Keep containers of liquid fuels full to prevent the build-up of vapours.
- Do not inhale their vapours as some are toxic and/or carcinogenic.

Table 3.3 summarises some precautions needed when dealing with specific alkanes.

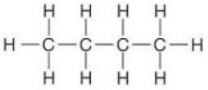
**Table 3.3** Precautions for using some alkanes.

| Hydrocarbons | Precautions |
|---|---|
| Methane and ethane | Flammable gases. Store in high pressure cylinders in cool places. Check valves and cylinders often. Small quantities of smelly chemical added to detect leaks. |
| Propane and butane | Flammable gases stored as liquids, under low pressure, in steel cylinders. Store and use in ventilated areas. Inspect cylinders and valves regularly. |
| Kerosene, petrol and diesel | Volatile, flammable liquid fuels. Store in metal tins with lids, away from flames and sparks. Use outside, explosive fuel/air mixtures form easily. |

**Figure 3.1** Petrol pumps on fire.

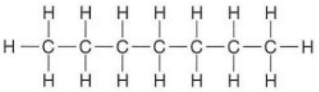
## QUESTIONS

1. Draw structural and semi-structural formulas for:
   (a) Propane.
   (b) Octane.
   (c) Methane.
2. Write molecular formulas for:
   (a) Ethane.
   (b) Pentane.
   (c) Hexane.
3. Name the following compounds.
   (a)



$$\begin{array}{ccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

   (b)



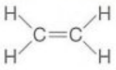
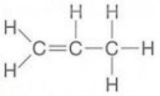
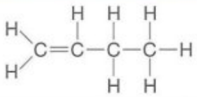
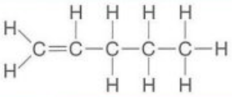
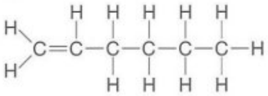
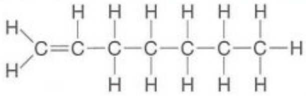
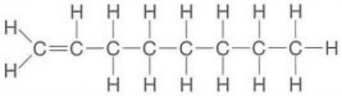
$$\begin{array}{ccccccccccccccc} & & H & & H & & H & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & H & & H & & \end{array}$$

4. (a) State the general formula for an alkane.
   (b) Identify three alkanes that occur naturally as gases.
5. (a) Justify the application of the term 'homologous series' to alkanes.
   (b) Describe how you have modelled the structure of alkanes. Use a diagram to show one model of a named alkane.
   (c) Draw a diagram of two molecules of ethane and label them to show intramolecular covalent bonds and intermolecular dispersion forces.

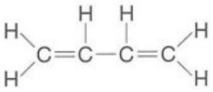
# 4 Hydrocarbons – Alkenes

**Alkenes** are an homologous series of hydrocarbons with the general formula $C_nH_{2n}$. Each alkene has a **carbon-carbon double bond**, so alkenes are described as **unsaturated**. The double bond makes alkenes **more reactive** than alkanes.

**Table 4.1** The first seven alkenes.

| Name | Molecular formula | Structural formula |
|---|---|---|
| Ethene | $C_2H_4$ |  |
| Propene | $C_3H_6$ |  |
| But-1-ene | $C_4H_8$ |  |
| Pen-1-tene | $C_5H_{10}$ |  |
| Hex-1-ene | $C_6H_{12}$ |  |
| Hept-1-ene | $C_7H_{14}$ |  |
| Oct-1-ene | $C_8H_{16}$ |  |

- Notice that methene does not exist. You cannot have a double bond between two carbon atoms if the molecule only contains one carbon atom.
- If two double bonds are present in a hydocarbon, it is called a diene, for example buta-1,3-diene.



## Uses of alkenes

Because alkenes are more reactive than alkanes they are widely used in industry. For example:

**Ethene** (ethylene) is widely used in the petrochemical industry, in the manufacture of such things as polymers, cosmetics, detergents, brake fluid and antifreeze.

**Propene** is used in the manufacture of polypropylene, glycerine and nitroglycerine.

## Cycloalkenes

Alkenes can form cyclic compounds such as cyclohexene. Cyclohexene is a clear, colourless liquid which is insoluble in water and less dense than water.

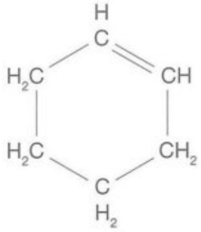
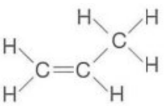


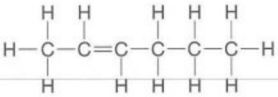
**Figure 4.1** Cyclohexene ($C_6H_{10}$).

## QUESTIONS

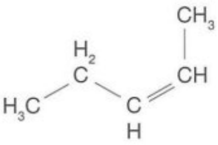
1. (a) State the general formula for an alkene.
   (b) Use this general formula to determine the molecular formula of:
      (i) An alkene with 11 carbon atoms per molecule.
      (ii) An alkene with 34 hydrogen atoms per molecule.
   (c) Identify the functional group for alkenes.
   (d) Are alkenes saturated or unsaturated compounds?
2. Name the following alkenes.
   (a)



   (b)



   (c) $C_6H_{12}$
   (d)



3. Write molecular, semi-structural (condensed) and structural formulas for the following compounds.
   (a) Prop-2-ene.
   (b) But-1-ene.
   (c) Hept-3-ene.
   (d) Hex-3-ene.

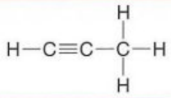
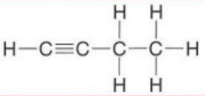
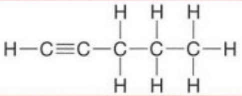
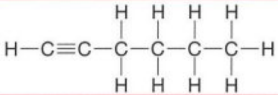
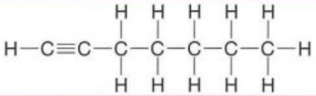
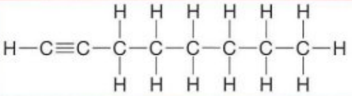
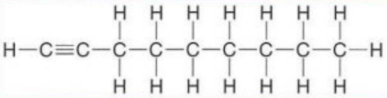
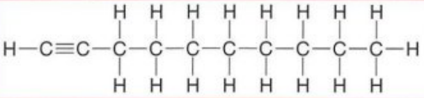
# 5 Hydrocarbons – Alkynes

**Alkynes** are a homologous series of hydrocarbons with the general formula $C_nH_{2n-2}$. Each alkyne has one or more **carbon-carbon triple bonds**.

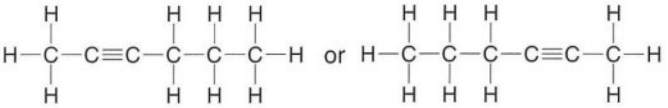
Alkynes are described as **unsaturated** because of the presence of triple bonds and, like alkenes, they are **more reactive** than alkanes.

The following table shows the first nine alkynes. Notice methyne does not exist.

Table 5.1 Alkynes.

| Name | Molecular formula | Structural formula |
|---|---|---|
| Ethyne | $C_2H_2$ | $H-C\equiv C-H$ |
| Propyne | $C_3H_4$ |  $H-C\equiv C-\overset{H}{\underset{H}{C}}-H$ |
| Butyne | $C_4H_6$ |  $H-C\equiv C-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$ |
| Pentyne | $C_5H_8$ |  $H-C\equiv C-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$ |
| Hexyne | $C_6H_{10}$ |  $H-C\equiv C-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$ |
| Heptyne | $C_7H_{12}$ |  $H-C\equiv C-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$ |
| Octyne | $C_8H_{14}$ |  $H-C\equiv C-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$ |
| Nonyne | $C_9H_{16}$ |  $H-C\equiv C-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$ |
| Decyne | $C_{10}H_{18}$ |  $H-C\equiv C-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$ |

Alkynes are named in a similar way to alkenes. The ending –yne indicates the presence of a triple bond. A number before the name indicates the position of the triple bond. As for alkenes, you number from whichever end gives the smallest number (see Figure 5.1).



$$H-\overset{H}{\underset{H}{C}}-C\equiv C-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H \text{ or } H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-C\equiv C-\overset{H}{\underset{H}{C}}-H$$

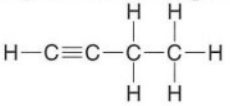
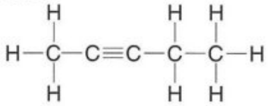
Figure 5.1 2-Hexyne (or hex-2-yne).

**Ethyne** ($C_2H_2$) is commonly called acetylene and is used as a fuel. Acetylene produces a high temperature flame and it is used in oxyacetylene torches to cut and weld metals. Ethyne changes from a solid to a gas at –84°C without becoming a liquid. That is, it sublimes.

## QUESTIONS

1. Identify the following.
   (a) Molecular formula for ethyne.
   (b) Structural formula for ethyne.
   (c) Common name for ethyne.
2. Explain what is meant by:
   (a) Alkyne. (b) Triple bond. (c) Sublimes.
3. Complete the following table to compare ethane, ethene and ethyne.

| Factor | Ethane | Ethene | Ethyne |
|---|---|---|---|
| Formula | | | |
| Boiling point (°C) | –89 | –104 | –84 (sublimes) |
| Homologous series | | | |
| Common feature | | | |
| Difference in reactivity | | | |
| Saturated/ unsaturated | | | |
| Uses | | | |

4. Use the boiling points in the table in Question 3 to determine which of the three compounds, ethane, ethene or ethyne has the weakest dispersion forces. Justify your answer.
5. Justify the classification of alkanes, alkenes and alkynes as hydrocarbons.
6. Identify the following compounds.
   (a)  $H-C\equiv C-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$
   (b)  $H-\overset{H}{\underset{H}{C}}-C\equiv C-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$
   (c) $CHC(CH_2)_3CH_3$
7. For the compound 3-heptyne, write the:
   (a) Molecular formula. (b) Structural formula.
   (c) Condensed structural formula.
8. Check your knowledge with this quick quiz.
   (a) Hydrocarbons with a triple bond belong to which homologous series?
   (b) In a triple bond, ........................ electrons are shared.
   (c) Name the alkyne with three carbon atoms.
   (d) Write the molecular formula for the alkyne with five carbon atoms.
   (e) Identify the systematic name for acetylene.
   (f) State the functional group of the alkynes.
   (g) How many carbon atoms in heptyne?
   (h) Are alkynes saturated or unsaturated?

# 6 Naming Hydrocarbons

You already know that organic compounds are named systematically according to IUPAC nomenclature, with IUPAC standing for the International Union of Pure and Applied Chemistry.

Here we will recap what we already know about naming organic compounds.

- The **stem** (prefix) of the name tells us the length of the carbon chain, for example:

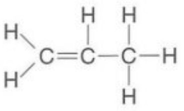
| | | | |
|---|---|---|---|
| $C_1$ meth- | $C_2$ eth- | $C_3$ prop- | $C_4$ but- |
| $C_5$ pent- | $C_6$ hex- | $C_7$ hept- | $C_8$ oct- |
| $C_9$ non- | $C_{10}$ dec- | | |

- The **suffix** (ending) of the name indicates the functional group present and thus the family of organic compounds to which the compound belongs.

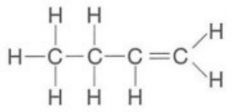
Table 6.1 Suffixes of some organic compounds.

| Suffix | Homologous series | Example |
|---|---|---|
| -ane | Alkane | Ethane $C_2H_6$ |
| -ene | Alkene | Ethene $C_2H_4$ |
| -yne | Alkyne | Ethyne $C_2H_2$ |

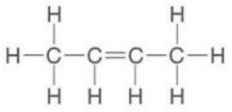
- **Types of formulas** include:
  - Molecular formula, e.g. propene $C_3H_6$.
  - Semi-structural formulas (also called condensed structural formulas), e.g. $CH_2CHCH_3$.
  - Structural formula, e.g. propene.



- **Carbon atoms are numbered** so that the carbon with the functional group attached has the lowest possible number.



But-1-ene or 1-Butene



But-2-ene or 2-Butene

Although these two compounds have the same molecular formula ($C_4H_8$), they are different compounds with different properties.

- Notice that the compound **can be numbered from either end**, e.g. hept-2-ene has the double bond on the second carbon from the end and it can be drawn from either direction – numbering from the left or from the right as shown in Figure 6.1.

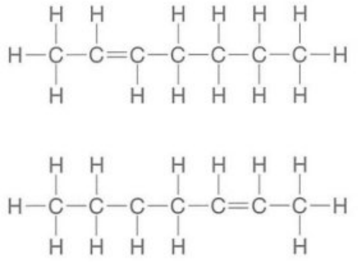
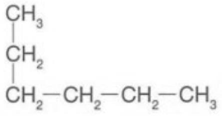


Figure 6.1 Two ways of drawing hept-2-ene.

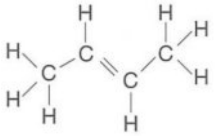
- Watch out for **twisted or bent chains**. The following formula is hexane, not ethylbutane.



$CH_3$–$CH_2$–$CH_2$–$CH_2$–$CH_2$–$CH_3$

Hexane

- Formulas can be **drawn in different ways**. For example, this structural formula of but-2-ene gives a better idea of the structural orientation within the molecule.

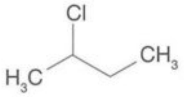


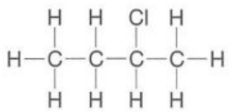
But-2-ene

Also the carbon atoms in the main chain may be omitted as in this example of a structural formula for non-2-ene.

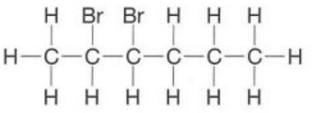
Of course, in an examination you would always give the full formula with all carbon and hydrogen atoms included.

- The position of atoms of **other elements** attached to a carbon chain, is also indicated by a number. Make sure you can see that each of the following formulas could be used to represent 2-chlorobutane.





- If there is more than one attachment, we number both in the same way. For example:



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{Br}{\underset{H}{C}}{-}\overset{Br}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}H}$$

This compound would be called 2,3-dibromohexane.

Notice that you use commas between numbers and dashes between a number and a word.

## Naming hydrocarbons with branched chains

Carbon compounds can have branched chains, and the position along the main chain of any attached groups is indicated by numbering.

To name a compound, first you find the longest chain. Then you identify any side chains by their length and their position along the chain.

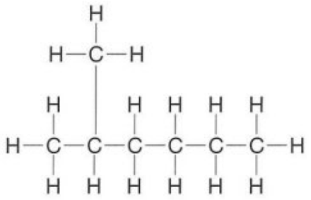
**Table 6.2** Naming side chains.

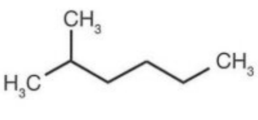
| Number of C atoms in chain | Formula | Name |
|---|---|---|
| 1 | $CH_3$ | Methyl |
| 2 | $CH_3CH_2$ | Ethyl |
| 3 | $CH_3CH_2CH_2$ | Propyl |
| 4 | $CH_2CH_2\ CH_2CH_2$ | Butyl |
| 5 | $CH_3CH_2CH_2\ CH_2CH_2$ | Pentyl |
| 6 | $CH_3CH_2CH_2CH_2CH_2CH_2$ | Hexyl |
| 7 | $CH_3CH_2CH_2CH_2CH_2CH_2\ CH_2$ | Heptyl |
| 8 | $CH_3CH_2CH_2CH_2CH_2CH_2\ CH_2\ CH_2$ | Octyl |

## Attachments to alkanes

Here are some examples to give you an idea of how naming branch chains works using alkanes.

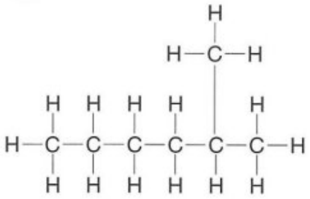
**Example 1:**





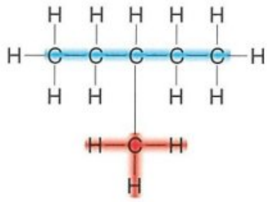
This structure is a 6 carbon chain, with all single C–C bonds, so it is hexane. And it has a $CH_3$ (methyl) group attached to the second carbon. So its name is **2-methylhexane**.

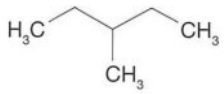
Notice that, as with other examples, this formula can also be written in reverse.



This is still 2-methylhexane – you number from whichever end will give you the smallest number for the attached group.

**Example 2:**

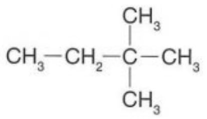




This is a 5 carbon alkane chain – pentane, with a methyl ($CH_3$) chain attached to the third carbon, **3-methylpentane**.

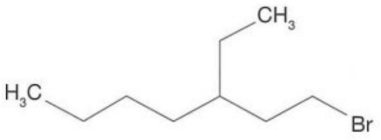
**Example 3:**

Compounds can have more than one side chain attached to the same main chain. Here is an example. It has two attached methyl groups, making it dimethyl, and they are both attached on carbon 2, so its name is **2,2-dimethylbutane**.



$$CH_3{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3$$

**Example 4:**

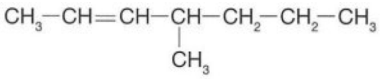


Numbering from the right again gives you the smallest numbers. The side attachments – bromo- and ethyl- ($C_2H_5$) are listed in alphabetical order. Bromine is on carbon 1 and the ethyl group is on carbon 3, so the name is **1-bromo-3-ethylheptane**.

## Attachments to alkenes and alkynes

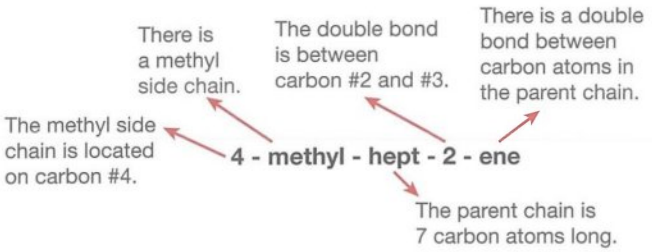
So far we have only used alkanes for the main chain. It works the same way for alkenes and alkynes, but when numbering, you always begin with the carbon closest to the double or triple bond. Here are some examples using just the carbon skeleton.

**Example 1:**

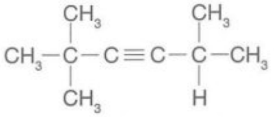


$$CH_3{-}CH{=}CH{-}\underset{CH_3}{CH}{-}CH_2{-}CH_2{-}CH_3$$

The main chain is 7 carbons with a double bond on the second C so it is hept-2-ene (or 2-heptene). The side chain is methyl (1 carbon) and it is attached to the fourth C in the main chain. So the name reflects all of this information.



**Example 2:**



$$CH_3-C(CH_3)_2-C\equiv C-CH(CH_3)-CH_3$$

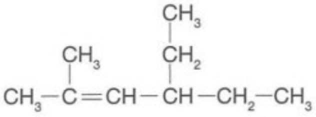
This compound has a 6 carbon chain with a triple bond on the third carbon – so it is hex-3-yne. There are 3 attached methyl groups. So we name it **2,2,5-trimethyl-hex-3-yne.**

## Writing formulas

Now, let's try this in reverse – **start with a name** and try to draw a compound. Start with the carbon skeleton first.

Example:

You are asked to write the structural formula for **2-methyl-4-ethyl-hex-2-ene**. Draw the carbon chain first, the hex-2-ene. Add the two side chains and then add all the hydrogen atoms.

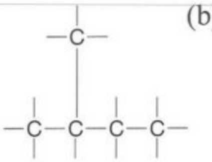


$$CH_3-C(CH_3)=CH-CH(CH_2-CH_3)-CH_2-CH_3$$

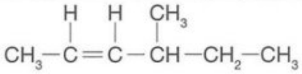
## QUESTIONS

1. Name the following compounds based on their carbon backbones.

(a)

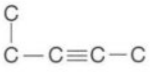


(b)



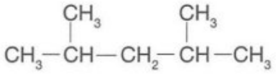
$$CH_3-C(H)=C(H)-CH(CH_3)-CH_2-CH_3$$

(c)



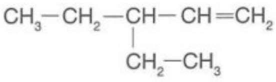
$$C(C)-C\equiv C-C$$

(d)



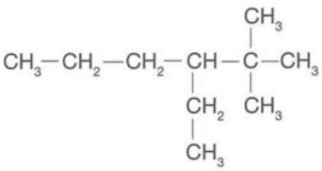
$$CH_3-CH(CH_3)-CH_2-CH(CH_3)-CH_3$$

(e)



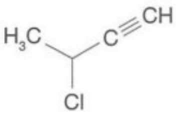
$$CH_3-CH_2-CH(CH_2-CH_3)-CH=CH_2$$

(f)



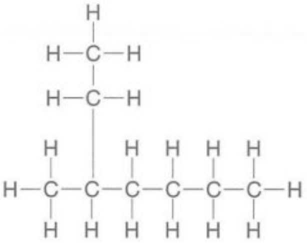
$$CH_3-CH_2-CH_2-CH(CH_2-CH_3)-C(CH_3)_2-CH_3$$

(g)

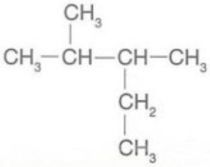


2. A student named each of the following structures incorrectly. State the correct name for each and explain why the student's answers were incorrect.

(a) This structure was named incorrectly as 2-ethylhexane.



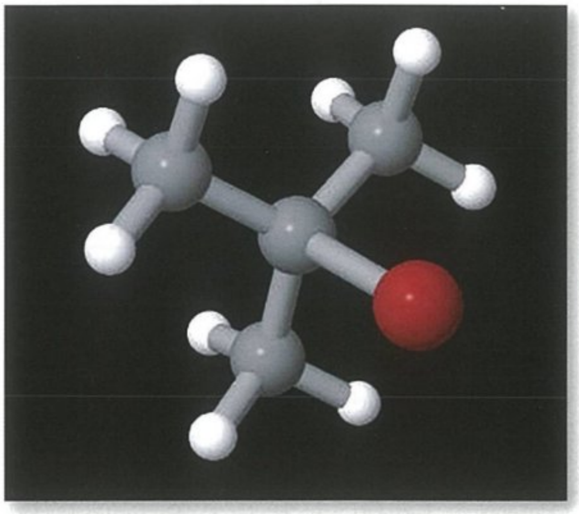
(b) This structure was named incorrectly as 2-methyl-3-ethylbutane.



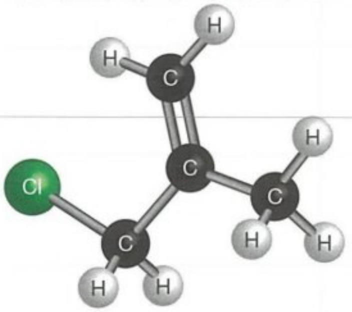
$$CH_3-CH(CH_3)-CH(CH_2-CH_3)-CH_3$$

3. Write structural formulas for the following compounds.
   (a) 1-Chloro-prop-1-yne.
   (b) 4-Ethyl-hex-2-ene.
4. Name the following models.

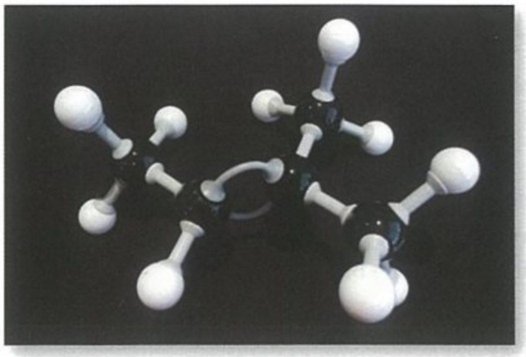
(a)



(b)



(c)



# 7 Alcohols

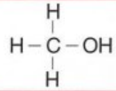
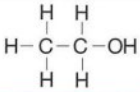
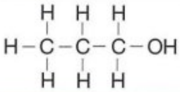
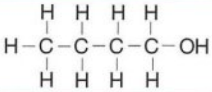
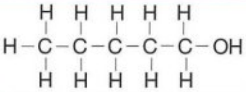
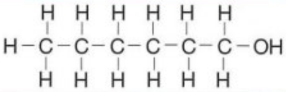
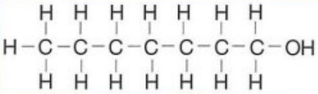
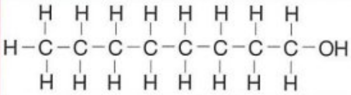
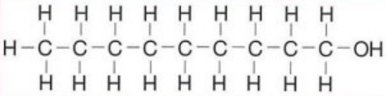
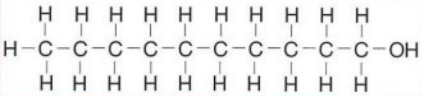
Another homologous series of organic compounds is the alcohols. They all contain the **hydroxyl functional group** (–OH) and their names all end with –anol as a suffix, for example, methanol, ethanol and propanol.

Alcohols made from an alkane and a hydroxyl group are called **alkanols** and have a general formula $C_nH_{2n+1}OH$.

## Naming alcohols

The stem (prefix) tells you the length of the carbon chain in an alcohol.

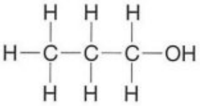
**Table 7.1** A series of alcohols.

| Name | Molecular formula | Structural formula |
|---|---|---|
| Methanol | $CH_3OH$ |  |
| Ethanol | $C_2H_5OH$ |  |
| Propanol | $C_3H_7OH$ |  |
| Butanol | $C_4H_9OH$ |  |
| Pentanol | $C_5H_{11}OH$ |  |
| Hexanol | $C_6H_{13}OH$ |  |
| Heptanol | $C_7H_{15}OH$ |  |
| Octanol | $C_8H_{17}OH$ |  |
| Nonanol | $C_9H_{19}OH$ |  |
| Decanol | $C_{10}H_{21}OH$ |  |

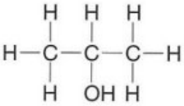
**Methanol** ($CH_3OH$) is the simplest alcohol; it is present in methylated spirits. This is not suitable for drinking, as methanol causes blindness.

Perhaps the best known alcohol is **ethanol** ($C_2H_5OH$) which is used in alcoholic drinks, in medicines, as a solvent and as a fuel.

In Table 7.1, the hydroxyl group is at one end of each molecule, but it can occur in other positions as indicated by numbering in the name of the alcohol.



Propan-1-ol

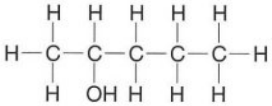


Propan-2-ol

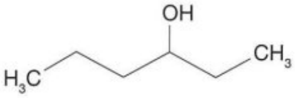
## QUESTIONS

1. Name the following alcohols.
   (a) $C_4H_9OH$ (b) $C_7H_{15}OH$ (c) $C_3H_7OH$
2. Write molecular formulas for the following alcohols.
   (a) Methanol. (b) Ethanol. (c) Hexan-3-ol.
3. Name the following alcohols.

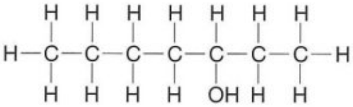
(a)



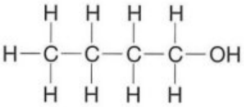
(b)



(c)

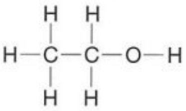


(d)



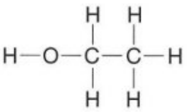
4. Is there any difference between the four compounds as illustrated below?

(a)

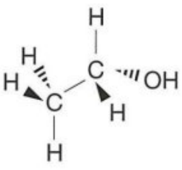


(b)

(c)



(d)



4. Does the compound butan-3-ol exist? Explain.
5. Distinguish between the following.
   (a) Hydroxide and hydroxyl groups.
   (b) Primary, secondary and tertiary alcohols.

# 8 Carboxylic Acids

This is revision of work you covered in year 11. Carboxylic acids are organic acids which contain a **–COOH group**. The COOH group is the functional group of carboxylic acids and is called a **carboxyl group**.

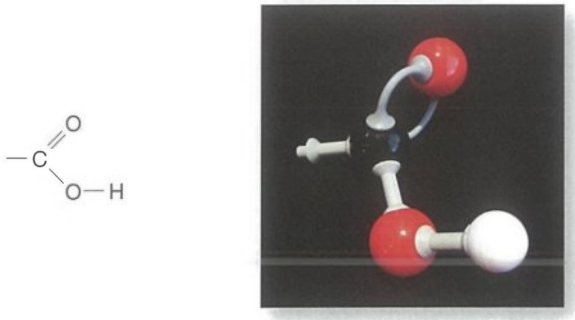
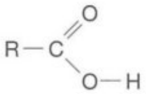


Figure 8.1 Carboxyl group formula.

In carboxylic acids, the carboxyl group is attached to a hydrogen atom or to a saturated carbon chain (an alkyl group) with the formula $C_nH_{2n+1}$. The general formula is RCOOH where R is a hydrogen atom or an alkyl group, $C_nH_{2n+1}$.

The general structure of **carboxylic acids** (also called alkanoic acids) is shown in the diagram.



## The carboxyl group

The carboxyl group COOH is the functional group for carboxylic acids. In the carboxyl group, a carbon atom is bonded to two different oxygen atoms, one by a single C–O bond and the other by a double C=O bond.

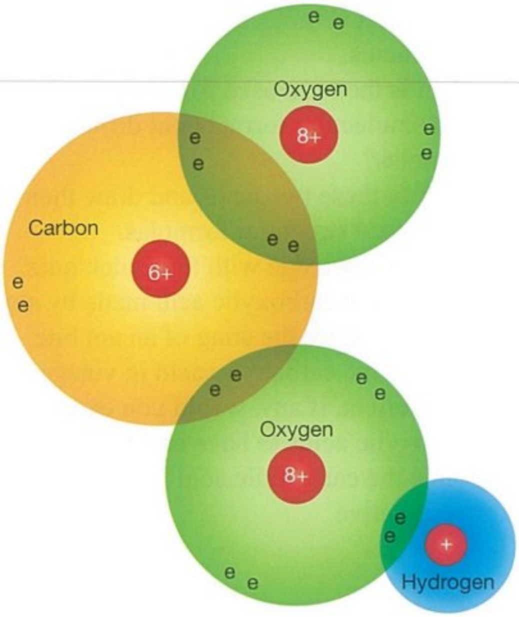


Figure 8.2 Structure of carboxyl group.

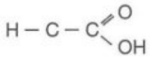
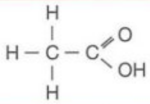
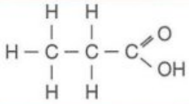
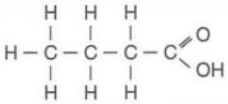
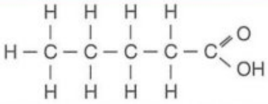
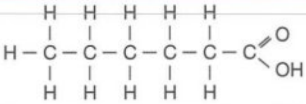
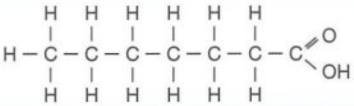
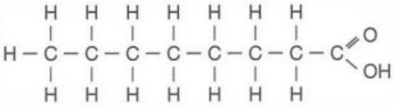
## Examples of carboxylic acids

**Methanoic acid** (HCOOH) is the simplest carboxylic acid. Pure methanoic acid has a pungent irritating odour and can blister the skin. Methanoic acid is also called formic acid as it was first isolated from ants (Latin: formica = ants). Ant stings can be neutralised with sodium hydrogen carbonate. Methanoic acid is **used** as a preservative and an antibacterial agent.

**Ethanoic acid** ($CH_3COOH$) is also called acetic acid and is the main component of vinegar. Vinegar is approximately 4% to 8% acetic acid. It is used to flavour and preserve food. Ethanoic acid is corrosive, and has a sour taste and a strong odour. It is **used** extensively in the production of glues and synthetic fibres.

Examples of carboxylic acids are shown in Table 8.1.

Table 8.1 Carboxylic acids.

| Name | Structural formula | Molecular formula |
|---|---|---|
| Methanoic acid |  | HCOOH |
| Ethanoic acid |  | $CH_3COOH$ |
| Propanoic acid |  | $C_2H_5COOH$ |
| Butanoic acid |  | $C_3H_7COOH$ |
| Pentanoic acid |  | $C_4H_9COOH$ |
| Hexanoic acid |  | $C_5H_{11}COOH$ |
| Heptanoic acid |  | $C_6H_{13}COOH$ |
| Octanoic acid |  | $C_7H_{15}COOH$ |

As with other chemicals which are important in industry, some of the carboxylic acids are known by common names as well as their IUPAC names. Table 8.2 lists some examples.

**Table 8.2** Names of carboxylic acids.

| Formula | IUPAC name | Common name |
|---|---|---|
| HCOOH | Methanoic acid | Formic acid |
| $CH_3COOH$ | Ethanoic acid | Acetic acid |
| $C_2H_5COOH$ | Propanoic acid | Propionic acid |
| $C_3H_7COOH$ | Butanoic acid | Butyric acid |
| $C_7H_{15}COOH$ | Octanoic acid | Caprylic acid |
| $C_{11}H_{23}COOH$ | Dodecanoic acid | Lauric acid |
| $C_{15}H_{31}COOH$ | Hexadecanoic acid | Palmitic acid |

## Strength of carboxylic acids

The strength of an acid is determined by how easily it can release (donate) protons when it goes into solution. The easier the protons ($H^+$ ions) are released into solution, the stronger the acid.

The carboxyl group (–COOH) contains a double bonded oxygen atom (=O) and a single bonded hydroxyl group (–OH). The hydroxyl group can ionise and release hydrogen ions ($H^+$) in solution, forming a conjugate base ($-COO^-$). This ability to release hydrogen ions makes it an acid.

Carboxylic acids are described as **weak acids** because they do not ionise completely. Most of the acid (about 95%) is present as un-ionised molecules.

The ionisation of a weak acid can be shown as an equilibrium equation where the equilibrium lies far to the left.

$$AH + H_2O \rightleftharpoons A^- + H_3O^+$$

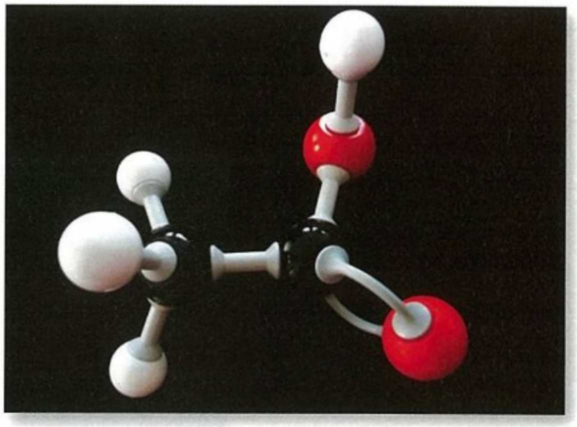
Or more simply as:

$$AH(aq) \rightleftharpoons A^-(aq) + H^+(aq)$$

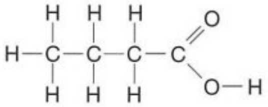
In these equations A stands for the anion (negative ion) in the acid.

## QUESTIONS

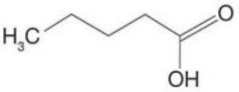
1. (a) Describe the meaning of a carboxylic acid.
   (b) Identify the general structure of a carboxylic acid.
2. Distinguish between a hydroxyl group and a carboxyl group.
3. Use diagrams to compare the size of molecules of ethanoic acid and methanoic acid.
4. Name the following carboxylic acids.
   (a) $CH_3CH_2COOH$
   (b) $CH_3CH_2CH_2CH_2CH_2CH_2CH_2COOH$
   (c)



   (d)



5. Sometimes formulas are drawn as follows. Each bend in the chain indicates the position of a carbon atom. Add the missing atoms to this chain and name the compound.



6. Research information on the following organic acids such as the number of carbon atoms in their hydrocarbon chains, and where they are found or used.
   (a) Lauric acid.
   (b) Stearic acid.
7. Justify the classification of organic acids as weak acids.
8. $C_3H_7COOH$ is the molecular formula of two carboxylic acids.
   (a) What is the term used for compounds with the same molecular formula but different structural formulas?
   (b) Identify these two acids and draw their condensed structural formulas.
9. Check your knowledge with this quick quiz.
   (a) Identify the carboxylic acid made by ants and responsible for the sting of an ant bite.
   (b) Identify the carboxylic acid in vinegar.
   (c) What effect, if any, would you expect carboxylic acids to have on litmus paper?
   (d) Name the carboxylic acid used as a food preservative.

# 9 Aldehydes and Ketones

Aldehydes and ketones are considered together as they both contain the same functional group. This is called the **carbonyl functional group** and consists of an oxygen atom attached to a carbon atom by a double bond.

**Figure 9.1** Carbonyl group.

Although aldehydes and ketones both have the carbonyl functional group, it is attached in a different position. In aldehydes, the carbonyl group is attached at the end of the carbon chain. In ketones the carbonyl group is attached along the chain, not at either end. This causes differences in some of the chemical reactions of aldehydes and ketones, especially oxidation reactions.

Where R and R′ are alkyl chains.

**Figure 9.2** General formulas of aldehydes and ketones.

## Aldehydes

Aldehydes (also called **alkanals**) are organic compounds with the general formula RCHO and a **carbonyl group attached to a terminal (end) carbon atom of the chain**.

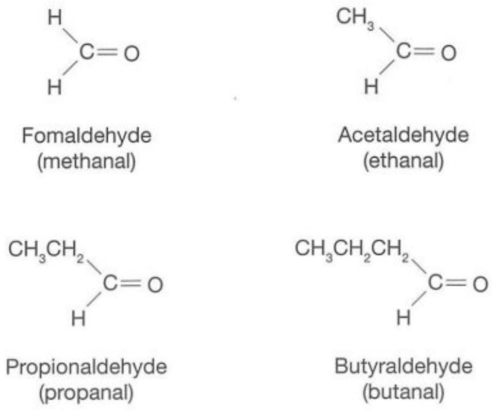


**Figure 9.3** Examples of aldehydes.

**For IUPAC naming:**

1. Choose the longest unbranched chain containing the carbonyl group.
2. Number from the C with the attached =O.
3. Replace the 'e' at the end of the alkane with –'al'. For example: Methanal is an aldehyde which contains one C and ethanal contains two C's .

## Ketones

Ketones (also called **alkanones**) are organic compounds with general formula RCOR′ where R and R′ are alkyl chains. In ketones the carbonyl group is on a carbon atom which is not in a terminal position (not at either end). The simplest ketone, called acetone or propanone has three carbon atoms.

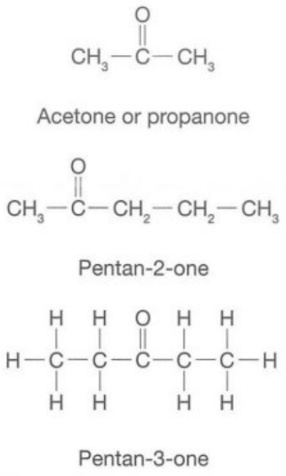


**Figure 9.4** Examples of ketones (alkanones).

**For IUPAC naming:**

1. Choose the longest unbranched chain containing the carbonyl group.
2. Number so that the C with the attached =O has the smallest possible number.
3. Replace the 'e' at the end of the alkane name with 'one'. For example:
   Acetone has 3 carbon atoms and is called propanone. Pentanone (with 5 C atoms in the chain) can be pentan-2-one or pentan-3-one depending on the position of the carbonyl group.

## QUESTIONS

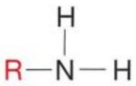
1. Identify the functional group in aldehydes and ketones.
2. Distinguish between aldehydes and ketones.
3. Name the following substances.
   (a) $CH_3CH_2CH_2COCH_3$
   (b) $CH_3CH_2CH_2CH_2CH_2COCH_3$
   (c) $CH_3CH_2CH_2CHO$
4. Write structural formulas for:
   (a) Butanal.
   (b) Butanone.
   (c) The simplest aldehyde.
   (d) The simplest ketone.

# 10 Amines and Amides

**Amines and amides** are two groups of organic compounds whose members have a **–$NH_2$** group as their functional group.

## Amines

An **amine** is an organic compound which contains the functional group –$NH_2$ attached to a hydrocarbon chain or ring. The general formula for an amine is R–$NH_2$.



$$R{-}\overset{\displaystyle H}{\overset{|}{N}}{-}H$$

Amines are named using the suffix -amine. Some examples are shown in Figure 10.1.

As with alcohols, amines can be **primary, secondary or tertiary** amines depending on the number of hydrocarbon groups attached to the nitrogen atom.

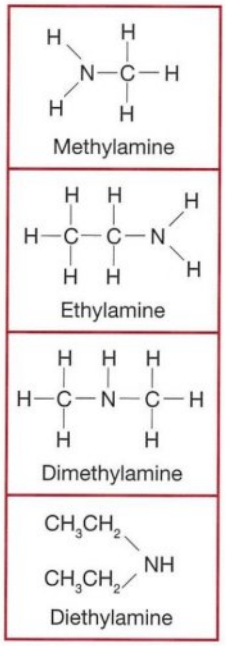


**Figure 10.1** Examples of amines.

## Importance of amines

Amines are **important in biology**. The **amino acids** which make up proteins have an amine group, so amines are found in all living organisms. Many neurotransmitters in the body are amines, e.g. serotonin, histamine and dopamine. Amines are also important in determining the 3-D structure of proteins.

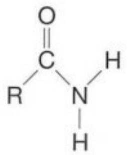
**Foods also contain amines**, e.g. histamine in wine and phenylethylamine in chocolate. Amines are present naturally in some foods such as fruits and vegetables. In other foods, e.g. meat, dairy products, alcoholic drinks and fermented foods, amines are usually formed by the action of bacteria.

Amines in foods we eat are broken down with the help of a special enzyme. In some people, genetic variations mean that this enzyme is missing, or its action may be blocked. When this happens, the amine called tyramine builds up in the body and can cause a range of symptoms including headaches, skin rashes, diarrhoea and aggressive behaviour disorders.

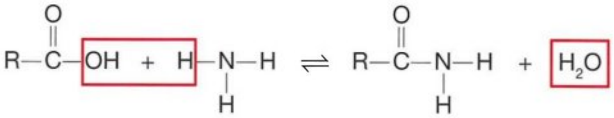
Many **drugs** used by doctors today have been designed to mimic or interfere with amine neurotransmitters, e.g. antihistamines used to relieve allergic reactions. The drugs morphine, codeine and heroin are all tertiary amines. Nicotine and caffeine also contain amine groups.

## Amides

An amide is an organic compound which contains the –$CONH_2$ group as its functional group. The general formula of an amide is:



Amides are formed from carboxylic acids when the –OH (hydroxyl group) of the carboxyl group is replaced by a –$NH_2$ (amine) group.



$$R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\boxed{OH + H}{-}\underset{\displaystyle H}{\underset{|}{N}}{-}H \rightleftharpoons R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\underset{\displaystyle H}{\underset{|}{N}}{-}H + \boxed{H_2O}$$

Amides are named by replacing the -oic suffix of the carboxylic acid by -amide.

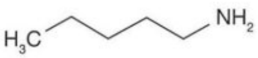
**Table 10.1** Examples of amides.

| Amide | Formula | Produced from |
|---|---|---|
| Methanamide | $HCONH_2$ | Methanoic acid |
| Ethanamide | $CH_3CONH_2$ | Ethanoic acid |
| Propanamide | $C_2H_5CONH_2$ | Propanoic acid |

## Uses of amides

Amides are used extensively in industries such as the manufacture of plastics, rubber, paper, crayons, pencils and inks, explosives and adhesives. They are also used as a coating for many household appliances.

## QUESTIONS

1. What is an amine?
2. Name and state the molecular formula for each of the following amines.
   (a) $CH_3{-}CH_2{-}CH_2{-}NH_2$
   (b)


   (c)

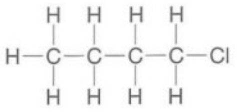

3. Research uses for two named amines.
4. What is an amide?
5. Copy and complete the table to summarise information about the homologous series you have studied.

| Homologous series | Functional group | General formula | Name of example | Formula of example |
|---|---|---|---|---|
| Alcohol | | | | $C_2H_5OH$ |
| Carboxylic acid | | R–COOH | | |
| Amine | –$NH_2$ | | | |
| Amide | | | | |
| Aldehyde (alkanal) | | | | |
| Ketone (alkanone) | | | | |

# 11 Halogenated Organic Compounds

You will recall that halogens are the elements in group 7 of the periodic table. When one or more halogen atoms are substituted into molecules of alkanes, alkenes and alkynes, the compounds are called **haloalkanes, haloalkenes and haloalkynes**.

An example of a haloalkane is 1-chlorobutane.



The bond between a halogen atom and a carbon atom is **polar covalent** because there is a large difference in electronegativity between the two atoms.

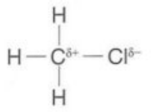


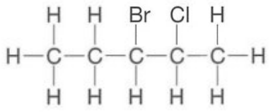
**Figure 11.1** Polar bond in chloromethane.

As this bond is not balanced by any other bonds, the molecule will be polar. This will result in the formation of dipole-dipole intermolecular forces (as well as the dispersion forces found between all molecules). So halogenated compounds will have higher melting and boiling points than other hydrocarbons of similar size.

Haloalkanes also tend to be more dense than similar molecules without halogen atoms, and also more dense than water.

**To name these compounds**, follow these rules.

- Use prefixes for the halogen, e.g. fluoro, chloro, bromo or iodo.
- If more than one halogen atom is present in the molecule, then list them in alphabetical order.
- Number the carbon with the halogen attached, giving preference to any double bond, otherwise giving the lowest number to the halogen group, for example 3-bromo-2-chloropentane.



3-bromo-2-chloropentane

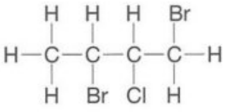
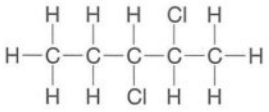
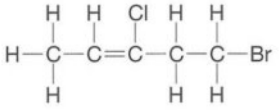
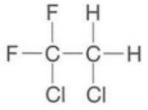
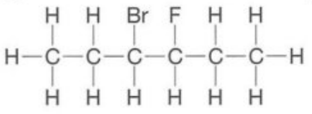
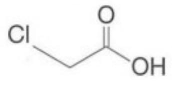
## Haloalkanes and the ozone layer

Haloalkanes have been used as anaesthetics, e.g. chloroform $CHCl_3$, as solvents and dry-cleaning fluids, e.g. $CCl_4$, as insecticides, e.g. DDT, dieldrin and lindane, and as propellants in aerosol spray cans, e.g. $CCl_2F_2$ (dichloro-difluoromethane). Many of these have been discontinued because of their effect on the environment, especially the ozone layer of the atmosphere.

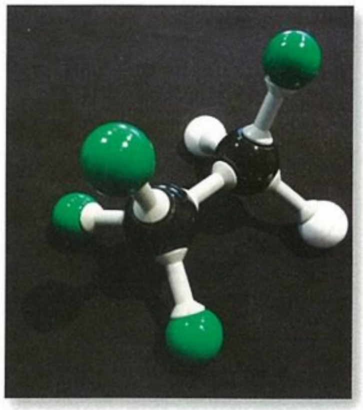
When these compounds contain both chlorine and fluorine replacing all the hydrogen atoms, they are called **chlorofluorocarbons or CFCs**. CFCs were first developed to replace ammonia in refrigerators and they have also been used as aerosol propellants, solvents and plastic foam-blowing agents.

CFCs are important because they rise to the upper atmosphere where they destroy the ozone layer. They are very stable compounds and persist in the upper atmosphere, doing damage, for years. We need the ozone layer because it protects the Earth from the sun's ultraviolet radiation. Ultraviolet radiation causes skin cancers and cataracts, suppresses the immune system, reduces lung function, breaks down polymers and paints, and contributes to the formation of photochemical smog. An international agreement, called the Montreal Protocol, has led to a reduction in the use of these ozone-depleting CFCs and most have been phased out.

## QUESTIONS

1. What is meant by a haloalkane?
2. Haloalkanes have higher densities and higher melting and boiling points than their corresponding alkanes. Explain.
3. Name the following compounds.
   (a) $CH_3CH_2Cl$
   (b) $C_6H_{13}I$
   (c)
   
   (d)
   
   (e)
   
   (f)
   
   (g)
   
   (h)
   
4. Write structural formulas for the following.
   (a) 2-Bromo-1-fluoro-2-iodohexane.
   (b) 1,1-Dibromoethene.
   (c) 2-Bromo-3-chloro-1-fluorobutane.
   (d) 2,3-Dibromo-4-chloropentane.
   (e) 3,4-Dibromo-2-chloro-pent-2-ene.

5. Name the compounds represented by the model. Black balls represent carbon, white balls represent hydrogen and green balls represent fluorine.



6. Graph the following information about the boiling points of haloalkanes and outline the trends illustrated by the graphs.

(a)

| Chemicals | Boiling points (°C) |
|---|---|
| $CH_3CH_2F$ | –37.7 |
| $CH_3CH_2Cl$ | 12.3 |
| $CH_3CH_2Br$ | 38.4 |
| $CH_3CH_2I$ | 72.3 |

(b)

| Chemicals | Boiling points (°C) |
|---|---|
| $CH_3CH_2Cl$ | 12.3 |
| $CH_3CH_2CH_2Cl$ | 46.6 |
| $CH_3CH_2CH_2CH_2Cl$ | 78.4 |
| $CH_3CH_2CH_2CH_2CH_2Cl$ | 107.8 |

7. A code is used to name CFCs. To work out the formula of a CFC from its code we add 90. For example, for a compound named CFC-12, we add 90 and this becomes CFC-102. The three digits tell us, in order, the number of atoms of carbon, hydrogen and fluorine atoms in a molecule. We can then work out the number of chlorines needed to complete the structure. CFC-102 has 1 carbon, 0 hydrogen and 2 fluorine atoms in its molecules.
That leaves room for 2 chlorine atoms. So its name is dichlorodifluoromethane.
Using this code, work out the names of CFC-11 and CFC-13.

8. Research the problems associated with the use of CFCs and assess the effectiveness of steps taken to reduce these problems.

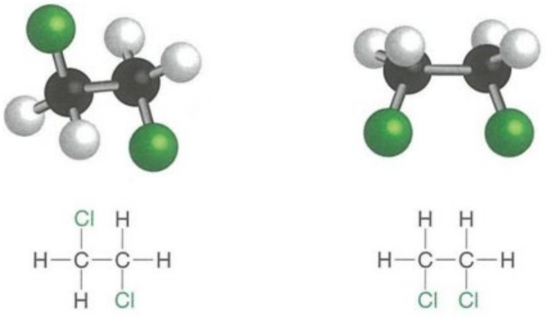
# 12 Structural Isomers

**Isomers** are molecules which have the same molecular formula, but their atoms are arranged differently in space. Although they have the same molecular formula, isomers are different compounds, with different structures and different properties.

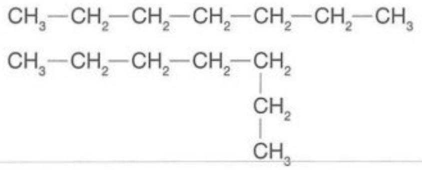
This ability for the same group of atoms to be arranged differently, forming a different compound, adds to the diversity of carbon compounds.

Don't be tricked by molecules where atoms have simply been rotated freely around –C–C–bonds. These are **NOT isomers**. For example, in Figure 12.1 you can see two images of 1,2-dichloroethane and of heptane. These are not isomers. They are two views of the same compound as they have the same formula and properties. One carbon atom has just rotated about the single –C–C– bond.

(a) Two diagrams of 1,2-dichloroethane showing rotation – these are NOT isomers.



(b) Two diagrams for heptane – these are NOT isomers.



$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$$

$$\begin{array}{l} CH_3-CH_2-CH_2-CH_2-CH_2 \\ \qquad\qquad\qquad\qquad\quad\ | \\ \qquad\qquad\qquad\qquad\quad CH_2 \\ \qquad\qquad\qquad\qquad\quad\ | \\ \qquad\qquad\qquad\qquad\quad CH_3 \end{array}$$

Figure 12.1 Examples that can be mistaken for isomers.

If you have not made models of carbon compounds yet, then you should do so now and investigate how the appearance of compounds such as alkanes can change as you rotate the atoms without forming an isomer.

If you have not had to take the molecule apart to make the second compound, then you have not made an isomer of your original structure.

## Types of isomers

There are a number of different types of isomers, as illustrated in Figure 12.2.

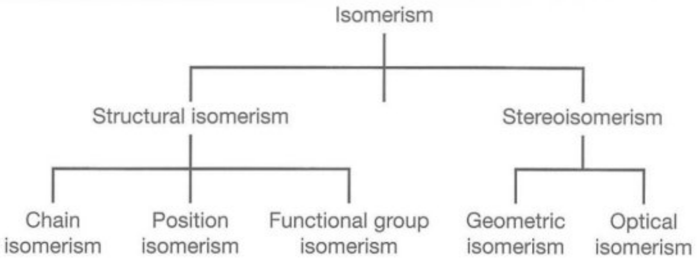


Figure 12.2 Types of isomers.

We will be looking at the three types of structural isomers – chain isomers, position isomers and functional group isomers.

## Structural isomers

Structural isomers are molecules with the same molecular formula, but with their atoms arranged in a different order.

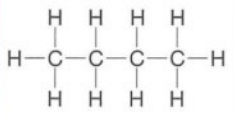
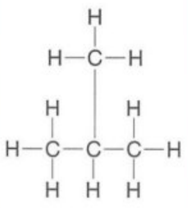
This can occur when:

- Chains can be straight or they can branch in different ways.
- The basic chain stays the same, but attached groups such as a chlorine atom, or a hydroxyl group can be attached at different positions.
- Atoms are arranged in different ways that lead to the isomers belonging to different homologous series.

### Structural isomerism caused by straight and branching chains

Butane and 2-methylpropane are structural isomers. They have the same molecular formula ($C_4H_{10}$), but their atoms are arranged in different orders so their molecules have different structures, different names and different properties as shown in Table 12.1.

Table 12.1 Structural isomers of butane ($C_4H_{10}$).

| Feature | Butane | 2-Methylpropane |
|---|---|---|
| Structural formula |  |  |
| Boiling point (°C ) | $-1$ | $-11.7$ |
| Density (g mL$^{-1}$) | 2.48 | 2.51 |
| Uses | A fuel | A refrigerant |

Notice that their differences are not due to rotation around carbon bonds, the atoms are actually arranged differently.

Larger molecules have more isomers. Pentane ($C_5H_{12}$) has three structural isomers.

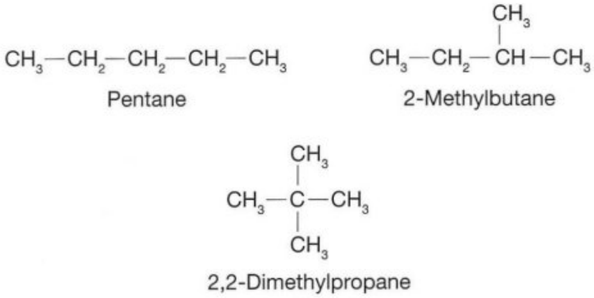


**Figure 12.3** Structural isomers of $C_5H_{12}$.

### Structural isomerism caused by change in position of attached groups

An example of this type of isomer is the compounds 2-chloropentane and 3-chloropentane. These are structural isomers because they have the same molecular formula ($C_5H_{11}Cl$), but the chlorine atom is attached in a different position in each compound.

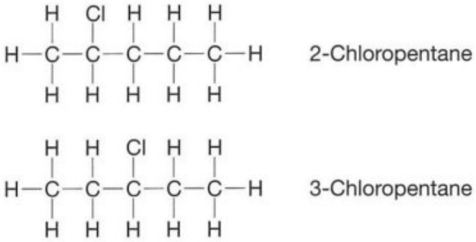
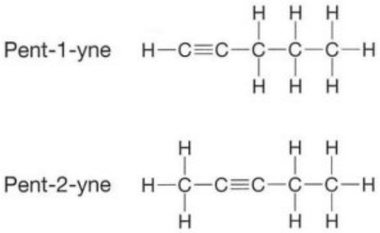


**Figure 12.4** Isomers of $C_5H_{11}Cl$.

### Structural isomerism due to position of a double or triple carbon-carbon bond

For example, the compounds pent-1-yne and pent-2-yne are structural isomers of $C_5H_8$.



### Structural isomers with different functional groups

You will see samples of these isomers as you study different homologous groups in more detail. For example, $C_4H_8O_2$ could be arranged to form either a carboxylic acid or an ester.

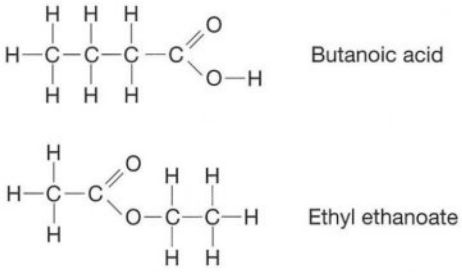
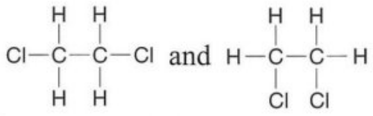


**Figure 12.5** Isomers of $C_4H_8O_2$.

## QUESTIONS

1. (a) What are structural isomers?
   (b) Identify three ways in which structural isomers can occur.
2. Figure 12.2 shows the formula for three compounds. Explain why these compounds are said to be isomers of pentane.
3. Use structural formulas to show structural isomers with the molecular formula of $C_4H_9Br$. Name these compounds.
4. Draw carbon skeletons to illustrate the structure of the five isomers for hexane $C_6H_{14}$. Name them.
5. Decide whether each of the following pairs of structures represent isomers and justify your decision.
   (a) $CH_2{=}CH{-}CH_2{-}CH_3$ and $CH_3{-}CH{=}CH{-}CH_3$
   (b) $CH_2{=}CH{-}CH_2{-}CH_3$ and $CH_3{-}CH_2{-}CH{=}CH_2$
   (c) 
6. The compounds 1-chloropropane and 2-chloropropane are isomers.
   (a) Write structural formulas for these compounds.
   (b) What is their molecular formula?
   (c) Use information from a chemical data book to help account for these two substances being considered as different chemicals despite the fact that they have the same molecular formula.
7. Draw and name six structural isomers for $C_7H_{16}$.
8. Check your knowledge with this quick quiz.
   (a) Compounds with the same molecular formula but different arrangement of their atoms in space are called (isomers/allotropes).
   (b) Name two different types of isomers.
   (c) Which type of bond is not free to rotate, a single –C–C– bond or a double –C=C– bond?

# 13 Revision Of Nomenclature

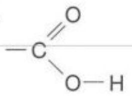
Before you go any further you should use these revision questions to check that you fully understand the work covered in the first section of this course on organic compounds.

Once you understand the principles of naming organic chemicals you will see that it is very logical. However, you do need to learn the basics thoroughly.

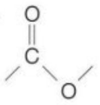
After you have answered the questions, check your answers against those in the back. If you have made any errors, be sure that you understand why your answer was not correct.

## QUESTIONS

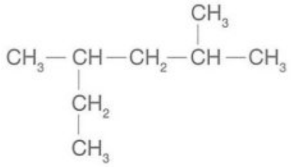
1. Organic chemistry refers to the study of:
   (A) The human body and its chemical structure.
   (B) The chemicals present in all living things.
   (C) Hydrocarbons only.
   (D) Carbon and its compounds.
2. The molecular formulas for butane and butene are respectively:
   (A) $C_4H_{10}$ and $C_4H_8$
   (B) $C_4H_{10}$ and $C_4H_6$
   (C) $C_4H_8$ and $C_4H_{10}$
   (D) $C_4H_6$ and $C_4H_8$
3. Which alternative correctly states the general formula and functional group for alkynes?
   (A) $C_nH_{2n}$ and C–C
   (B) $C_nH_{2n+2}$ and C–C
   (C) $C_nH_{2n}$ and C=C
   (D) $C_nH_{2n-2}$ and C≡C
4. The functional group for carboxylic acids is:
   (A) The carboxyl group.



   (B) The carbonyl group. $-C{=}O$
   (C) The carbon-carbon double bond. $C{=}C$
   (D) The acetyl group.

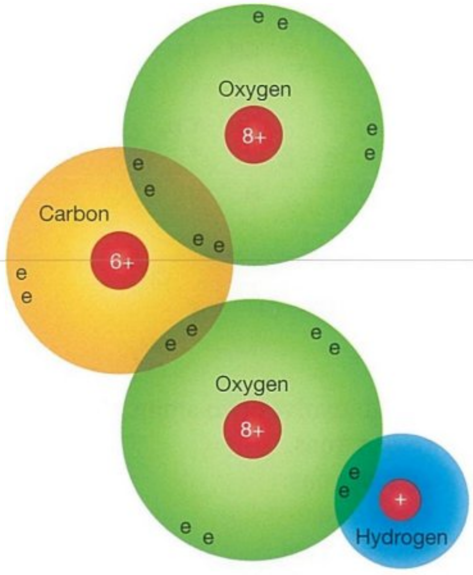


5. All compounds in an homologous series have the same:
   (A) Molecular formula.
   (B) Structural formula.
   (C) Functional group.
   (D) Physical and chemical properties.
6. Three carbon compounds belonging to the same homologous series could be:
   (A) $C_5H_8$, $C_5H_{10}$, $C_5H_{12}$
   (B) $C_5H_{12}$, $C_6H_{14}$, $C_7H_{16}$
   (C) $CH_4$, $C_2H_4$, $C_3H_4$
   (D) $C_3H_7OH$, $C_3H_7Cl$, $C_3H_7I$
7. Which alternative correctly names the following compound?



$$CH_3-CH(CH_2CH_3)-CH_2-CH(CH_3)-CH_3$$

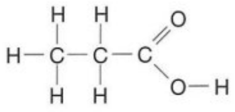
   (A) 2-Ethyl-4-methylpentane.
   (B) 2-Methyl-4-ethylpentane.
   (C) 2,4-Dimethylhexane.
   (D) 3,5-Dimethylhexane.
8. The functional group of an amide is:
   (A) $-NH_2$ (B) –COO
   (C) $-CONH_2$ (D) –COOH
9. An aldehyde has the general formula:
   (A) ROH
   (B) RCOOH
   (C) RCOR′
   (D) RCHO
10. The structure illustrated represents a model of a functional group. This group can be attached to a hydrogen atom or a carbon chain.



| | The name of the structure | The homologous group it defines |
|---|---|---|
| (A) | Hydroxyl | Hydrocarbon |
| (B) | Hydroxide | Alcohol |
| (C) | Carboxyl | Carboxylic acid |
| (D) | Carbonyl | Amide |

**11.** Aldehydes and ketones both have the:
(A) Carboxyl functional group.
(B) Carbonyl functional group.
(C) Hydroxyl functional group.
(D) Oxide functional group.

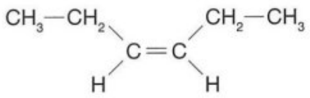
**12.** Identify the homologous group to which the following compound belongs.

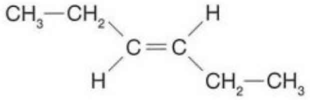


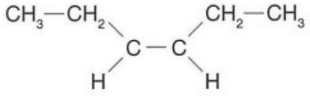
(A) Carboxylic acid.
(B) Alkane.
(C) Amide.
(D) Amine.

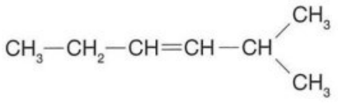
**13.** If a saturated hydrocarbon exists as isomers, these will have:
(A) The same structure.
(B) Different elemental composition.
(C) The same molecular formula.
(D) Ability to rotate a light beam.

**14.** Hexene exists as geometric isomers. Which formula correctly represents the trans form of hex-3-ene?

(A)


(B)


(C)


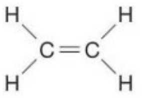
(D)

$CH_3-CH_2-CH=CH-CH(CH_3)_2$

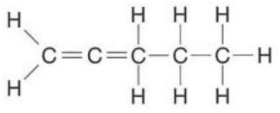
**15.** A triple bond involves two atoms sharing:
(A) Two electrons.
(B) Four electrons.
(C) Six electrons.
(D) Eight electrons.

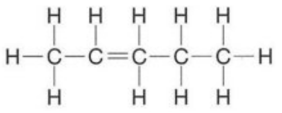
**16.** Which of the following equations correctly shows the ionisation of a carboxylic acid.
(A) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$
(B) $CH_3CH_2COOH \rightleftharpoons CH_3CH_2O^- + H^+$
(C) $CH_3CH_2OH \rightleftharpoons CH_3CH_2O^+ + OH^-$
(D) $CH_3COOH \rightleftharpoons CH_3CO^- + OH^+$

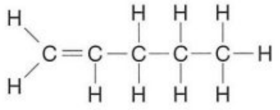
**17.** Carboxylic acids can be described as:
(A) Weak acids because they are present in the food we eat.
(B) Weak acids because they do not ionise completely.
(C) Strong acids because they have very polar ions.
(D) Strong acids because they react with metals.

**18.** The formula of the compound pent-2-ene is:

(A)


(B)


(C)


(D)


**19.** Of the following compounds, the one which is a saturated organic compound is:
(A) Water.
(B) Hexene.
(C) Cyclohexene.
(D) Hexane.

**20.** Which of the following hydrocarbons has structural isomers?
(A) $C_2H_6$
(B) $C_2H_4$
(C) $C_3H_8$
(D) $C_4H_{10}$

**INQUIRY QUESTION**

Discuss the role of the functional group in the systematic naming of organic chemicals.

# 14 Models Of Hydrocarbons

Hydrocarbons are molecular compounds. There are many ways in which we can represent molecular substances, all of which have limitations. We can use electron dot formulas, structural formulas, valence structures, ball and stick models and space-filling models.

We have already seen how **electron dot structures** use dots to show only the outer valence shell of electrons around an atom. These structures can provide a helpful tool in working out bonding between atoms and we can see at a glance if a stable outer shell will be formed when the atoms lose, gain or share electrons.

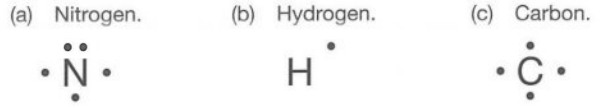
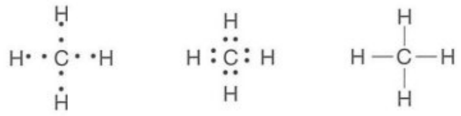

(a) Nitrogen. (b) Hydrogen. (c) Carbon.

**Figure 14.1** Electron dot structures for single atoms.

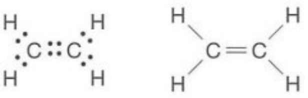
When electrons are shared we can either use just the dots close together, or draw a line to represent the shared pair of electrons or else draw a circle around the shared pair of electrons.

(a) Hydrogen gas.

(b) Methane ($CH_4$)



(c) Ethene



(d) Ethyne

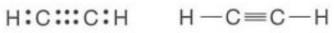
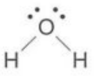


**Figure 14.2** Electron dot structures showing shared electrons.

## Structural formulas

Structural formulas can be used as models of compounds. They use 'sticks' to join atoms of elements. Structural formulas provide information about how atoms are bonded in covalent molecules, but they do not tell us about the shape of the molecule. For example, the structural formula of water can be written as H–O–H. This suggests the molecule is a linear (straight line) shape, whereas it is really a bent shape.


Bent shape of water molecule

Another problem with using diagrams as models, is that they usually only show two-dimensional forms of three-dimensional structures, although some do attempt to show 3-D structure such as the following diagram of methane.

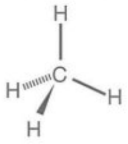


**Figure 14.3** Structure of methane.

## Space filling models

Space filling models can give a more accurate idea of three-dimensional structure of molecules, including the relative sizes of atoms.

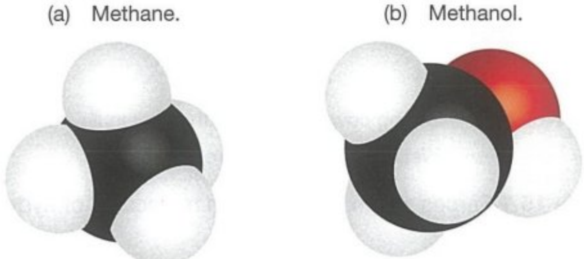

(a) Methane. (b) Methanol.

**Figure 14.4** Space filling models.

## Ball and stick models

Ball and stick models such as the model of ethanol ($C_2H_5OH$) shown can give an idea of the arrangement and relative size of atoms and can also provide information about bond length and angle.

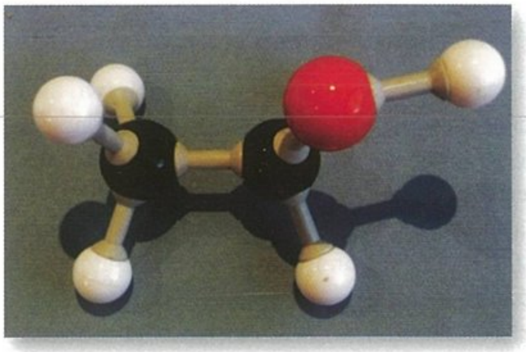


**Figure 14.5** Ball and stick model of ethanol.

## QUESTIONS

1. Describe different types of models you have constructed for organic chemicals, and explain why you found some more useful than others.
2. All these types of models have advantages but also limitations. Discuss this statement.

# 15 Revision – Intramolecular Forces

You already know that:

- Atoms of covalent substances share electrons.
- Most covalent substances exist as molecules.
- The atoms within these molecules are held together by strong covalent bonds – intramolecular forces.
- The whole molecules are attracted to each other by weaker forces – intermolecular forces.

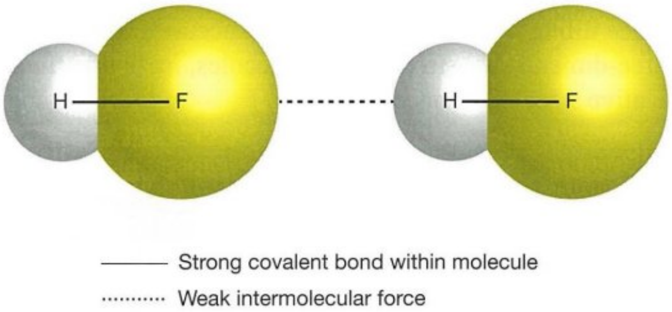


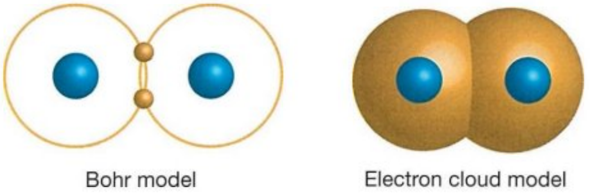
**Figure 15.1** Forces within and between molecules of hydrogen fluoride.

**The nature and strength of intermolecular forces can explain observable properties** such as vapour pressure, melting point, boiling point and solubility. However, to understand this, **we first need to look at bonds and forces in more detail**.

## Covalent bonds – non-polar bonds

When atoms share valence electrons to form covalent bonds the shared pair of electrons orbits both nuclei. Covalent bonds are very strong bonds.

In a molecule such as hydrogen ($H_2$), the two atoms are identical hydrogen atoms, so the bonding electrons are attracted equally to each nucleus and shared equally between them. The two shared electrons spend equal time in the area around each atom and this sharing of electrons forms the covalent bond which holds the atoms together. Such bonds are referred to as **non-polar covalent bonds**. Figure 15.2 shows two different types of models which can be used to illustrate this.



Bohr model

Electron cloud model

**Figure 15.2** Molecule of hydrogen gas with non-polar bond between its atoms.

## Covalent bonds – polar bonds

When the atoms joining together are not identical, then their electrons are not shared equally. For example, this happens when hydrogen and chlorine atoms share a pair of electrons to form hydrogen chloride (HCl). The shared electrons are more strongly attracted to the chlorine nucleus than to the hydrogen nucleus, so the electrons spend more time near the chlorine. This makes the chlorine end slightly more negative than the hydrogen end. A bond with unequal sharing of electrons is called a **polar covalent bond**. The bond forms a **dipole**, a structure with two oppositely charged ends and it can be shown as follows.

$$\delta^+ \mathrm{H} - \mathrm{Cl}\ \delta^-$$

The Greek lower case delta (δ) is used to represent a partial (small amount of) electrical charge, a much smaller charge than that on a proton or an electron. $\delta^+$ and $\delta^-$ symbols indicate the areas on the molecule surface which are slightly more positive or slightly more negative due to unequal sharing of electrons.

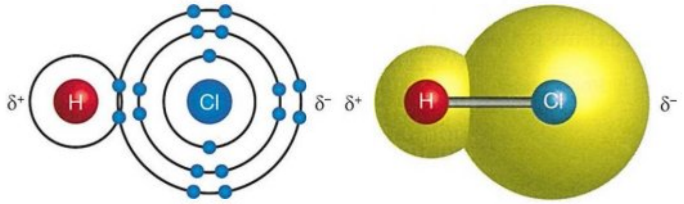
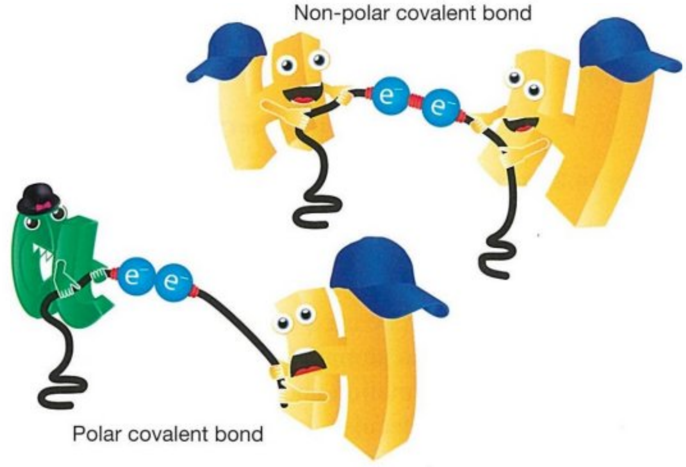


**Figure 15.3** Electron dot and electron cloud diagrams to illustrate the polar bond in hydrogen chloride.

## Polar and non-polar molecules

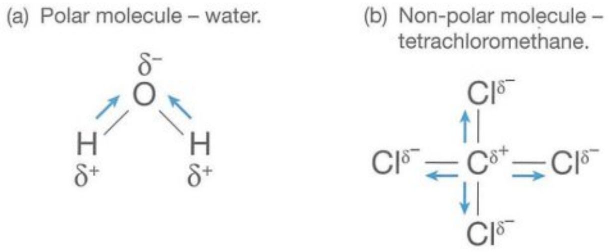
You could think about polar and non-polar bonds like this:



A molecule which consists of **only non-polar bonds**, e.g. $H_2$, $Cl_2$ will be called a **non-polar molecule**.

A molecule which contains **one polar bond**, e.g. HCl will have an unequal charge distribution so it will form a **polar molecule** with a slightly positive area at one end and a slightly negative area at the other end.

A molecule which has **more than one polar bond** may have **polar molecules**, such as in water $H_2O$, or **non-polar molecules** such as in tetrachloromethane $CCl_4$ (which used to be called carbon tetrachloride). Molecules such as $CCl_4$ have non-polar molecules because the way that the polar bonds are arranged means that they cancel each other out.


(a) Polar molecule – water.

(b) Non-polar molecule – tetrachloromethane.

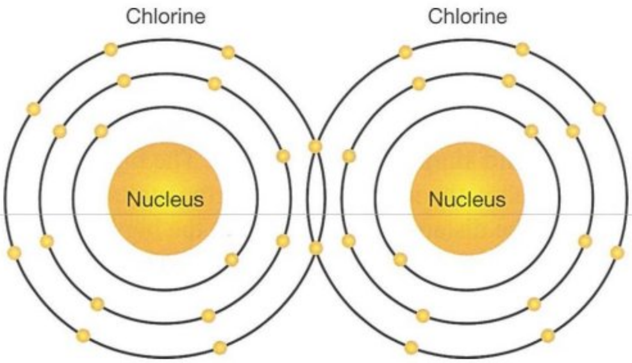
**Figure 15.4** Polar and non-polar molecules.

With these non-polar molecules, the charge distribution is even over the surface of the molecules even though polar covalent bonds are present.

The shape of a molecule helps to determine whether or not polar bonds cancel each other out and thus whether the molecule will be polar or non-polar. You will be learning about shapes of molecules soon.

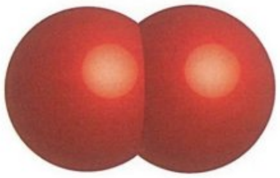
## QUESTIONS

1. A molecule of chlorine is drawn below.
   (a) Identify the shared electrons in this molecule.
   (b) Explain why the chlorine molecule is said to contain a non-polar covalent bond.

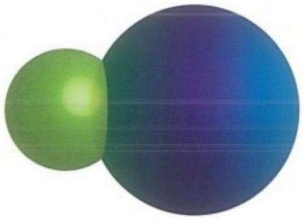


2. The following diagrams are said to illustrate the difference between an ionic bond, a non-polar covalent bond and a polar covalent bond. Identify which is which and justify your decisions.

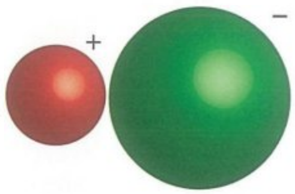
(a)



(b)



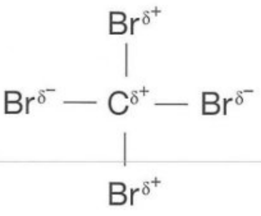
(c)



3. Copy and complete the table to show whether or not each of the substances listed has polar or non-polar bonds within its molecules.

| Substance | Formula | Polar/non-polar bonds |
|---|---|---|
| Hydrogen | | |
| Ammonia | | |
| Hydrogen bromide | | |
| Water | | |
| Carbon dioxide | | |
| Argon | | |

4. The word 'polar' can be applied to a bond, a molecule and a substance. Discuss this statement.
5. Explain the difference in polarity between a hydrogen molecule and a hydrogen fluoride molecule.
6. Why is the tetrabromomethane molecule non-polar, even though it contains polar bonds.



7. Identify each of the following statements as true or false and justify your answer.
   (a) Oxygen molecules are non-polar.
   (b) Sodium chloride contains molecules of NaCl.
   (c) Chlorine contains polar covalent bonds.
   (d) Covalent bonds are strong forces of attraction within molecules.
8. Check your knowledge with this quick quiz.
   (a) A polar bond is an attraction between two atoms which are (the same/different).
   (b) The covalent bond in a bromine molecule is a (polar/non-polar) bond.
   (c) The covalent bond in a hydrogen fluoride molecule is (polar/non-polar).
   (d) Covalent bonds occur when electrons are (shared/donated/received).

# 16 Revision – Intermolecular Forces

This chapter and the next look at the types of forces that exist between covalent molecules.

**Intermolecular forces** (also called van der Waals forces) are the attractive electrostatic forces holding covalent molecules together.

These have to be broken for a covalent molecular substance to dissolve or change state. When a covalent substance dissolves, melts or evaporates, the molecule itself does not break up. Instead, whole molecules move away from each other.

**Figure 16.1** Intermolecular forces.

There are three main **types of intermolecular forces** – dispersion forces, dipole-dipole forces and hydrogen bonds. We will look at the first two in this chapter, and then in Chapter 17 we will compare them to hydrogen bonding.

## Dispersion forces

Dispersion forces are very weak, constantly changing, electrostatic forces of attraction between covalent molecules.

Dispersion forces occur between **all covalent molecules**. In non-polar substances, dispersion forces are the only forces between the molecules. Polar substances have other types of intermolecular forces as well as dispersion forces.

Dispersion forces are caused by changes in the electron distribution of atoms in nearby molecules. This is due to the shifting of electron clouds as electrons orbit the nuclei of atoms within the molecule.

At any one instant all the electrons might be on one side of the atom, at the next instant they might be evenly spread, or they might be at the other end. These constant changes in charge distribution within molecules cause constantly fluctuating forces of attraction. As the electron clouds are distorted, they form – just for an instant – a temporary dipole.

When one of these temporary dipoles comes close to another molecule it can induce a charge in it also.

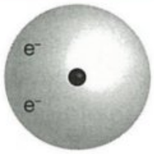
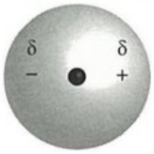
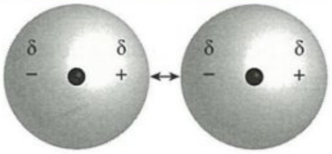
| | |
|---|---|
| (a) Just for an instant the electrons in a helium atom are close together – the distribution of electrons is uneven. |  |
| (b) A temporary dipole forms in this atom just for the instant that the electrons are on the same side. |  |
| (c) Two nearby dipoles are attracted to each other while their temporary charges last. |  |

**Figure 16.2** Electrons are constantly moving.

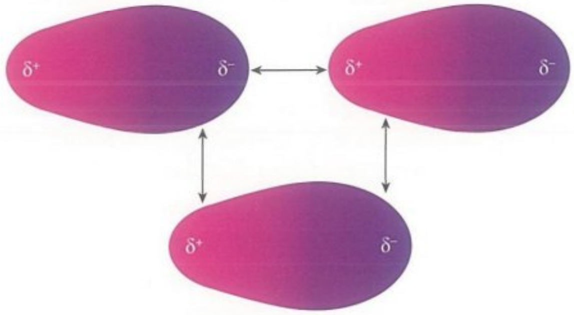
These temporary dipoles, and the dispersion forces they cause, are constantly being formed and broken. They attract each other briefly and then disappear as the electrons move on and form different dipoles.

Generally, not much energy is needed to break dispersion forces, as they are often quite weak. Non-polar substances, with only dispersion forces holding their molecules together, e.g. hydrogen, methane and nitrogen, have very low melting and boiling points. This is because their only intermolecular forces are dispersion forces which are weak and easy to break.

However, dispersion forces do **vary in strength** depending on the **size and shape of the molecule**. The bigger the molecular mass, the more electrons in the molecule, and the greater the distance they can move, the bigger the dispersion forces. Also long thin molecules have greater dispersion forces than short fat ones with the same number of electrons – they develop bigger dipoles and are more strongly attracted as they can get closer together.

## Dipole-dipole forces

**Dipole-dipole forces** are stronger, permanent, electrostatic forces of attraction between **polar molecules**. Polar molecules are dipoles – they have permanently charged positive and negative ends. The slightly positive end of one molecule attracts the slightly negative end of another molecule. This electrostatic attraction between opposite charges is the dipole-dipole force. Because they are stronger attractive forces, more energy is needed to break dipole-dipole forces than to break dispersion forces.



Dipole-dipole force between molecules

**Figure 16.3** Polar molecules are attracted to each other by dipole-dipole forces between opposite charges.

Sometimes a polar molecule induces a charge in a non-polar molecule and they are then attracted while they are close to each other.

(a) A non-polar molecule and a polar molecule come near each other.

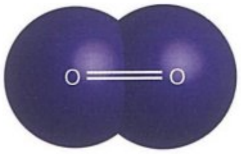
(b) A temporary charge is induced in the non-polar molecule, so it forms a temporary dipole.

**Figure 16.4** Inducing dipoles.

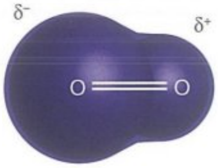
In the next chapter we will compare these dispersion forces and dipole-dipole forces with the third type of intermolecular force – hydrogen bonding.

## QUESTIONS

1. Dispersion forces are present between all molecules.
   (a) Describe the formation of dispersion forces between molecules.
   (b) Outline what determines the strength of dispersion forces.
2. Outline two differences between dispersion forces and dipole-dipole forces.
3. (a) Define a dipole.
   (b) Where would you expect to find a dipole?
   (c) What is a dipole-dipole force?
4. An oxygen molecule usually looks like this:



In a textbook it was shown looking like this:



Suggest a reason for it being drawn this way.

5. Would sodium chloride have any type of intermolecular forces? Justify your answer.
6. The following substances exist as molecules. Divide them into two groups based on the nature of their intermolecular forces.
   Chlorine, ethane, nitrogen, sulfur dioxide.
7. Explain how a molecule can be non-polar when it has polar covalent bonds.
8. Research the relevance of dispersion forces to lizards called geckoes.

9. Identify whether each statement is true or false and justify your decision.
   (a) Dispersion forces are permanent forces between all molecules.
   (b) Dispersion forces occur between all molecules, both polar and non-polar molecules.
10. Check your knowledge with the following quick quiz.
   (a) Intermolecular forces are those (within/between) molecules.
   (b) Identify the intermolecular forces that occur between all covalent molecules.
   (c) The temporary forces of attraction between molecules are called ........................ forces.
   (d) What do we call permanent attractive forces between molecules?
   (e) Which are weaker forces, dispersion forces or dipole-dipole forces?
   (f) Dipole-dipole forces occur between (polar/non-polar) molecules.

# 17 Revision – More Intermolecular Forces

In Chapter 16 you looked at two types of forces between molecules (intermolecular forces) – dispersion forces and dipole-dipole forces.

The third type of electrostatic attractive force that can occur between covalent molecules is the hydrogen bond.

**Hydrogen bonds** are strong electrostatic attractions between the slightly positive **hydrogen** atoms of one molecule and a highly electronegative atom (**oxygen, nitrogen or fluorine)** in another nearby molecule. Hydrogen bonding is sometimes regarded as a special type of dipole-dipole force.

Just having a hydrogen atom in a molecule is not enough for hydrogen bonds to form between molecules. Hydrogen bonds only occur in highly polar molecules – those which contain at least one hydrogen atom and *also* either oxygen, nitrogen or fluorine. They are found in compounds such as water, ammonia, hydrogen fluoride and ethanol.

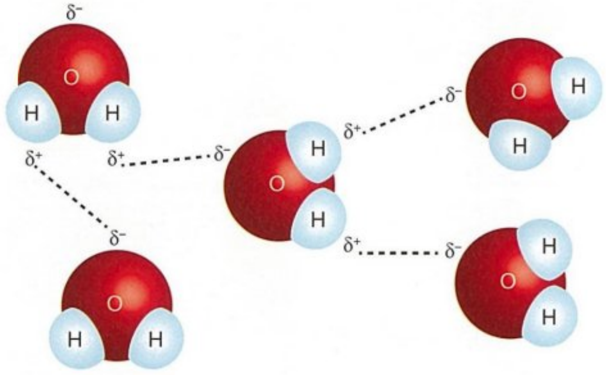


**Figure 17.1** Hydrogen bonds between water molecules. (*Note*: Dispersion forces and dipole-dipole forces also exist between these molecules but are not shown here.)

Remember that dispersion forces, dipole-dipole forces and hydrogen bonds are all **intermolecular forces** – they occur between molecules.

**Intermolecular forces vary in strength**. However, they are not the strongest forces that exist in the atomic world. None of the intermolecular forces, not even hydrogen bonds, are nearly as strong as the covalent forces between atoms inside the molecule, nor are they as strong as the forces between positive and negative ions in ionic compounds.

## QUESTIONS

1. Compare the three main types of intermolecular forces. Tabulate your answer.
2. (a) Describe what is meant by a hydrogen bond.
   (b) Use a diagram to show hydrogen bonding between ammonia molecules.
   (c) A student wrote that, 'Hydrogen bonds hold the hydrogen atoms together in a molecule of ammonia gas.' For this answer the student received no marks. Explain why the teacher marked the answer with a zero.
3. Copy and complete the table to summarise the types of intermolecular forces between molecules of the substances listed.

| Substance | Dispersion forces | Dipole-dipole forces | Hydrogen bonds |
|---|---|---|---|
| Helium He | | | |
| Oxygen $O_2$ | | | |
| Water $H_2O$ | | | |
| Methane $CH_4$ | | | |
| Hydrogen sulfide $H_2S$ | | | |
| Ammonia $NH_3$ | | | |
| Hydrogen fluoride HF | | | |
| Acetic acid $CH_3COOH$ | | | |
| Carbon dioxide $CO_2$ | | | |
| Hydrogen chloride HCl | | | |
| Bromine liquid $Br_2$ | | | |
| Ethanol $C_2H_5OH$ | | | |

4. Identify each of the following statements as true or false and justify your decision.
   (a) Hydrogen bonding occurs in a molecule of water between the hydrogen and the oxygen atoms.
   (b) Dipole-dipole forces are the weakest intermolecular forces.
5. List the following substances in order of decreasing strength of intermolecular forces: hydrogen sulfide, ethane, water, argon.
6. Check your knowledge with this quick quiz.
   (a) What do we call the strongest of the intermolecular forces of attraction?
   (b) Name a substance which would have hydrogen bonding.
   (c) Name two atoms that must be present in two molecules for hydrogen bonding to occur between the molecules.

# 18 Properties and Bonding Of Hydrocarbons

Hydrocarbons are molecular compounds. Their bonding includes intramolecular bonding and intermolecular bonding as shown below.

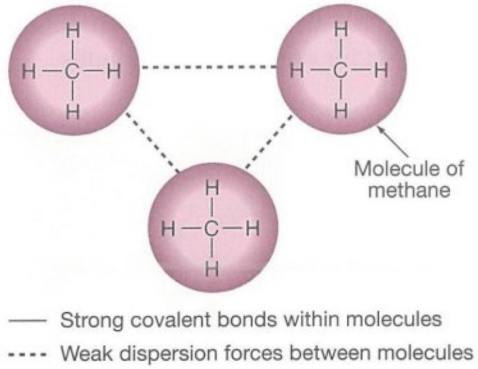


**Figure 18.1** Bonding in the alkane, methane.

## Intramolecular bonding

**Intramolecular bonds** in alkanes, alkenes and alkynes are strong covalent bonds between carbon atoms (C–C) and between carbon and hydrogen atoms (C–H).

The only difference between the bonds in these hydrocarbon series is that alkenes have one or more double bonds, and alkynes have one or more triple bonds.

## Intermolecular bonding

The only intermolecular bonds (between molecules) are weak dispersion forces.

Alkanes, alkene and alkynes are **non-polar** as there is little difference between the electronegativity of carbon and hydrogen atoms, so there are no dipole-dipole forces. There are only carbon and hydrogen atoms present, so there is no hydrogen bonding because alkanes do not contain any N, O or F atoms.

## Physical properties

Physical properties of molecular compounds, such as melting and boiling points, solubility, density and viscosity, depend on the strength of intermolecular forces. You will have investigated some of these physical properties of hydrocarbons in the laboratory. However, because many organic compounds are highly flammable, and some are poisonous substances you may find you are limited to just a few to compare. When we do not have access to chemicals, or cannot carry out experiments on them, we can compare their properties using data tables to obtain information such as melting and boiling points. If you look at the boiling points of hydrocarbons in Table 18.1, you will realise we cannot achieve some of those temperatures in a school laboratory.

## Melting and boiling points

In hydrocarbons there are only dispersion forces, which are weak and relatively easily broken when a hydrocarbon is heated.

Alkanes, alkenes and alkynes change state at relatively low temperatures – they have **low melting and boiling points**.

The molecule itself does not break up when substances are heated and change state, it is just the forces holding the molecules together that are broken. As molecules become larger, the dispersion forces increase, so more energy is needed to break them and the boiling point increases.

C1 to C4 have the lowest boiling points. Larger molecules have higher boiling points because the dispersion forces increase as the mass of the molecule increases. It takes more energy to pull larger molecules apart.

Because of these low melting and boiling points, at 25°C, C1 to C4 alkanes are gases, C5 to C16 are liquids and those with larger molecules are solids.

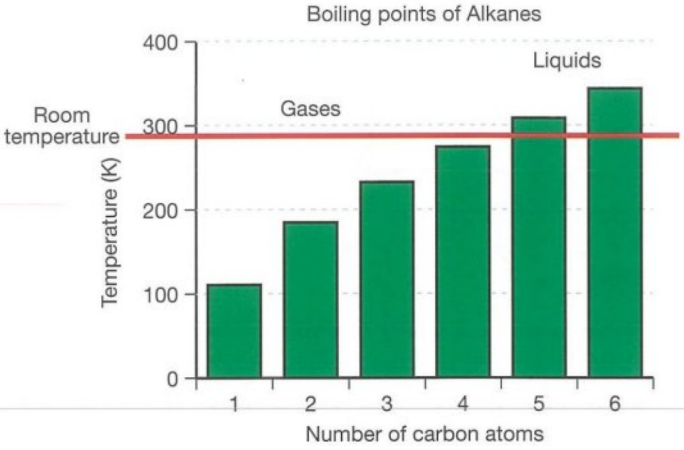


**Figure 18.2** Boiling points of some alkanes.

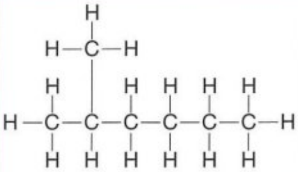
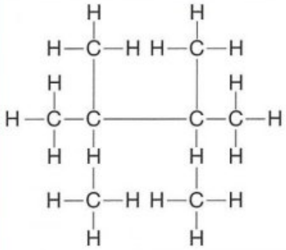
If you compare molecules with the same number of carbon atoms, there is little difference between the melting and boiling points of alkanes and alkenes while those of alkynes are just a little higher, as you can see in Table 18.1.

**Table 18.1** Some boiling points of alkanes, alkenes and alkynes.

| Boiling points (°C) | | |
|---|---|---|
| Propane –42 | Propene –47.6 | Propyne –23.2 |
| Pentane 36.1 | Pentene 30.0 | Pentyne 40.2 |
| Hexane 68 | Hexene 63 | Hexyne 81 |

Whether a hydrocarbon is branched or not has an effect on the melting and boiling point. The presence of branching chains in hydrocarbons lowers the boiling point slightly. An unbranched chain has a more extended shape and this increases the intermolecular forces that need to be broken, making the boiling point higher. For example, Table 18.2 shows the boiling points of three isomers of octane. Each isomer has the same number of carbon and hydrogen atoms and thus the same mass. However, their boiling points differ. This can only be because of the way the atoms are arranged in the molecule. Octane has the longest chain, and the highest boiling point.

**Table 18.2** Boiling points of branched and unbranched isomers of $C_8H_{18}$.

| Formula | Name | Boiling point (°C) |
|---|---|---|
| $CH_3(CH_2)_6CH_3$ | Octane | 126 |
|  | 2-Methylheptane | 118 |
|  | 2,2,3,3-Tetramethylbutane | 107 |

## Density

Hydrocarbons have **lower densities than water**, so hydrocarbons float on water. This is also related to intermolecular forces. Water has stronger intermolecular forces as it is polar and forms hydrogen bonds, increasing the mass per unit volume (density). You could compare the density of hydrocarbons with water by adding the two together in a test tube.

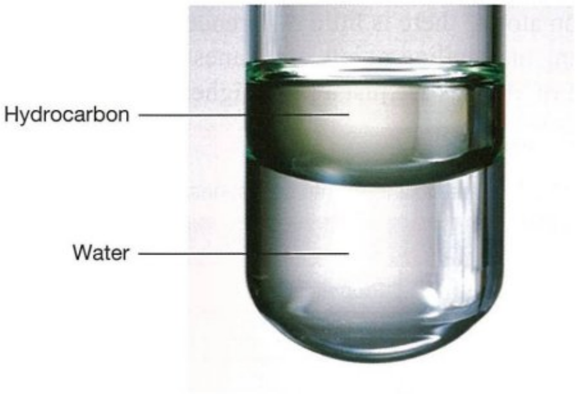


**Figure 18.3** Hydrocarbons are less dense than water.

## Solubility

Hydrocarbons are **not soluble in water – they are insoluble.** Water is polar – it will dissolve substances that it can form bonds with – other polar substances and those that it can form hydrogen bonds with. It cannot bond with non-polar hydrocarbons, so they are not soluble in water.

However, hydrocarbons do **dissolve in organic solvents**, substances which are also non-polar. Also, liquid alkanes can act as solvents for non-ionic compounds.

## Viscosity

Viscosity means resistance to flow. This depends on intermolecular forces. Larger hydrocarbons with larger intermolecular forces will be more viscous – more resistant to flow.

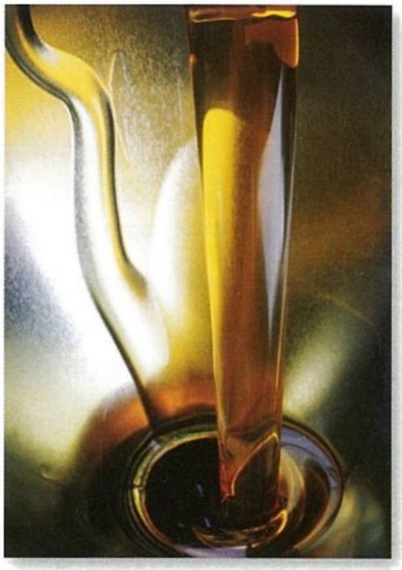


**Figure 18.4** Pouring motor oil.

## Chemical properties

In chemical reactions, it is the intramolecular covalent bonds that are broken and re-formed.

Alkanes are not very reactive compared to alkenes and alkynes. The double –C=C– bond in alkenes and the triple –C≡C– bond in alkynes, are more easily broken than single –C–C– bonds, making alkenes and alkynes more reactive than alkanes.

## Combustion

Hydrocarbons undergo **complete combustion** in a plentiful supply of air or oxygen to form carbon dioxide and water. Combustion is an exothermic reaction, which accounts for the use of hydrocarbons, especially alkanes, as fuels.

$$\begin{array}{lclcccc}
\text{Ethane} & + & \text{oxygen} & \rightarrow & \text{carbon dioxide} & + & \text{water} \\
C_2H_6(g) & + & \tfrac{7}{2}O_2(g) & \rightarrow & 2CO_2(g) & + & 3H_2O(l) \\
\text{Ethene} & + & \text{oxygen} & \rightarrow & \text{carbon dioxide} & + & \text{water} \\
C_2H_4(g) & + & 3O_2(g) & \rightarrow & 2CO_2(g) & + & 2H_2O(l) \\
\text{Ethyne} & + & \text{oxygen} & \rightarrow & \text{carbon dioxide} & + & \text{water} \\
C_2H_2(g) & + & \tfrac{5}{2}O_2(g) & \rightarrow & 2CO_2(g) & + & H_2O(l)
\end{array}$$

Alkenes and alkynes burn more vigorously than alkanes due to their double and triple bonds.

In a restricted supply of oxygen, **combustion is incomplete**. Hydrocarbons burn to produce water and either carbon monoxide or carbon, depending on the availability of oxygen. The carbon is formed as soot.

Ethane + oxygen → carbon + carbon monoxide + water

$$C_2H_6(g) + 2O_2(g) \rightarrow C(s) + CO(g) + 3H_2O(l)$$

Ethene + oxygen → carbon + carbon monoxide + water

$$C_2H_4(g) + \tfrac{3}{2}O_2(g) \rightarrow C(s) + CO(g) + 2H_2O(l)$$

Ethyne + oxygen → carbon + carbon monoxide + water

$$C_2H_2(g) + O_2(g) \rightarrow C(s) + CO(g) + H_2O(l)$$

Alkenes and alkynes tend to burn with a more sooty flame than alkanes because the percentage of carbon is higher in alkenes than in alkanes, and some carbon may not combine with oxygen.

## Dehydrogenation of alkanes

The dehydrogenation of alkanes is mentioned here because the dehydrogenation of ethane to produce ethene for the manufacture of polymers is an important industrial reaction.

$CH_3 - CH_3 \rightarrow CH_2{=}CH_2 + H_2$

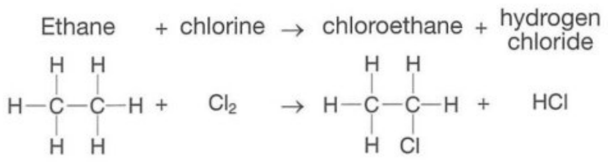
Ethene is produced in huge quantities as it is the starting point in the manufacture of a vast range of chemicals, including polymers, antifreeze and solvents. Ethene is also used to accelerate the ripening of fruit.

## Substitution reactions of alkanes

Alkanes are saturated compounds and not very reactive, however they can undergo substitution reactions in which an atom of another element is substituted for one of their hydrogen atoms. Substitution reactions **cannot take place in the dark**; **energy is needed** in the form of ultraviolet light for substitution reactions to take place.

Alkanes can undergo substitution reactions with halogens (group 7 non-metals) such as chlorine.

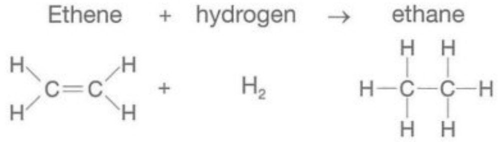
Two products are always produced in substitution reactions.



Alkenes and alkynes do not generally undergo substitution reactions.

## Addition reactions of alkenes and alkynes

Addition reactions occur in unsaturated organic compounds such as alkenes and alkynes. In an addition reaction, the double or triple bond is broken and other atoms are added. Energy is not needed for addition reactions to occur, they can take place **in the dark, as well as in UV light**. Alkenes can undergo addition reactions with hydrogen, water, halogens and hydrogen halides. For example, the addition of hydrogen to an alkene produces the corresponding alkane.



Alkanes do not have a double or triple bond, so they cannot undergo addition reactions.

You will learn more about substitution and addition reactions in the next section.

## QUESTIONS

1. Describe an investigation you carried out to compare the properties of hydrocarbons in an homologous series.
2. Account for the relatively low boiling points of most hydrocarbons.
3. Compare the following flames and suggest possible reasons why they differ.

(a)

(b)

3. Hydrocarbons undergo combustion.
   (a) Name the products of complete combustion.
   (b) Name the products of incomplete combustion.
   (c) Which would be more likely to produce a sooty flame, in the same oxygen supply, an alkane or an alkene?
4. Write balanced equations for the complete combustion of:
   (a) Methane.
   (b) Propane.
   (c) Butene
   (d) Ethyne (acetylene).
5. Hydrocarbons undergo substitution and addition reactions.
   (a) Which type of reaction needs energy in order to take place, substitution or addition reactions?
   (b) Name a hydrocarbon series that undergoes each of these reaction types.
6. (a) Would you expect hydrocarbons to be soluble or insoluble in water? Explain.
   (b) Would you expect hydrocarbons to be soluble or insoluble in organic solvents? Explain.

# 19 Shapes Of Hydrocarbon Molecules

The overall shape of an organic molecule is determined by its carbon atoms and the bonds between them.

You have seen that carbon atoms can join in single, double, or triple bonds.

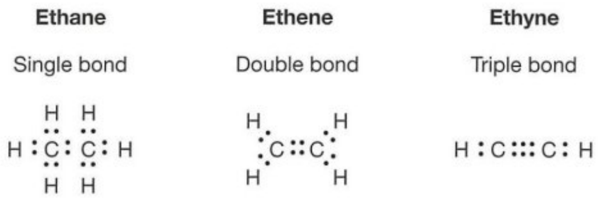


**Figure 19.1** Carbon-carbon bonds.

These diagrams are useful as they show the sharing of electrons between atoms, but they give no indication of the sizes and shapes of the molecules which are determined by the lengths and directions of their chemical bonds.

These are represented in ball and stick models such as the following.

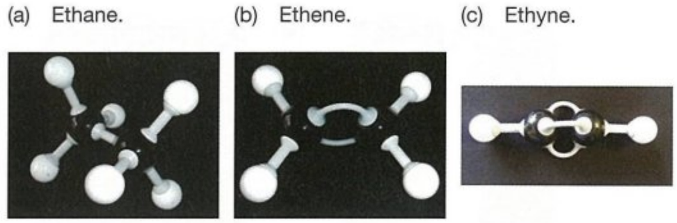

(a) Ethane. (b) Ethene. (c) Ethyne.

**Figure 19.2** Ball and stick models.

From these models we can see that the shapes of their molecules are very different.

| Ethane ($C_2H_6$) | Ethene ($C_2H_4$) | Ethyne ($C_2H_2$) |
|---|---|---|
|  |  |  |
| Two overlapping tetrahedrons | Trigonal planar | Linear |

**Figure 19.3** Shapes of molecules.

Larger molecules are more complex. In each case you look at each carbon atom and its bonds individually.

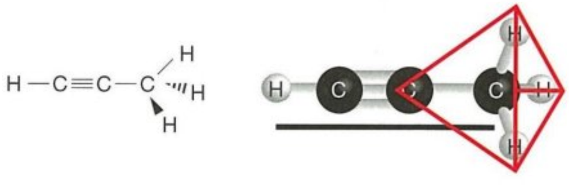


**Figure 19.4** Shape of propyne $HC=C-CH_3$.

Propyne is linear at the carbon 1 and 2 end with a tetrahedron at carbon 3 as this carbon atom has 4 attached bonds.

Most high school molecular model kits are useful for showing the angles and shapes and even the lengths of bonds. They are also useful to help visualise the rotation that can occur around single bonds but not double or triple bonds. However, remember that, in real life, the bonds are really much smaller than the diameter of atoms, and the atoms are bunched much closer together, more like space filling models.

We can draw 2-D organic molecules that show 3-D structure by using the following symbols.

**Table 19.1** Drawing 3-D shapes.

| Type of bond | Description |
|---|---|
| — | The bond lies in the plane of the paper. |
| IIIIIIIIIIIII<br>or<br>·····IIIIIIII | The bond extends backwards, away from the viewer. |
| ◀ | The bond protrudes forwards, towards the viewer (comes out of the paper towards you). |

As an example of this, compare the diagram of methane on the left to the ball and stick model on the right.

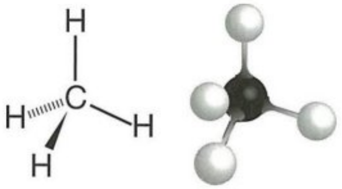


**Figure 19.5** Representing methane in 3-D.

## QUESTIONS

1. Describe the 3-D shape of ethane and illustrate it.
2. Describe the shape of an ethene molecule.
3. What is the shape of the ethyne molecule?

# 20 Safety With Organic Compounds

Special precautions are needed when handling or using many organic compounds.

## General safety rules for laboratories

Of course, you will still take all of the usual precautions for chemistry experiments, such as:

- Wear safety glasses.
- Wear suitable clothing, including covered footwear, and keep long hair tied back.
- Never take food into a chemistry laboratory.
- Keep the benches tidy and clean and the aisles free.
- Clean up any spills immediately and if it is large or hazardous always inform your teacher.
- Never taste anything or inhale directly. If it is necessary to smell a chemical you should waft it towards you with your hand.

- Do not return unused chemicals to the stock container.
- Never heat a closed system or mix chemicals in front of your face.
- Do not remove concentrated acids and bases from the fume cupboard.
- Test tubes and flasks containing reacting chemicals should always be pointed away from other people.
- Dispose of wastes as instructed and do not take any materials from the laboratory.
- Do you know where to find eyewash, a safety shower and a fire blanket?
- Wash your hands before leaving the laboratory.

There is a **Material Safety Data Sheet** (MSDS) available with information about any chemicals you will be using. You should always consult this before you use a chemical.

## Safety rules for organic substances

As well as these general precautions, when dealing with organic substances, you need to consider that:

Many organic chemicals are **volatile** – they vaporise easily and may be inhaled or absorbed via the skin. To avoid inhaling toxic vapours you should work in a fume cupboard or hood.

Organic substances are also often **flammable** and can **irritate skin and eyes**. Flammable and combustible substances such as methanol, ethanol, acetone, hexane and pentane should never be heated on a hotplate, and of course they should be kept away from naked flames. If you need to heat them use a hot water bath.

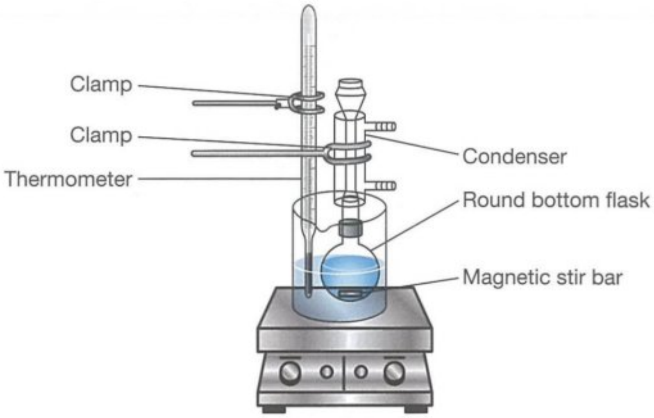


**Figure 20.1** Hot water bath.

Many organic solvent vapours are heavier than air and will flow along the ground.

Organic chemicals are not poured down the sink; your teacher will provide you with **a container for them so they can be disposed of safely**.

## QUESTIONS

1. List five general safety rules for working in the laboratory.
2. (a) Why are special precautions taken when using organic chemicals in a laboratory?
   (b) List three such precautions.
3. Work in a group to devise a poster advertising one or more safety rules for the laboratory.

# 21 Revision – Fossil Fuels

We obtain fossil fuels from the earth and use them for many purposes, but principally as fuels and for the production of polymers. You will have covered some of this in year 11, so Chapters 21 to 24 are for revision – to remind you of how we extract and use fossil fuels and also some of the environmental, economic and societal effects of our use of the hydrocarbons we extract from the earth. You will be learning more about polymers soon.

## Fossil fuels

Fossil fuels are energy sources that have been made by the action of geological processes (heat and pressure), over millions of years, on carbon compounds which are present in the buried remains of once living organisms. Fossil fuels include coal and petroleum (crude oil and natural gas), coal seam gas and also shale oil and gas. Fossil fuels are finite and **non-renewable** – they take millions of years to form and once we have used up available supplies, we cannot replace them.

## Coal

Coal is a rock consisting mainly of carbon (from 50% to 98%). It also contains hydrogen, oxygen and small amounts of other elements such as nitrogen and sulfur, together with varying amounts of water and inorganic matter. The inorganic matter does not burn, it remains as ash after the coal burns.

## Formation of coal

**Coal is formed** from the heat and compression of buried remains of plants over millions of years to form peat, then brown coal, black coal and finally anthracite.

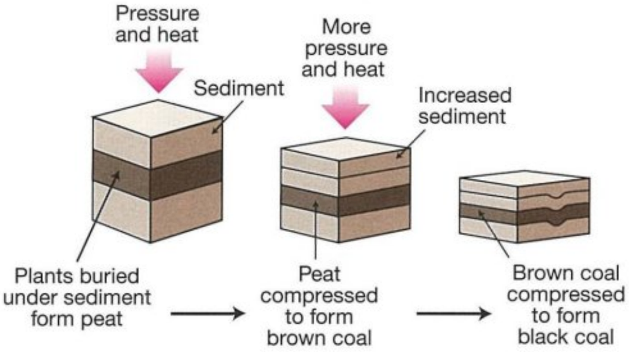


Figure 21.1 Formation of coal.

## Coal resources

The largest coal reserves are found in the USA, Russia, China and Australia. World coal consumption has been growing rapidly, especially in developing areas such as China, which is now the biggest producer and consumer of coal.

## Coal in Australia

In Australia, coal is found in every state and in the Northern Territory. However, New South Wales, Victoria and Queensland are our main producers. It has been estimated that Australia has 6% of the world's black coal and about 25% of the world's brown coal deposits. Most (95%) of our black coal is mined in New South Wales and Queensland, and most (96%) of our brown coal is mined in Victoria.

## Uses of coal

- Coal is a major source of energy, especially for the generation of electricity. In Australia, coal produces about 80% of our electricity.
- Coal is also a major source of export income for Australia. Australian black coal is highly valued because of its high energy, low ash and low sulfur content.
- Coal is used in industry, to make products such as cement, glass and aluminium.
- In some areas, coal is used for domestic heating.
- Some black coal is heated without air or oxygen to make coke which is used in the production of iron and steel.

## Petroleum – crude oil and natural gas

Petroleum consists of **crude oil and natural gas**. These are both formed from once-living organisms, mainly single celled marine organisms, so they are called fossil fuels. Supplies of petroleum are finite and non-renewable.

## Formation of petroleum

Petroleum has been formed by the action of geological processes (heat and pressure) on the remains of animals, especially microscopic marine organisms such as diatoms. These must be buried under sediment and compressed for millions of years to form petroleum. The petroleum formed is trapped in porous rocks when the rock layers above and below are impervious (won't let liquids through). Natural gas forms with the liquid petroleum and slowly rises to the top.

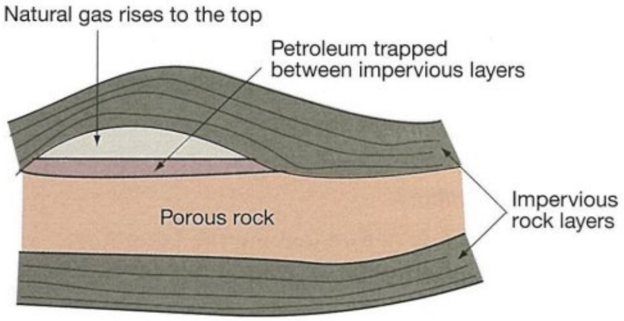


Figure 21.2 Formation of petroleum.

## Composition of petroleum

**Crude oil** is a mixture of **liquid** compounds, mainly hydrocarbons. Petroleum contains up to 300 compounds of hydrogen and carbon (hydrocarbons) as well as sulfur and nitrogen. It undergoes fractional distillation to separate out groups of chemicals (called fractions) which can be used for specific purposes, for example petrol for motor vehicles, aviation fuel, kerosene, diesel fuel and lubricating oil.

**Liquefied petroleum gas** (LPG) mainly consists of propane ($C_3H_8$) and/or butane ($C_4H_{10}$). It can be produced during natural gas processing and during the refining of crude oil. LPG is stored and transported as a cooled liquid under pressure.

**Natural gas** is a mixture of combustible **gases**, mostly methane with small amounts of other gases. The composition of natural gas varies, but typical figures are as follows.

Hydrocarbons such as:

- methane 91.6%
- ethane 5.0%
- propane 0.4%
- butane 0.1%

Natural gas can also contain small amounts of other substances such as nitrogen, oxygen and carbon dioxide.

## Petroleum resources

The largest oil reserves are in Venezuela, the Middle East (especially Saudi Arabia, Iran, Iraq and Kuwait) and Canada. The world's largest reserves of natural gas are in the Middle East (about 40%) and the Russian Federation (about 27%). At the current rate of production and consumption, resources worldwide could last about 50 to 60 years.

**Figure 21.3** Offshore oil rig.

## Petroleum in Australia

Australia has about 0.3% of the world oil reserves, mostly associated with giant offshore gas fields, off the coast of Western Australia. We also have large reserves of natural gas. At present we export liquefied natural gas (LNG) to other countries such as Japan, China and South Korea.

## Using fossil fuels

**Crude oil** – the liquid part of petroleum is mainly used for the production of fuels – petrol, diesel fuel, heating oil and jet fuel. At present, about 80% of the transport fuels used worldwide are derived from petroleum. Other uses include the production of lubricants, waxes and asphalt. A small percentage is used as petrochemical feedstock – to manufacture other chemicals, e.g. polymers.

**Natural gas is used** mainly to produce energy for:

- Manufacturing (36%), e.g. for making bricks, cement, glass and aluminium.
- Producing electricity (32.5%), e.g. to produce steam to turn turbines.
- Mining (12.5%).
- Homes (12.0%) – heating, cooling and cooking.
- Commercial (3.8%), e.g. smelting ore.
- Transport (3.2%), e.g. as a fuel in vehicles.

Natural gas is also used as a source of chemicals to manufacture plastics and other chemicals such as fertilisers.

As a fuel, natural gas has the following advantages.

- It produces less carbon dioxide per energy unit than any other fossil fuel.
- It is a cleaner burning fuel, producing less sulfur dioxide, nitrogen oxides, particles and volatile products than other fossil fuels.
- Methane is lighter than air and boils at –181°C, so natural gas will easily disperse if there is a leak.

**Coal seam gas** is natural gas, mostly methane, which has collected near underground coal seams. The surrounding rock is fractured using a mixture of water, sand and chemicals pumped in at high pressure. This is called fracking. Fracking is noisy and the waste water from extracting coal seam gas is often contaminated with salt, toxic or radioactive substances and heavy metals.

Recently there has been growth in the development of this gas associated with coal seams. Most (about 90%) of Queensland's gas supply is coal seam gas.

Australian coal seam gas resources (mainly methane) may be particularly useful as they are close to our major population centres along the east coast.

However, this proximity to population centres is making the mining of coal seam gases very controversial, and there is a great deal of opposition to its extraction. This is because of the noise and possible associated pollution. Coal seam gas has 20 times the global warming effect of carbon dioxide if it escapes to the atmosphere.

**Shale oil and gas** are fuels extracted from fine-grained sedimentary rocks (oil shale) which contain a solid mixture of organic compounds. Major deposits occur in the United States and Canada. There are also deposits in other countries including Australia.

There is controversy about the use of shale oil as it is presently more costly to extract than petroleum and its extraction involves fracking with multiple wells and has considerable environmental impact.

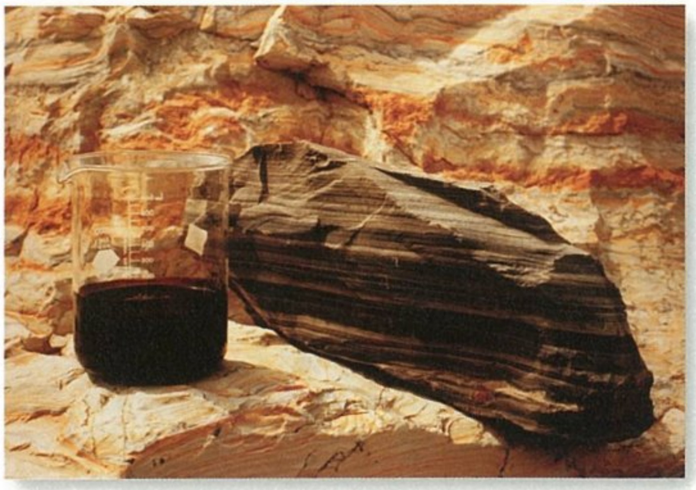


**Figure 21.4** A block of shale oil and beaker of crude oil extracted from this type of rock.

## QUESTIONS

1. (a) Outline how coal is formed.
   (b) Use the data in the table to help explain why black coal and anthracite are the most highly regarded forms of coal.

| Factor | Peat | Brown coal | Black coal | Anthracite |
|---|---|---|---|---|
| Carbon content (%) | 60 | 60 to 71 | 77 to 87 | 94 |
| Average energy value (kJ kg$^{-1}$) | 16000 | 23000 | 36000 | 35000 |

2. (a) Explain why carbon, hydrogen, oxygen, sulfur and nitrogen are present in fossil fuels.
   (b) A sample of coal was analysed and found to contain 75% carbon, 10% ash, 8% oxygen, 5% hydrogen, 1.5% nitrogen and 0.5% sulfur. Use these figures to graph the composition of coal – use a pie or column graph.
   (c) Why would a line graph not be suitable to represent this information?
3. (a) Describe the range of compounds found in natural gas and include the structural formulas of the main components.
   (b) Use the information in the text to construct a pie graph to summarise the uses of energy produced from natural gas.
   (c) Outline three advantages of natural gas, as a source of fuel, over other fossil fuels.
   (d) Do you think it would be a good idea to replace all other fossil fuels with natural gas?
   (e) Research to find when natural gas was first used in Australia.
4. Liquefied petroleum gas (LPG) is a source of energy that is sometimes confused with natural gas. Compare the composition of liquefied petroleum gas to natural gas.
5. Research the elemental composition of crude oil.
6. (a) Justify the application of the term fossil fuel to petroleum.
   (b) Research the use of petroleum as a petrochemical feedstock.
7. (a) Explain why carbon dioxide is produced when fossil fuels are burnt to produce energy.
   (b) Define the term 'non-renewable'.
   (c) Justify the use of the term non-renewable being applied to fossil fuels.
8. Decide whether each of the following statements is true or false and justify your decisions.
   (a) Natural gas is a compound.
   (b) Methane is a hydrocarbon.
   (c) Coal, oil, natural gas and metals come from the ground, so they are all fossil fuels.
9. (a) What is fracking?
   (b) Identify pros and cons of the use of this technique.
10. Use a diagram or tables to revise and summarise the carbon cycle.
11. Check your knowledge with this quick quiz.
    (a) Name three types of coal.
    (b) Identify the type of coal that is best for fuel.
    (c) Is coal formed mainly from plants or animals?
    (d) Identify the main use for coal in Australia.
    (e) Identify the original source of the chemical energy in coal.
    (f) Identify two geological processes that contribute to the formation of fossil fuels.
    (g) Name the main type of energy in fossil fuels.
    (h) Name the main component of coal.
    (i) Fossil fuels that we use cannot be replaced; we say they are a ........................ resource.
    (j) Identify the fossil fuel that produces the least carbon dioxide per unit of energy.
    (k) Identify the main compound in natural gas.
    (l) Name two chemicals, other than methane, that may be present in natural gas in small amounts.

# 22 Revision – Fractional Distillation

**Fractional distillation** is a method of separating the components of a mixture containing two or more liquids or gases. Its use depends on the components having different **boiling points**. Figure 22.1 shows typical equipment used in a school laboratory to carry out fractional distillation to separate the components of a mixture of liquids.

To separate a mixture of ethanol (boiling point 78°C) and water (boiling point 100°C), the mixture is gently heated. At 78.3°C, the ethanol vaporises, rises to the top and passes out through the condenser.

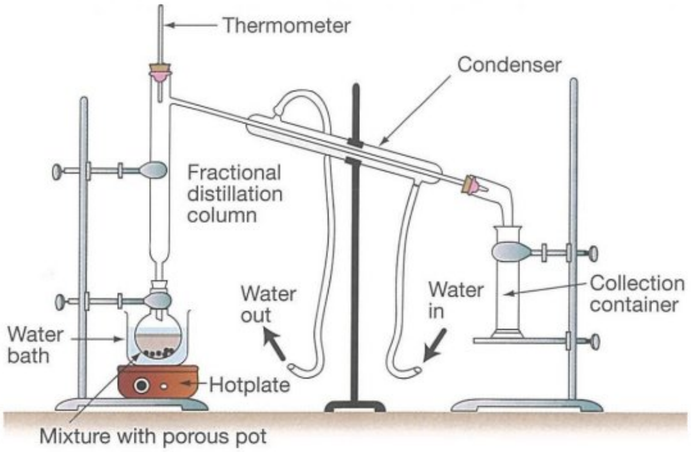


**Figure 22.1** Fractional distillation.

As the ethanol vapour passes through the condenser, the cool water in the outside jacket cools the vapour and condenses it back to liquid ethanol, which is collected in a container.

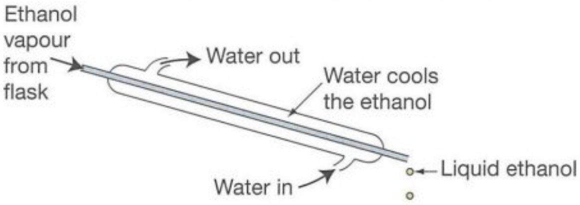


**Figure 22.2** Condenser.

Heating continues while the ethanol is evaporating, but its temperature stays at 78.3°C, the extra heat being used to change the state of the ethanol from liquid to gas. When all of the ethanol has vaporised and been condensed by the condenser, the two liquids have been separated. Ethanol is the distillate in the collection container, water is left in the original flask.

**Fractional distillation is used** in industry to separate mixtures such as air and the liquid part of petroleum which is extracted from the earth.

**Crude oil is the liquid part of petroleum**. It is:

- A **mixture** of chemicals. It contains up to 300 hydrocarbons as well as varying amounts of sulfur and nitrogen.
- Formed from **marine micro-organisms**. They are buried quickly and then compressed, for millions of years, by overlying sediments.
- A **fossil fuel** – a fuel, because it is burned as a source of heat energy; a fossil because it has formed from once-living things that existed on Earth many millions of years ago.
- A **non-renewable** resource.
- Extracted from underground deposits, on land and under oceans, by oil wells; transported to refineries; then separated into components by **fractional distillation**.

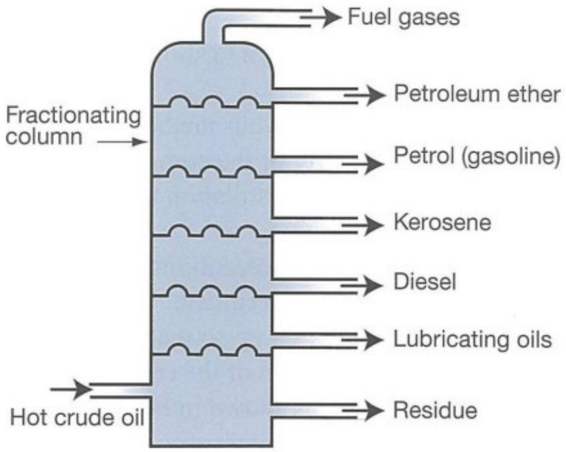


**Figure 22.3** Simplified distillation tower.

**Fractional distillation of crude oil** is carried out in a steel **fractionating column**, about 50 metres high. Crude oil heated to about 300°C to 400°C is piped into the base of the column. Molecules vaporise and rise in the column through a series of perforated trays. The smallest molecules have the lowest boiling points, so they vaporise first and rise to the top of the column where they are removed. Different-sized molecules liquefy out at different heights. The largest molecules have the highest boiling points, so they settle out on the lowest trays.

The original source of the oil and the refinery conditions will determine the composition of the fractions produced.

**Table 22.1** Petroleum fractions.

| Fraction | Boiling point range (°C) | Number of carbon atoms | Uses |
|---|---|---|---|
| Fuel gases | Less than 40 | 1 to 4 | Fuel for homes and industry, LPG.<br>Production of ethene and polymers. |
| Petroleum ether | 40 to 110 | 5 to 6 | Industrial solvents. |
| Petrol | 110 to 200 | 4 to 12 | Petrol for cars. |
| Kerosene | 180 to 230 | 10 to 14 | Aviation fuel. |
| Diesel oil | 200 to 425 | 12 to 19 | Diesel fuel. Industrial heating oils.<br>Some is converted to petrol by cracking. |
| Lubrication oil | Over 425 | 19 to 40 | Lubricating oils. |
| Paraffin wax | Melts 50 to 55 | Over 20 | Candles. Waterproofing fabrics. |
| Bitumen | Residue | Over 35 | Road surfacing (asphalt/bitumen). |

**Figure 22.4** Petroleum refinery.

## QUESTIONS

1. You may have performed an investigation of fractional distillation, using the process to separate the components of a mixture. If so, answer the following questions.
   (a) Identify the components of the mixture you separated.
   (b) Use a labelled diagram to show the equipment you used.
   (c) Outline the steps in your method.
   (d) Name the property of the components that allowed fractional distillation to be used as a separation technique.
   (e) Explain any safety precautions necessary when carrying out this experiment.
2. A condenser is always set up so that the cooling water goes into the bottom of the condenser and comes out of the top, as shown in Figure 22.1.
   (a) Explain why this is necessary.
   (b) Does the cooling water in the condenser have any contact with the mixture or the ethanol distilled off? Explain.
3. Explain why the mixture being distilled in Figure 22.1 is being heated with a hot water bath rather than with a direct Bunsen flame.
4. Fractional distillation is used in industry to separate the components of crude oil. It is also used to separate the components of air after it has been liquefied.
   (a) Describe how you could liquefy air.
   (b) Check the boiling points of oxygen and nitrogen in a data book. Use this information to decide which element would evaporate first if a mixture of liquid oxygen and liquid nitrogen underwent fractional distillation.
   (c) Outline ways in which the distillation of petroleum and air are similar to each other and to the laboratory distillation process.
5. Identify some areas in which the development of the technique of fractional distillation has had an impact on science and society and discuss this impact.
6. A variety of carbon compounds is extracted from organic sources such as crude oil.
   (a) Justify calling petroleum an organic source.
   (b) Identify a method used to separate crude oil into components.
   (c) Classify the method mentioned in (b) as physical or chemical. Justify your answer.
7. Identify four fractions that can be obtained by the fractional distillation of petroleum and identify the uses of each of these fractions.
8. Explain why fossil fuels such as crude oil frequently contain varying amounts of nitrogen and sulfur.
9. The presence of high levels of nitrogen and sulfur in fossil fuels is a problem. Explain.
10. Check your knowledge with this quick quiz.
    (a) When carrying out fractional distillation of ethanol and water, which is produced first?
    (b) What process is carried out by the condenser?
    (c) Fractional distillation can be used to separate a mixture of liquids with different .......................... ...........................
    (d) The function of the condenser is to .......................... and .......................... the vapour.
    (e) Identify a use for liquid petroleum.
    (f) Name three alkanes present in crude oil.
    (g) Crude oil is made from once-living things so we call it a .......................... ...........................
    (h) Petroleum cannot be replaced as it is used up, so we describe it as ...........................

# 23 Revision – Products Of Combustion Of Fossil Fuels

Some of the products of combustion of fossil fuels and biofuels are pollutants. Fossil fuels and biofuels all contain carbon and hydrogen so they release carbon dioxide, carbon monoxide and water as products of combustion. Most fuels contain sulfur and nitrogen so oxides of these elements are formed during combustion. Also, unburned particles and ash are formed.

**Carbon dioxide** is a colourless, odourless gas formed by complete combustion of carbon and carbon compounds. Large amounts of carbon dioxide are produced by power plants burning coal (mainly carbon), gas (mainly methane), by motor vehicles burning petrol (e.g. octane) and by burning biofuels (e.g. ethanol).

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

$$2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l)$$

$$CH_4(g) + 2O_2 \rightarrow CO_2(g) + 2H_2O(l)$$

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

Carbon dioxide is acidic. It is a major cause of the enhanced greenhouse effect and it also contributes to acid rain and acidification of rivers, lakes and oceans.

**Carbon monoxide** is a colourless, odourless gas produced by incomplete combustion when the oxygen supply is restricted, e.g. when a car is idling. It is toxic because it combines with haemoglobin in red blood cells in preference to oxygen, reducing the ability of blood to transport oxygen. The use of unflued heaters and barbecues inside homes where there is not a free flow of fresh air can cause carbon monoxide poisoning.

$$2C_8H_{18}(l) + 17O_2(g) \rightarrow 16CO(g) + 18H_2O(l)$$

$$C_2H_5OH(l) + 2O_2(g) \rightarrow 2CO(g) + 3H_2O(g)$$

$$CH_4(g) + \tfrac{3}{2}O_2 \rightarrow CO(g) + 2H_2O(l)$$

Carbon monoxide is not acidic, so it does not contribute to acid rain.

**Sulfur dioxide** is formed by the combustion of sulfur which is present in fossil fuels.

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

Sulfur dioxide is one of the main causes of acid rain and it also causes respiratory problems such as asthma.

Australian black coal generally has low sulfur content, but unfortunately we export most of our high quality black coal, burning the inferior, polluting coal here.

**Nitrogen oxides** (e.g. NO and $NO_2$) are formed by the combustion of nitrogen in fuels and atmospheric nitrogen when fuels undergo combustion at high temperatures.

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

Nitrogen oxides cause respiratory problems. Nitrogen dioxide is acidic and contributes to the formation of acid rain and photochemical smog.

**Particulates** are small particles, of solids (such as ash and carbon) and tiny droplets of liquids, that stay suspended in the air. Some coals contain up to 30% mineral matter (e.g. silicates and carbonates) which produces large amounts of ash when the fuel burns.

$$2C_8H_{18}(l) + 19O_2(g) \rightarrow 6C(s) + 10CO_2(g) + 18H_2O(l)$$

Particulates reduce visibility, cause respiratory problems, damage machinery and contribute to photochemical smog. Some are also carcinogens (cause cancer).

Figure 23.1 Photochemical smog over Sydney, NSW.

**Additives in petrol** can include a vast array of chemicals including antioxidants, stabilisers, antiknock agents, corrosion inhibitors, lubricants and fuel dyes, all of which can pollute the environment.

## Reducing pollution

Steps taken to reduce pollution include the following.

1. **Ensure complete combustion.**
   - Adjust the carburettor/fuel injector of motor vehicles so there is a lean fuel/air mixture to increase engine fuel efficiency and thus reduce exhaust emissions.
   - Recirculate the exhaust to burn any fuel that was not burnt initially.
   - Use catalysts in the exhaust system to reduce the toxic pollutants emitted. Carbon monoxide and unburned hydrocarbons undergo complete combustion with the help of a catalyst and nitrogen oxides are reduced to nitrogen gas. Catalysts can also be used to remove nitric oxide by increasing the rate of its reaction with carbon monoxide.
     $2NO(g) + 2CO(g) \rightarrow N_2(g) + 2CO_2(g)$
     Ensuring complete combustion not only produces less pollution it also results in more energy being produced per kilogram of fuel.

2. **Lower combustion temperatures** to prevent the formation of nitrogen oxides – use cooled air, and use multistage combustion.

3. **Remove pollution**.

   - Power stations use filtering devices and electrostatic precipitators to stop particulates being emitted into the atmosphere.
   - Water scrubbers are used to dissolve out carbon and sulfur oxides, e.g.
   - Carbon dioxide + water → carbonic acid
   - $CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$
   - Some industries find uses for waste products rather than releasing them into the environment. Sulfur dioxide is used to make sulfuric acid and carbon dioxide is used in fire extinguishers and to make soft drinks.

4. **Develop other less polluting energy sources** such as wind power, solar energy and tidal generators. Australia has the highest average solar radiation per square metre of any continent in the world. What do you think we should be developing as our main energy source in Australia?

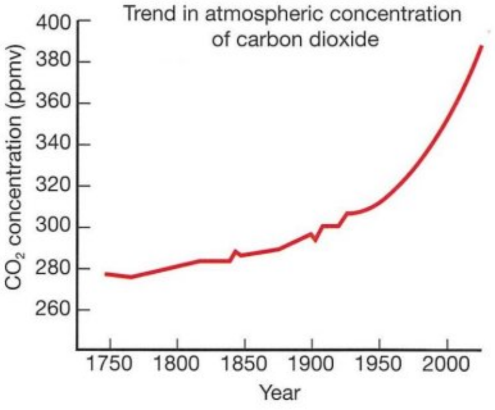
## QUESTIONS

1. Write balanced equations to show the incomplete combustion of:
   (a) Methane to produce carbon monoxide and water.
   (b) Methane to produce carbon and water.
   (c) Propane to produce carbon and water.
2. Write equations to show the complete combustion of:
   (a) Butane. (b) Hexane.
3. Copy and complete the following table about the products of combustion of fossil fuels.

| Name of product | Formula | Harmful effect |
|---|---|---|
| | $CO_2$ | |
| | | Toxic – preferentially combines with haemoglobin. |
| Particulates, e.g. carbon | | |
| | NO and $NO_2$ | |
| | $SO_2$ | |
| Volatile organic compounds (VOCs) | | |

4. Research photochemical smog and answer the following questions about it.
   (a) Define photochemical smog.
   (b) What causes photochemical smog?
   (c) Account for the concern about photochemical smog.
   (d) What gives the brown tinge to photochemical smog?
   (e) When is photochemical smog most common?
5. Many countries recommend turning off your car's engine if you are stopped for longer than 10 to 60 seconds. Account for the presence of the following road sign placed outside a primary school.

6. For every litre of petrol used in a car, approximately 2.3 kilograms of carbon dioxide is produced.
   (a) If a car uses, on average, 40 L of petrol per week, calculate how much carbon dioxide this car would release in one year.
   (b) Calculate how much carbon dioxide your family produces per year and consider how you could reduce this.
7. Carbon dioxide is present naturally in the atmosphere. The graph below shows changes in atmospheric concentration of carbon dioxide over time.
   (a) Describe the trend shown by the graph.



   (b) Outline the main causes of this change in atmospheric carbon dioxide concentration.
8. Check your knowledge with this quick quiz.
   (a) Name a toxic gas that combines with haemoglobin in blood in preference to oxygen.
   (b) Identify a device used to remove small particles from exhaust gases.
   (c) Name a colourless, odourless gas produced by complete combustion of carbon-based fuels.
   (d) Name an acidic nitrogen oxide.
   (e) Name an acidic gas produced by combustion of sulfur present in coal.

# 24 Revision – The Greenhouse Effect

## The demand for energy

Two hundred years ago, the main energy source was wood, with a little help from wind and water. In the 1800s the Industrial Revolution led to the need for more energy and we came to rely on fossil fuels. However, their combustion releases huge amounts of carbon dioxide, sulfur dioxide and ash particles into the atmosphere, causing pollution, contributing to acid rain and also to the greenhouse effect and global warming.

## Greenhouse gases

**Greenhouse gases** are gases that absorb heat, keeping it in the atmosphere, making the Earth warmer and causing changes in climate. Greenhouse gases include water vapour ($H_2O$), carbon dioxide ($CO_2$), methane ($CH_4$), dinitrogen monoxide (nitrous oxide $N_2O$), and fluorinated gases such as hydrofluorocarbons, perfluorocarbons and sulfur hexafluoride ($SF_6$).

Carbon dioxide has had the most effect on climate change as so much of it has been produced. However, water, methane and nitrous oxide are actually more effective at trapping heat.

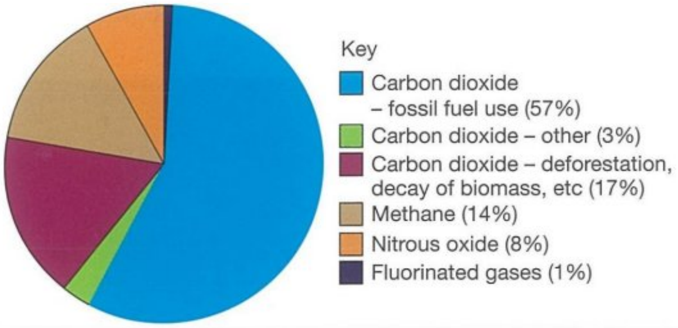


Figure 24.1 Contribution of gases to the greenhouse effect.

The demand for energy continues to grow worldwide, with an ever increasing population and the escalating use of energy dependent appliances and motor vehicles. Carbon dioxide concentrations are at their highest level in the last million years. **Australia is one of the world's worst polluters. Per person, we emit more than four times the world average carbon dioxide**.

## Energy use

In Australia, the **generation of electricity** and **transport** together account for half of our greenhouse emissions.

The largest contributor is electricity production – 96% of which is still made from fossil fuels. Motor cars account for most of the greenhouse emissions in the transport sector and the agriculture sector produces most of our methane and nitrous oxide emissions.

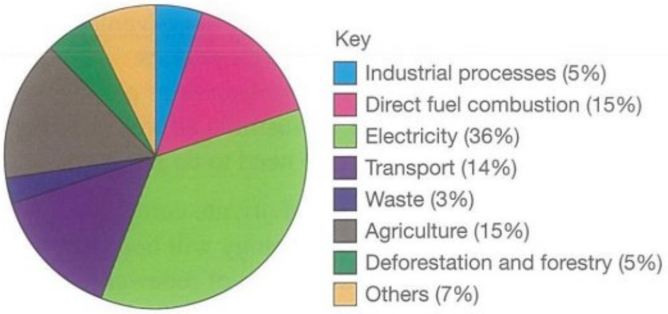


Figure 24.2 Greenhouse emissions from Australia, classified by their source.

In Australia, we have a high standard of living and on the whole we live a very comfortable life. To achieve that same standard of living for all people throughout the world would require more fossil fuels than the Earth can provide. There is not enough fossil fuel in the world to allow even half the world's population to live the way we do. Australians have the highest carbon footprint per person for any developed country in the world. Industries as well as individuals need to look for ways to reduce the energy they use in order to reduce our greenhouse emissions.

## Alternatives

Australia is energy rich. We have approximately 10% of the world's coal, 2% of the world's gas resources, 0.3% of the world's oil reserves. Australia is the world's ninth largest energy producer, contributing about 2.5% of the world energy production and 5% of world energy exports. We also have the highest average solar radiation per square metre of any continent in the world. And every year more than 10 000 times the energy needed by the whole country reaches Australia via the Sun – a resource that is obviously currently underutilised.

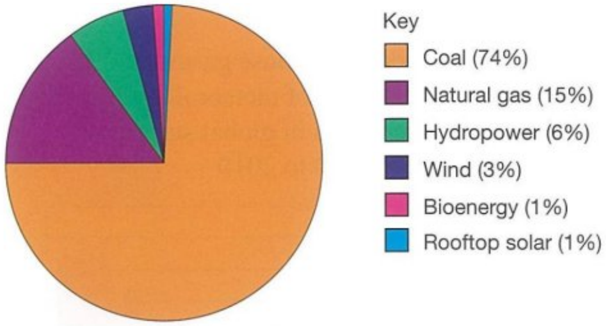


Figure 24.3 Sources of energy in Australia.

Recently, the rising price of fuels and knowledge that fossil fuels are contributing to high levels of pollution, combined with the realisation that fossil fuels are a finite resource and their use is not sustainable, has led to more demand for renewable energy sources.

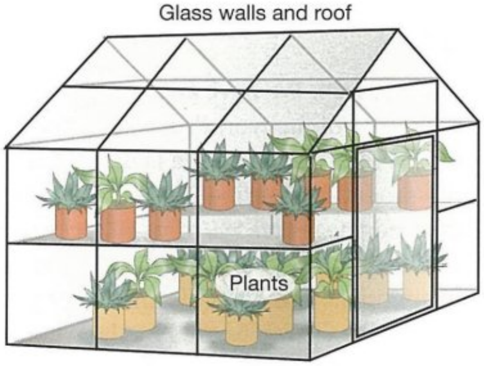
People are finally realising that our present way of life, with its dependence on fossil fuels, is not sustainable. Many are thinking about how they can personally reduce energy wastage and evaluating the advantages and disadvantages of different energy sources.
Since 2007 more than a million rooftop solar photovoltaic systems have been installed in Australia as well as many solar hot water systems. But we need to do more.

With backing by government and private companies, continued developments in technology will hopefully allow more access to reliable sources of renewable energy on a larger scale in the future.

At the global level, most scientists and nations agree that the risks of increasing global temperatures more than 2°C are too high, but we are already approaching 1°C. To slow this increase we need to reduce carbon dioxide emissions close to zero by 2050. All major economies are taking steps to reduce emissions and develop renewable energy sources.

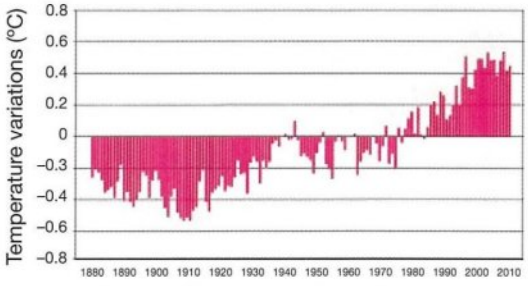
## QUESTIONS

1. The figure below shows plants growing inside a greenhouse.



   (a) How is this related to the greenhouse effect?
   (b) The greenhouse effect is not new. Comment on this statement.
   (c) Identify five greenhouse gases.

2. The Australian Bureau of meteorology has released data that show changes in global surface air temperature from 1880 to 2010.



Changes in global surface air temperatures

   (a) Comment on any trend evident in this graph.
   (b) Can such a minor change affect us?
   (c) The Earth's temperature is constantly changing. Why is this change concerning scientists?

3. The following table provides information about the mass of carbon dioxide emitted when equivalent amounts of four fossil fuels are burnt to produce energy. Discuss any implications of this information for global warning. (*Note:* 1 GJ = $10^9$ joules.)

**Table 24.1** Emissions of carbon dioxide from some fossil fuels.

| Fuel | Carbon dioxide emitted per GJ of energy produced (kg) |
|---|---|
| Brown coal | 93.3 |
| Black coal | 90.7 |
| Liquid petroleum | 68.2 |
| Gas | 50.9 |

4. The decision about which fuel we should use in any situation – whether it is in industry, the home etc can reflect social, economic, cultural and political values associated with the source of the fuel.
Discuss this statement.

5. The pictures show two methods of obtaining energy without increasing greenhouse gases. Research the methods used to obtain energy in your home, your school, your local community and in the state where you live.

6. Check your knowledge with this quick quiz. Name the following substances.
   (a) An acidic gas caused by the combustion of carbon compounds in fossil fuels.
   (b) The major cause of the enhanced greenhouse effect.
   (c) A toxic gas caused by incomplete combustion of fossil fuels.
   (d) An acidic gas produced by combustion of sulfur in coal.
   (e) A greenhouse gas released as a result of digestion especially in sheep and cattle.
   (f) The fuel from which most of our electricity is generated in Australia.

# 25 Revision Of Hydrocarbons

You have seen that organic chemicals, and especially hydrocarbons play an important role in our lives. We use them to make pharmaceuticals, fuels and polymers and thus meet the needs of society. The bonding in hydrocarbons determines their properties and thus how we use them.

When you have revised this section of work, try answering the following multiple choice questions to check your knowledge and understanding. If in doubt, as always, speak to your teacher,

## QUESTIONS

**1.** Identify which forces are the weakest.
(A) Dispersion forces.
(B) Covalent bonds.
(C) Hydrogen bonds.
(D) Dipole-dipole forces.

**2.** Which physical property is characteristic of molecular substances such as hydrocarbons?
(A) Hardness.
(B) Good conductors of electricity.
(C) Low melting points.
(D) Very soluble in polar solvents such as water.

**3.** Which method of representing molecular substances provides the most information about both the bond length and the shape of a molecule?
(A) Ball and stick models.
(B) Structural formulas.
(C) Lewis electron bond structures.
(D) Space filling models.

**4.** Which product of combustion is mainly responsible for the formation of acid rain?
(A) Carbon monoxide.
(B) Carbon dioxide.
(C) Sulfur dioxide.
(D) Dinitrogen monoxide.

**5.** Natural gas is composed mostly of:
(A) Methane.
(B) Ethane.
(C) Propane.
(D) Butane.

**6.** In Australia, the main fuel used to produce electricity is:
(A) Ethanol.
(B) Coal.
(C) Solar energy.
(D) Hydroelectricity.

**7.** The process used to separate crude oil into its component fractions is:
(A) Centrifuging.
(B) Condensation.
(C) Fracking.
(D) Fractional distillation.

**8.** The continent with the highest average solar radiation per square metre in the world is:
(A) South America.
(B) Australia.
(C) Antarctica.
(D) Africa.

**9.** The list containing only greenhouse gases is:
(A) Carbon dioxide, methane, nitrous oxide.
(B) Fluorinated hydrocarbons, sulfur dioxide, oxygen.
(C) Ozone, chlorine, ammonia.
(D) Sulfur hexafluoride, sulfur dioxide, ammonia.

**10.** The products of complete combustion of hydrocarbons are:
(A) Carbon dioxide and water.
(B) Carbon monoxide.
(C) Carbon dioxide and hydrogen.
(D) Carbon monoxide and hydrogen.

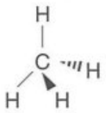
**11.** Many hydrocarbons:
(A) Are soluble in water.
(B) Are volatile and flammable.
(C) Are safe to heat with a naked flame.
(D) Can be disposed of by pouring down the sink.

**12.** Alkanes are non-polar because:
(A) They only have weak dispersion forces within their molecules.
(B) They contain strong covalent bonds.
(C) The electronegativity values of carbon and hydrogen are similar.
(D) They have low melting and boiling points.

**13.** Which of the following hydrocarbons would you expect to have the highest boiling point?
(A) Methane.
(B) Ethane.
(C) Propane.
(D) Butane.

**14.** Which alternative provides the general formula for alkanes?
(A) $C_nH_{2n}$
(B) $C_nH_{2n+1}$
(C) $C_nH_{2n+2}$
(D) $C_nH_{2n-2}$

**15.** In the formula shown:



The wedge shape represents:
(A) A bond that comes out of the paper towards you.
(B) A bond that goes away from you, into the paper.
(C) A bond that lies in the plane of the paper.
(D) A bond that is about to be shared.

16. Which alternative correctly describes the shape of the molecules of the named hydrocarbons?

| | Propane | Propene | Propyne |
|---|---|---|---|
| (A) | Linear | Trigonal planar | Overlapping tetrahedrons |
| (B) | Trigonal planar | Linear | Overlapping tetrahedrons |
| (C) | Linear | Overlapping tetrahedrons | Trigonal planar |
| (D) | Overlapping tetrahedrons | Trigonal planar | Linear |

17. Which statement summarises the concept behind the use of fractional distillation?
    (A) Each pure substances has a definite boiling point.
    (B) All elements boil at the same temperature.
    (C) Boiling points of compounds depend on the elements they are made of.
    (D) Any two substances can be separated by chemical methods.

18. What is the function of the water in the outer jacket of a condenser during fractional distillation?
    (A) It dilutes the product so it is easier to collect.
    (B) It washes the desired product from the condenser.
    (C) It cools and condenses volatile reactants and products without mixing with them.
    (D) It enters the flask and dissolves volatile reactants and products so they cannot escape into the environment.

19. Which alternative best describes crude oil?
    (A) A renewable fossil fuel.
    (B) A re-usable mixture of fossil fuels.
    (C) A source of renewable polymers.
    (D) A non-renewable mixture.

20. A double bond involves two atoms sharing:
    (A) Two electrons.
    (B) Four electrons.
    (C) Six electrons.
    (D) Eight electrons.

**INQUIRY QUESTION**

How can hydrocarbons be classified based on their structure and reactivity?

# 26 Substitution Reactions

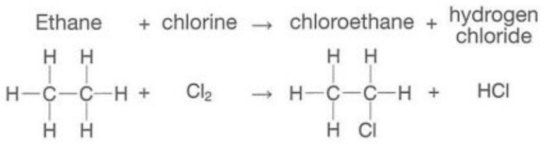
**Substitution reactions** are chemical reactions in which another atom replaces a hydrogen atom in a saturated organic compound. The new atom substitutes for (takes the place of) a hydrogen atom and two products are formed. Substitution reactions occur in saturated compounds such as alkanes and haloalkanes.

## Substitution reactions in alkanes

Alkanes are saturated organic compounds as they only have single carbon-carbon bonds, so they undergo substitution reactions. One type of atom that is often substituted into alkanes is a halogen atom. You will recall that halogens are elements in group 7/17 such as fluorine, chlorine, bromine and iodine.

When alkanes undergo substitution reactions with halogens they form a haloalkane and a hydrogen halide. For example:

Ethane + chlorine $\xrightarrow{UV}$ chloroethane + hydrogen chloride



Notice that **two products** are formed from this substitution reaction, the **haloalkane**, chloroethane and the **hydrogen halide**, hydrogen chloride.

Halogens differ in their degree of reactivity and this affects the extent to which they take part in substitution reactions.

Fluorine reacts explosively, even when cold and in the dark.
Chlorine and bromine will not react in the dark, but will react when provided with energy from ultraviolet light or a flame.

However iodine tends not to react with alkanes at all.

Under some conditions, more than one atom can be substituted into an alkane, producing a mixture of haloalkane products. For example, when methane is mixed with chlorine, in sunlight or UV light, a series of reactions takes place as more H atoms are substituted with Cl atoms.

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

Chloromethane

$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$

Dichloromethane

$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$

Trichloromethane

$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$

Tetrachloromethane

To react bromine with alkanes, you can either mix the alkane with liquid bromine or with bromine dissolved in water (which is essentially HOBr). In UV light bromine or bromine water reacts, losing its red-brown colour and becoming colourless. For example:

Propane + bromine liquid $\xrightarrow{UV}$ bromopropane + hydrogen bromide

$C_3H_8(g) + Br_2(l) \rightarrow C_3H_7Br(l) + HBr(g)$

Propane + bromine water → bromopropane + water

$C_3H_8(g) + BrOH(aq) \rightarrow C_3H_7Br(l) + HOH(l)$

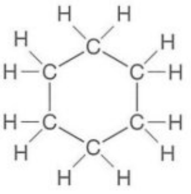
Under different conditions the actual haloalkane formed can vary, forming isomers such as 1-bromopropane or 2-bromopropane.

## Substitution in cycloalkanes

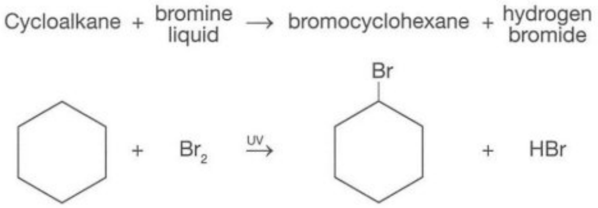
**Cycloalkanes** are also saturated compounds, so they also take part in substitution reactions with halogens.

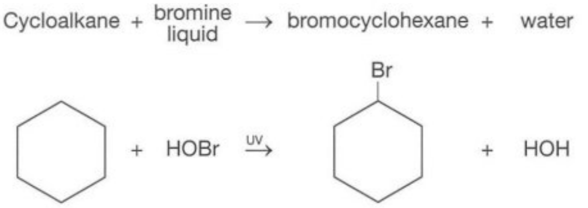
You may have used the cycloalkane called cyclohexane ($C_6H_{12}$) to investigate substitution reactions in the laboratory. Cyclohexane is used because it is liquid at room temperatures.

As with the alkanes, UV light is needed for substitution reactions with cycloalkanes to occur.



Cyclohexane





Remember, substitution reactions will only take place slowly and in the presence of ultraviolet light. They will not occur in the dark.

This is important as it gives us a way to distinguish alkanes from alkenes and alkynes. Saturated alkanes will only react with bromine in light (by substitution) whereas unsaturated hydrocarbons such as alkenes will react with bromine even in the dark (by addition reactions).

## Substitution reactions in haloalkanes

Haloalkanes such as chloroethane ($C_2H_5Cl$) are also saturated hydrocarbons, so they can also undergo substitution reactions, for example with an hydroxyl group (–OH).

In this case, the halogen atom in the compound is replaced with another atom or group because halogen atoms are more readily removed from a haloalkane than hydrogen atoms.

The speed of the reaction depends on which halogen atom is present (F, Cl, Br or I) as the strength of their bonds with carbon varies (see Table 26.1)

**Table 26.1** Strength of bonds. (Note that the values of these bonds can vary in different sources.)

| Bond | C–C | C–F | C–Cl | C–Br | C–I |
|---|---|---|---|---|---|
| Bond strength (kJ $mol^{-1}$) | 413 | 467 | 346 | 290 | 228 |

You can see from these figures that the carbon-fluorine bond is very strong, even stronger than a carbon-carbon bond, so fluoroalkanes are very unreactive. You might have predicted this – fluorine and alkanes react explosively so they form very stable compounds.

The most active haloalkanes are the iodoalkanes, then the bromoalkanes and chloroalkanes.

The hydroxyl group (–OH) can be substituted into a haloalkane, replacing a Cl, Br or I atom. To do this, the haloalkane is heated, under reflux conditions, with a solution of sodium or potassium hydroxide. This provides a way to make an alcohol. For example:

Chloroethane + sodium hydroxide → ethanol + sodium chloride

$$CH_3{-}CH_2{-}Cl + NaOH_{(aq)} \rightarrow CH_3{-}CH_2{-}OH + NaCl_{(aq)}$$

## QUESTIONS

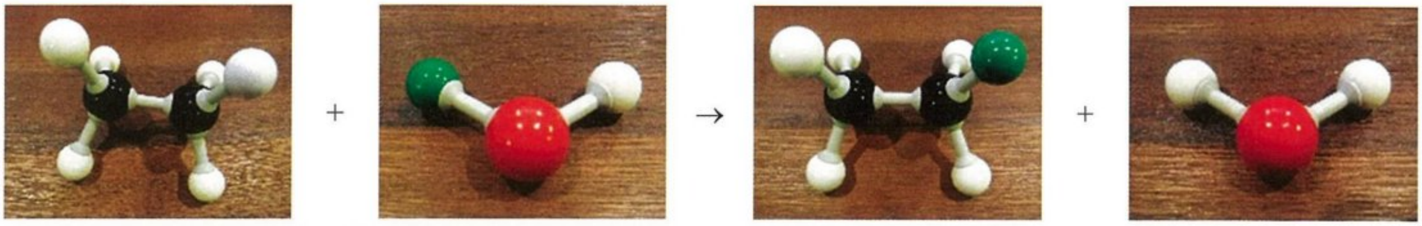
1. (a) Explain what is meant by a substitution reaction.
   (b) Name two homologous series that take part in substitution reactions.
2. Write equations to show the following substitution reactions with alkanes.
   (a) Propane and chlorine.
   (b) Hexane and bromine.
   (c) Hexane and bromine water.
3. Write equations, using words and symbols, to show the substitution reaction of bromoethane and potassium hydroxide.
4. Substitution into haloalkanes occurs under reflux conditions. What does this mean?
5. Name the products of reactions between:
   (a) Pentane and chlorine gas.
   (b) Chloropentane and sodium hydroxide.
   (c) Butane and bromine water.
   (d) Octane and bromine water.
6. Use a model kit to illustrate five substitution reactions and draw diagrams or photograph your models and name all reactants and products.
7. Complete the following sentence.
   Substitution reactions occur in (saturated/unsaturated) compounds such as (alkanes/alkenes) in the (light/dark) and these reactions produce (one/two) products.

## Modelling substitution reactions

You could use structural diagrams or model kits to illustrate substitution reactions. For example:

Ethane + bromine water → bromoethane + water

$$CH_3{-}CH_3 + HO{-}Br \rightarrow CH_2Br{-}CH_3 + H{-}O{-}H$$

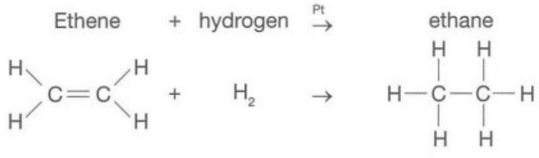


# 27 Addition Reactions

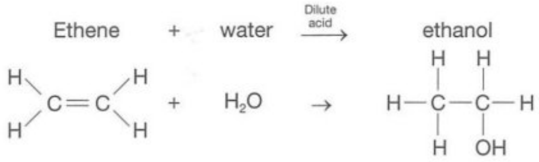
**Addition reactions occur in unsaturated organic compounds** when a double bond is broken and other atoms are added. In addition reactions, two molecules combine to form one larger molecule. Energy is not needed for addition reactions, they can even occur in the dark. Some reactions require the presence of a catalyst.

**Addition reactions occur in unsaturated compounds such as alkenes**, but not in alkanes or haloalkanes, which are saturated hydrocarbons. Alkenes are more reactive than alkanes because of the presence of their double bonds. Some substances that undergo addition reactions with alkenes are hydrogen, water, halogens and hydrogen halides.

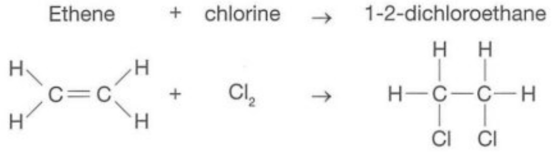
Addition of hydrogen to ethene:



Addition of water to ethene:

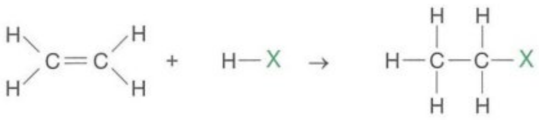


Addition of a halogen (group 7/17 non-metal such as chlorine or bromine) to ethene:



The halogen bromine can be added to bromine in the form of bromine water (HOBr).

Additition of hydrogen halide to ethane. In this eqution, X could represent I, Cl or Br.



The reactivity of alkenes and their ability to take part in addition reactions makes alkenes such as ethene important raw materials in the manufacture of polymers, which you will learn more about later.

## Distinguishing test for an alkene

When liquid bromine or bromine water (BrOH) is added to a saturated alkane and an unsaturated alkene they react differently, so the reaction with bromine, or bromine water, can be used to test whether an unknown hydrocarbon is a saturated alkane or an unsaturated alkene.

When you **add bromine water to a sample of an alkene**, it reacts very rapidly, even in the absence of light, the bromine water changing from red-brown to colourless. This is an addition reaction.

However, when you **add bromine water to an alkane**, it reacts very slowly, and only in the presence of UV light. So the bromine water remains a red-brown colour and only fades very slowly. The substitution reaction is very slow unless UV light is present.

For example, if **bromine water is added, in the dark, to ethene and ethane**, only ethene will discolour the bromine.

So, if you are **not sure if a hydrocarbon is an alkane or an alkene**, you can add bromine water to it, under dark conditions.

If the bromine water changes colour from yellow-brown to colourless, then you know that the hydrocarbon is an unsaturated compound – an alkene – not an alkane. If it does not change colour, then the hydrocarbon is an alkane.

Note that **bromine water is poisonous and corrosive** and should be handled with care and used in a fume cupboard or hood. Any vapour given off should not be breathed in. If any comes in contact with your skin it must be washed immediately with a large volume of running water.

The chemicals used **to demonstrate this distinguishing test for an alkene** are usually cyclohexane ($C_6H_{12}$) and cyclohexene ($C_6H_{12}$).

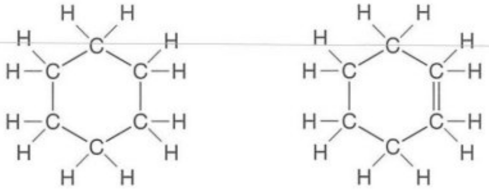
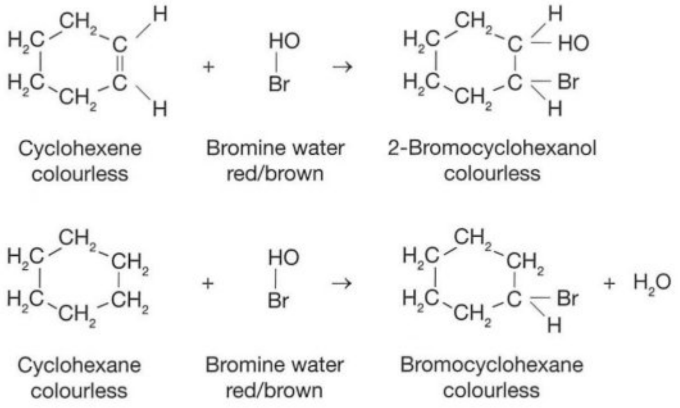


**Figure 27.1** Cyclohexane and cyclohexene.

The **reasons for using these cyclic alkanes** are that they occur as liquids at room temperature and they are not quite as reactive as hexane and hexene.

However, you should be aware that **cyclohexane and cyclohexene are poisonous, volatile and flammable** and must be handled with care. They should be used in a fume cupboard or hood, away from any sparks or flames, and you should take care not to inhale any vapour. If any spills on the skin it should be washed off under running water. Eye protection must be worn.

In the presence of UV light, the following reactions occur.



When these reactions are carried out in the dark, the colour change to bromine water only happens with the cyclohexene.

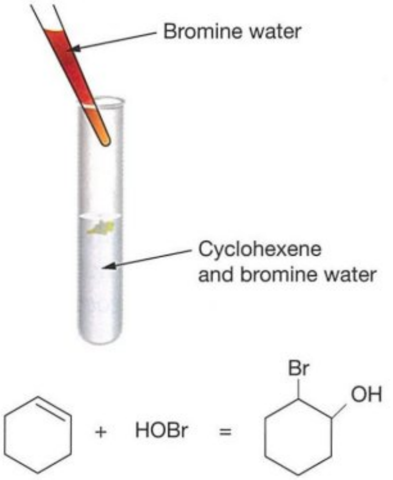


**Figure 27.2** Bromine water is decolourised by cyclohexene.

The cyclohexene does not decolourise the bromine water. It would need UV light to react with the bromine water.

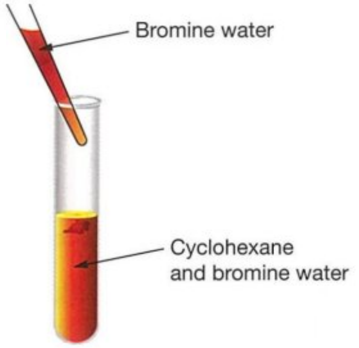


**Figure 27.3** Bromine water is not decolourised by cyclohexane.

The reactivity of alkenes such as ethene, and its ability to take part readily in addition reactions, makes ethene an important material in the manufacture of polymers.

## QUESTIONS

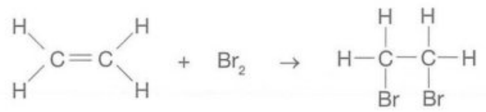
1. What is meant by an addition reaction?
2. Write balanced equations to show the addition reactions that occur when the following chemicals react. Name any products.
   (a) Hydrogen and propene.
   (b) Hydrogen and pent-2-ene.
   (c) Chlorine and but-1-ene.
   (d) Water and ethylene.
   (e) Hydrogen chloride and propene.
3. Describe an investigation you carried out to compare the reaction of bromine water on an alkane and an alkene.
   (a) In your answer include your method, observations and equations for any reaction.
   (b) Outline any safety precautions necessary during this investigation and explain their necessity.
4. Use a model kit to illustrate five addition reactions with different alkenes. Draw diagrams or photograph your models and name all reactants and products.
5. Check your knowledge with this quick quiz.
   (a) Addition reactions occur in (alkanes/alkenes).
   (b) Addition reactions occur with (saturated/unsaturated) hydrocarbons.
   (c) When bromine reacts with hydrocarbons, how does its colour change?
   (d) To test an unknown to see if it contains a double bond, you would add .......................... .
   (e) Name two chemicals you used to demonstrate the test for the presence of a double bond.
   (f) A chemical which can discolour bromine water in the dark is (cyclohexane/cyclohexene).

# 28 Revision Of Products Of Reactions Involving Hydrocarbons

Answer the multiple choice questions to help you revise this section of reactions of hydrocarbons. Many of these reactions are used to manufacture other organic chemicals and of course the reaction with bromine water can be used to distinguish whether a hydrocarbon is saturated or unsaturated.

## QUESTIONS

1. The reaction between ethene and hydrogen to form ethane is an example of:
   (A) Combustion.
   (B) Hydrolysis.
   (C) Addition.
   (D) Substitution.
2. Which statement is correct?
   (A) Addition reactions make two products.
   (B) Substitution reactions make two products.
   (C) Addition reactions occur with saturated hydrocarbons.
   (D) Substitution reactions do not need energy.
3. The list that correctly shows halogens in order of decreasing reactivity is:
   (A) F, Cl, Br, I
   (B) I, Br, Cl, F
   (C) Cl, Br, F, I
   (D) Cl, Br, I, F
4. When carbon reacts with halogens, it forms the strongest bonds with:
   (A) Bromine.
   (B) Chlorine.
   (C) Fluorine.
   (D) Iodine.
5. A haloalkane is an organic compound and it:
   (A) Resembles an alkane with delocalised electrons arranged in the shape of a halo.
   (B) Can be converted to an alcohol by heating under reflux conditions with sodium hydroxide.
   (C) Has a lower melting and boiling point than its corresponding alkane.
   (D) Is most likely to undergo addition rather than substitution reactions.
6. An alcohol can be made by:
   (A) Substituting an hydroxide ion into an alkane.
   (B) Adding an hydroxide ion to an alkane.
   (C) Adding an hydroxyl group into a haloalkane.
   (D) Substituting an hydroxyl group into a haloalkane.
7. What type of reaction does this equation represent?



   (A) An addition reaction.
   (B) An oxidation reaction.
   (C) An explosion.
   (D) A substitution reaction.
8. When chloroethane reacts with sodium hydroxide:
   (A) The only product is hydroxychloroethane.
   (B) Hydroxide is added into the chloroethane.
   (C) Chlorine is substituted for the hydroxide.
   (D) Hydroxide is substituted for the chlorine.
9. The addition of hydrogen to ethene will produce:
   (A) Hydroethene.
   (B) Ethane and water.
   (C) Ethane only.
   (D) Water only.
10. Hydrogen halides are sometimes referred to as HX, where X can be:
   (A) An alkane or alkene.
   (B) A chlorine, bromine or iodine atom.
   (C) A chloroalkane.
   (D) Substituted water.
11. The hydrogen halide named hydrogen bromide, reacts in an addition reaction with propene. The product(s) will be:
   (A) Bromopropene and bromine.
   (B) Bromopropane and bromine
   (C) Bromopropene only
   (D) Bromopropane only
12. Two chemicals used to demonstrate the test for the presence of a double bond were:
   (A) Ethene and ethane.
   (B) Chloroethene and chloroethane.
   (C) Hexanol and hexenol.
   (D) Cyclohexane and cyclohexene.
13. Which one of the following substances could decolourise bromine water in the dark?
   (A) Ethane.
   (B) Methane.
   (C) Methene.
   (D) Butene.
14. Which substance(s) would most likely be the product(s) of the incomplete combustion of a hydrocarbon?
   (A) Water, carbon dioxide and carbon.
   (B) Water, carbon monoxide and carbon.
   (C) Carbon monoxide and carbon only.
   (D) Carbon dioxide only.

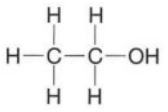
**INQUIRY QUESTION**

What are the products of reactions of hydrocarbons and how do they react?

# 29 Alcohols

You have seen that alcohols are organic compounds that contain the hydroxyl (–OH) functional group.

Most of the alcohols you will come across are the alkanols – alkanes with a hydroxyl group attached – such as ethanol.



Ethanol

Alcohols can occur **as structural isomers**, for example, propanol can occur as propan-1-ol or propan-2-ol depending on the position of their functional (–OH) group.

Propan-1-ol

Propan-2-ol

**Figure 29.1** Structural isomers of propanol.

## Bonding in alcohols

The atoms that make up alcohols are held together by **strong covalent bonds**.

Their **molecules are polar** because of the presence of their hydroxyl group. The **oxygen** in the hydroxyl group is highly electronegative.

The carbon chain of the alcohol is non-polar.

The **intermolecular forces** that hold alcohol molecules together include dispersion forces, dipole-dipole forces and also strong hydrogen bonds.

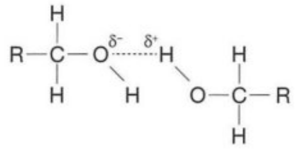


**Figure 29.2** Hydrogen bond between two alcohol molecules.

## Properties of alcohols

- Alcohols are **soluble in water** because their polar hydroxyl group can form hydrogen bonds with water molecules. The smallest molecules such as methanol and ethanol are the most soluble. As the molecules become larger, the solubility in water decreases.
- Alcohols are good solvents of both **polar and non-polar** substances because of the presence of both polar and non-polar areas in their molecules.
- **Boiling and melting points** of alcohols **increase as the length of the carbon chain increases**. This is because as the chain becomes longer, intermolecular forces increase so more energy is needed to break these intermolecular forces.
- Alcohols have slightly **higher melting and boiling points than hydrocarbons** because the alcohols have stronger intermolecular bonding – dipole-dipole forces and hydrogen bonds – that are not present between hydrocarbon molecules.

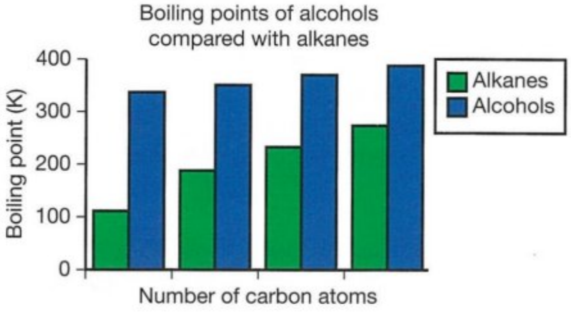


**Figure 29.3** Boiling points of some alkanes and alcohols.

- Alcohols are **flammable**, especially those with smaller molecules such as methanol and ethanol which can be used as fuels. During combustion, the covalent bonds holding the molecule together are broken, and the atoms recombine to form water and carbon dioxide, carbon monoxide or carbon depending on the oxygen supply.

**Figure 29.4** Ethanol burning.

## Uses of alcohols

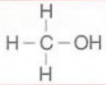
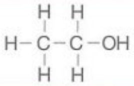
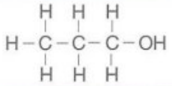
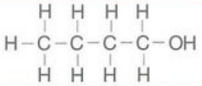
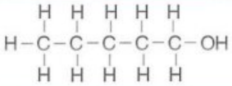
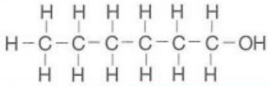
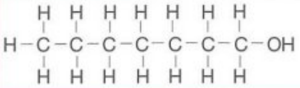
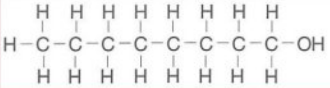
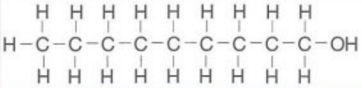
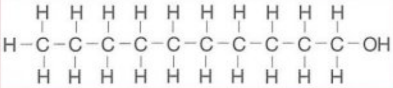
Alcohols are used as **solvents** in the manufacture of medicines, varnishes, adhesives and plastics.

The alcohol **ethanol** is used as an alcoholic drink, however it is toxic to cells and can cause damage to organs such as the brain and liver. **Methanol**, which is present in methylated spirits, is also toxic and causes blindness if consumed.

Alcohols such as ethanol are also used as fuels, providing a source of heat and energy, and bioethanol is used as a supplement to fossil fuels such as petrol in motor vehicles.

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

**Table 29.1** A series of alcohols.

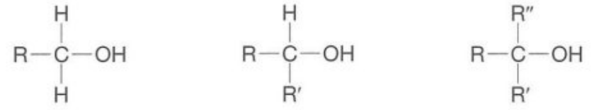
| Name | Molecular formula | Structural formula |
|---|---|---|
| Methanol | $CH_3OH$ |  $H-\overset{H}{\underset{H}{C}}-OH$ |
| Ethanol | $C_2H_5OH$ |  $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$ |
| Propanol | $C_3H_7OH$ |  $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$ |
| Butanol | $C_4H_9OH$ |  $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$ |
| Pentanol | $C_5H_{11}OH$ |  $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$ |
| Hexanol | $C_6H_{13}OH$ |  $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$ |
| Heptanol | $C_7H_{15}OH$ |  $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$ |
| Octanol | $C_8H_{17}OH$ |  $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$ |
| Nonanol | $C_9H_{19}OH$ |  $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$ |
| Decanol | $C_{10}H_{21}OH$ |  $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$ |

## Types of alcohols

Alcohols can be classified as **primary, secondary or tertiary alcohols** depending on the position of their hydroxyl (–OH) group.

Alkanols with the hydroxyl group at the end of the carbon chain are called **primary alcohols**. The carbon with the hydroxyl (–OH) group attached is terminal (at the end of the chain). We can write this as R–OH where R indicates an alkyl group or carbon chain. Some simple primary alcohols are shown in Table 29.1.

In **secondary** alcohols, the carbon with the hydroxyl (–OH) group is bonded to two other carbon atoms. In **tertiary** alcohols, the carbon with the hydroxyl (–OH) group is bonded to three carbon atoms.


$R-\overset{H}{\underset{H}{C}}-OH$ $\quad R-\overset{H}{\underset{R'}{C}}-OH$ $\quad R-\overset{R''}{\underset{R'}{C}}-OH$

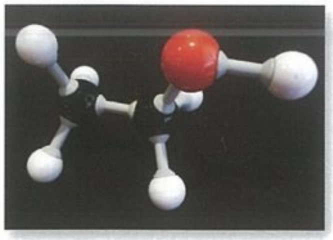
Primary alcohol Secondary alcohol Tertiary alcohol

**Figure 29.1** Primary, secondary and tertiary alcohols.

In these formulas, **R, R′ and R″** refer to an alkyl chain which can be one or more carbon atoms long.

## QUESTIONS

1. Write structural formulas for each of the following alcohols and state whether each is a primary, secondary or tertiary alcohol.
   (a) Pentan-2-ol. (b) Hexan-3-ol.
2. Distinguish between the following.
   (a) Hydroxide and hydroxyl groups.
   (b) Primary, secondary and tertiary alcohols.
3. Write an equation to show the substitution of a hydroxyl group into 1-chloropropane.
4. Name the alcohol illustrated and discuss how its polar nature affects its solubility in water and its ability to act as a solvent.



5. Examine the table below and describe how the solubility of alcohols changes as the length of the carbon chain increases. Suggest a reason.

| Compound | Formula | Solubility (g/100 g water) |
|---|---|---|
| Methanol | $CH_3OH$ | Infinite |
| Ethanol | $CH_3CH_2OH$ | Infinite |
| Propan-1-ol | $CH_3CH_2CH_2OH$ | Infinite |
| Butan-1-ol | $CH_3CH_2CH_2CH_2OH$ | 8.0 |
| Pentan-1-ol | $CH_3CH_2CH_2CH_2CH_2OH$ | 2.7 |
| Hexan-1-ol | $CH_3CH_2CH_2CH_2CH_2CH_2OH$ | 0.6 |

6. Research the formulas and uses for these more complex alcohols.
   (a) Ethane-1,2-diol (ethyl glycol).
   (b) 1,2,3-Propanetriol (glycerol).
7. Use structural formulas to illustrate eight structural isomers of pentanol ($C_5H_{11}OH$). Name each isomer and indicate whether it is primary, secondary or tertiary.
8. Check your knowledge with this quick quiz.
   (a) Identify the functional group of alcohols.
   (b) Name three types of alcohols.
   (c) Identify three uses of alcohols.
   (d) Are alcohols polar or non-polar?
   (e) List three properties of alcohols.
   (f) Identify three types of bonds between molecules of alcohols.
   (g) Alcohols have (higher/lower) boiling points than hydrocarbons.
   (h) Name two structural isomers of pentanol.

# 30 Enthalpy Of Combustion Of Alcohols

You already know that combustion is an exothermic chemical reaction that uses oxygen and produces one or more oxides.

The **heat of combustion** refers to the energy released when a substance undergoes complete combustion. This is always a positive value, as combustion is an exothermic reaction, always releasing heat energy.

**Enthalpy of combustion** ($\Delta H_{combustion}$) refers to the change in the total change of a system during a combustion reaction. Combustion always releases energy – it is always an exothermic reaction – so the enthalpy of combustion must always be written as a negative value.

## Investigating heat of combustion

A technique used to determine the enthalpy of combustion of liquid fuels such as ethanol (alcohol) and methanol is to burn the ethanol in a spirit burner and use the heat from the combustion of the ethanol to heat a measured volume of water. The water can be held in a flask, or if available, in a metal calorimeter.

Obviously, the simple polystyrene cup calorimeter would not be suitable.

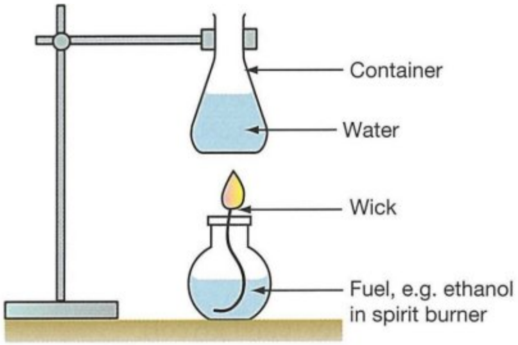


**Figure 30.1** Measuring heat of combustion for alcohols.

The idea of the experiment is to measure the temperature rise, of a measured volume of water, caused by burning a measured mass of a fuel in a spirit burner, and then use those values to calculate how much energy would be released by burning a mole of that fuel – the molar heat of combustion for that alcohol fuel.

The **steps in this method** are as follows.

- Measure the mass of a spirit burner containing a fuel such as ethanol.
- Measure out 100 mL of water.
- Pour the water into the beaker, metal can or flask that will be used as a calorimeter.
- Measure the temperature of the water.
- Place the water container directly above the spirit burner.
- Light the wick of the spirit burner and allow it to burn for a short time, e.g. 1 minute.
- Measure the highest temperature reached by the water and calculate the change in temperature. Note that in your calculations the unit (Celsius or kelvin) does not matter as you are only interested in the change in temperature, not the actual temperature.
- When cool, measure the mass of spirit burner + remaining fuel, and calculate the change in mass. This tells you the mass of fuel that burned and heated the water.
- Calculate the enthalpy change using the formula:
  $\Delta H = -mC\Delta T$, where:
  $\Delta H$ = enthalpy change in joules
  $m$ = mass of water (g)
  $C$ = thermal heat capacity of water
  $= 4.18\ \text{J g}^{-1}\ \text{K}^{-1}$
  $\Delta T$ = change in temperature (in kelvins or Celsius).

This tells you the enthalpy change from burning a small mass of fuel. You can then calculate the molar heat of combustion of the fuel.

The results using this technique are not very accurate. An assumption made is that all the heat from the burning alcohol has gone into heating the water. Of course, this is not the case, as a great deal of heat can be lost to the surroundings – the water container and the air around the experiment. Also, combustion may be incomplete as indicated by the deposition of any soot on the outside of the water container. However, this method still provides a valid technique for comparing the relative amounts of heat energy released when different fuels are burned.

Table 30.1 provides some figures for the heats of combustion and the enthalpy of combustion for four alcohol fuels often used in questions on heat of combustion.

**Table 30.1** Heats of combustion for some alcohols.

| Fuels | Formula | Theoretical heat of combustion (kJ mol$^{-1}$) | Theoretical enthalpy of combustion (kJ mol$^{-1}$) |
|---|---|---|---|
| Methanol | $CH_3OH$ | 726 | –726 |
| Ethanol | $C_2H_5OH$ | 1367 | –1367 |
| Propanol | $C_3H_7OH$ | 2021 | –2021 |
| Butanol | $C_4H_9OH$ | 2676 | –2671 |

We can show the enthalpy of combustion when we write combustion equations. For example:

$$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)\ \Delta H_{comb} = -726\ \text{kJ mol}^{-1}$$

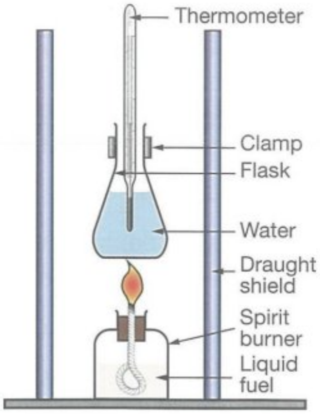
Table 30.2 shows enthalpies of combustion for some alcohols that can be used as fuels. This is the energy released by the complete combustion of 1 mole of each alcohol, with the final products being carbon dioxide and water. In this table the values are expressed in kJ mol$^{-1}$.

**Table 30.2** Enthalpy of combustion of alcohols.

| Fuel | Formula | State | $\Delta H$ (kJ mol$^{-1}$) |
|---|---|---|---|
| Methanol | $CH_3OH$ | Liquid | –726 |
| Ethanol | $C_2H_5OH$ | Liquid | –1368 |
| Propan-1-ol | $C_3H_7OH$ | Liquid | –2021 |
| Butan-1-ol | $C_4H_9OH$ | Liquid | –2671 |

## QUESTIONS

1. Describe the experiment you carried out to investigate the enthalpy of combustion for a range of alcohols.
2. (a) Distinguish between the heat of combustion and the molar enthalpy of combustion.
   (b) Write a balanced equation for the combustion of propanol including the molar enthalpy of combustion.
3. A chemistry student performed a first-hand investigation to determine the heat of combustion of ethanol. He burned ethanol in a spirit burner and used it to heat 100.0 mL of water. His results were:
   Initial temperature of 100.0 mL water = 23.5°C
   Final temperature of 100.0 mL water = 33.5°C
   Initial mass of spirit burner + ethanol = 245.42 g
   Final mass of spirit burner + ethanol = 244.80 g
   Specific heat of water = $4.18 \times 10^3$ J kg$^{-1}$ K$^{-1}$
   (a) Use these results to calculate the experimental heat of combustion of ethanol.
   (b) Comment on the accuracy of these results.
   (c) Suggest ways to reduce the heat loss during this experiment.
   (d) In view of the inaccuracy of results, is there any value in carrying out these experiments? Explain.
   (e) Outline any safety measures necessary when doing such an experiment.
4. Methanol is toxic and can cause blindness. It is present in methylated spirits, making it unsuitable to drink.
   (a) Write the thermochemical equation for the complete combustion of liquid methanol.
   (b) How much energy would be released by the complete combustion of 1 mol of methanol?
   (c) Deduce the energy released by the complete combustion of 2 mol of methanol.
   (d) Calculate the molar mass of methanol.
   (e) Calculate the energy that would be released by the complete combustion of 500 g of methanol.



5. A conical flask containing 100.0 mL (100 g) of water is suspended over a spirit burner containing ethanol as shown in the diagram.
   (a) Calculate the amount of heat absorbed by the water in the flask if its temperature increases by 16°C.
   (b) The amount of ethanol burned to bring about this temperature rise was 0.49 g. Assuming all of the heat produced enters the water, how much heat energy would be released by one mole of ethanol?
6. Using the method described in this chapter, some students determined the heat released from the combustion of 1 gram of three different alcohols.

| Alcohol | Heat energy produced by combustion (kJ g$^{-1}$) | Molar mass (g mol$^{-1}$) |
|---|---|---|
| Methanol | 15.5 | 32 |
| Ethanol | 20.8 | 46 |
| Propanol | 25.0 | 60 |

   (a) Use the values in the table above to calculate the experimental molar heat of combustion for these three alcohols.
   (b) Compare these experimental values for molar heats of combustion to the theoretical values in Table 30.1.
   (c) State the value of the experimental enthalpy of combustion for these three alcohols.

# 31 Reactions Of Alcohols

The reactions of alcohols include the following.

## Combustion

Alcohols are flammable. They burn in air or oxygen, forming water and carbon dioxide. For example:

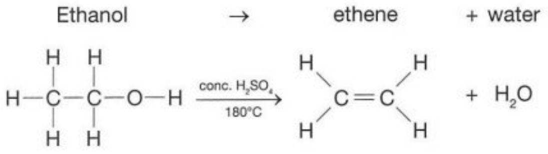
$C_2H_5OH(l) + 3O_2(g) \rightarrow 3H_2O(l) + 2CO_2(g)$

In a restricted oxygen supply, carbon monoxide and/or carbon can be formed.

$C_2H_5OH(l) + 1\frac{1}{2}O_2(g) \rightarrow 3H_2O(l) + CO(g) + C(s)$

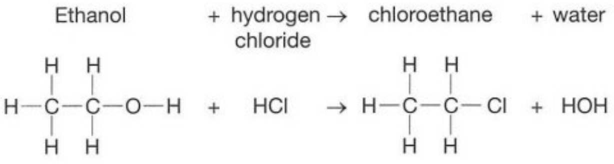
## Dehydration

Alcohols can be dehydrated (have a molecule of water removed) by heating with concentrated sulfuric or phosphoric acid. This produces an alkene. For example:



## Substitution with HX (a hydrogen halide)

Alcohols undergo a substitution reaction with a hydrogen halide such as hydrogen chloride. For example:



## Oxidation of alcohols

**Primary and secondary alcohols** react **with oxidising agents** such as acidified potassium permanganate ($KMnO_4$) and acidified potassium dichromate ($K_2Cr_2O_7$). (Acidified means that an acid such as dilute sulfuric acid is added.)

Dichromate ions ($Cr_2O_7^{2-}$) are orange. When reduced, they are converted to chromate ions ($Cr^{3+}$) which are green as shown in Figure 31.1.

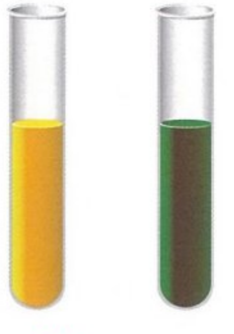
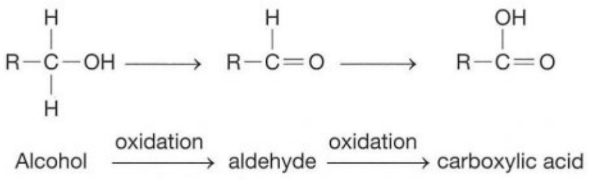
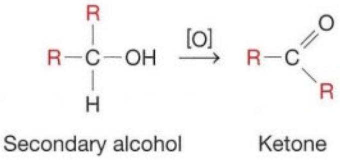


**Figure 31.1** Reduction of dichromate to chromate ions.

**Primary alcohols** are oxidised to **aldehydes**, which can be further oxidised, under suitable conditions, to **carboxylic acids**.



- **Secondary alcohols** are oxidised to **ketones**, which do not get oxidised any further. Note that an [O] placed over an arrow is another way of indicating an oxidation reaction with an oxidising agent.



- **Tertiary alcohols** are not able to be oxidised.

Looking at Figure 31.2 might help you understand and remember these reactions. You can see that in primary and secondary alcohols the oxidising agent is removing a H from a C atom and from a hydroxyl group attached to that C. However, in tertiary alcohols, there is no H (attached to the C atom) to be removed – so no oxidation can occur.

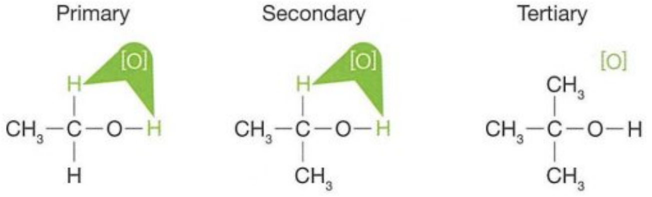


**Figure 31.2** Oxidation of alcohols.

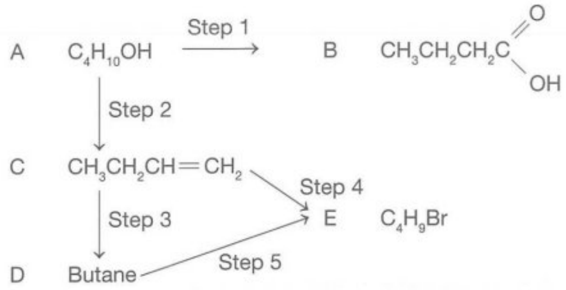
## Esterification

Alcohols react with carboxylic acids to form esters in a process called esterification – but more on that later.

## QUESTIONS

1. Write equations to show the following reactions.
   (a) The complete combustion of 1-propanol.
   (b) The dehydration of 1-butanol by heating with concentrated phosphoric acid.
   (c) The substitution of hydrogen bromide into 1-pentanol.
2. (a) Is ethanol a primary, secondary or tertiary alcohol?
   (b) Use equations to show the oxidation of ethanol.
3. Use an equation to show the oxidation of methanol.
4. Use a table to summarise the oxidation of primary, secondary and tertiary alcohols.

5. Consider the following flow chart showing a series of reactions involving organic compounds and answer the questions below.



(a) Identify the chemicals A, B, C and E.

(b) How would you distinguish between chemicals B and D using a physical property.

(c) Complete the table to show which step illustrates each of the following types of reactions.

| Type of reaction | Step number |
|---|---|
| Addition | |
| Substitution | |
| Dehydration | |
| Oxidation | |

# 32 Production Of Alcohols

Primary alcohols have their hydroxyl (OH) group attached to a terminal carbon in the molecule. They are produced mainly by fermentation, hydration (hydrolysis) and substitution reactions. They can also be produced by complex redox reactions.

## Fermentation of sugars

One of the most important alcohols is **ethanol** which is used as a fuel, in drinks, as a solvent, and in many industrial processes including the production of vinegar and adhesives. Ethanol can be **synthesised** by the **fermentation of sugars** using enzymes produced by fungi such as the yeast *Saccharomyces cerevisiae* or by genetically engineered bacteria such as *E. coli.*

$$C_6H_{12}O_6(aq) \xrightarrow{\text{Yeast}} 2C_2H_5OH(aq) + 2CO_2(g)$$

## To make ethanol by fermentation in the laboratory

The container in which fermentation will occur and all equipment must be very clean. After being washed, it should be rinsed with a sterilising agent, such as sodium metabisulfite, then rinsed with boiled water and allowed to dry.

Sugar or commercial wort water is added to the clean container and stirred until dissolved.

Commercial wort is the liquid extract from mashing barley and it contains sugars. Alternatively, a solution of 1 gram of glucose to 10 mL of water can be used.

When the water has cooled, brewers yeast is added, about 1 gram of yeast to 500 mL of solution, and the container air-sealed to prevent the entry of microbes and allow carbon dioxide produced to escape. If you are using a home brewing kit, it may look something like this.

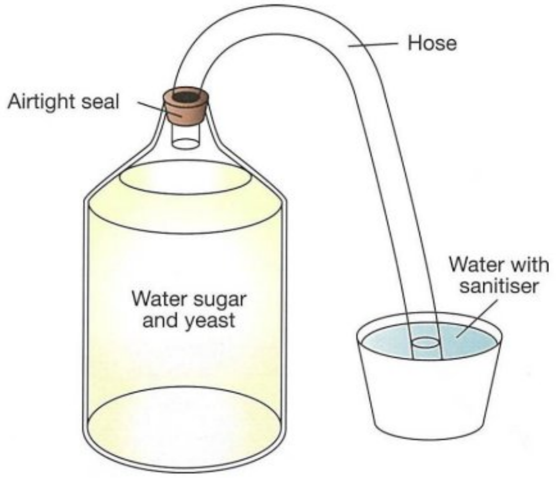


**Figure 32.1** Making ethanol.

Sugars such as glucose, fructose and sucrose can be used in this process.

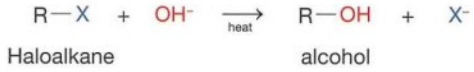
Allow your mixture to ferment for about a week, maintaining the flask and contents at a temperature of between 20°C and 25°C. Then remove a sample of the mixture and carry out fractional distillation of the sample to separate out any alcohol.

One problem with this process is that alcohol is lethal to living cells, including those of yeast.

## Substitution into haloalkanes

You already know that the **hydroxyl group** (–OH) can be **substituted into a haloalkane**, replacing a chlorine, bromine or iodine atom. To do this, the haloalkane is added to a solution of sodium or potassium hydroxide and the mixture is heated, under reflux conditions.

The general equation is:



$$\underset{\text{Haloalkane}}{R{-}X} + OH^- \xrightarrow[\text{heat}]{} \underset{\text{alcohol}}{R{-}OH} + X^-$$

Where X is a halogen, e.g. Cl, Br, I.

For example, the reaction of chloroethane and sodium hydroxide heated under reflux conditions can be shown as follows.

$$CH_3CH_2Cl + OH^-(aq) \rightarrow CH_3CH_2OH + Cl^-$$

The ease with which this reaction occurs depends on the strength of the C–X bond, with C–F being least likely to react as it is very stable and strong, and thus least likely to react. Fractional distillation can be used to separate the alcohol from the reaction mixture.

## QUESTIONS

1. (a) Define primary alcohol and give an example.
   (b) List four types of reactions that could produce a primary alcohol.
2. Describe a hydrolysis reaction that can produce an alcohol.
3. Describe the production of propan-1-ol from 1-chloropropane. Include an equation in your answer.
4. Name a primary alcohol that could be produced by reduction reactions of the following compounds.
   (a) Methanal.
   (b) Propanoic acid.
   (c) Ethanoic acid.
5. Research other methods of making a primary alcohol from other organic compounds.
6. Research the production of a primary alcohol from the oxidation of an alkane.

# 33 Biofuels

Biofuels are produced from **biomass**, material that comes from living or recently living organisms, either plant or animal. The main types of biofuels in use are biogas, bioethanol and biodiesel.

The development of biofuels has been in response to concerns about:

- Pollution caused by the combustion of fossil fuels, especially by transport vehicles such as cars which are among the top emitters of greenhouse gases.
- Fears that supplies of fossil fuels are running out as they are a finite resource and non-renewable.
- Lack of availability of fuels at times of political unrest.
- Instability of world markets, the cost of importing fuel and its effect on inflation. In Australia we import petrol.

The first production of biofuels used sugar cane, corn and vegetable oils as **biomass**. These are sometimes called **first generation biofuels**. The sugars are extracted from these crops and then fermented by yeast to produce bioethanol. Biodiesel produced from vegetable oils is also considered a first generation biofuel.

Other **biomass sources** now being used as feedstocks, include waste residues from the production of crops such as sugar cane, corn, sorghum, grains such as wheat, sugar beets, olives and palm nuts. Wastes from the wood industry are also used. These crop residues are mostly cellulose which is more difficult to treat.

**Garbage, as well as animal waste** (including human waste) can be used to produce methane gas as a biofuel (biogas). Animal fats and vegetable oils are used, including waste cooking oil, to produce biodiesel. Also **algae** are being cultivated and fermented to produce biomass for the production of biofuels.

## Biofuels are renewable

Biofuels obviously have the advantage that they are **renewable**, whereas fossil fuels are non-renewable. They are renewable because we can replace them as they are used up. The use of fossil fuels for energy production is not sustainable as they are a finite resource – they will eventually run out and we cannot make new supplies.

## Are biofuels carbon neutral?

Biofuels do **produce less carbon dioxide** overall than fossil fuels. This is because the amount of carbon dioxide released when they burn is the same as the amount absorbed by the plants (during photosynthesis) as they grow.

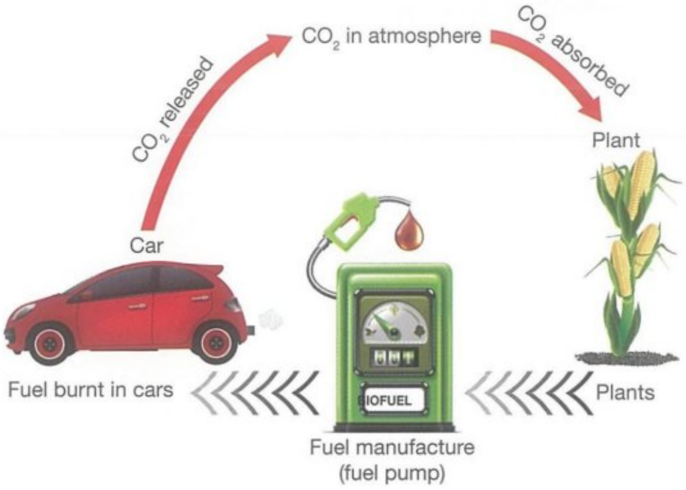


**Figure 33.1** Carbon neutral.

Of course, fossil fuels such as coal were also once living plants using carbon dioxide to photosynthesise and grow, but that was millions of years ago. The carbon dioxide released when fossil fuels burn has been trapped in the coal or petroleum for millions of years. When biofuels burn they release carbon dioxide into the atmosphere which was only recently absorbed by the plants used to make them.

However, biofuels are **not carbon neutral** because fossil fuels are also used in their production, for example in the making of fertilisers and pesticides, for growing plants to produce biomass and for providing the energy for industrial processes, such as distillation, that are needed to produce the biofuel.

## Disadvantages of biofuels

The production of biofuels such as bioethanol and biodiesel in large quantities is difficult because **sustainable and acceptable raw materials** and **affordable energy sources** for their production are not always available.

The use of food crops to produce biofuels contributes to **increases in food prices**. The production of crops such as corn and sugar in the United States and sugar in Brazil has increased by 30% to 50% over recent years. This might have been expected to stabilise food prices and help the thousands of hungry people throughout the world. However, this has not happened because these crops were grown not for food but for the production of biofuels.

Other issues associated with the use of crops to make fuels such as ethanol include the spread of **large scale commercial agriculture** and the spread of **monoculture**. This leads to a decrease in the diversity of species and also if an infection or insect pest attacks the crop, then the whole crop is more likely to be wiped out than if there is variation. These crops also tend to use a **large volume of water** in their production.

There is no doubt that we need to stop burning fossil fuels, but we must be careful that we do not choose alternatives with even worse problems.

## Fuels from cellulose

The answer may lie in the production of **second generation biofuels** which are made from a wider variety of biomass types. This includes cellulose sources such as the non-food parts of crops, the waste from food production, human and animal waste, and industrial waste such as woodchips. **Cellulose** in many of these sources can be thought of as a potential source of sugars, which can be released by processes such as hydrolysis by enzymes, and then fermented to produce biofuels. The biofuels are extracted from the fermentation mix by distillation. This cellulosic biofuel is the fuel with lowest carbon emissions. Unfortunately, most of the production by this method so far has used corn or similar crops as the source of cellulose.

Research into the use of biomass wastes as a source of cellulose is ongoing. There are a number of processes that have been developed to break down such waste materials, but high cost and the disposal of waste products tend to be problems for their implementation.

## Present use of biofuels

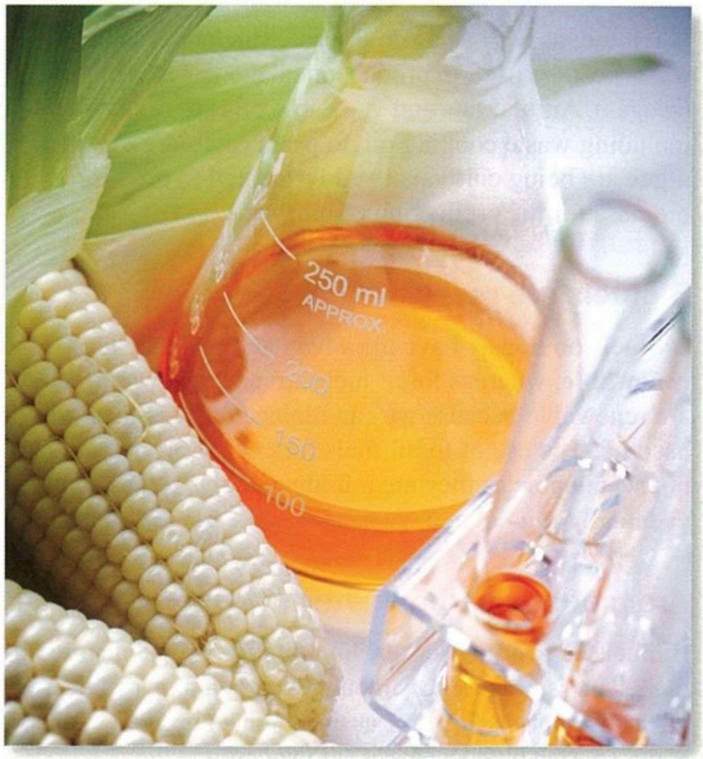
With present methods of production, biofuels can only be considered as a **supplement to petrol**, for example E10 petrol which contains 10% ethanol. It is not yet possible to manufacture nearly enough biofuel to replace the amount of petrol currently used in motor vehicles.

The three biggest producers and users of biofuels are China, Brazil and the USA, and many countries, including Australia, have established targets aimed at reducing their reliance on fossil fuels and increasing their consumption of biofuels such as ethanol and biodiesel, or using other sustainable and more environmentally friendly energy sources such as solar energy. The European Commission aimed to replace 10% of its transport fuels with renewable fuels by 2020, but this has now been reduced. Brazil already has 20% ethanol content of fuel and aims to increase this.

Current research and development projects on biofuels are focused on developing cost-competitive advanced technologies to convert wastes into fuels and producing fuels that are compatible with existing engines.

## QUESTIONS

1. (a) Define 'biofuel' and name two examples of biofuels.
   (b) Outline three concerns that have led to the development of biofuels.
2. Biofuels are claimed to be 'carbon neutral'.
   (a) What is meant by this term?
   (b) Is it correct to describe biofuels as carbon neutral?
3. Biofuels are made from biomass.
   (a) What is meant by the term biomass?
   (b) Identify five sources of biomass used to produce biofuels.
4. Research and write a report about the production of a named biofuel in Australia and consider whether or not this is a sustainable practice.
5. Distinguish between first and second generation biofuels.
6. Why is the production of biofuels from cellulose more difficult than production from sugars?
7. The governments of several countries, including the United States of America and Canada have invested millions of dollars into research on the use of algae to manufacture biofuels.
   Research the use of algae to produce biofuels.
8. Global conferences in chemical engineering frequently include sessions that target the spread of up to date information about biofuels. Identify some examples of this.
9. Check your knowledge with this quick quiz.
   (a) Plant and animal matter from recently living organisms is used to make biofuels. What is this called?
   (b) Identify three possible sources of biomass.
   (c) Fuels made from biomass are collectively called .......................... .
   (d) The three main biofuels are .........................., .......................... and .......................... .
   (e) Identify the three countries which are the biggest producers and users of biofuels.



# 34 Biogas

Biogas consists of a mixture of gases, and is rich in methane. Biogas is produced by the breakdown of organic matter in the absence of oxygen.

The organic matter used includes natural wastes derived from agriculture and from households – components such as manure from farm animals, human sewage, plant wastes such as sugar cane stalks and food processing wastes. Such wastes are decayed by bacteria producing flammable gases such as methane which can be collected and used as a fuel.

Biogas can then be used for the production of electricity or to provide a fuel to heat boilers, making steam for industrial processes. Waste material from the production of biogas can be used as a fertiliser.

In some areas, household wastes are being used in homes to produce biogas to provide lighting, fuel for cooking, heating water, central heating and even the generation of electricity.

Australia has been estimated to produce about 20 million tonnes of organic waste annually from domestic and industrial sources. If used to make biogas, this organic waste could potentially produce energy to power almost 1 million homes. So converting wastes to a useful fuel in the form of biogas could reduce our wastes, provide a useful fuel and also reduce our greenhouse emissions.

**Melbourne Water** makes biogas from wastes at their treatment plant at Werribee and uses it to make its own electricity. This is the largest biogas power station in the Southern Hemisphere. Any excess electricity is exported to the electricity grid. This plant is said to generate 71 500 megawatt hours of electricity. The combustion of fossil fuels to produce this much energy would result in the release of 87 000 tonnes of carbon dioxide.

**Sydney Water** also collects its own biogas (mainly methane) generated from the treatment of waste water. This biogas is used as a fuel to generate electricity, thus reducing greenhouse gas emissions as in Victoria.

**Industries** such as dairy, cattle and poultry farms as well as abattoirs are also developing biogas technology to reduce their energy bills and also their carbon footprints.

## Synthesis of biogas

To produce biogas, waste is placed into a closed structure called a **digester** where it is broken down by bacteria in the absence of oxygen (anaerobic change).

The digester is kept at an even temperature and suitable pH to facilitate bacterial growth. The gas released by this breakdown process is rich in methane and may also contain carbon monoxide and hydrogen, making it suitable as a fuel.

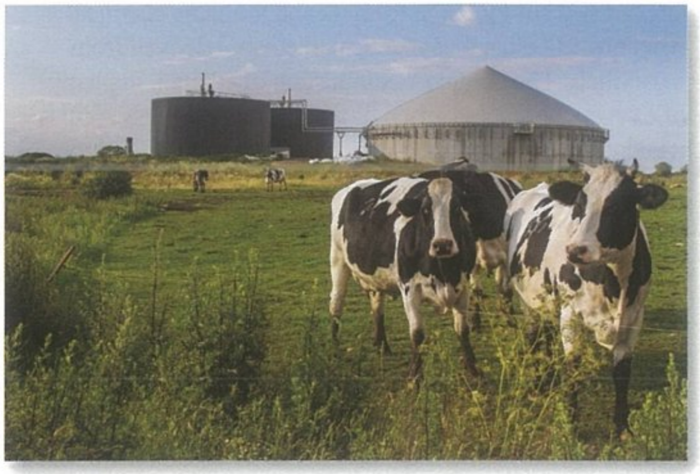


**Figure 34.1** A digester used to make biogas.

Some hydrogen sulfide may also be produced and this can be removed by using lime scrubbers. In this process the gas produced is passed through a scrubber tower filled with a solution of limewater (calcium hydroxide) or iron(II) oxide. These chemicals can absorb and remove the hydrogen sulfide from the biogas.

## QUESTIONS

1. (a) What is biogas?
   (b) Justify the classification of biogas as a renewable fuel.
   (c) Suggest sources of biomass suitable for the production of biogas.
   (d) What is a digester?
2. Identify some ways in which biogas is utilised.
3. What effect would the use of biogas have on the greenhouse effect?
4. (a) Identify an unwanted gas that can also be produced in a biogas digester.
   (b) Outline why this gas could be a problem and how it can be removed to prevent it entering the atmosphere.

# 35 Bioethanol and Biodiesel

## Bioethanol

Bioethanol is a renewable source of ethanol that has been made by the fermentation of carbohydrates (sugars, starch, cellulose) from biomass, particularly sugar cane, corn and wheat crops.

As with all compounds, no matter how it is obtained or made, ethanol still has the same formula and the same chemical reactions. Bioethanol is identical to ethanol derived from fossil fuels. The complete combustion of ethanol, in plenty of oxygen, produces carbon dioxide and water. This applies whether the fuel is produced from petroleum or from biomass.

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

Most bioethanol is still produced from starch based crops such as corn. The crop is ground up and fermented by yeast, producing ethanol and carbon dioxide. However, Brazil which is a very successful sustainable producer of biofuels, produces its bioethanol from sugar cane.

**Figure 35.1** Bioethanol refinery.

Ethanol is mainly blended in different concentrations with petrol, e.g. E10. Thus it acts as a supplement to petrol supplies, and it also acts as an octane enhancer, reducing pinging in the motor. Blends containing higher concentrations of ethanol, such as E85 are only suitable for vehicles designed for its use such as the flexible-fuel vehicles used in Brazil which can run on any proportion. Ethanol to be used as a fuel has chemicals added, before it leaves the factory, to make it unfit for human consumption.

Ethanol has been mainly used in cars, but in Brazil its use is being extended to use in trucks, buses and planes, sometimes in conjunction with biodiesel. It is also used in hybrid vehicles.

## Synthesis of bioethanol

The leading producer of bioethanol is the United States. Here it is mainly being produced from corn, although other sources of starch can be used.

**Bioethanol** is formed by **fermenting carbohydrates** derived from biomass using enzymes produced by fungi, such as the yeast *Saccharomyces cerevisiae,* or by using genetically engineered bacteria such as *E. coli*.

$$C_6H_{12}O_6 \xrightarrow[\text{enzymes}]{\text{yeast}} 2C_2H_5OH(aq) + 2CO_2(g)$$

The industrial processs can be carried out in many ways; one such process is illustrated in Figure 35.2.

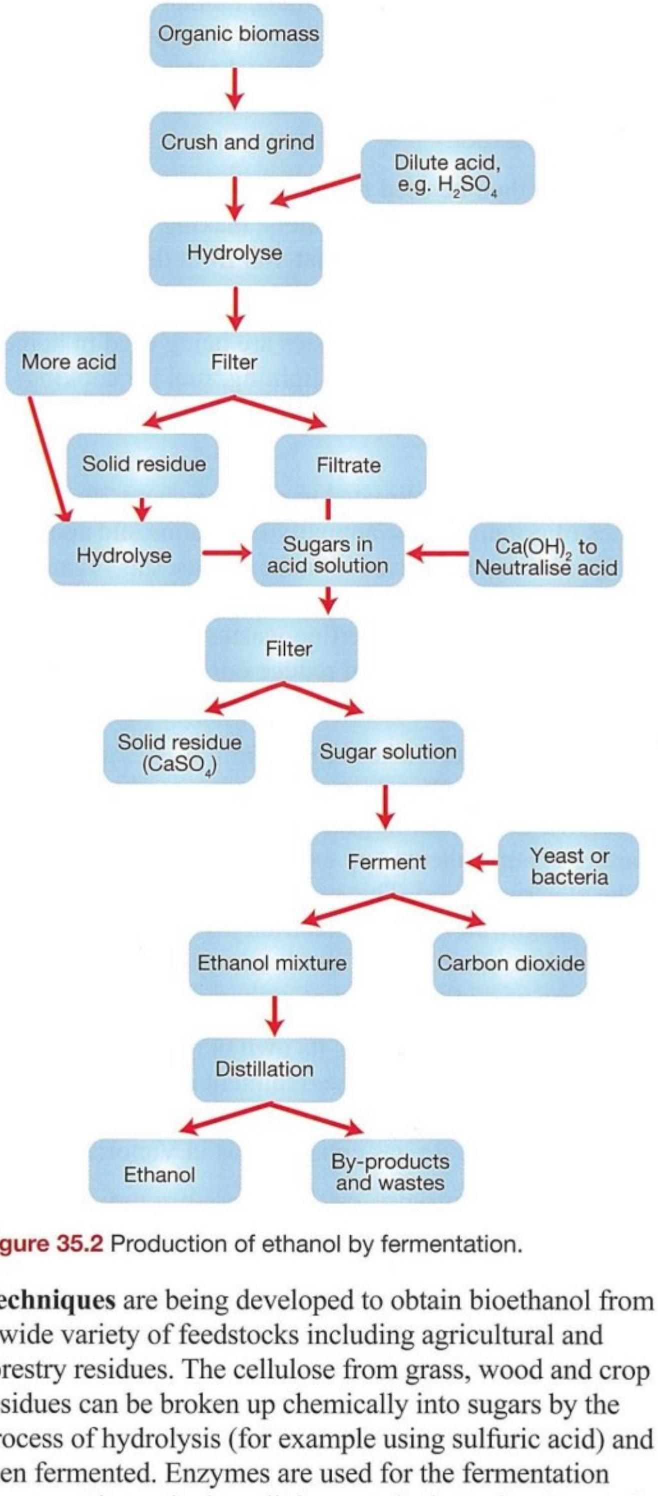


**Figure 35.2** Production of ethanol by fermentation.

**Techniques** are being developed to obtain bioethanol from a wide variety of feedstocks including agricultural and forestry residues. The cellulose from grass, wood and crop residues can be broken up chemically into sugars by the process of hydrolysis (for example using sulfuric acid) and then fermented. Enzymes are used for the fermentation process. Alternatively, cellulose can be heated and treated with chemicals to produce syngas which is a mixture of carbon monoxide and hydrogen. Syngas can then be converted into bioethanol using microbial catalysts.

Genetic modification of plants is being investigated to produce plants with cell walls that are easier to break down. Also recently discovered proteins called tapirins, which occur in bacteria found in hot springs, can bind onto and break down cellulose, so their use is also being investigated as an aid in the production of biofuels.

## Biodiesel

Biodiesel is a liquid fuel composed of methyl/ethyl esters of long chain fatty acids. Biodiesel is used as a fuel additive in petroleum based diesel fuel and is the most commonly used biofuel in Europe.

Biodiesel produces fewer emissions than diesel fuel, so its use releases lower levels of particulates, carbon monoxide and hydrocarbons into the atmosphere. It is renewable, biodegradable and non-toxic. It is also relatively safe to use as it has a high flash point.

## Synthesis of biodiesel

Biodiesel is made from renewable sources such as:

- Vegetable oils, e.g. soybean, coconut, sunflower oils, and waste vegetable oils from commercial cooking sources.
- Animal fat, e.g. lard, tallow, chicken fat and waste fish oil.
- Algae and sewage sludge.

These fats and oils (triglycerides) are reacted with a short chain alcohol (methanol or ethanol) in the presence of a base, such as sodium or potassium hydroxide, which acts as a catalyst. This process is called esterification.

It can also be carried out at low temperatures and pressures, using enzymes. This is a cost effective process that produces high yields and does not need difficult separation techniques to separate the products – biodiesel and glycerol.

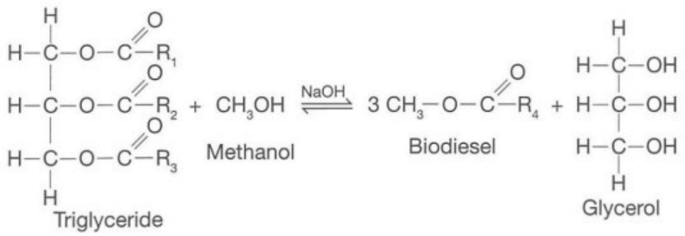


**Figure 35.3** Triglyceride converted to biodiesel by transesterification.

Glycerol (also called glycerine) is produced as a by-product of biodiesel production and it can be used in soap as well as in the pharmaceutical and cosmetics industries.

Biodiesel is also produced by **fermentation of sugars produced from cellulose** in sources such as agricultural waste. This is a process similar to the production of ethanol.

## QUESTIONS

1. Justify the classification of both bioethanol and biodiesel as renewable fuels.
2. Ethanol can be used as a renewable alternative to fossil fuels.
   (a) Write an equation for the combustion of ethanol.
   (b) Justify the classification of ethanol as a renewable fuel.
   (c) One argument against using ethanol as fuel is that the crops required, and the land needed to grow these crops, could be better used in providing food for starving people. Evaluate this argument.
3. (a) Describe the composition of petrol.
   (b) Describe the composition of bioethanol.
   (c) Evaluate the usefulness of ethanol as a fuel source in comparison to petrol.
4. (a) Distinguish between bioethanol and biodiesel in their sources, composition and uses.
   (b) Biofuels can use biomass in their manufacture. Define biomass.
5. Research the production of ethanol or biodiesel in Australia for use as a fuel and consider if this is a sustainable practice.
   Write a report based on your research. Before you begin, you should discuss the format and length of your report with your teacher.
6. Check your knowledge with this quick quiz.
   (a) State the formula for the ethanol in bioethanol fuels.
   (b) Name two products of the combustion of both bioethanol and biodiesel.
   (c) Bioethanol and biodiesel are both made of carbon compounds. Which contains the longer chain carbon compounds, bioethanol or biodiesel?
   (d) Identify two substances used to make bioethanol.
   (e) Name two substances used to make biodiesel.

# 36 Comparing Fossil Fuels and Biofuels

We use a great deal of energy, especially in the area of transport. This is costly, and the air pollution produced can have severe and multiple impacts.

A sustainable energy supply is essential for any nation that wants a healthy economy and good standard of living. So the choice of which fuels to use is important and should be based on factual comparisons.

Fossil fuels (coal, crude oil, natural gas and coal seam gas) can be compared with biofuels (biogas, bioethanol and biodiesel) with reference to their energy content, efficiency, renewability and environmental impacts related to sourcing and combustion.

## Energy content of fossil fuels and biofuels

Table 36.1 gives some approximate figures to illustrate that fuels vary in the energy that can be released during their combustion. You will find variations in values quoted, one reason being that some are quoted for reactions in which the water produced remains as a liquid, other lower values assume the water is all vaporised.

**Table 36.1** Energy content of some fuels.

| Fuel | Approximate energy content (MJ/kg) |
|---|---|
| Propane | 50.0 |
| LPG (propane + butane) | 49.7 |
| Butane | 49.3 |
| Kerosene | 46.8 |
| Petrol | 46.8 |
| Diesel | 46.4 |
| Petroleum oil | 45.0 |
| Natural gas | 38.9 |
| Black coal | 29.9 |
| Brown coal | 10.1 |
| Biodiesel | 39.2 |
| Ethanol | 29.9 |
| Methanol | 23.0 |
| Dry wood | 15.8 |
| Green wood | 9.0 |
| Agricultural crop residues | 9.0 to 18.0 |
| Municipal waste | 7.2 to 9.0 |

## Fuel efficiency

The actual energy content per mass of a fuel is important, but not the only factor to consider. For example, an electric powered car is about twice as expensive as a petrol driven car, but electric motors are more efficient than internal combustion motors using petrol and/or ethanol. This is partly because internal combustion engines have more moving parts so more energy is lost overcoming friction. The 'lost' energy refers to energy that is changed to heat, rather than bringing about movement of the vehicle, and which is released into the atmosphere. Heat is also lost via the radiator, and exhaust system, friction with the road, and the atmosphere.

A fuel efficient engine uses less fuel to travel any given distance, resulting in a lower use of fuel and thus less pollution. Fuel efficiency can be measured by the litres of fuel needed to travel a stated distance, such as litres per km or litres per 100 km. Sometimes it is more relevant to consider how far a vehicle can travel per unit of fuel, e.g. km per litre.

## Fuel efficiency of LPG and petrol

In Australia, **petrol** is the most widely used fuel in motor vehicles. However, over recent years LPG and also diesel have become more popular.

**LPG** is a less efficient fuel. Converting from petrol to LPG means an increase in fuel consumption of up to 40% – you need 40% more fuel to cover the same distance. At present LPG is cheaper per litre to buy, so that compensates economically for the reduced efficiency of the fuel, making it a popular choice. People seem to forget (or do not know) that LPG is, like petrol, a fossil fuel and is thus also an unsustainable fuel choice.

## Renewability

Obviously, when it comes to renewability, the biofuels have an enormous advantage over fossil fuels. Fossil fuels cannot be renewed, once used they cannot be replaced. Biofuels are manufactured from sources such as biomass which are renewable. The problem here is finding enough biomass that has no other use such as for the production of food for humans and farm animals, and finding land on which to grow the required biomass. We have already seen that this problem may be at least partly addressed by using cellulosic wastes for biomass.

We know that fossil fuels are not renewable, they are a finite resource and they are running out. Some will last longer than others, but they will all run out eventually, and as the population continues to increase, and more of the world's population demand a Western style of high energy living, they will be used up faster. Fossil fuels are not a sustainable resource. We need to change our way of life and/or find new sources of fuel.

Table 36.2 Advantages and disadvantages of using bioethanol compared to using petrol.

| Advantages of bioethanol | Disadvantages of bioethanol |
|---|---|
| **Production:**<br>Renewable.<br>Made by fermenting carbohydrate biomass.<br>$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$<br>Technology is being developed to use waste cellulosic feedstocks.<br>Local production of bioethanol could reduce the amount of petrol we need to import. | To grow feedstocks, large areas of land are needed which could otherwise be used to grow food crops.<br>Waste products of cellulose fermentation are difficult to dispose of.<br>A lot of water is used.<br>High production costs, e.g. for distillation or membrane separation and also to remove water from ethanol. |
| **Emissions:**<br>Ethanol molecule contains oxygen atom, so combustion is more complete. Ethanol burns more cleanly producing less carbon monoxide and carbon particles when burnt under the same conditions as petrol.<br>Ethanol has a **lower greenhouse impact** than petrol. However, emissions benefits of ethanol depend on fuel blend used, vehicle type and age, engine calibration and maintenance. | Biofuels such as bioethanol produced from biomass are **not greenhouse neutral**. Greenhouse gases are released during its production, e.g. during cultivation of crops, production of fertilisers, distillation of fermented sugars and waste disposal. This reduces its ecological effectiveness. |
| **Additives:**<br>No high octane additives are needed as ethanol has a higher octane rating than petrol. | Other additives are added, e.g. corrosion inhibitors.<br>Ethanol can cause corrosion of metals and deterioration of some rubber engine components. |
| **Spills of fuel:**<br>Spills biodegrade more readily and can more easily be diluted to non-toxic levels. | Spills are difficult to contain and recover as the hydroxyl group (OH) bonds with water and thus the fuel cannot be skimmed off the top of water like petrol. |
| **Fuel economy:**<br>Nil. Petrol has higher fuel economy than biodiesel. | Lower fuel economy so higher fuel consumption – you use more ethanol than petrol to go the same distance (and travel less km per litre of ethanol). |

## Environmental impacts

It is obvious that many of the problems we face today, such as climate change, pollution of air, land and water, oil spills and acid rain, are all a direct result of our use of fossil fuels to produce electricity and provide for transport.

Concerned scientists worldwide have united in condemning the use of fossil fuels to provide energy because of all its undesirable side effects.

We can look at these differences by comparing the use of petrol and bioethanol as fuel in a car. Table 36.2 summarises some advantages and disadvantages of using bioethanol, compared to using petrol.

## QUESTIONS

1. Ethanol and petrol can both be used as fuels. Petrol is a mixture, but a major component is octane and this can be used for comparison purposes. The heats of combustion of ethanol and octane are respectively −1367 and −5450 kJ mol$^{-1}$.
   (a) Write equations to represent the combustion reactions for ethanol and octane in oxygen.
   (b) Convert the heat of combustion of ethanol and octane from kJ mol$^{-1}$ to kJ g$^{-1}$.
   (c) If the fuels were the same price per gram, which would be the more economical to use, petrol or ethanol?
   (d) Would your car travel further when you use petrol containing 10% ethanol or when filled with the same amount of petrol without ethanol?
   (e) If ethanol is less economical than petrol, why is it added to petrol? Suggest three reasons.
2. Research the current use of fuel containing bioethanol, especially in Australia. In your answer you should consider such issues as the following.
   - The production of bioethanol in Australia and compare this with its production in Brazil, China or the United States of America.
   - The availability of various blends in Australia compared to overseas and reasons for any differences.
   - The availability of petrol containing ethanol at service stations in different regions of Australia.
   - Does acceptance of bioethanol vary between states in Australia?
3. Do you think that ethanol will ever replace petrol as a fuel for motor vehicles in Australia? Justify your opinion.

# 37 Petrodiesel and Biodiesel As Transport Fuels

Transport fuels are fuels used to power motor vehicles including cars, trucks, heavy machinery, planes, trains and boats.

The Australian government classifies the fuels we use for transport as conventional and alternative fuels.

**Conventional transport fuels** are those derived from crude oil and used to power motor vehicles and aircraft – petrol, diesel and jet fuel, all obtained by the fractional distillation of crude oil. These make up the largest volume of fuel use in Australia.

**Alternative transport fuels** include **biofuels**, **gaseous fuels** (compressed natural gas (CPG), liquefied petroleum gas (LPG) and **synthetic fuels** such as shale oils. Don't be fooled by this classification. Only the biofuels are renewable, the others are produced from fossil fuels – classifying them as alternative fuels does not mean that they are renewable.

In Australia, **petrol** is the most widely used transport fuel. However, over recent years diesel fuels have become more popular, both petrodiesel and biodiesel. Before we compare these fuels we need to look at some properties of fuels and how they relate to fossil fuels and biofuels.

## Properties of fuels

Petrol is more **volatile** than both diesel and biodiesel, the petrol has a greater tendency to vaporise, making the fuel more hazardous. This has little influence on engine performance, but is an important property to consider for storage and transport. The formation and build-up of petrol fumes may cause fires and explosions, whereas this is not a problem with diesel fuels

**Viscosity** is the resistance of a fluid to flow. (Honey is more viscous than water, especially when the honey is cold.) Fuel is pumped from the fuel tank through a fuel filter and into fuel injectors which inject a fine spray of fuel into the cylinders where they burn. Viscosity affects the spray pattern when the fuel is injected into the cylinder and the viscosity needs to be kept low to prevent wear of the fuel injection pump and ensure smooth combustion. Petrodiesel is more viscous than petrol or biodiesel so it acts as a lubricator and prevents wear to fuel lines. At low temperatures the viscosity of fuels increases and this may cause problems for diesel fuels. Petrol does not freeze, even in severe weather conditions, but diesel fuels have higher melting and freezing points, so waxy crystals may form in the fuel lines of diesel engines at low temperatures. This can be overcome by additives which prevent crystal formation, but these additives lower the energy efficiency of the fuel.

**Hygroscopic properties** refer to the ability of the fuel to absorb water from the air. Petrol is not hygroscopic, but diesel, biodiesel and bioethanol are, and a small amount of water may dissolve in these fuels. The water present in these fuels may cause corrosion and has the potential to freeze in cold climates. It also reduces the ability of the fuel to act as a lubricant. Additives can be used to disperse the moisture through the fuel, forming a stable emulsion of the water in the fuel to reduce the problem. Diesel engines may also have a water separator in the fuel filter.

## Petrodiesel

Petrodiesel is diesel fuel produced through the fractional distillation of crude oil. It contains a mixture of hydrocarbon molecules that vary in size from 8 to 21 carbon atoms.

**Diesel engines** are generally claimed to have the advantage of **greater fuel efficiency** than petrol engines. The use of compression ignition instead of spark plugs makes the engines more fuel efficient. Also they usually have a lot of pulling power and use less fuel in each gear.

Diesel engines do produce less toxic carbon monoxide in their exhaust, however they also produce more particulate matter and nitrogen oxides (NOx) so they have a greater adverse environmental impact.

The particulate matter consists of fine particles of organic and inorganic compounds and unburnt carbon and it poses a health risk as it may affect the respiratory system and also some of the substances are carcinogenic.

The nitrogen oxides released include a large percentage of harmful nitrogen dioxide. Petrol driven cars also produce some nitrogen oxides, but only 10% to 15% $NO_2$. In some places NOx pollution is so bad that some countries are considering banning diesel vehicles in cities and/or offering cash incentives to switch from diesel to electric or hybrid vehicles.

NOx pollution, especially $NO_2$ contributes to the production of ozone in the lower atmosphere and also fine particulate matter. Both of these harm human health. $NO_2$ also has a direct effect, aggravating heart and lung disease. In the United Kingdom alone an estimated 23 500 deaths can be attributed directly to $NO_2$ each year.

There are technologies available to help reduce emissions from vehicles, but these come with drawbacks. For example:

- Recirculating exhaust gases back through the engine – but this reduces engine performance.
- Using a trap (LNT) to remove gases – but these rapidly become saturated and extra fuel is used to regenerate them, increasing fuel consumption.
- Using a selective catalytic reducer (SCR, e.g. AdBlue) which reacts urea with NOx to form harmless nitrogen gas and water. However, the tanks are large so are only fitted to larger vehicles and they have to be repeatedly refilled.

The development of biodiesel may help to address some of these problems with petrodiesel.

## Biodiesel

Biodiesel is a diesel fuel obtained by esterification of oil derived from plant or animal matter (see Chapter 33). It is a renewable liquid fuel which can be used in pure form (B100) or it can be blended in different concentrations with petroleum diesel, e.g. B2 (2% biodiesel), B10 (10% biodiesel) and B20 (20% biodiesel).

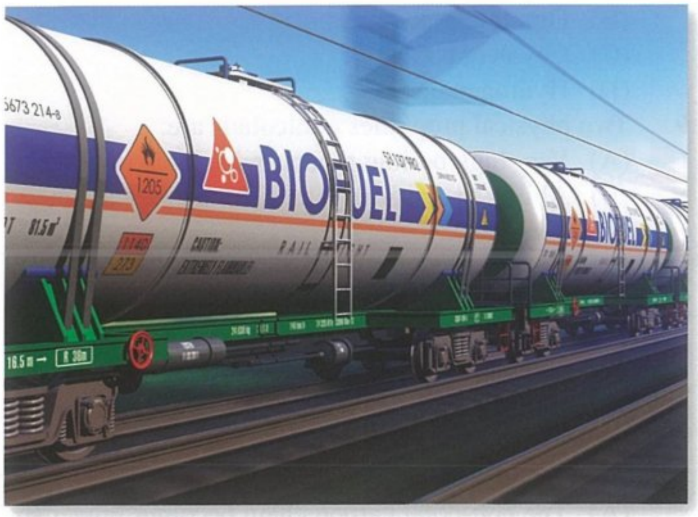


**Figure 37.1** Transport of biodiesel.

The **advantages of biodiesel** are as follows.

- It is renewable.
- Low level blends, e.g. B20 and lower, can be used in existing diesel engines without modification. However, not all manufacturers cover the use of biodiesel in their warranties.
- It can improve engine lubrication and increase engine life as it does not contain any sulfur.
- It produces less of some pollutants when used in older engines, e.g. less CO, $CO_2$, $SO_2$, particulates, and hydrocarbons.
- Reduction in $CO_2$ released to the atmosphere can help reduce the greenhouse effect. Using B20 could reduce emissions by about 15%.
- Biodiesel is non-toxic and highly biodegradable, breaking down about four times faster than petrodiesel in the event of a spill.
- It has a higher flash point than petrodiesel making it safer to handle and transport.
- It can be made locally thus helping to create local jobs and also reduce our dependence on imported fuel supplies.

There are however some **disadvantages to the use of biodiesel**.

- It is more expensive to use than petrodiesel. B20 will have 1% to 2% less energy than petrodiesel.
- The quality varies as it can be made from a variety of crops, although it does have to comply with Australian standards.
- The use of crops which could be used to provide food is not acceptable. This applies not just to human food but also food for farm animals such as pigs. There is also the problem of the use of water to produce crops as water shortages are also a problem.
- It is not suitable for use in low temperatures, especially in high level blends.
- Biodiesel may cause corrosion of some metals such as zinc, tin and copper based alloys. It also causes some polymer seals to swell or harden.
- Although biodiesel does remove dirt from engines, decoking combustion chambers, this dirt collects in filters and causes clogging there.
- Biodiesel produces higher nitrogen oxide emissions than other petroleum products, including petrodiesel.
- The energy needed to produce the biomass to make biofuels must be considered. The feedstock accounts for about 80% of the cost of biodiesel. It is only economically viable at present because of government subsidies paid for non-food crops and the absence of oil tax.

### QUESTIONS

1. It is claimed that new cars have become much cleaner over the last 20 years mainly due to strong emission standards introduced by authorities. Identify some technologies and innovations that have helped to make cars cleaner.
2. (a) Why is the release of nitrogen oxides from the exhaust of motor vehicles considered undesirable?
   (b) Explain why diesel engines produce more NOx than petrol engines.
3. The energy contents of biodiesel and petrodiesel are approximately 39 MJ/kg and 46 MJ/kg respectively.
   (a) Which fuel would you theoretically use less of on a 100 km trip?
   (b) Explain why biodiesel is claimed to produce less net carbon dioxide compared to petrodiesel.
4. Check your knowledge with this quick quiz.
   (a) Rank these fuels in efficiency – petrodiesel, petrol, biodiesel.
   (b) Name a fuel which contains esters.
   (c) What is B5?
   (d) Which of these elements is not present in biodiesel – C, H, O or S?
   (e) Which has a lower flash point, petrol or petrodiesel?
   (f) Which fuel does not perform well in cold weather?

# 38 Revision Of Alcohols

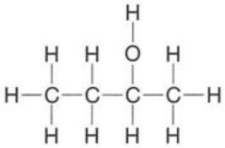
In this topic you have been learning about the homologous series of alcohols. You should be able to describe the types of alcohols – primary, secondary and tertiary, the bonding of alcohols and how this affects their properties, methods used to manufacture alcohols, their use as fuels and the energy produced when they undergo combustion as fuels.

Check your knowledge and understanding by working through these multiple choice questions, and consult your teacher about any problems.

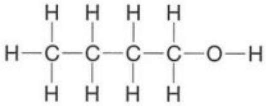
## QUESTIONS

1. Which of the following structures is an example of a secondary alcohol?

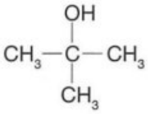
(A)



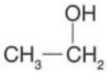
(B)



(C)

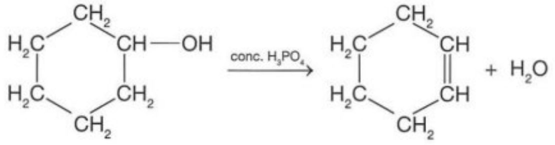


(D)

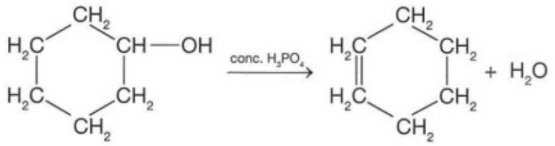


2. Dehydration of an alcohol would produce an:
   (A) Alkane.
   (B) Alkene.
   (C) Alkanoic acid.
   (D) Ester.
3. Complete combustion of an alcohol will produce:
   (A) Carbon and water.
   (B) Carbon dioxide and water.
   (C) A secondary or tertiary alcohol.
   (D) Oxygen and a carboxylic acid.
4. Ethanol is flammable in air. A substance which cannot be a product of the combustion of ethanol is
   (A) Hydrogen.
   (B) Carbon.
   (C) Carbon monoxide.
   (D) Water.
5. The hydroxyl group of a tertiary alcohol is bonded to:
   (A) The terminal carbon atom.
   (B) Two carbon atoms.
   (C) Three carbon atoms.
   (D) Four carbon atoms.
6. Primary alcohols are oxidised to:
   (A) Aldehydes and then to carboxylic acids.
   (B) Aldehydes and then ketones.
   (C) Directly to ketones.
   (D) None of the above, they cannot be oxidised.
7. An oxidising agent used in organic chemistry is:
   (A) A primary alcohol.
   (B) Acidified potassium permanganate.
   (C) A carboxylic acid.
   (D) All of the above.
8. Which is not an intermolecular attractive force in alcohols?
   (A) Dispersion forces.
   (B) Dipole-dipole forces.
   (C) Covalent bonds.
   (D) Hydrogen bonds.
9. Two physical properties of alcohols are:
   (A) Very high boiling points and soluble in water.
   (B) Ability to dissolve polar substances and non-flammable.
   (C) Soluble in non-polar substances but insoluble in water.
   (D) Soluble in water and dissolve polar and non-polar substances.
10. The boiling points of alcohols increase as you move through the group from methanol to octanol. This happens because:
   (A) The non-polar carbon chain becomes bigger so dispersion forces increase.
   (B) There are more covalent bonds present in bigger molecules.
   (C) The number of hydrogen bonds increases as bigger molecules contain more oxygen atoms.
   (D) Bigger molecules are less likely to spontaneously combust.
11. Cyclohexanol is treated with phosphoric acid to bring about its dehydration. The equation that shows the most likely products of this reaction is:

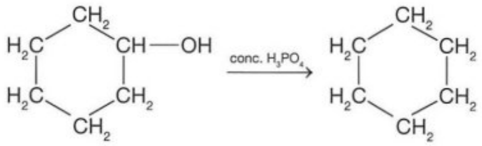
(A)



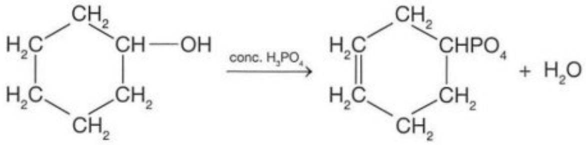
(B)



(C)



(D)



12. Which statement is correct about using spirit burners in the laboratory to determine enthalpy of combustion of alcohols?
    (A) This is too dangerous to attempt as alcohols are very flammable.
    (B) This is a waste of time as the results are so inaccurate.
    (C) This provides inaccurate results but they are still useful for comparing fuels.
    (D) This is a very accurate method to determine the enthalpy of combustion of alcohols.

13. If hydrogen bromide reacted with ethanol, the products formed would be:
    (A) Bromoethene and water.
    (B) Bromoethane and water.
    (C) Bromoethene only.
    (D) Bromoethane only.

14. A primary alcohol can be produced by
    (A) Fermentation of sugar.
    (B) Hydrolysis of an ethene.
    (C) Substituting a hydroxyl group into a haloalkane.
    (D) All of the above.

15. The reaction between hydrogen chloride and propan-1-ol will produce:
    (A) Chloropropane.
    (B) Chloropropene and water.
    (C) Chlorine gas and water.
    (D) Hydrogen and chlorine gases.

16. An example of a hydrogen halide is:
    (A) Water.
    (B) Ethene.
    (C) Chloroethane.
    (D) Hydrogen chloride.

17. The conditions needed to ferment a sugar and produce alcohol include:
    (A) Warmth.
    (B) Presence of enzymes, e.g. in yeast.
    (C) Remove the alcohol as it forms.
    (D) All of the above.

18. A fuel which cannot be a biofuel is:
    (A) Biogas.
    (B) Petroleum.
    (C) Diesel.
    (D) Ethanol.

19. Which statement is not correct about bioethanol.
    (A) Biethanol can be produced by fermenting carbohydrates derived from biomass.
    (B) Bioethanol is chemically exactly the same as ethanol made from petroleum sources.
    (C) Bioethanol will soon be produced in large enough amounts to replace the use of petrol in cars in Australia.
    (D) Raw materials used for the production of bioethanol include corn, sugar cane, wheat and cellulose.

20. The development and use of biofuels is encouraged because:
    (A) They occur naturally and do not have to be made.
    (B) They are made from renewable resources.
    (C) They do not contain any additives.
    (D) You use less ethanol than petrol to drive the same distance in the same car.

**INQUIRY QUESTION**

Without looking at any notes or textbooks:

1. Write down all you can remember about the production of alcohols, but do it as concisely as possible, using as few words as possible.
2. Use a table to show links between the properties of alcohols and their structure and bonding. Again keep this as brief as possible.

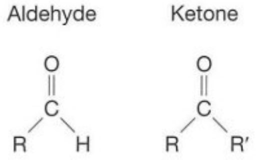
# 39 Aldehydes and Ketones

You will recall that **aldehydes and ketones** both have the same functional group, called the **carbonyl group**.

Figure 39.1 The carbonyl group.

In **aldehydes** the functional group is attached at the end of the carbon chain.

In **ketones** the carbonyl group is attached along the chain, not at either end.



Where R and R′ are alkyl chains.

Figure 39.2 General formulas for aldehydes and ketones.

## Properties of aldehydes and ketones

**Solubility** – Aldehydes and ketones both have a polar carbonyl group, so small aldehydes are soluble in water as they can accept hydrogen bonds from water molecules. Solubility decreases as the size of the molecule increases.

**Density** – Aldehydes and ketones are generally less dense than water

**Reduction** – Aldehydes and ketones can be reduced by hydrogen, using a platinum catalyst, to primary and secondary alcohols.

**Oxidation** – Aldehydes can be distinguished from ketones by the different effects on them of oxidising agents. Aldehydes will be oxidised and will turn acidified potassium dichromate from orange to blue-green.

Ketones will not be oxidised; they do not change the colour of such oxidising agents.

## Formation of aldehydes

Aldehydes can be formed by the oxidation of a primary alcohol, using acidified potassium permanganate or dichromate as the oxidising agent.

Further oxidisation of the aldehyde will form the carboxylic acid.

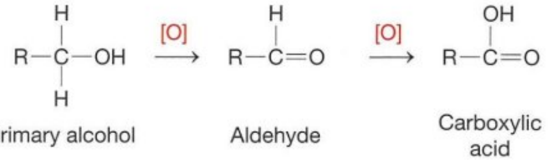


Figure 39.3 Oxidation reactions.

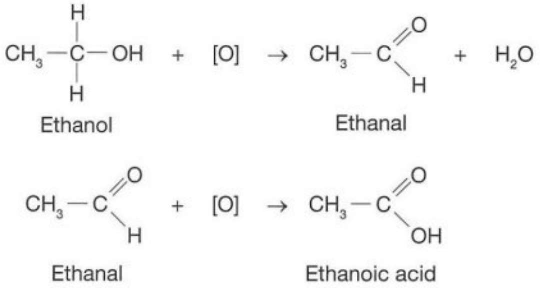


Figure 39.4 Example – Oxidation of ethanol and ethanal.

To produce the ethanal, you must control the reaction conditions in order to prevent ethanal being further oxidised to ethanoic acid.

## Formation of ketones

Ketones can be formed by the oxidation of secondary alcohols. For example, propanone is produced when propan-2-ol is oxidised.

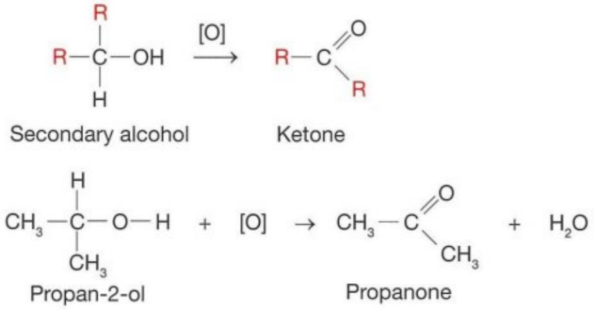


Figure 39.5 Formation of ketones.

## QUESTIONS

1. (a) Identify two properties that aldehyde and ketones have in common.
   (b) Identify a property which is different for aldehydes and ketones.
2. A group of students add oxidising agents to samples of propanone and propanal. Identify any products that would be formed.
3. The oxidation of butan-1-ol is carried out under controlled conditions designed to produce butanal.
   (a) Write an equation for this reaction.
   (b) Identify a basic chemical test you could carry out to determine whether you had actually produced butanal or butanoic acid.
4. Explain why acetone and propanal are classified as isomers.

# 40 Amines and Amides

You will recall that amines and amides both contain nitrogen.

## Amines

For **amines**, the functional group is $-NH_2$ and its general formula is $R-NH_2$. For example, methylamine is $CH_3NH_2$ and ethylamine is $C_2H_5NH_2$.

## Making amines

**Amines can be formed** from ammonia ($NH_3$) when one or more of its hydrogen atoms is replaced by a hydrocarbon group. They can also be made by a substitution reaction between ammonia and a haloalkane. For example:

Chloroethane + ammonia → ethylamine + hydrogen chloride

$$C_2H_5Cl + NH_3 \rightarrow C_2H_5NH_2 + HCl$$

## Properties of amines

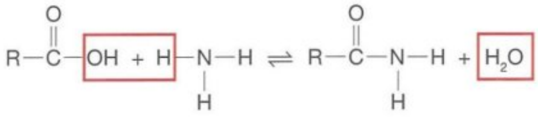
- Amines **are polar molecules**.
- Amines have **lower boiling points than similar sized alcohols**. They can form hydrogen bonds as well as dipole-dipole forces and dispersion forces. However, their hydrogen bonding is not as strong as in alcohols because there are fewer lone pairs on the N atom.
- The small molecule amines are **soluble in organic solvents**, and **also in water**, because they can form hydrogen bonds. However, solubility decreases as the chain gets longer.
  $$CH_3CH_2NH_2 + H_2O \rightleftharpoons CH_3CH_2NH_3^+ + OH^-$$
- Amines are **weak bases** (like ammonia).
  $$CH_3NH_2 + HCl \rightleftharpoons CH_3NH_3^+ + Cl^-$$
- Amines have a similar smell to ammonia. Larger amines have a sickly 'fishy' smell.

## Amides

For **amides** the functional group is the $-CONH_2$ group and its general formula is $R-CONH_2$. For example, methylamide is $HCONH_2$ and ethyl amide is $CH_3CONH_2$.

## Making amides

Amides can be made when the carboxyl group (COOH) of a carboxylic acid has its –OH replaced by a $-NH_2$ group.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-\boxed{OH + H}-\underset{\underset{\displaystyle H}{|}}{N}-H \rightleftharpoons R-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{N}-H + \boxed{H_2O}$$

## Properties of amides

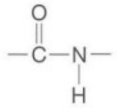
- Amides have **polar molecules**.
- Amides have **high melting points** because of the presence of hydrogen bonds.
- Amides are **soluble in water** as they form hydrogen bonds with water molecules.
- Amides are **neutral** to litmus paper. Although they contain a $NH_2$ group, they do not act as bases.
- Amides can be **reduced** to form amines. For example:
  $$CH_3CONH_2 + 4[H] \xrightarrow{\text{Catalyst}} CH_3CH_2NH_2 + H_2O$$
  Ethanamide Ethylamine

## Test for an amide

To test an unknown organic chemical in order to see if it is an amide, you add sodium hydroxide solution and then heat. If the unknown chemical gives off ammonia on heating, but not when cold, then it is an amide. Ammonia is detected by its characteristic odour and it also turns red litmus paper blue.

## Polyamides

Polyamides are polymers made of amide groups (–CONH–) linked together to form a polymer. The amide groups are linked together by what is called an amide link – and it is also called a peptide bond.

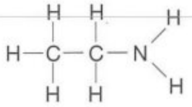


Peptide bond

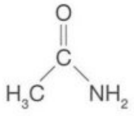
## QUESTIONS

1. What do amines and amides have in common?
2. How do amines and amides differ?
3. How can amides be converted to amines?
4. Name the following compounds.

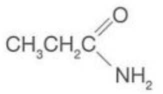
(a)



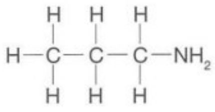
(b)



(c)



(d)



5. Write formulas for:
   (a) Butanamide.
   (b) Hexylamine.

# 41 Carboxylic Acids

You have seen that carboxylic acids are organic acids which contain a carboxyl (–COOH) group and they have a general formula of RCOOH where R is a hydrogen atom or an alkyl group $C_nH_{2n+1}$.

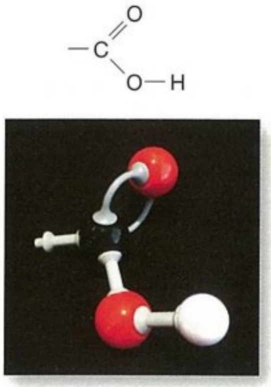


**Figure 41.1** The carboxyl group.

## Properties of carboxylic acids

Carboxylic acids are organic acids with **strong odours**, e.g. acetic acid (vinegar) and butyric acid (smells like vomit). They can be identified by techniques such as infra-red spectroscopy.

- Carboxylic acids are **more polar** than alcohols, and they also have **higher melting and boiling points**, due to the presence of the carboxyl group and more hydrogen bonding.
- They are **weak acids**. In water solution they release hydrogen ions from the COOH group to a water molecule. For example:

  $$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

  This can also be written as:

  $$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+$$

  Ethanoic acid + water ⇌ ethanoate ion + hydronium ion

  Notice that the ion produced when ethanoic acid ionises, is called an ethanoate ion ($CH_3COO^-$) and it has a single negative charge.
- Shorter chain carboxylic acids are **soluble in water**, but as the hydrocarbon chain increases in size, their solubility decreases. Longer chain carboxylic acids that are insoluble in water are called fatty acids and they are important components of lipids (fats and oils) in organisms. They also form part of soaps and detergents.

**Table 41.1** Solubility of carboxylic acids.

| Name | Formula | Solubility in water (g/100 mL) |
|---|---|---|
| Methanoic acid | $HCOOH$ | Very large |
| Ethanoic acid | $CH_3COOH$ | Very large |
| Propanoic acid | $CH_3CH_2COOH$ | Very large |
| Butanoic acid | $CH_3(CH_2)_2COOH$ | Very large |
| Pentanoic acid | $CH_3(CH_2)_3COOH$ | 3.7 |
| Hexanoic acid | $CH_3(CH_2)_4COOH$ | 1.0 |

## Reactions of carboxylic acids

- **Reactions with metals**

  Carboxylic acids react with active metals to produce a salt and hydrogen. For example:

  $$2CH_3COOH(aq) + Mg(s) \rightarrow (CH_3COO)_2Mg(aq) + H_2(g)$$

  Ethanoic acid + magnesium → magnesium ethanoate + hydrogen
- **Reactions with bases such as metal hydroxides**

  Metal hydroxides, e.g. sodium hydroxide, are bases so they can be **neutralised** by carboxylic acids.

  $$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

  Ethanoic acid + sodium hydroxide → sodium ethanoate + water

  As with other acid-base reactions this can be represented by the ionic equation:

  $$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$
- **Reactions with carbonates and hydrogen carbonates**

  Organic acids react with carbonates and hydrogen carbonates to produce water, carbon dioxide and a salt. (You will recall that inorganic acids, e.g. HCl also react in this way.) For example:

  $$2CH_3COOH + Na_2CO_3 \rightarrow 2CH_3COONa + H_2O + CO_2$$

  Ethanoic acid + sodium carbonate → sodium ethanoate + water + carbon dioxide

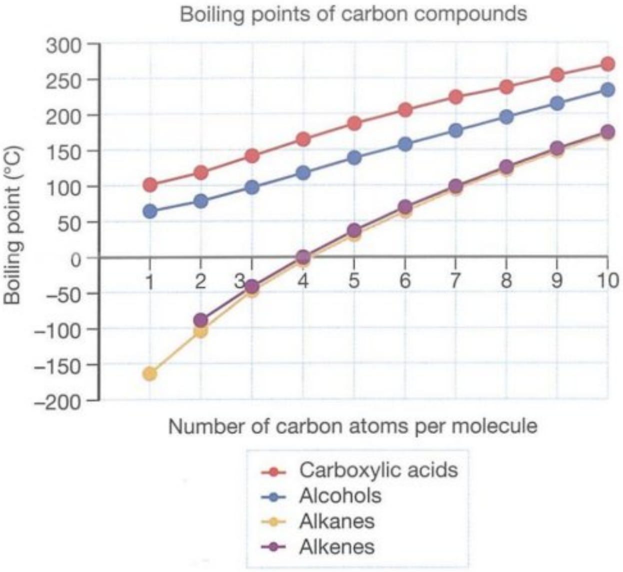
## QUESTIONS

1. Copy and complete the table to compare properties of carboxylic acids with those of alcohols.

| Factor | Alcohols | Carboxylic acids |
|---|---|---|
| Functional group | | |
| General formula | | |
| Polarity | | |
| Solubility in water | | |
| Melting and boiling points | | |

2. $C_3H_7COOH$ is the molecular formula of two carboxylic acids.
   (a) What is the term used for compounds with the same molecular formula but different structural formulas?
   (b) Identify these two acids and draw their condensed structural formulas.

3. There is a relationship between the presence of functional groups and the physical properties of compounds. For example, the following graphs show the boiling points of four homologous groups of carbon compounds.
Describe two trends in these graphs and account for the differences in terms of functional groups.



4. Check your knowledge with this quick quiz.
   (a) Identify the carboxylic acid made by ants and responsible for the sting of an ant bite.
   (b) Identify the carboxylic acid in vinegar.
   (c) Name the products when a carboxylic acid reacts with an active metal.
   (d) What effect, if any, would you expect carboxylic acids to have on litmus paper?
   (e) Name the carboxylic acid used as a food preservative.
   (f) Identify the gas produced when a carboxylic acid reacts with a carbonate.

# 42 Comparing Homologous Groups

Here we will compare some properties of a number of homologous groups, especially in terms of their intermolecular bonding. We can see a clear relationship when we look at melting and boiling points.

## Melting and boiling points

The temperature at which a molecular substance changes state depends on the strength of the bonds which have to be broken. For organic compounds, the bonds that break to allow change of state are the intermolecular forces which attract molecules to each other. Covalent bonds are *not* broken during change of state. The strength of these intermolecular forces, and thus the melting and boiling points, depends on the molecular weights of substances and the shape and polarity of their molecules.

The stronger the intermolecular forces, the more energy is needed to break them and the higher their melting and boiling points.

Remember, hydrogen bonds > dipole-dipole forces > dispersion forces.

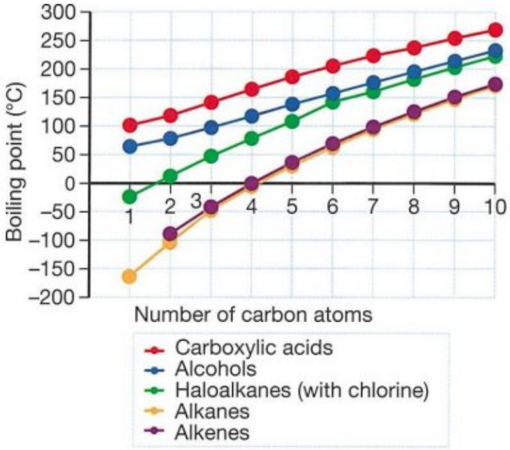


**Figure 42.1** Boiling points of members of some homologous groups.

From these graphs you can see that for all homologous series, as the **number of carbon atoms** in the molecules increases, the boiling point increases. So for all homologous series, the greater the mass of the molecule, the higher the boiling point. And we know that this is because the dispersion forces increase with mass of the molecules.

If we compare compounds with the same number of carbon atoms in each homologous series, we can see another trend. Boiling points increase as we go from **hydrocarbons (alkanes and alkenes) to haloalkanes to alcohols to carboxylic acids**. This trend is due to the bonding of members of each series.

**Alkanes and alkenes** of similar size have similar boiling points. They have only dispersion forces acting between their molecules. They are not polar molecules so they do not have dipole-dipole bonds. They do not form hydrogen bonds as they do not contain any O, N or F atoms.

**Haloalkanes** have higher boiling points than alkanes and alkenes. They have slightly higher molecular mass (halogen atoms are heavier than the hydrogen atoms they have replaced), so their dispersion forces are greater. They are also polar molecules, so they have dipole-dipole forces to overcome in order to melt.

**Alcohols** have even higher boiling points because they have dispersion forces, plus dipole-dipole forces due to their polar hydroxyl group, plus they can form hydrogen bonds between molecules of alcohol.

**Carboxylic acids** have the highest boiling points of the homologous series included in Figure 42.1. They are even more polar than alcohols with similar sized molecules as they have polar C=O, C–O and O–H bonds. Also, they can form double the number of hydrogen bonds with their two O atoms.

Other groups are not shown in this graph, but we can still compare them and then you can add lines to the graph to show where they would fit.

**Aldehydes**, e.g. ethanal **and ketones**, e.g. ethanone, have molecules that are more polar then alcohols. However, they cannot form hydrogen bonds between their molecules the way alcohol molecules do. So their boiling points are higher than for alkanes and alkenes, but lower than for alcohols. Draw a line on the graph for aldehydes.

**Amines**, e.g. methylamine have dispersion forces. They are polar molecules so they have dipole-dipole forces. However, the N in amines is less electronegative than the O in the OH group of alcohols and carboxylic acids, so amines are less polar than members of those series. So their boiling points tend to be lower than alcohols but higher than alkanes and alkenes. Draw a line on the graph for amines.

**Amides**, e.g. methanamide, contain an $NH_2$ group with none, one or two of the H atoms replaced by an alkyl group.

Amides are even more polar than carboxylic acids because amides can hydrogen bond and accept hydrogen bonds on both the oxygen and the nitrogen. They can also form hydrogen bonds between their molecules. So amides tend to have higher boiling points than carboxylic acids.

Similar comparisons can be made with **melting points** as they also depend on the molecular structure and intermolecular forces.

Other properties can be compared across homologous series, for example flash point, viscosity and solubility.

## Flash point

The flash point of a substance is the lowest temperature at which it can vaporise to form a flammable mixture with air so that it can be ignited by a spark or flame.

The flash point indicates how flammable and combustible substances are – how easily a chemical will ignite and burn, so it is important to consider the flash point of a fuel when determining safe handling and transport methods.

Flash points can be measured, or they can be estimated from boiling points. The boiling point of a compound shows a strong correlation with its flash point as the boiling point is closely related to the amount of vapour present. Generally, the higher the boiling point, the higher the flash point.

## Viscosity

**Viscosity** is the ability of a substance to flow or to resist flowing. It is a measure of the force per unit area resisting flow. A viscous substance, like cold honey, does not flow freely.

Viscosity, like melting and boiling points, also **depends on** the strength of intermolecular forces, size and shape of molecules and polarity. Viscosity increases as the molecular mass increases and the size of molecules increases.

The heavier the molecule, the stronger the intermolecular dispersion forces between molecules, and so the less easily the substance will flow. The size and shape of molecules both affect their polarity and thus their ability to form intermolecular dipole-dipole forces and hydrogen bonds. Also longer, linear molecules become tangled up more easily, which prevents easy flow, increasing viscosity.

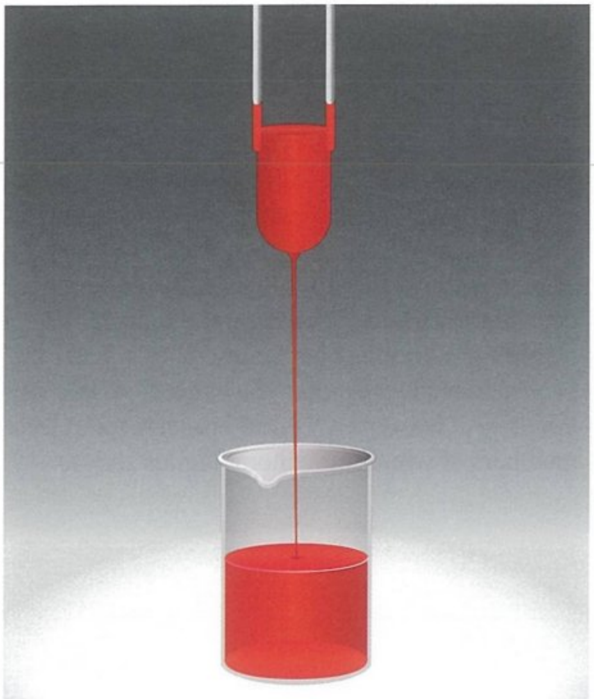


Figure 42.2 Measuring viscosity of paint by determining the time it takes to empty a small cup of paint through a hole in the bottom.

**Viscosity changes with temperature**. This can be seen when comparing the flow of honey at room temperature, when refrigerated, and when warmed. Heating a substance makes it more runny (less viscous). As the substance is heated, the heat gives the molecules more energy to move around, so they can escape more easily. As they are moving more, they may also become un-entangled more quickly.

## Solubility

Solubility depends on the ability of molecules to form bonds with the solvent. The size of the molecule also affects solubility.

**Hydrocarbons**, being non-polar, tend to be not soluble in polar substances such as water as they cannot form bonds with water. However, they are soluble in non-polar solvents such as ethanol and acetone.

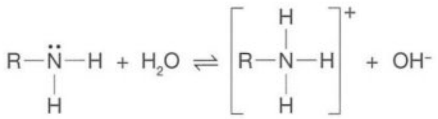
**Haloalkanes** are more soluble in water as they are polar and can form bonds with the water.

**Alcohols** are soluble in water because they are polar and can form hydrogen bonds. As the alcohols become bigger they are les soluble in water and more soluble in non-polar solvents.

**Carboxylic acids** – The ability to form intermolecular hydrogen bonds with its two O atoms, in addition to its polar C=O, C–O and O–H bonds, makes small molecule carboxylic acids quite soluble.

As the molecule becomes larger, the increasing length of the non-polar chain means they become less soluble in water.

**Amines** have a lone pair on their nitrogen atom. This can form a hydrogen bond with water, making them more soluble in water than hydrocarbons. Notice that the lone pair also makes the amine a Lewis base, it can form a covalent bond with a hydrogen ion from water or an acid.



$$R{-}\ddot{N}H{-}H + H_2O \rightleftharpoons [R{-}NH_3]^+ + OH^-$$

**Aldehydes and ketones** have highly polar molecules and can accept hydrogen bonds with water, increasing their solubility in water.

**Amides** with small molecules are soluble in water as they can hydrogen bond with water. However, they are less soluble than similar sized amines and carboxylic acids.

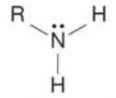
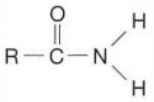
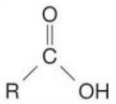
## Carboxylic acids, amines and amides

The following table summarises some properties of three homologous series to help you compare them.

You should be able to refer to differences in intermolecular bonding in these series to account for differences in their properties.

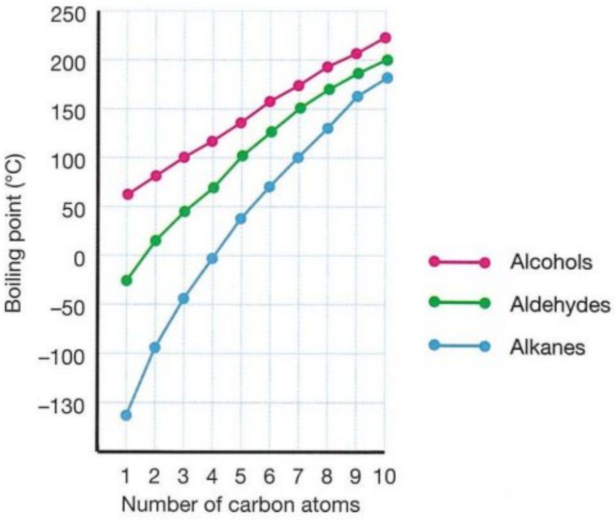
You should be able to account for similarities within homologous series in terms of their intramolecular bonding.

**Table 42.1** Comparing amines, amides and carboxylic acids.

| Feature | Amine | Amide | Carboxylic acid |
|---|---|---|---|
| Functional group | $-NH_2$ | $-CONH_2$ | $-COOH$ |
| General formula |  |  |  |
| Name of example | Methylamine | Methylamide | Methanoic acid |
| Polarity | Slightly polar | Polar | Most polar |
| Solubility | Soluble and solubility decreases as size of molecule increases. | | |
| Melting and boiling points | High | Highest | Very high |
| Hydrogen bonds | Weaker | Strong | Strong |
| Effect on indicators | Weak bases | Neutral | Weak acids |
| Reduced to | Not reduced | Amines | Alkanals |

## QUESTIONS

1. Some homologous series that you have studied include:
   Alcohols, alkenes, alkanes, carboxylic acids, haloalkanes, amines, amides.
   (a) List these homologous series in order of decreasing boiling points.
   (b) List the homologous series in order of decreasing strength of intermolecular forces.
2. The graph compares boiling points of alcohols, aldehydes and alkanes.



   (a) How do the boiling points of aldehydes compare to those of alkanes and alcohols?
   (b) Account for these observations.
   (c) Compare the graphs for alcohols and alkanes. You will notice that for small molecules the difference between their boiling points is large, but the graphs converge showing that for larger molecules, there is a smaller difference between their boiling points. Account for this observation.
3. The flash point of petrol is about −43°C whereas the flash point of diesel is over 50°C. Suggest how this difference would affect the handling and storage of these two fuels.
4. Investigate how you could compare the viscosity of substances such as honey, water, ethanol and glycerol. In your answer you should include:
   (a) The method used.
   (b) The variables you would need to control.
   (c) Predict the order in which the substances flow down a slope and justify your prediction based on the strength of intermolecular forces.
5. The physical properties of organic compounds depend on the functional group, molecular size and resulting intermolecular forces.
   Describe an investigation you carried out that studied trends in at least one physical property for at least five members of two or more homologous series.

# 43 Esters

This is revision of work you covered in year 11. An ester is an organic compound with the functional group –COO– and general formula RCOOR′ where R and R′ are hydrocarbon chains.

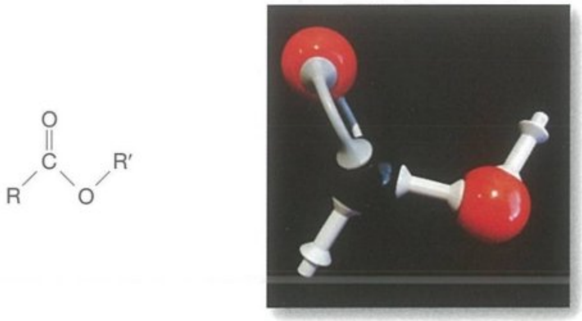


**Figure 43.1** General formula and model of an ester functional group.

Some examples of esters are shown in Figure 43.2.

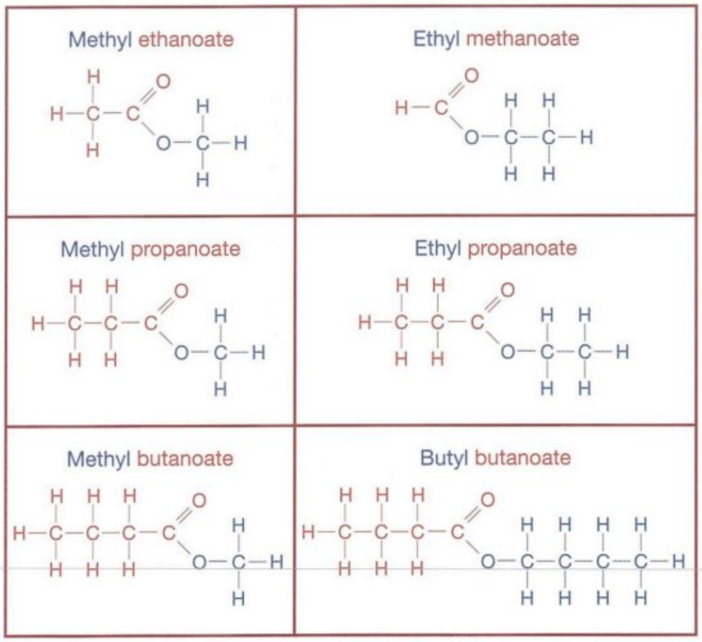
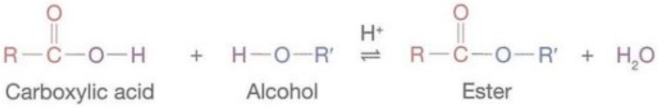


**Figure 43.2** Examples of esters.

You will understand the naming of esters better if you see how esters are made – they are produced by the reaction of a **carboxylic acid** and an **alcohol**. The process of producing an ester from a carboxylic acid and an alcohol is called **esterification**.

In the table above, the red part of each formula comes from the acid and the blue part from the alcohol.

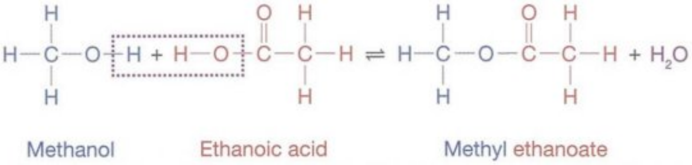
During esterification, OH is removed from the carboxyl (–COOH) group of a carboxylic acid and H is removed from the alcohol. The **–OH group from the –COOH** (carboxyl group) combines with the **H from the –OH** (hydroxyl group) to produce a molecule of water.



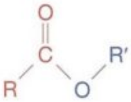
$$R-\overset{\overset{O}{\|}}{C}-O-H + H-O-R' \overset{H^+}{\rightleftharpoons} R-\overset{\overset{O}{\|}}{C}-O-R' + H_2O$$

(Note that this is different from inorganic chemistry – where the H$^+$ ion from an acid combines with the hydroxide ion (OH$^-$) from an alkali during neutralisation.)

For example:

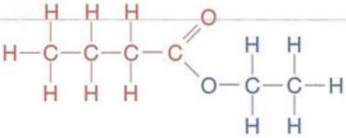


Now, if you look again at the structure of an ester, you will see that the remains of the carboxylic acid can readily be identified because it contains a double bonded oxygen atom (=O). The single bonded O atom unites what is left of the acid and the alcohol after $H_2O$ is removed. So in the figure below, RCO is from the acid and R′O is from the alcohol.



The tricky part when naming esters is to remember that the part from the alcohol is the first part of its name, then the acid part and finally the suffix – anoate is added to the name. However, the structural formula can be drawn with either the acid first (as in the table) or it can be drawn with the acid part last (as in the equation above).

Here is another example – ethyl butanoate.



This would be made by reacting ethanol with butanoic acid.

Ethanol + butanoic acid → ethyl butanoate + water

$C_2H_5OH(aq) + C_3H_7COOH(aq) \rightarrow C_3H_7COOC_2H_5(l) + H_2O(l)$

## Properties and uses of esters

- **Occurrence** – Many esters occur naturally, in living things. Fats and oils are esters and many have a fruity odour and give perfume or flavour to flowers and fruits.
- **State** – Most esters have low melting points so are liquids at room temperature. Larger esters are solids due to their stronger intermolecular forces.

- **Polarity** – Ester molecules are polar, but not as polar as alcohols. They cannot form hydrogen bonds with other ester molecules.
- **Solubility** – Esters are insoluble in water except for the very small molecule esters. Small ester molecules, e.g. ethyl methanoate are soluble in water because hydrogen bonds form with water molecules. Solubility decreases as the hydrocarbon chain increases in size and gets in the way, preventing the formation of hydrogen bonds.
- **Uses** – Because of their fruity odour and flavour many esters are manufactured to use in perfumes, cosmetics and processed foods.

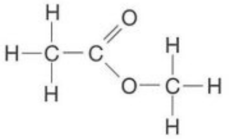
You will have experienced esters in many products.

*Note:* In carbon chemistry, as you have already seen, you will often find alternative names being used. This is because many of these substances were produced by industries and named according to their origin or use before the systematic IUPAC system of naming was developed. So you will find examples such as formate/methanoate; acetate/ethanoate.

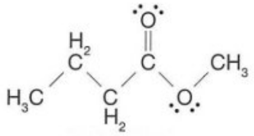
## QUESTIONS

1. Name the following compounds.

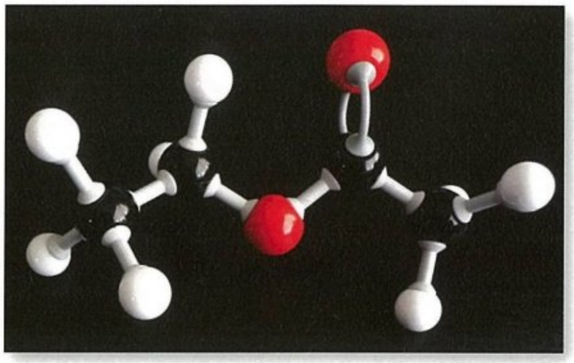
(a)



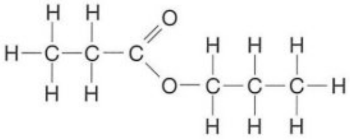
(b)



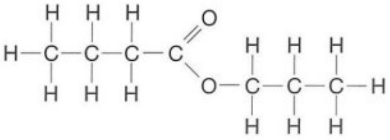
(c)



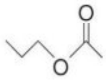
(d)



(e)



2. (a) Write this formula out in full and name the chemical represented.



(b) How can you tell, from the formula and name that this substance is an ester?

3. Write structural formulas for the following esters.
   - (a) Butyl propanoate.
   - (b) Methyl methanoate (also called methyl formate).
   - (c) Ethyl hexanoate.
4. Name the alcohol and organic acid from which each of the following esters would be made.
   - (a) Methyl hexanoate.
   - (b) Propyl methanoate.
   - (c) Butyl ethanoate.
   - (d) Ethyl ethanoate.
5. (a) State the general formulas for an alcohol, a carboxylic acid and an ester.
   - (b) State the functional group for an alcohol, a carboxylic acid and an ester.
6. Comment on any relationship between molar mass and boiling point based on the figures in the table below.

| Condensed structural formula | Molar mass (g) | Boiling point (°C) |
|---|---|---|
| $HCOOCH_3$ | 60 | 32 |
| $CH_3COOCH_3$ | 74 | 57 |
| $CH_3COOCH_2CH_3$ | 88 | 77 |
| $CH_3CH_2CH_2COOCH_3$ | 102 | 102 |
| $CH_3CH_2CH_2COOCH_2CH_3$ | 116 | 121 |

7. Outline the safety precautions you used when making an ester in the laboratory.
8. Check your knowledge with this quick quiz.
   - (a) Identify the general formula of an ester.
   - (b) Identify the functional group of esters.
   - (c) Write the condensed structural (semi-structural) formula for methyl ethanoate.
   - (d) Write the condensed structural (semi-structural) formula for ethyl butanoate.
   - (e) Name the process of producing an ester.
   - (f) Esters are made from an .......................... and a .......................... .

# 44 Esterification

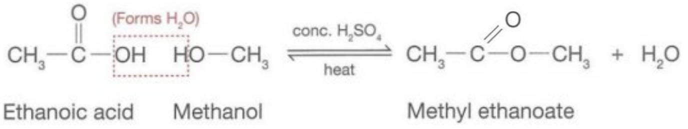
**Esterification** is the production of an ester by the reaction between an alcohol and a carboxylic acid. Water is produced as a by-product so this reaction is sometimes called a condensation reaction or a dehydration reaction.

The **general equation** for esterification is:

Carboxylic acid + alcohol ⇌ ester + water

$RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$

For example, methanol reacts with ethanoic acid to produce methyl ethanoate and water. Concentrated sulfuric acid is used as a **catalyst**. It absorbs water, pushing the equilibrium to the right.



$$CH_3-\overset{O}{\overset{\|}{C}}-OH + HO-CH_3 \xrightleftharpoons[heat]{conc.\ H_2SO_4} CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3 + H_2O$$

## Refluxing

This reaction is carried out using a technique called **refluxing**. The reactants are heated in a flask, placed in a warm water bath, with a cooling condenser attached vertically to the top of the flask. Using this technique, the reaction can be carried out at a higher temperature than would otherwise be possible. The reactants and products all tend to be volatile, so heating would lead to them vaporising into the environment. Using the condenser allows volatile substances to be cooled so they condense and fall back into the flask instead of being released into the environment.

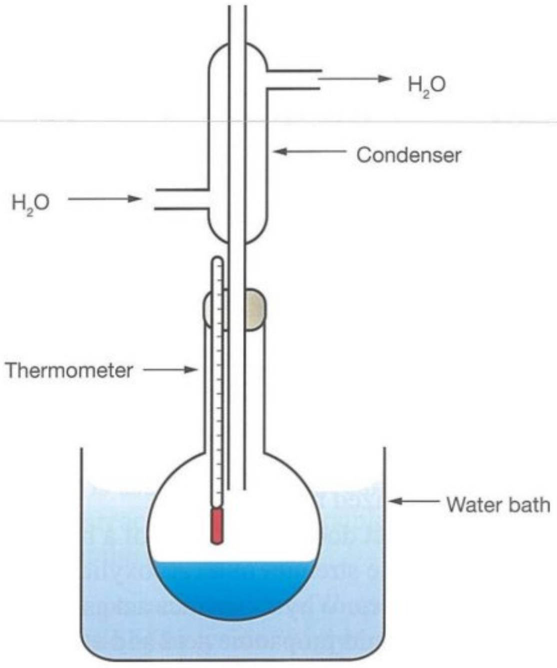


**Figure 44.1** Esterification.

Using the condenser is essential, as some organic chemicals have a very strong odour, which can be unpleasant, e.g. butanoic acid smells rather like vomit. Some are a health hazard, they may cause headaches and irritate the respiratory system. Also many are flammable, so they could become a fire hazard if released into the environment. The concentrated sulfuric acid used as a catalyst is very corrosive.

## QUESTIONS

1. (a) What is esterification?
   (b) Write the general equation for this process, indicating from which reactants the water is produced.
   (c) Write a word equation for the production of the ester propyl methanoate.
2. (a) Outline the meaning of the term refluxing.
   (b) In Figure 44.1, why is the condenser connected so that water enters the bottom of the condenser jacket and exits from the top?
   (c) What is the purpose of the water in the condenser jacket?
   (d) Does the water in the condenser jacket mix with the vapour coming out of the flask?
   (e) Explain the advantage of using reflux when an ester is being produced.
3. Name the esters produced by the following reactions.
   (a) Propanol and ethanoic acid.
   (b) Methanol and butanoic acid.
   (c) Ethanol and propanoic acid.
4. Copy and complete the table to show formulas, names and odours of some esters. You may need to research the aromas.

| Formula | Name | Aroma |
|---|---|---|
| $HCOOCH_2CH_3$ | | |
| | Methyl butanoate | |
| | | Pineapple |
| $CH_3COO(CH_2)_4CH_3$ | | |
| | Pentyl butanoate | Apricot |
| $CH_3COO(CH_2)_7CH_3$ | | |

5. Check your knowledge with this quick quiz.
   (a) Identify a use of esters.
   (b) Name the ester made from pentanoic acid and butanol.
   (c) Write the structural formula for pentyl propanoate.
   (d) Identify the term for the production of esters.
   (e) Esters are produced using a technique called
   ............................ .
   (f) Name the substance used as a catalyst during esterification.

# 47 Soaps

**Soaps and detergents** are materials which, when dissolved in water, help to clean a surface by removing dirt or other foreign matter.

Soaps and detergents are both **surfactants** – which means they reduce surface tension. They are also both **emulsifying agents** – this means they keep grease and dirt suspended in water so they can be washed away from the object (e.g. skin or clothes) being washed.

We will look at soaps first and then look at detergents in the next chapter.

## Soap

Soap is the **salt of a long chain fatty acid** with an **alkali metal ion** attached. You will recall that fatty acids are carboxylic acids with more than 10 carbon atoms in their hydrocarbon chains, for example stearic acid is $CH_3(CH_2)_{16}COOH$. Soaps contain anions (negative ions) of fatty acids combined with cations (positive ions) such as sodium ions. An example of a soap is sodium stearate, $CH_3(CH_2)_{16}COO^-Na^+$.

You will see shortly that the metal cations (positive ions) play no part in the cleaning action of soap. It is the negative fatty acid ion which acts as both a surfactant and as an emulsifier.

**Figure 47.1** Soaps.

## Historical development of soaps

The use of cleaning agents has evolved over a long period of time. We know that soaps were used by Egyptians as early as 3000 BC, and around 300 BC the Romans were using soaps for bathing and washing clothes.

However, the increasing population in towns and cities together with harsh economic factors led to a decrease in personal hygiene and an increase in unsanitary living conditions. People could not afford soap, and water supplies were often contaminated. The things we take for granted today, such as running hot and cold water within the home and sanitation systems, just did not exist.

Even if people did realise the link between lack of hygiene and the spread of disease, the soaps of the time were expensive and tended to be smelly as well as harsh on the skin, causing alkaline burns. Early soaps were made by boiling oil or animal fats with plant ashes and lime (calcium oxide) and sometimes with the addition of urine (which decomposes to form ammonia – a good cleaning agent). Soap was used initially in the cloth industry, to prepare wool for dyeing, rather than for personal hygiene.

During the 18th and 19th centuries, commercial soap became available for personal use and costs gradually decreased. Eventually soap became a necessity rather than a luxury.

The **impact of soap** on society was considerable and positive. The increased availability of soap eventually led to an improvement in hygiene and decrease in the spread of disease. Thus the development of soap contributed to an improved standard of living and a lower death rate. Soaps were biodegradable, so they had little impact on the environment – although the industrial processes used to make them had a significant impact.

## Industrial production of soap

The main steps in the industrial production of soap are as follows.

- Fats and oils are blended.
- These fats and oils are boiled with an hydroxide solution such as sodium hydroxide, potassium hydroxide or ammonium hydroxide.
- Concentrated sodium chloride solution (brine) is added to this soapy mixture in order to dissolve the glycerol and separate it from the soap. Glycerol will dissolve in salt water but the soap will not dissolve, so the soap precipitates out, forming a surface layer.
- The soap is separated and washed to remove any remaining hydroxide or brine. Any unused fatty acids left in the brine will separate out as an oily layer which solidifies on cooling and can be removed. Glycerol is recovered by vacuum distillation of the remaining solution.

Perfume and colour can be added to the soap, and translucent soaps can be made by adding alcohol, sugar and glycerol to slow down the growth of soap crystals as it solidifies.

## Cleaning action of soap

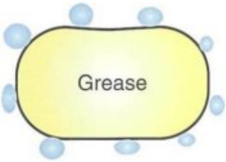
The cleaning action of soap relies on its negatively charged fatty acid ions such as the stearate ion, $CH_3(CH_2)_{16}COO^-$, acting as both a surfactant and an emulsifier.

## Soap as a surfactant

A **surfactant** is a substance that acts on the surface of another substance, changing its surface tension. The fatty acid ions in soap act as a surfactant, lowering the surface tension of water by disrupting hydrogen bonds between water molecules. This increases the ability of water to wet a surface and thus to remove any dirt or grease and clean it. It works as follows.

(a) Water acts as if it has a skin, its surface tension keeps water in round droplets.

(b) If the water comes in contact with dirt and grease, it forms droplets on the grease, not wetting it very effectively at all.



(c) When soap is added to the water, this reduces the surface tension so the soapy water can wet the grease.

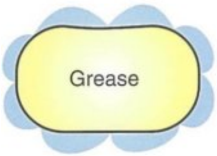


Figure 47.2 Soap acting as a surfactant.

## Emulsions

Emulsions are important in the cleaning process.

An **emulsion** is a suspension of liquid droplets in another liquid. It occurs when you mix together two liquids that will not dissolve in each other so that droplets of one of the liquids remain dispersed (spread) and suspended (held in place) through the other liquid.

Soaps help to clean people and objects by making grease/oil and dirt become suspended in water – they produce an emulsion, so they are called emulsifiers.

## Soap as an emulsifier

**An emulsifier** (or emulsifying agent) is a substance that helps to keep one substance suspended in another – in other words to keep it **existing as an emulsion**. For example, **milk** is an emulsion of fat droplets in water. Chemicals which act as emulsifying agents are added to milk to keep the fat suspended (floating) in the milk so that it does not float to the top as cream. Another example is **mayonnaise**. This is an emulsion of oil, water and vinegar with egg added to act as an emulsifier, keeping it from separating out into layers.

**Soap acts as an emulsifier**, keeping the grease/dirt suspended in water so it can be rinsed away from the object being washed. The reason soap can act like this is because of its structure. The fatty acid part of the soap molecule has a long non-polar hydrocarbon tail and a negatively charged polar head.

Figure 47.3 Structure of soap.

The polar head is referred to as **hydrophilic** – which just means that it is attracted to water molecules. The non-polar tail is **hydrophobic** – which just means that it repels water molecules.

Because of this structure, soap molecules do not spread evenly through water, they form little clumps as shown in Figure 47.4.

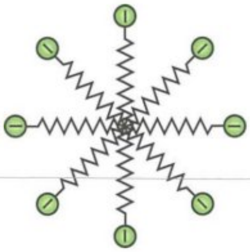


Figure 47.4 Soap molecules clump together in water.

Non-polar grease/dirt molecules come out of the clothes and move to the centre of the soap clump. The negative ends interact with water molecules keeping the whole clump suspended in the water.

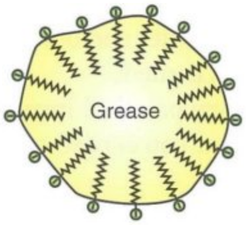


Figure 47.5 Soap molecules and grease/dirt.

In this way, soap, water and grease/dirt together form an emulsion. The soap is acting as an emulsifier (emulsifying agent), suspending the grease/dirt in the water so it does not return to the clothes.

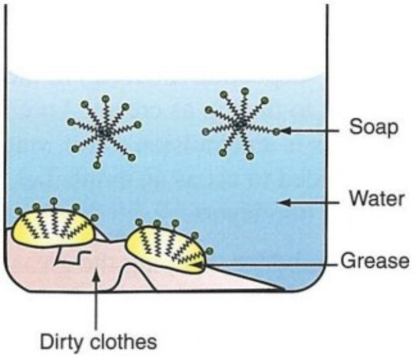


**Figure 47.6** Soap removing grease/dirt from clothes.

## QUESTIONS

1. Define each of the following terms.
   - (a) Emulsion.
   - (b) Emulsifier.
   - (c) Hydrophobic.
   - (d) Hydrophilic.
   - (e) Cation.
   - (f) Anion.
   - (g) Surface tension.
2. (a) What is a surfactant?
   - (b) Justify the description of soap as a surfactant.
   - (c) Outline how soap's acting as a surfactant helps to clean clothes.
3. Soap acts as an emulsifier.
   - (a) Justify the description of soap as an emulsifier.
   - (b) Identify three common examples of emulsions.
4. Recall what is meant by hard water.
5. Perform an experiment in which you make an emulsion and study its properties.
   - (a) Describe how you made your emulsion.
   - (b) Describe how you tested your emulsion and determined its properties.
   - (c) Outline a use for your emulsion.
   - (d) Relate the properties of your emulsion to its uses.
   - (e) Outline any safety issues involved in this investigation.
6. Research the difference between hard and soft water to answer the following questions.
   - (a) What is meant by hard water?
   - (b) What is the main concern about hard water?
   - (c) Distinguish between temporary and permanent hardness of water and outline ways in which they can be treated.
   - (d) Describe any practical investigation of hardness of water that you carried out in the laboratory.
7. Perform an investigation to demonstrate the effect of soap as an emulsifying agent.
   - (a) Outline the method and results of your investigation.
   - (b) State a conclusion you can draw from your results.
   - (c) Comment on the validity of your conclusion.
8. Check your knowledge with this quick quiz.
   - (a) Identify the term used to describe a mixture in which droplets of one liquid remain dispersed and suspended in another liquid.
   - (b) List the names of three commercial emulsions.
   - (c) A chemical that lowers the surface tension of water is described as a .......................... .
   - (d) Is water polar or non-polar?
   - (e) Is grease polar or non-polar?
   - (f) Identify an anion in soap molecules.
   - (g) Identify a cation in soap molecules.
   - (h) Identify any role sodium ions have in the cleaning action of soap.

# 48 Detergents

Detergents are cleaning products that are produced synthetically. Detergents, like soaps, are surfactants and emulsifying agents.

**Figure 48.1** Detergents.

The surfactant molecules in detergents, like soap, have a polar head and a non-polar chain. The most efficient detergents have 12 to 15 carbon atoms in their chain. Early detergents had branched chains, but today most have straight chains as these are easier to break down in the environment, so they are less polluting.

There are three types of surfactant molecules, with anionic, cationic and non-ionic heads.

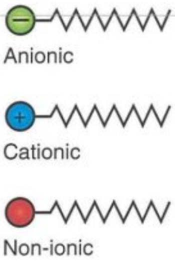


**Figure 48.2** Surfactants in detergents.

## Anionic surfactants

Anionic surfactants have molecules with a negatively charged head and they are the most widely used surfactants.

**Figure 48.3** Anionic surfactants.

The most common ones have a negatively charged (anionic) head with a sulfate group ($SO_4^{2-}$) or a sulfonate group ($SO_3^-$). This is attached to a long hydrocarbon end that has a special ring structure made of six carbon atoms called a benzene ring. Because of this they are sometimes called alkyl benzene sulfonates or sulfates.

Anionic surfactants are used in dishwashing liquids and laundry detergents. They are highly sudsing and have excellent cleaning properties, especially for natural fabrics that absorb water readily such as cotton, wool and silk.

## Cationic surfactants

Cationic surfactants are made of molecules with a positively charged head, and are usually ammonium compounds.

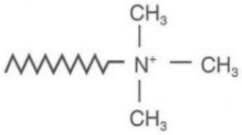


**Figure 48.4** Cationic surfactants.

Cationic surfactants are used as fabric softeners because their positive charge adheres to fabrics that usually carry negative charges, thus reducing static. They are also used as germicides in mouthwashes, nappy washes, and antiseptic soaps. This is because ammonium ions can disrupt the cell walls of some pathogenic bacteria.

Cationic detergents are not used in dishwashers, because glass has a negatively charged surface which would attract the positive ends of their molecules, leaving the tails free to make the glass slippery.

## Non-ionic surfactants

Non-ionic surfactants have non-polar ends to interact with non-polar grease. Scattered along their hydrocarbon chain there are many polar oxygen atoms forming a polar and a non-polar area. The polar oxygen atoms can form hydrogen bonds with hydrogen atoms in nearby water molecules.

Non-ionic surfactants do not ionise in water and they are low sudsing. They are used as detergents in the laundry, in washing up liquids, automatic dishwashers and for washing cars and are useful for cleaning synthetic fabrics.

## Historical development of detergents

During World War I (1914-1918) a shortage of fats and oils led to a shortage of soap. At the same time, petroleum production was starting up and scientists were looking for new uses for this substance. Detergents were developed from petroleum and its products, and they had the added advantage that they could be used with hard water without producing a scum. By the 1950s more detergent was being made than soap.

During the 1900s soaps and detergents increased in volume and variety due to a rapid increase in **technological development**. Liquid soaps and fabric softeners were developed, detergents were developed that could be used effectively in cold water, and, with the invention of washing machines and dishwashers, suitable detergents were designed for them also.

Additives were also used such as chemicals to reduce water hardness, enzymes to decompose protein stains, organic molecules to make clothes look brighter and antimicrobial agents to kill micro-organisms.

## Impact of detergents

The development of detergents had a **positive impact on society**, but a **negative effect on the environment**.

The availability of cheaper and more effective cleaning agents reduced the spread of infection and also the time and energy needed for cleaning.

However, early detergents produced a long-lasting foam in waterways that killed organisms. Also these detergents did not decompose, due to their branched chains (soaps have linear chains), so they persisted in the environment. Early detergents also contained a large amount of phosphate that contributed to algal blooms and eutrophication of waterways, leading to stagnation of waterways and the death of aquatic organisms.

**Figure 48.5** An ibis near a stagnant pool.

Many of these problems are now being addressed. For example, biodegradable detergents have been developed and their phosphate content reduced.

## QUESTIONS

1. (a) What are detergents?
   (b) Explain why detergents were developed by chemists.
   (c) Identify and distinguish between the three types of surfactants that may be present in detergents.
2. (a) Which product is more environmentally friendly, soap or detergent? Justify your answer.
   (b) Relate the structure of soaps and detergents to biodegradability.
   (c) Outline three ways in which both soaps and detergents have had a positive impact on society.
3. Copy and complete the table to compare and contrast the chemical composition of soaps and detergents.

| Feature | Soaps | Detergents |
|---|---|---|
| Made from | | |
| Composition | | |
| Structure | | |
| How it works | | |
| Synthesis | | |
| Other relevant properties | | |
| Effect on hard water | | |
| Environmental concerns | | |

4. Recall what is meant by eutrophication.
5. Research four types of additives developed to improve the action of synthetic detergents.
6. Dodecylbenzene ($C_{12}H_{25}C_6H_5$) is a chemical used in the manufature of ionic detergents. Research to answer the following questions.
   (a) Show the structural formula of dodecylbenzene.
   (b) How is this compound used in the production of detergents?
7. Check your knowledge with this quick quiz.
   (a) The first detergents had (branched/straight) carbon chains.
   (b) Soaps have (branched/straight) carbon chains.
   (c) Detergents are (more/less) stable than soaps.
   (d) Detergents are (more/less) soluble than soaps.
   (e) Soaps are made from ........................ .
   (f) Detergents are made from ........................ .

# 49 Organic Reaction Pathways

For many organic compounds that are manufactured on an industrial scale, the raw materials are obtained from petroleum. Often there is **more than one possible pathway** that could produce the desired chemical.

For example, you can convert propene to bromopropane by either of the following pathways.

- Reacting it with hydrogen bromide – a single step reaction.
  $CH_3CH{=}CH_2 + HBr \rightarrow C_3H_7Br$
- Adding hydrogen to convert propene to propane and then substituting in bromine – a two step process.
  $CH_3CH{=}CH_2 + H_2 \rightarrow CH_3CH_2CH_3$
  $CH_3CH_2CH_3 + Br_2 \rightarrow C_3H_7Br + HBr$

When more than one step is involved like this, any chemical produced during the process is called an intermediate, so here propane is an intermediate.

**Intermediates** in a synthesis process may also be unstable molecules, or highly reactive fragments of molecules which exist only briefly. Free radicals, such as the hydroxyl radical ($OH^•$), may be intermediates in chemical reactions such as combustion and they play an important role in the chemistry of the atmosphere. They can also be important in industrial synthesis.

In organic chemistry pathways, carbon-carbon bonds need to be broken or formed and functional groups may need to be interchanged. Catalytic cracking of petroleum, to produce short chain compounds such as ethene from longer chains is a multi-step process, e.g.

$C_{16}H_{34} \rightarrow C_8H_{16} + C_8H_{18}$
$C_8H_{18} \rightarrow C_2H_6 + C_6H_{12}$
$C_2H_6 \rightarrow C_2H_4 + H_2$

The **costs** of reactants involved in each possible pathway and of maintaining the necessary conditions for the reaction are factors that will impact on the decision as to which reaction process is preferable to use. Industrial chemists need to work out pathways that produce the highest possible yield most economically. This often means the pathway with fewest steps as some matter and energy is likely to be lost at each step. There are specific reagents that can be used to facilitate some chemical changes for example, concentrated sulfuric acid in the formation of esters, hydrogen and metal catalysts for converting alkenes to alkanes.

**Safety** is another issue to be considered when deciding on a chemical pathway to use. If a possible reactant or intermediate is toxic or explosive then a different pathway may be used. If high pressures and temperatures are needed then extra precautions are needed to ensure safety of workers and the environment.

## Reaction pathways in living cells

There are many organic reaction pathways occurring continually in organisms as part of their metabolism. Organic synthesis and decomposition in living cells is usually multi-step. Some are simple, others are very complex with many branches and many of these pathways are cyclical. They concern important processes such as the manufacture of essential chemicals, the production of energy, and the breakdown of waste products from reactions.

Two reactions in cells with which you are already familiar are photosynthesis and respiration.

Photosynthesis involves the splitting of water using light, to hydrogen and oxygen. The hydrogen atoms are then used, in a complicated series of reactions, with carbon dioxide to form glucose. We summarise the series of reactions as follows.

$$6CO_2(g) + 6H_2O(l) + \text{energy} \rightarrow C_6H_{12}O_6(aq) + 6O_2(g)$$

Likewise, the respiration of glucose to release energy involves many steps, although we write the overall equation as follows.

$$C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) + \text{energy}$$

Associated with respiration is an important series of organic reaction pathways called the Krebs cycle, which involves the oxidising of sugars and other organic molecules to make ATP (adenosine triphosphate), a high energy molecule which transfers energy to where it is needed.

Enzymes, which are organic catalysts, play important roles in the reaction pathways within living organisms.

## Fermentation

Fermentation involves a natural process using sugars such as glucose in a multi-step organic reaction pathway to make commercial products such as ethanol, lactic acid, vinegar and biopolymers such as PHAs. The enzymes (biological catalysts) needed for fermentation are provided by yeast or bacteria such as *E. coli.*

Some common organic reaction pathways are summarised in Figure 49.1.

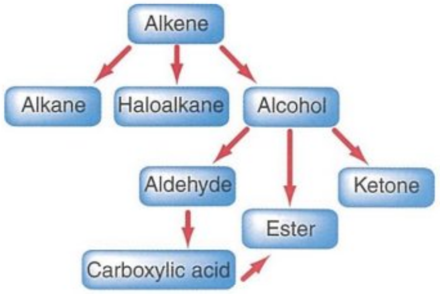


**Figure 49.1** Organic reaction pathways.

## Protein synthesis

Proteins are synthesised in the body using chemicals in our diet – the amino acids that make up the proteins we eat. We digest the proteins we eat, breaking them down to amino acids, and then build up the amino acids into the protein our bodies need.

**Amino acids** are carboxylic acids with an attached amine (–$NH_2$) group. Each amino acid has along its length at least one amino (–$NH_2$) and one carboxyl (–COOH) group.

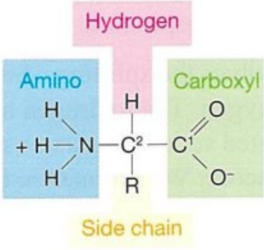


**Figure 49.1** Structure of an amino acid.

Twenty different amino acids have been isolated from the proteins of organisms. These twenty amino acids can bond together to make long chains called polypeptides. The bond between amino acids is called a peptide bond.

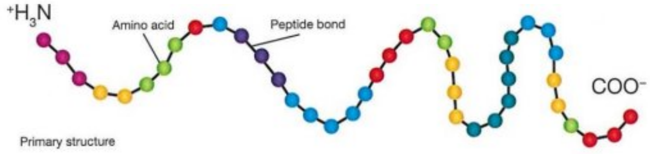


**Figure 49.2** A polypeptide.

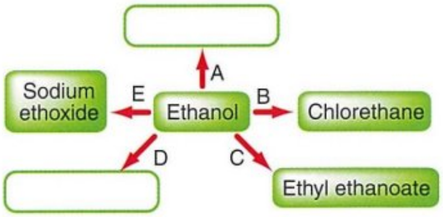
The polypeptide chain can twist into a spiral shape (a helix) or form pleats, by itself or with other chains. It can then form complex folded shapes. The shapes it forms depend on its bonding and they determine its properties. Folding in sheets produces a protein that is flexible but not elastic, such as the protein keratin in silk. Helix shaped proteins can be elastic, such as elastin in connective tissue. Proteins that are fibrous may be tough, rigid and insoluble in water such as those that make up nails and hair.

The structures of proteins are as varied as their functions. They can form soft, flexible structures, rigid structures, soluble crystals or insoluble fibres. Their functions include strengthening and protecting body structure, transport, contraction, defence and regulation of metabolic activities.

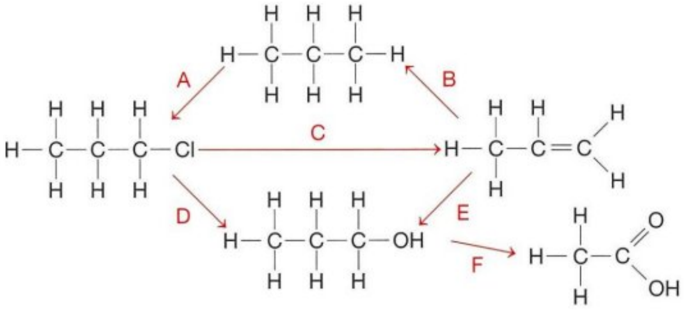
Building up these proteins involves a multi-step reaction process.

## QUESTIONS

1. (a) What is meant by an organic compound?
   (b) Copy Figure 49.1 and add in the names of chemical reactions or processes that could bring about each change.
2. The diagram below shows a number of connected reactions involving organic chemicals.



   (a) Reaction A is dehydration; identify the product.
   (b) Reaction D is oxidation; identify the product.
   (c) Identify the types of reactions occurring in reactions B, C and E.
3. Recall names of the following functional groups and the type(s) of organic compounds that contain each of these functional groups.
   (a) –C=C– (b) $H_2C=O$ (c) –C–OH
   (d) –COOH (e) –COO–
4. Name two organic reaction pathways that occur in living cells.
5. Describe an organic reaction pathway you carried out in the laboratory.
6. Using the diagram below, outline two reaction pathways that could both produce 1-propanol from propene.

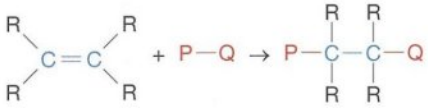
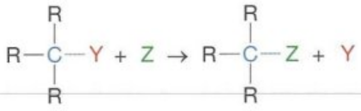
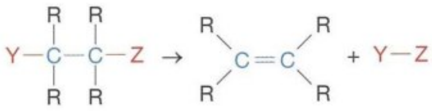
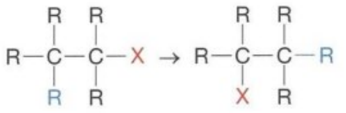


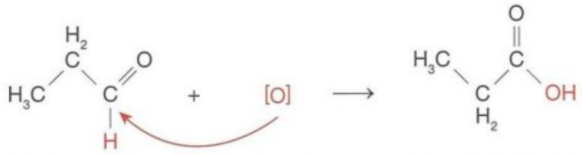
7. A compound A, with molecular formula $C_3H_7Cl$, reacts with sodium hydroxide solution to form compound B, which reacts with acidified potassium permanganate to form compound C, which then reacts with sodium carbonate to release carbon dioxide gas. Compound B can also react with ethanoic acid, in the presence of concentrated sulfuric acid, to form compound D which has a characteristic smell. Identify compounds A, B, C and D and use a flow diagram to illustrate these reaction pathways.

# 50 Revision Of Reactions Of Organic Acids and Bases

By now you should be familiar with the formulas, bonding, properties and some reactions of the main groups of organic compounds. There is a lot to remember about the different groups and their interactions, so at the end of this revision activity, you will find a table and a flow chart to help you summarise this information.

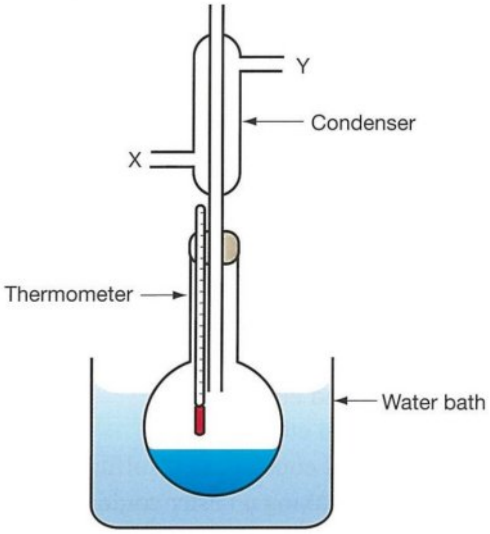
## QUESTIONS

1. The reaction of an alcohol on a carboxylic acid is referred to as:
   (A) Neutralisation.
   (B) Polarisation.
   (C) Isomerisation.
   (D) Esterification.
2. Alkenes are more reactive than alkanes because:
   (A) Alkenes have stronger dispersion forces.
   (B) Alkenes have stronger covalent bonds.
   (C) Alkenes can form stronger hydrogen bonds.
   (D) Alkenes have double –C=C– bonds.
3. When organic compounds interact with other chemicals, there are four main types of reactions that occur to cause structural changes in their molecules – addition, substitution, elimination and rearrangement. These are summarised in the following equations. Which equation shows a substitution reaction?
   (A)
   
   (B)
   
   (C)
   
   (D)
   
4. Which of these compounds is not produced by the oxidation of an alcohol?
   (A) A carboxylic acid.
   (B) A ketone.
   (C) An aldehyde.
   (D) An ester.
5. Alkanoic acids have a –COOH functional group that determines the properties of the group. Which statement is not correct about this series?
   (A) All members of this group are weak acids that turn blue litmus red.
   (B) As the chain length increases, the melting points increase.
   (C) Solubility in water is the same for all members of the group due to hydrogen bonding with water.
   (D) They react with alcohols to form esters.
6. In order to make ethyl propanoate you would use:
   (A) Ethanol and propanoic acid.
   (B) Propanol and ethanoic acid.
   (C) Propyne and ethyne.
   (D) Ethanol and concentrated sulfuric acid.
7. The process of making an ester could be described as:
   (A) Condensation.
   (B) Dehydration.
   (C) Esterification.
   (D) All of the above.
8. The catalyst used during the manufacture of an ester is:
   (A) Dilute sulfuric acid.
   (B) Concentrated sulfuric acid.
   (C) Platinum.
   (D) Ziegler-Natta catalyst.
9. Which of the following substances would you expect not to undergo oxidation?
   (A) Aldehyde.
   (B) Primary alcohol.
   (C) Haloalkane.
   (D) Ketone.
10. Consideer the following reaction.



This chemical reaction shows:
   (A) The oxidation of the aldehyde propanal to propanoic acid.
   (B) The oxidation of the ketone propanone to propanoic acid.
   (C) The reduction of the aldehyde propanal to propanoic acid.
   (D) The reduction of the ketone propanone to propanoic acid.

**11.** The equipment illustrated is used for reflux reactions.



In this experiment:

(A) Water enters at X and exits at Y.
(B) Water enters at Y and exits at X.
(C) Water mixes with the gases produced to help them cool and condense.
(D) Different reactants are added at X and at Y to mix in the flask.

**12.** A suspension of liquid droplets in another liquid is called:

(A) A surfactant.
(B) An emulsion.
(C) A cation.
(D) An emulsifying agent.

**13.** The part of a soap which acts as an emulsifier and a surfactant is the:

(A) Positive metal ions.
(B) Negative metal ions.
(C) Positive fatty acid ion.
(D) Negative fatty acid ion.

**14.** The impact on society of the development of soap included:

(A) Improved hygiene. (B) Less disease.
(C) Lower death rate. (D) All of the above.

**15.** Saponification is the synthesis of:

(A) Soap. (B) An ester.
(C) Sulfuric acid. (D) A polymer.

**16.** Early synthetic detergents were harmful to the environment because they:

(A) Produced large amounts of foam which did not last long.
(B) All contained linear hydrocarbon chains which persisted in the environment.
(C) Contained phosphate which contributed to algal bloom and eutrophication of waterways.
(D) Were completely biodegradable.

**17.** Bromopropane can be produced by the following two-step process:

Reaction X: $CH_3CH{=}CH_2 + H_2 \rightarrow CH_3CH_2CH_3$

Reaction Y: $CH_3CH_2CH_3 + Br_2 \rightarrow C_3H_7Br + HBr$

Which alternative correctly describes these two reactions.

| | Reaction X | Reaction Y |
|---|---|---|
| (A) | Addition | Addition |
| (B) | Substitution | Substitution |
| (C) | Addition | Substitution |
| (D) | Substitution | Addition |

**18.** Which one of the following elements is present in all organic compounds?

(A) Oxygen.
(B) Nitrogen.
(C) Carbon.
(D) Chlorine.

**19.** Which of the following pairs of chemicals would you use to synthesise the ester butyl propanoate.

(A) $C_3H_7OH$ and $C_4H_9COOH$
(B) $C_3H_7OH$ and $C_2H_5COOH$
(C) $C_4H_9OH$ and $C_3H_7COOH$
(D) $C_4H_9OH$ and $C_2H_5COOH$

**20.** Which of the following types of reaction is involved when an alcohol reacts with a carboxylic acid?

(A) Elimination.
(B) Esterification.
(C) Addition.
(D) Substitution.

**21.** Which of the following compounds would you expect to be the most soluble in water?

(A) Propane.
(B) Propene.
(C) Propanol.
(D) Propanoic acid.

**22.** Alkenes have lower boiling and melting points than alcohols or carboxylic acids because:

(A) Alkenes have a double bond which weakens the intermolecular forces.
(B) The smallest alkenes exist as gases.
(C) Only weak dispersion forces hold their molecules together.
(D) Their atoms are held together by strong covalent bonds.

**23.** Which list shows compounds in increasing order of polarity?

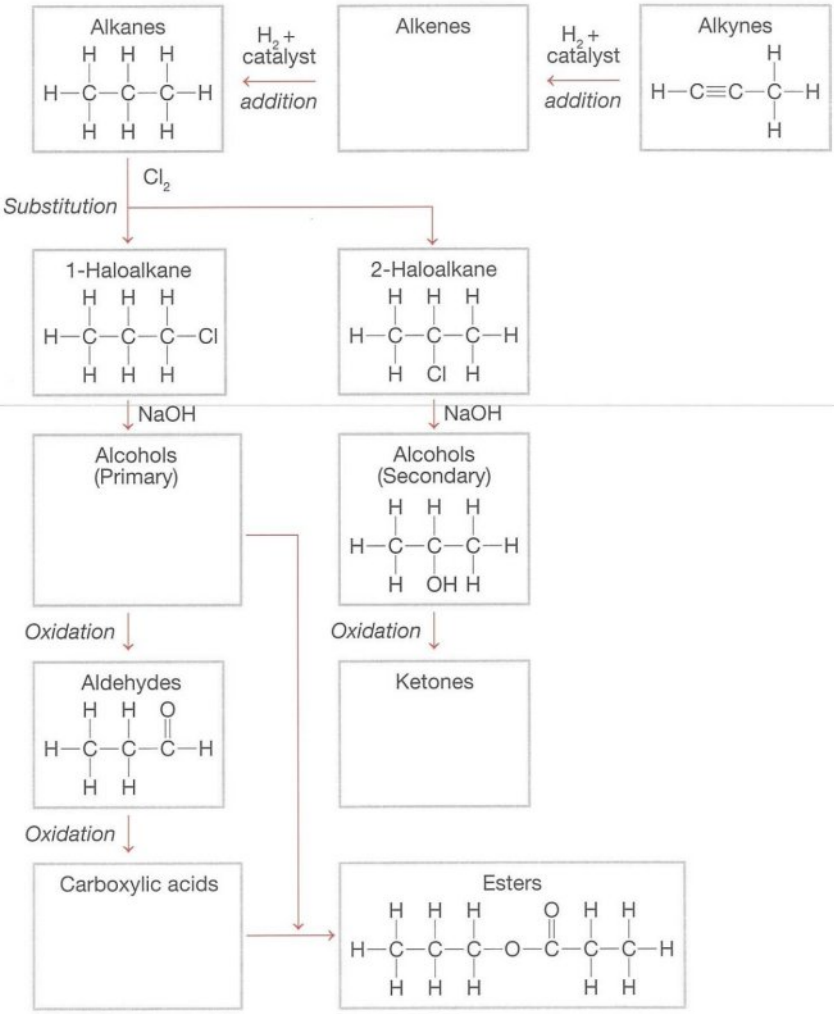
(A) Water, alkanes, alkenes, alkynes.
(B) Esters, alkynes, aldehydes, amides.
(C) Carboxylic acids, alcohols, alkenes, alkanes.
(D) Alkanes, alkenes, alcohol, carboxylic acids.

**INQUIRY QUESTION**

1. Complete the table below to summarise homologous series, their reactions and the products of these reactions.

| Homologous series | Important reaction types | Reagent and conditions | Product(s) |
|---|---|---|---|
| Alkanes $C_nH_{2n+2}$ | Combustion | Air/oxygen, heat | |
| | Free radical substitution of halogens | Halogen, UV light | |
| Alkenes $C_nH_{2n}$ | Combustion | Air/oxygen, heat | |
| | Addition of halogens or hydrogen halides | Halogen or hydrogen halide | |
| | Addition of hydrogen | Hydrogen | |
| | Addition of water (hydrolysis) | Water, acid catalyst | |
| | Polymerisation | Monomer(s) with a catalyst | |
| Alcohols (alkanols) $C_nH_{2n+1}OH$ | Combustion | Air/oxygen, heat | |
| | Dehydration (elimination) | Phosphoric or sulfuric acid | |
| | Oxidation of primary alcohol | Oxidising agent, e.g. acidified dichromate | |
| | Oxidation of secondary alcohol | Oxidising agent, e.g. acidified dichromate | |
| | Esterification | Reflux with carboxylic (alkanoic) acids, concentrated sulfuric acid | |
| Aldehydes (alkanals) RCHO | Oxidation | Oxidising agent, e.g. sulfuric acid | |
| Carboxylic acids (alkanoic acids) $C_nH_{2n+1}COOH$ | Carboxylic acid-base reactions | Base (e.g. sodium hydroxide) | |
| | Esterification | Reflux with alcohol (alkanol) and concentrated sulfuric acid | |
| Halogenoalkanes (haloalkanes) $C_nH_{2n+1}Cl$ | Substitution of halogen for hydroxide | Sodium hydroxide | |

2. Complete the flow chart to summarise the main conversion reactions you have studied.



# 51 Monomers and Polymers

A **monomer** is a small molecule that is able to bond in long chains to form a very large molecule called a polymer. Most monomers are organic compounds with double bonds such as ethene, propene and chlorethene.

A **polymer** is a large molecule that consists of many small molecules (monomers) joined together chemically.

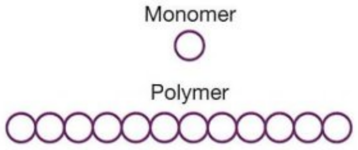


**Figure 51.1** Monomer and polymer.

## Natural and synthetic polymers

Many **naturally occurring** substances are polymers, for example starch, cellulose, proteins, wool, silk, amber and natural rubber (extracted from rubber trees).

**Synthetic** polymers include polyethylene, polypropylene, polystyrene, synthetic rubber, teflon and synthetic textiles such as rayon, nylon, polyester and viscose.

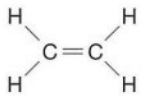
Many polymers are made from **ethene** which is produced from petroleum. In Europe and Japan, ethene is obtained from crude oil by fractional distillation and then cracking (breaking up) of larger alkanes into smaller ethene molecules. In Australia and the United States, ethene is mostly produced by cracking ethane, propane and butane, which are obtained from natural gas and crude oil.

Alkenes such as ethene have a double bond which makes them reactive. They undergo **addition reactions** and join together readily to form the long chain of a polymer. We will look at the simplest polymer first – polyethylene.

## Polyethylene

Polyethylene – also called polythene, polyethene or poly(ethene) – is the simplest polymer and also the most common polymer used worldwide in daily life.

(a) The monomer ethene.



(b) The polymer polyethylene.

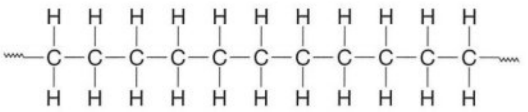
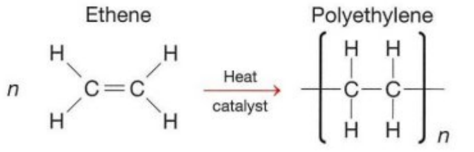


**Figure 51.2** Ethene and polyethene.

Polyethylene is **made from the monomer ethene**.

Polyethylene is called an addition polymer because it is made by addition reactions in a process called **polymerisation**.



(where *n* is a large number)

## Properties and uses of polyethylene

Polyethylene is insoluble and is stable and inert. Polyethylene is easily processed as a flexible film. It is tough and strong due to strong dispersion forces between the long chains and the physical tangling of these chains.

Because of these properties it has many uses. For example, to make cling wrap, supermarket bags, dry-cleaning bags, garbage bags, bottles for milk, detergent and shampoo, lids, toys, mixing bowls, garbage bins, laundry baskets, boats, canoes, buoys and playground equipment as well as irrigation and sewerage pipes and telecommunications cables.

### QUESTIONS

1. Distinguish between a monomer and a polymer.
2. (a) Polyethylene is an addition polymer. Explain the meaning of this term.
   (b) Write an equation to show the formation of polyethylene from ethene.
   (c) Why is ethene important in polymer production?
3. Identify uses of polyethylene that would depend on it having the following properties.
   (a) Insoluble in water.
   (b) Stable and inert.
   (c) Flexible film.
   (d) Tough and strong.
4. (a) Draw a section of a polyethylene chain showing three monomer units.
   (b) What is the repeating unit in this chain?
   (c) Name the monomer.
5. Check your knowledge with this quick quiz.
   (a) What do we call a large molecule formed by many identical small molecules joined together?
   (b) Name the small molecule repeated many times in a polymer.
   (c) Identify the process of making a polymer from monomers.
   (d) Identify the polymer made from ethene.
   (e) List two properties of polyethylene.

# 52 Polyethylene and Its Production

**Polyethylene** is a polymer made from the monomer ethene. It is an odourless solid which is sold in pellet form and is easily processed to form a tough, flexible film or a firm container.

Figure 52.1 Polyethylene pellets.

Polyethylene is very stable and inert. It resists attack by most chemicals, including most acids and bases, and is insoluble in water. It will, however, dissolve in some hydrocarbons when heated. Also, some chemicals, such as detergents and oils, will cause stress cracking and discolouration.

This polymer was first made in 1933 when researchers studying the effects of pressure on ethene accidentally left some gas in a high pressure container over the weekend.

**Polymerisation** is the process of making a polymer from molecules of monomers. Polyethylene and polypropylene are produced by addition reactions.

Most polymers were initially manufactured in large vessels, under conditions of high temperature and pressure.

The **stages in the production** of polyethylene are:

1. **Initiation** – A chemical called an initiator starts (initiates) the reaction by opening the double bond of an ethene monomer. This forms a free radical which has an unpaired outer shell electron and so it is very reactive.
2. **Propagation** – Each time a free radical hits an ethene molecule, a new longer chain is formed. The monomers join, to form a long chain.
3. **Termination** – When two free radicals collide and join, the process stops. A complete polyethylene molecule is formed and we say the process is terminated.

These days, most polyethylene is made using relatively low pressure in a fluidised bed reactor with the help of transition metal catalysts.

Ethene is pumped, under pressure, into the bottom of a **fluidised bed reactor**, which contains a bed of polyethylene powder suspended over a perforated plate. Ethene gas is bubbled up through the powder, making it behave like a liquid (or fluid), so that it looks rather like boiling, bubbling water.

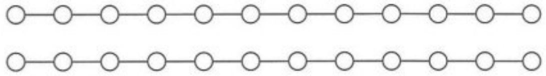
A transition metal **catalyst** is added to allow the reaction to occur at the relatively low pressure of 20 atmospheres. The polyethylene chains grow at the interface with this catalyst. As polymerisation is highly exothermic, the temperature of the reaction vessel must be monitored and maintained to prevent the polymer decomposing as it forms.

Transition metal catalysts are also called **Ziegler-Natta catalysts** after their inventors. These allow the production of linear, unbranched polyethylene chains consisting of over 10 000 monomer units. Recently nanosized metal catalysts have been developed which are more efficient and less expensive.

Ziegler and Natta realised that the catalyst used would not only affect the rate of the polymerisation reaction and the conditions under which it took place (e.g. pressure and temperature), but also the arrangement of units attached to its main chain. This in turn could affect the polymer's properties, such as its stability to heat, density and tensile strength.

The physical properties of a polymer depend on the monomers used, the length of the polymer molecules and the amount of branching.

(a) Linear polymer.



(b) Branched polymer chains.

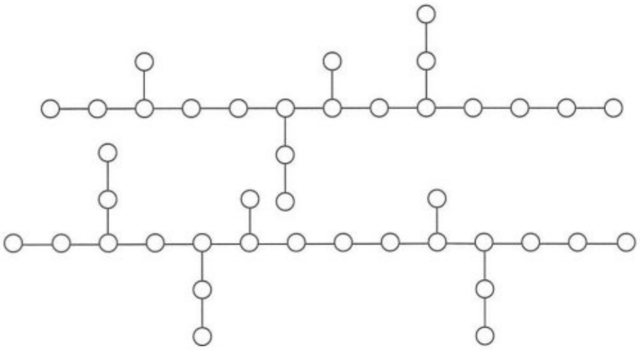


Figure 52.2 Linear and branched polymer chains.

## High and low density polyethylene

Polyethylene can be manufactured as high density polyethylene and low density polyethylene, both of which can be recycled.

**Figure 52.3** Recycling symbols for high and low density polyethylene.

**Low density polyethylene** (LDPE) has branched chains. Branched molecules cannot be packed together as tightly so they tend to be less dense than polymers with linear molecules. The first polyethylene produced, in the 1930s, was LDPE. High pressures (1000 to 3000 atmospheres) and temperatures (300°C) and an initiator are needed to produce LDPE.

LDPE is used to make toys, soft plastic bags and carrier bags, squeeze bottles, waterproof linings in tanks and construction, gas and water pipes. It is also used as a plastic coating on paper and packaging, e.g. milk bottles.

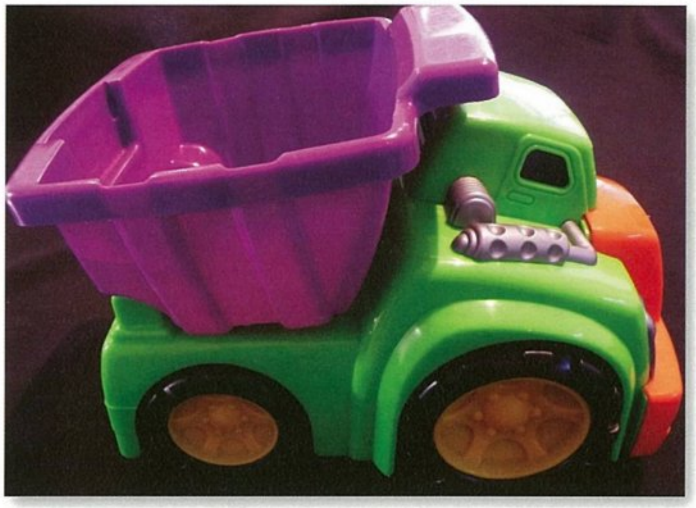


**Figure 52.4** Toy truck made of low density polyethylene.

**High density polyethylene** (HDPE) has linear molecules which can pack closely together with molecular weights between 100 000 and 500 000. HDPE is stronger and less flexible than LDPE. Polyethene can also be made under safer and less expensive conditions of relatively low pressures (a few atmospheres) and temperatures (about 60°C) with ultra high molecular weights of 3 to 6 million. This is used to make bulletproof vests and large sheets of artificial ice for skating rinks. HDPE is one of the most commonly used plastics. It is also used for many other purposes, for example, for car fuel tanks, hard hats, plastic bags and bottles, storage sheds, pipes, bottle caps and food storage containers.

**Figure 52.5** Containers and a child's swing made of high density polypropylene.

## QUESTIONS

1. (a) Identify the three main stages in the polymerisation of polyethylene.
   (b) Identify three factors that can be varied in the production of a polymer to change the properties of the finished product.
   (c) Outline two ways in which the long polymer chains that make up polyethylene give it strength.
2. Two forms of polyethylene are LDPE and HDPE.
   (a) Identify a scientific advance that made the development of the low pressure process possible.
   (b) Outline the commercial advantages of using the low pressure process.
   (c) Which of these types of polymers has a branched structure? Explain.
   (d) Use a table to compare differences between these forms of polyethylene.
3. Research and assess the impact of the discovery of polyethylene on society and the environment.
4. Check your knowledge with this quick quiz.
   (a) Identify two uses of polyethylene which has been made to have an ultra high molecular weight.
   (b) Which would be more dense, a polymer with a linear or a branched molecule?
   (c) What does LDPE stand for?

# 53 Other Addition Polymers

There are many other important polymers. Here we will look at two more addition polymers, polyvinyl chloride and polystyrene.

## Polyvinyl chloride or PVC

The **monomer** used to make polyvinyl chloride or PVC is chlorethene, which is commonly called vinyl chloride. The polymerisation process can be shown by the equation in Figure 53.1.

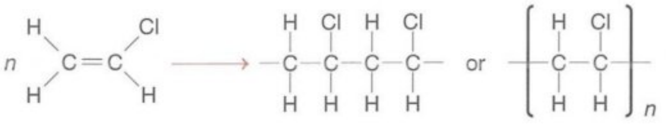


**Figure 53.1** Polymerisation of vinyl chloride.

**Polyvinyl chloride is used** for containers, e.g. for vegetable oil, for imitation leather, blister packaging, electrical insulation, pipes and hoses, vinyl flooring and outdoor furniture.

## Polystyrene

Polystyrene is made by the addition of many molecules of styrene. The IUPAC name for styrene is ethenylbenzene, and it is also known as vinyl benzene.

(a) Styrene.

$C_6H_5$ is a special ring structure called a benzene ring.

(b) Polystyrene.

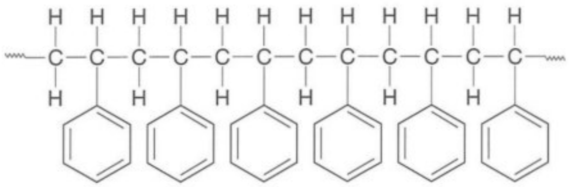


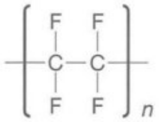
**Figure 53.2** Styrene and polystyrene.

**Polystyrene is used** for fruit boxes, packing foam, clothes hangers, foam egg cartons, meat trays, plastic cutlery, toys, surfboards and hot drink cups. It is suitable for these uses because it is light, tough and can be moulded. A gas can be blown through the molten polymer during manufacture, making the polymer foam-like with low density. Without the gas it forms a tough, transparent plastic used for such products as CD and DVD cases and toys.

## Polytetrafluoroethylene

Polytetrafluoroethylene (PTFE) is a polymer which is commonly called Teflon.

The monomer is tetrafluoroethylene.



Poly(1,1,2,2-tetrafluoroethylene)

This polymer is a hard, tough, non-flammable polymer. Its strong bonds, between its carbon atoms and highly electronegative fluorine atoms, make it resistant to chemical attack. It has a very low coefficient of friction and is hydrophobic (repels water). These properties make it suitable for a non-stick coating on such surfaces as cookware and skis. It is used to protect pipes carrying corrosive chemicals and as a coating on machinery and medical equipment such as artificial heart valves where it reduces friction and helps prevent infection.

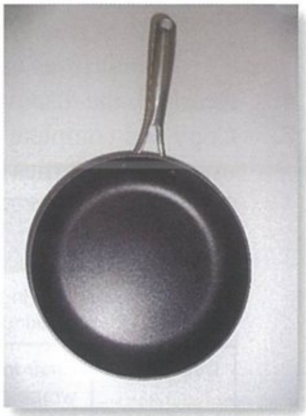


**Figure 53.3** Teflon coated frypan.

## Properties of these polymers

These **four** addition polymers have some properties in common. They are all insoluble in water, they are stable compounds and resistant to attack by chemicals, they have a relatively low density and are relatively inexpensive. They also tend to be tough and strong due to the large number of dispersion forces between their long chains and also tangling of chains.

In addition, **PVC** has fire-retardant properties and is a good electrical insulator and **polystyrene** can be moulded to fit products – it maintains its shape, and is a good insulator. **Polytetrafuoroethylene** is also non-flammable and can be used to coat surfaces to prevent friction and to prevent chemicals adhering to the surface.

## QUESTIONS

1. Research the meaning of the terms vinyl monomer and vinyl polymer.
2. Copy and complete the table to summarise information about two of the polymers you have studied that are produced by addition reactions.

| Monomer name | Ethene | Chloroethene |
|---|---|---|
| Formula of monomer | | |
| Polymer | | |
| Common name of polymer | | |
| Formula of polymer | | |

**3.** Vinyl chloride is a non-flammable liquid which evaporates slowly and mixes poorly with water.

(a) Vinyl chloride is classed as a severe explosion hazard and yet it is the monomer in the manufacture of polyvinyl chloride which has flame retardant properties. Explain why this difference in flammability of vinyl chloride and polyvinyl chloride is possible.

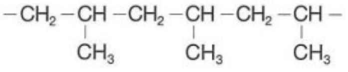
(b) Vinyl chloride irritates the eyes, skin and respiratory system, causes liver damage and may be carcinogenic. It is also highly toxic to marine life. What precautions need to be taken in industries using this chemical?

**4.** Research the discovery of polytetrafluoroethylene.

**5.** Copy and complete the table to summarise some uses and properties of polymers.

| Name of polymer | Use | Properties that allow this use |
|---|---|---|
| PVC | Flooring and carpet backing. | |
| PVC | Clear food wrapping, toys, blister packaging, child's float. | |
| HDPE | Natural gas pipes and coating for steel pipes. | |
| LDPE | | High tensile strength, low density, soft and flexible, insoluble in water. |
| Polystyrene | Sheathing for wire, phone and TV cables. | |
| Polystyrene | Disposable foam cups. | |
| Polystyrene | Surfboards. | |

**6.** The formula of a polymer can be illustrated by the small section of its molecule shown in the following structure.



$$-CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-$$

(a) Research to identify this polymer.

(b) Name and draw the condensed structural formula of the monomer used to make this polymer.

(c) Identify the process used to make this monomer.

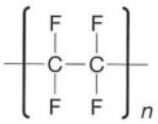
(d) Research information about this polymer.

**7.** The monomer iodoethene undergoes addition polymerisation.

(a) State the structural formula of iodoethene.

(b) Draw a small section of the polymer it forms, showing three monomer units.

(c) Name this polymer.

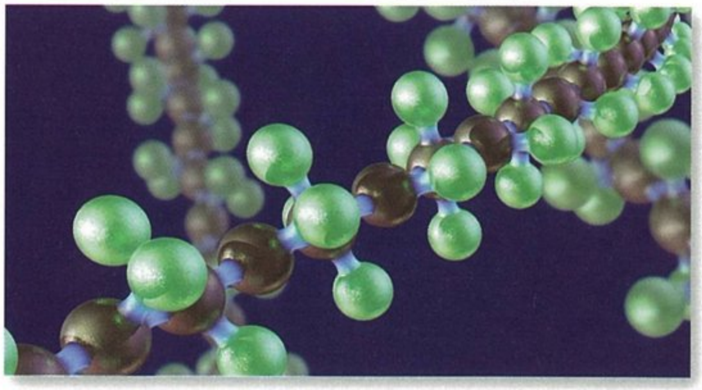


$$\left[-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-\right]_n$$

**8.** Polytetrafluoroethene is a high molecular weight polymer made of only carbon and fluorine. The strength of its C–F bonds also makes it resistant to chemical attack.

Because of these properties it is used to provide a non-stick coating on such surfaces as cookware and skis. The structure of polytetrafluoroethylene is shown in the diagram.

(a) The model illustrated shows a section of a PTFE molecule and you can see that it consists of atoms of only two elements. Name these elements.



(b) Identify and show the structural formula of the monomer that would be used to make this polymer.

(c) Calculate the molecular weight of this monomer.

(d) Calculate the molecular weight of the polymer if $n = 200$.

(e) Identify the type of chemical reaction used to link these monomer units together and form the polymer.

**9.** (a) Discuss the commercial and industrial importance of polymers.

(b) Outline the importance of the discovery of transition metal catalysts to the development of the polymer industry.

**10.** Check your knowledge with this quick quiz.

(a) What do we call a large molecule formed by the joining of many identical smaller molecules?

(b) What do we call the small molecule repeated many times in a polymer?

(c) Name the process of making a polymer such as PVC from monomers.

(d) Identify the polymer made from styrene.

(e) Which would be more dense, a polymer with a linear or a branched molecule?

(f) State three uses of polystyrene.

(g) Name three examples of addition polymers.

(h) Name and state the molecular formula for the ring structure that forms part of a styrene molecule.

(i) State one reason why vinyl chloride must be treated with extreme care.

# 54 Condensation Reactions

The polymers you have looked at so far have been addition polymers – manufactured by addition reaction. Another group of polymers, called condensation polymers, are produced by condensation reactions.

A **condensation reaction** is a chemical reaction which releases a small molecule such as water as one of its products. Here we will look at condensation reactions between a carboxylic acid and an amine.

Remember:

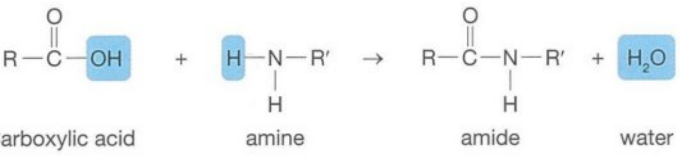
**Carboxylic acids contain R–COOH**

**Amines contain R–$NH_2$**

**Amides contain R–$CONH_2$**

Can you see how these groups might be related to each other?

When carboxylic acids react with amines they produce molecules of water and an amide. In amides the OH part of the carboxylic acid is replaced by a $NH_2$ group.



$$R-\overset{O}{\overset{\|}{C}}-OH + H-\underset{H}{\underset{|}{N}}-R' \rightarrow R-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-R' + H_2O$$

Amide groups can link together to form a polymer. This link is called an amide link. This reaction is important because of its role in the manufacture of condensation polymers and also in the production of peptides and amino acids in biochemistry.

## Formation of polyamides

Polymers called polyamides are formed by condensation reactions between an amine and a carboxylic acid. Amide links form between the monomers. Kevlar and nylon are two important polyamides.

## Formation of peptides and amino acids

Biochemists call an amide link a **peptide bond** because it can link together the chains of amino acids, that together make up peptides and proteins. Amino acids are the monomer units for peptides and proteins.

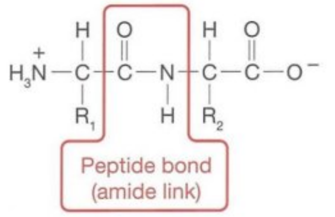
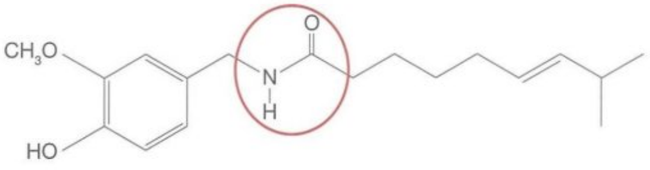


Figure 54.1 A peptide bond (amide link).

The condensation reaction to produce polyamides is also important because of its role in industries. Amide links are used to make polymers such as Kevlar bullet-proof vests; nylon carpets, clothing, ropes and tyres; and silicone adhesive tapes. They are also used to make paper, pencils, inks, explosives, and adhesives and are used in the treatment of sewage. Amide links are found in many common substances such as foods and dyes, medications and insecticides.

(a) Capsicim, found in capsicum, peppers, chilli and paprika.



(b) An insecticide ingredient.

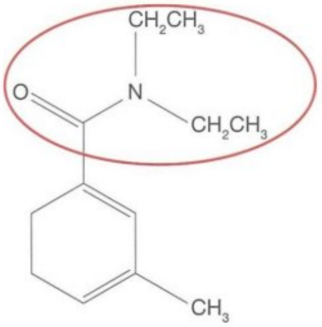
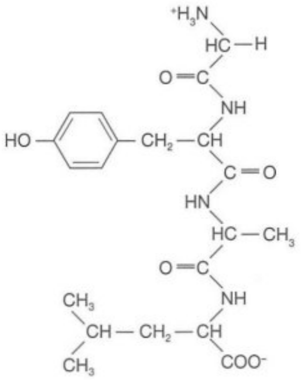


Figure 54.2 Amide links (circled) occur in many common substances, e.g. foods and insecticides.

## QUESTIONS

1. During this course, you have seen two types of condensation reactions involving carboxylic acids. Use general equations to summarise these.
2. Distinguish between an amine and an amide.
3. The diagram below shows a sequence of amino acids linked by peptide bonds (amide links). Circle the amide links.



4. Research to outline the formation of a condensation polymer.

# 55 Condensation Polymers

## Condensation polymers

In condensation reactions, a small molecule, such as a water molecule, is produced as a by-product.

Starch, cellulose and proteins are naturally occurring condensation polymers. Starch and cellulose are made from condensation reactions between glucose monomers. Proteins are made from amino acid monomers.

Many synthetic polymers are produced by condensation reactions. These include polyurethanes, PET plastics (polyterephthalic acid), Bakelite plastics, polycarbonates, nylon and polyesters such as Dacron. Polyesters include fabrics and also resins such as the fibreglass products used to make surfboards and car parts.

The monomers used to synthesise condensation polymers have two important features.

- They do not react at double bonds; instead they react at functional groups.
- Each monomer has two or more reactive sites, as they usually have more than one functional group. This means they often form side chains.

## Synthesis of nylon

**Nylon** is a condensation polymer produced by a condensation reaction involving chemicals obtained from petroleum. There are different types of nylon; the reactions for making two types of nylon are shown here.

**Nylon 6** is made from a compound, aminohexanoic acid, containing six carbon atoms in its molecules – hence the name, nylon 6.

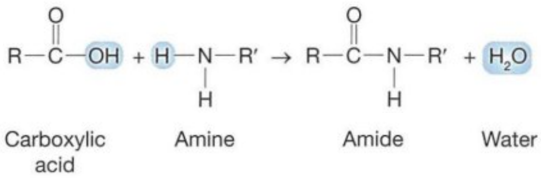
$$n(H_2N{-}(CH_2)_5{-}COOH) \rightarrow \left[ NH{-}(CH_2)_5{-}CO \right]_n + nH_2O(l)$$

6 Aminohexanoic acid → nylon 6 + water

**Nylon 6, 6** is made from two compounds, hexamethylenediamine and adipic acid, each containing six carbon atoms per molecule.

$$n\ HOOC{-}(CH_2)_4{-}COOH + n\ H_2N{-}(CH_2)_6{-}NH_2 \rightarrow \left[ OC{-}(CH_2)_4{-}CO{-}NH{-}(CH_2)_6{-}NH \right]_n + 2n\ H_2O$$

If we look at this reaction more carefully, we see that it is like a carboxylic acid reacting with an amine – a water molecule is removed and a bond is formed called an amide link.



$$R-\overset{\overset{O}{\|}}{C}-OH + H-\underset{\underset{H}{|}}{N}-R' \rightarrow R-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-R' + H_2O$$

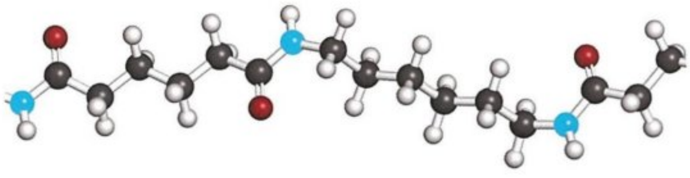


Figure 55.1 Model of nylon 6, 6.

Nylon was first developed in 1938 when it was used to make bristles in toothbrushes. It is one of a group of polymers called polyamides. Nylon can be moulded or drawn into fibres and used to make fabric.

Nylon is thermoplastic; it melts when heated. It is strong, elastic, waterproof and highly resistant to attack by insects and fungi. It has a wide variety of uses, including the manufacture of clothing, umbrellas, fishing lines, dental floss, tents, sleeping bags, luggage and carpets. Nylon 6, 6 is used when mechanical strength, rigidity and stability to heat and chemicals are required properties, for example in pipes and machine parts.

## Synthesis of PET

**PET (polyethylene terephthalate) plastics** are condensation polymers. About a third of PET manufactured is used to make bottles and containers. Most is used to make fibres that may be referred to by names such as polyester, Dacron and Terylene.

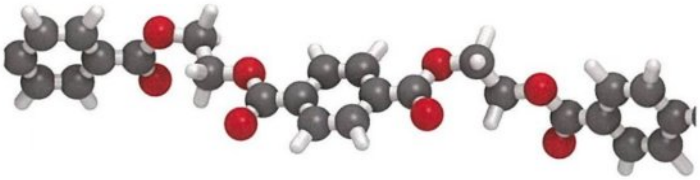


Figure 55.2 Model of PET.

PET plastics are made from two comonomers, terephthalic acid and ethylene glycol (the latter is also used as antifreeze).

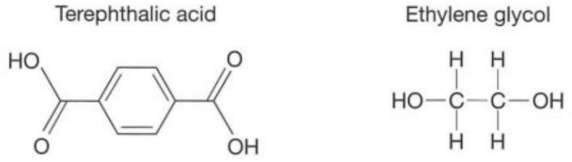
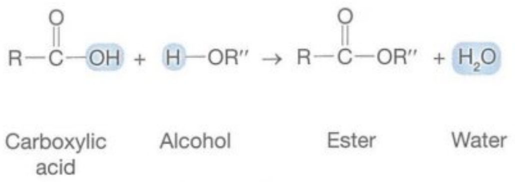


Figure 55.3 Monomers used in making PET plastics.

The reaction can be shown as follows.

$$n\,C_6H_4(COOH)_2 + n\,HOCH_2CH_2OH \rightarrow [(CO)C_6H_4(CO_2CH_2CH_2O)]_n + 2n\,H_2O$$

Notice that in this reaction a carboxylic acid is reacting with an alcohol and an ester link is being formed.



## Cellulose

Cellulose is another condensation polymer. It occurs naturally, being one of the main components of biomass – organic matter produced by plants. Cellulose makes up the cell walls of plants and is the most abundant carbohydrate on Earth.

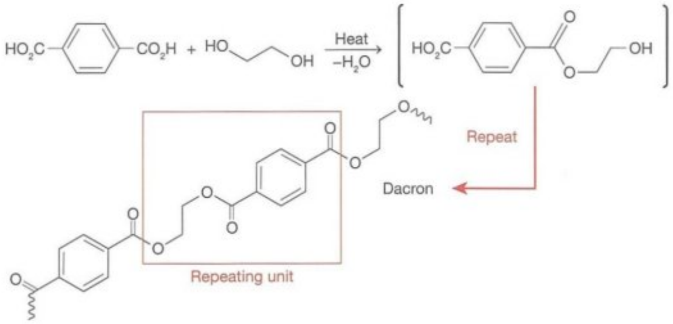
You have already seen that cellulose consists of about 2000 to 8000 $\beta$-glucose molecules joined in long chains by a condensation reaction, and it can be modified to make new polymers such as cellophane.

## QUESTIONS

1. Copy and complete the table to compare addition and substitution reactions.

| Feature | Addition reactions | Condensation reactions |
|---|---|---|
| What happens? | | |
| Occurs in saturated or unsaturated compounds. | | |
| One or two products. | | |
| Is energy needed? | | |
| Example | | |

2. Compare the synthesis of addition and condensation polymers.
3. Most polymers are currently manufactured from petroleum. Why is there a need to find alternative sources of raw materials for polymer production?
4. Polyethylene glycol (PEG) is a polymer which can be synthesised from ethylene oxide or ethylene glycol.
   (a) Research to distinguish between the compounds ethylene, ethanol, ethylene oxide, ethylene glycol and polyethylene glycol.
   (b) Research the manufacture and uses of polyethylene glycol.
5. The equations show the synthesis of a polyester called Dacron.



Is this an example of addition or condensation polymerisation? Justify your answer.

6. Check your knowledge with this quick quiz.
   (a) Monomers with double bonds react by (addition/condensation) reactions.
   (b) A small molecule such as water is released during the formation of (addition/condensation) polymers.
   (c) Name the three stages during polymerisation.
   (d) Classify the following polymers as addition or condensation polymers.
   Nylon, polyethylene, cellulose, polystyrene, polyesters, polyvinyl chloride, polyurethane.

# 56 Thermoplastic and Thermosetting Polymers

Addition and condensation polymers are often classified as thermoplastic and thermosetting polymers.

## Thermoplastic polymers

A **thermoplastic polymer** is one that becomes pliable and can be moulded when heated and solidifies when cooled. Thermoplastic polymers are mostly linear or only slightly branched so that in the molten state the molecules can flow past each other. Most thermoplastic polymers have a high molecular weight, and when heated, their intermolecular forces become broken and they melt.

Exposure to cold temperatures could make these polymers become brittle and crack. To prevent this, two different monomers may be used to form the polymer or chemicals called plasticisers can be added during the formation of the polymer.

Thermoplastic polymers can be **repeatedly melted and formed into new shapes**. Most thermoplastic polymers can be **recycled** – they can be repeatedly melted and remoulded into new products. They are shaped by a variety of techniques such as injection moulding, compression moulding and extrusion.

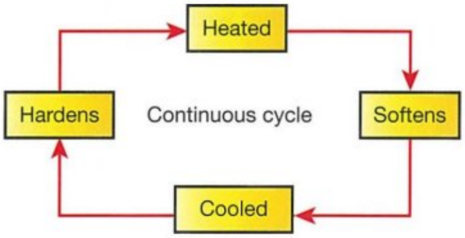
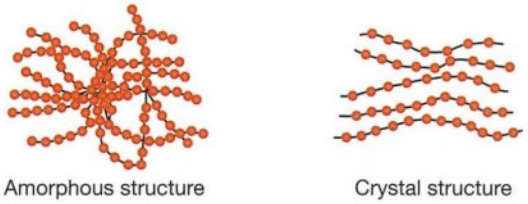


**Figure 56.1** Recycling thermoplastic polymers.

Thermoplastic polymers can be **amorphous** (chains all jumbled up) or **crystalline** (chains aligned).



Amorphous structure

Crystal structure

**Figure 56.2** Amorphous and crystal structure in polymers.

Amorphous structures tend to be more elastic; crystalline structures tend to be very strong but brittle rather than elastic. Linear polyethylene is nearly 100% crystalline, but with branches it becomed highly amorphous.

The addition polymers you have already studied are thermoplastic polymers – polyethylene, polypropylene, polystyrene and polyvinyl chloride. Polylactic acid, a renewable, biodegradable plastic made from corn starch and waste dairy and sugar cane is another thermoplastic polymer.

## Thermosetting polymers

**Thermoset polymers** contain cross-linked chains that form irreversible chemical bonds when heated.

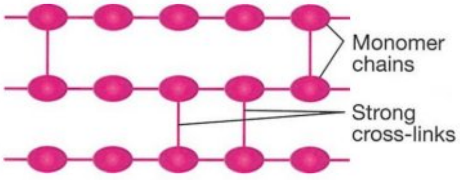


**Figure 56.3** Thermoset polymers.

Thermoset polymers are useful in situations where resistance to heat and deformity is needed such as in saucepan handles, electronics and electrical switches and appliances.

They cannot be softened by heating and reshaped, or remoulded, so they **cannot be recycled** as new products.

Thermoset polymers are made by **condensation reactions**. These include polyesters, polyamides such as nylon, melamine, Bakelite, polycarbonates and polyurethanes. They can be drawn into fine fibres and woven into cloth and they can be mixed with natural fibres such as cotton. You may like to find out more about some of these polymers.

## QUESTIONS

1. (a) Compare thermosetting and thermoplastic polymers. Tabulate your answer.
   (b) Use diagrams to show the structural difference between these two types of polymers.
2. Compare the terms 'polymer', 'plastic', 'thermoplastics' and 'elastomer'.
3. (a) Research the use of recycling numbers on polymers.
   (b) Are any of these polymers considered unsafe to recycle?
   (c) Collect (or take photographs of) samples of each type of polymer.

# 57 Designing Polymers

There are many new polymers being produced all the time and they can be designed with properties to suit a particular market. Properties of polymers that may be requested by a customer include their appearance, density, durability, flammability, strength, conductivity, hardness, chemical resistance, and flexibility.

An example of designing a polymer to meet customer requests is the development of **'breathable' fabrics** such as Gore-Tex which is used to make lightweight, waterproof shoes and clothing which repel water on the outside and allow water vapour to evaporate from the body. To do this they use a thin, porous layer of polytetrafluoroethylene (PTFE) that allows for the evaporation of water vapour. This type of clothing is particularly useful for activities out of doors in all weather.

This type of fabric is also used as an implant membrane in surgery and under casts on broken limbs to make the patient more comfortable.

**Figure 57.1** Porous membrane used under a cast.

Because of their versatility, polymers are replacing many materials traditionally used in vehicles, construction and manufacturing. A number of factors influence the properties of a polymer.

## Monomers

A suitable **monomer** is selected to produce the desired structure and properties.

**Mechanical properties** of a polymer, such as strength, flexibility, resistance to abrasion and ability to absorb shock, are affected by its monomer. Branching and long side chains result in a less dense polymer as the chains cannot pack so closely together. The nature of the side chain also affects the strength of the product.

**Electrical properties.** The monomer chlorethene produces a polymer with a high electrical resistance, making it a good insulator for wires and tubes. It has the added advantages of being inexpensive and it can be made flexible enough to bend around corners.

**Chemical reactivity.** You are already aware that polymers such as polyethylene and polypropylene can resist attack by most chemicals, including most acids and bases. However, hydrocarbons, esters, detergents and oils can damage these polymers.

**Copolymers.** Sometimes more than one monomer is used, forming a product called a copolymer. Synthetic rubber is an example, with monomers of styrene and 1,3-butadiene ($CH_2$=CH–CH=$CH_2$). Varying the proportion of each monomer and the amount of cross-linking, can produce products to suit particular purposes.

**Table 57.1** Some examples of copolymers.

| Monomer A | Monomer B | Copolymer | Uses |
|---|---|---|---|
| $H_2C$=CHCl | $H_2C$=$CCl_2$ | Saran$^R$ | A film sprayed on fighter planes |
| $H_2C$=$CHC_6H_5$ | $H_2C$=C–CH=$CH_2$ | Styrene butadiene rubber | Tyres |
| $H_2C$=CHCN | $H_2C$=C–CH=$CH_2$ | Nitrile rubber | Adhesive and hoses |
| $H_2C$=$C(CH_3)_2$ | $H_2C$–$(CH_3)$=CH–$CH_2$ | Butyl rubber | Car inner tubes |

## Reaction conditions and the type of catalyst

The conditions under which polymerisation occurs and the type of catalyst used can change the length of the chains formed and the properties of the polymer. Reaction conditions can affect its hardness, melting point, crystalline structure, transparency and stiffness. The longer the chain, the stronger and stiffer the polymer becomes and the higher its melting point.

You have already seen that:

- **Polyethylene** can be a high density or low density polymer depending on the degree of branching of the polymer chain. **HDPE** is more crystalline, has a higher melting point, is stronger and stiffer than **LDPE**.
- **Thermoset** polymers have cross-links between chains to form a 3-D solid structure. Heating does not change their permanent shape.
- **Thermoplastic** polymers have weak links between their chains. The chains can line up side by side forming tiny **crystals** which make the polymer solid.

- **Elastomers** can be developed, including flexible fibres such as spandex as well as artificial rubber-like products that are highly resistant to chemicals and stable at high temperatures.

Hundreds of specialised polymers can be made from the one basic polymer as different copolymers and additives are included in its manufacture.

## Additives

There are hundreds of additives that can be used to change polymer properties. We will look at just a few here.

**Plasticisers.** Adding a plasticiser increases the flexibility and ease of handling of a polymer. These are usually petroleum based oils, or fatty acids and esters. Plasticisers are frequently added to PVC, which would otherwise be rigid. Tiny particles of the plasticiser push their way between the polymer chains, keeping them apart so the attraction between chains is reduced and the chains become more flexible and can move more freely.

Some plasticisers not only increase flexibility of the polymer, they add other properties as well. For example, adding glycerol esters can reduce the flammability of the product.

The amount of plasticiser added will vary; thermoplastic materials may contain 10%, whereas elastomers may contain up to 60%.

In natural polymers, such as in natural fibres like silk, wool and cotton, water molecules act as a plasticiser. In muscles, water and fat molecules act as plasticisers.

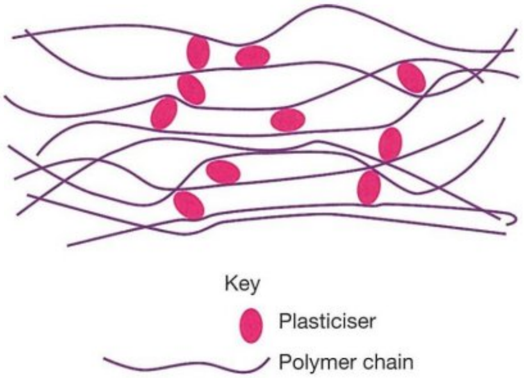


Figure 57.2 Plasticisers in a polymer.

A problem with plasticisers is that they can be mobile, and after some time they may migrate out of the polymer, leaving it feeling greasy and brittle.

There is concern about the use of some plasticisers because of their side effects. For example, diethyl phthalate (DEP) is toxic and causes endocrine disruption. This was previously used in products such as bottles for babies and childrens' toys. Also organophosphates are a concern as they are reported to be toxic to bees, humans and other animals, affecting the nervous system.

**Fillers.** Fillers are added to all sorts of products, not only polymers. They are often used to bulk up a product, reducing its cost. Fillers commonly used for this purpose are ground calcium carbonate and clay. However, fillers are also added to polymers to enhance properties such as stiffness and strength, for example, carbon black is added to some polymers for added strength. Also ground up glass fibre is used to improve thermal properties.

**Stabilisers.** Stabilisers are added to help protect a polymer exposed to heat, light and atmospheric contaminants. UV absorbers and antioxidants are frequently added to help resist discolouration and oxidation.

**Other additives.** Other additives include **fire retardants** in polymers for use in aeroplanes and clothing, additives to **prevent mildew** and **pigments** to enhance appearance of the polymer.

## QUESTIONS

1. Discuss properties of polymers that are affected by:
   (a) Chain length.
   (b) Chain branching.
   (c) Cross-linking.
2. Polymers can be designed to suit specific applications.
   (a) Identify three factors that can be varied to change the properties of polymers.
   (b) State three ways in which additives can change the properties of polymers.
3. (a) Where does natural rubber come from?
   (b) Research artificial (synthetic) rubber, identifying the monomers used and its properties.
   (c) What is meant by vulcanising of rubber?
4. Researchers have developed a renewable, biodegradable, thermoplastic polymer known as PLA.
   (a) What is PLA?
   (b) Discuss the advantages and disadvantages of PLA.
5. Research one of the following.
   (a) A polymer used in medicine.
   (b) A breathable fabric used for outdoor clothing in wet weather.

# 58 Advantages and Disadvantages Of Polymers

## The advantages of polymers

One advantage of polymers is the **flexibility and enormous variety** of their **structure and properties**. They can be solid structures or thin films. Some can be used as insulators (heat and electricity), others as conductors. Some are transparent and can be used for windows and lenses, whereas others are opaque. These can vary depending on the monomers used, the conditions of manufacture and additives employed. Many polymers are relatively cheap, strong and durable. They have low density, which means they are economical to transport, using less fuel in the process. They are easy to manufacture and do not need maintenance such as painting.

Many polymers have **advantages over traditional materials** such as glass, metals and ceramics including lower costs and lower density. Also bank notes made from polymers such as polyethylene are more durable and make counterfeiting more difficult.

Figure 58.1 Polymer banknotes.

Polymers provide the **ability to design and manufacture substances suitable for particular jobs** and some technology such as wind power would not be possible without polymers.

- Polymer based sprays have been developed to improve the penetration of water into soils. These are of particular use in Australia as up to thirty per cent of Australia's cropping land is water-repellent making it difficult to farm crops.
- Capsules have been developed to cover thin film solar cells and protect them from water and oxygen, thus allowing them to last longer in our harsh Australian climate.
- Fabrics that 'breathe' have been developed from polymers such as Teflon.
- Hydrogels have been developed to be used as devices to deliver drugs to nerve cells during stroke, spinal cord injury and traumatic brain injury.
- Polymers have been synthesised that mimic biological molecules – with similar properties to those of proteins and RNA allowing scientists to study how natural biopolymers fold.

## The disadvantages of polymers

One advantage of polymers is that they **last so long** – they are unreactive. However, this is also a disadvantage as they are **difficult to dispose of**. They do not decompose, take up a lot of space in landfill, and if you burn them they produce toxic gases such as dioxins and the greenhouse gas carbon dioxide. Many polymers can be recycled, but separating them out is difficult and expensive.

There are moves to solve this problem. Polymers are being produced which are **biodegradable**, and bags made of these polymers are available. They decompose to carbon dioxide – a greenhouse gas. However, if these are buried in landfill where no oxygen is available, they will decompose to methane a more potent greenhouse gas than carbon dioxide. Also water soluble polymers have been developed for some packaging.

There are still problems such as their pollutant effect on the ocean including the effect of discarded plastic bags on marine life

Polymers are also **using up a non-renewable resource** – petroleum. We need to consider if this is an acceptable way to use this resource and whether or not it is sustainable.

Another problem is the **toxicity** of many raw materials used to make polymers, exposing workers to risk in factories and the risk of leaks that can affect the environment and the general public. It has now also been found that some toxic substances such as bisphenols can leach out of polymers during use.

For example, the comonomers used in the synthesis of PVA (polyvinyl alcohol) include acrylamide, a neurotoxin; formaldehyde, a suspected carcinogen which also causes mutations; and vinyl chloride a carcinogen. The cross-linkage agent is also highly toxic causing burning effects similar to those of mustard gas.

## Biopolymers

The production and use of biopolymers has removed some of the objections to the use of polymers as these are made from plant material rather than from non-renewable fossil fuels.

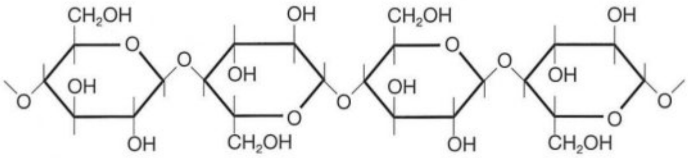
**Biopolymers** are polymers produced by living organisms or from biomass. Some occur naturally, others are made from biomass or by using organisms.

Biopolymers are **biodegradable** and they can decompose to carbon dioxide, water and biomass.

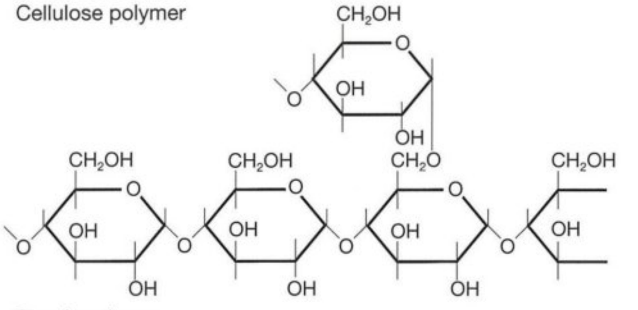
Biopolymers are also **biocompatible**. They do not react with living tissue so they have a market in the medical field. Sutures, staples and screws made of biodegradable polymers such as PHA (polyhydroxyalkanoate) and PLA (polylacticacid) have the advantage of providing structural support, without causing adverse reactions, and they eventually decompose without having to be removed.

**Naturally occurring biopolymers** include starch and cellulose which are both condensation polymers composed of long chains of glucose molecules. Proteins are also naturally occurring polymers and these are made of chains of amino acids.

**Biomass** is organic matter produced from plants and includes the waste plant matter from agricultural products such as waste from sugar cane, corn crops and forestry. Cellulose is a major component of biomass as it makes up the cell walls of plants.



Cellulose polymer



Starch polymer

Figure 58.2 Cellulose and starch are natural polymers of glucose.

Scientists are now manufacturing biopolymers from biomass using starch, sugars and cellulose.

**Starch based biopolymers.** Starch is a natural polymer in plant tissues such as rice, potatoes, wheat, maize, corn and tapioca. Corn starch is fermented by bacteria to produce xanthum gum, which is used as a thickener, emulsifier and stabiliser in a vast range of foods as well as other products including cosmetics and paints.

**Sugar based biopolymers.** Biopolymers based on lactose (milk sugar) can be made from waste products of the dairy industry. Lactose is converted to lactic acid which is polymerised to produce polylactic acid polymer (PLA), which is similar to polyethylene except that it is biodegradable.

**Cellulose based biopolymers.** Cellophane is a polymer made from plant cellulose. It is transparent and has good folding properties so it is used in sticky tape and as a packaging material for foods and gifts.

Much research is under way to produce biopolymers from plant products which do not deprive humans or other animals of food sources, using toxin-free processes. For example, PHAs (polyhydroxyalkanoates) are being produced by bacterial fermentation of sugars and fats. Medical applications include their use as sutures, stents, orthopaedic pins, valves for veins, ligament and tendon grafts and implants.

Figure 58.3 Cellophane.

## Polyhydroxyalkanoate biopolymers

Polyhydroxyalkanoates (PHAs) consist of two different monomers (copolymers) joined by a condensation reaction. These biopolymers are made by bacteria such as *Alcaligenes eutrophus* which is grown in tanks. The polymer is separated out and purified. The common bacterium *E. coli* can be genetically modified to produce PHAs. This may produce better yields in a shorter time.

The properties of PHAs make them suitable for use in packing, in medicine, and in the manufacture of disposable items such as razors, nappies, cosmetic and shampoo containers. They are renewable, biodegradable and biocompatible. They are also flexible and stable to heat so they are possible substitutes for PET and polypropylene.

## Biopolymers in the food industry

Plant biopolymers are used extensively in the food industry as gums, stabilisers, emulsifiers and thickeners. They are used in products such as salad dressings, ice creams, soft drinks, and syrups.

**Xanthum gum** is used to create a pleasant texture in foods, increasing the viscosity of liquids (it is a thickening agent) and stabilising emulsions so that oil does not separate. It is used in breads, cakes, sauces, dressings, ice creams and yoghurts. Xanthum gum is secreted by the bacterium *Xanthomonas campestris*. It can be made by fermenting glucose, sucrose or lactose.

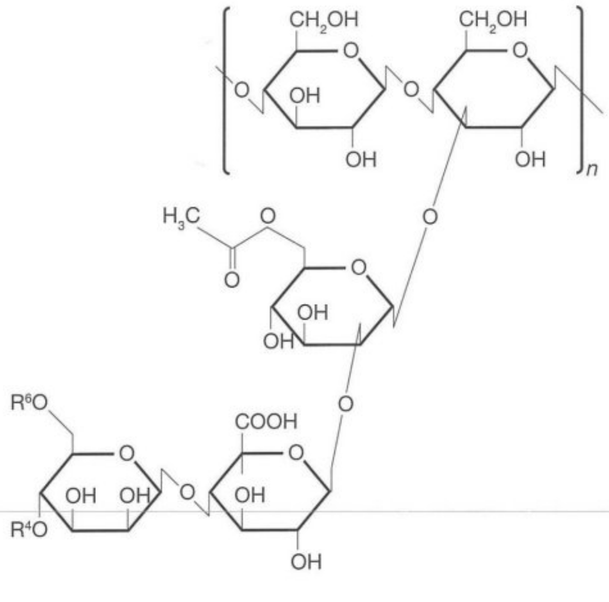


**Figure 58.4** Xanthum gum.

**Pectin** is a natural component of plants and is especially abundant in fruit such as apples and citrus fruit.

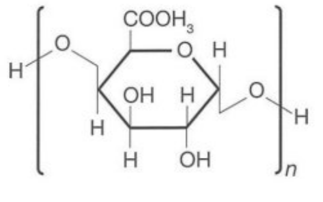


**Figure 58.5** Pectin.

Pectin is a gelling agent, thickening agent and stabiliser in foods such as jams. It is used as a protein stabiliser in acidified dairy products.

Research in Australia is looking at the industrial production of such biopolymers by plant cell culture, as this would provide an economic alternative to growing the whole plant.

## Advantages of biopolymers

- Biopolymers are **biodegradable**. Biodegradable packaging can be composted, reducing it to carbon dioxide, water and biomass. Coating paper with biodegradable polymers instead of polyethylene (polyethene) would eliminate the problem of plastic in paper compost.
- Biopolymers are being developed for medical uses such as artificial skin and organs for implants as well as coatings for medical devices and drugs. They are used to release medical ingredients slowly over time such as in slow release drug coatings and capsules. As they are **biocompatible**, the use of biopolymers in medical situations minimises possible adverse reactions by the body as happened with some breast implants. Sutures, staples and screws made of biopolymers such as PLA (polylactic acid), have the advantage of providing structural support, without causing reactions, and then eventually dissolving away.
- Biopolymers are made from **renewable** materials, rather than fossil fuels, thus conserving our finite fossil fuel resources.

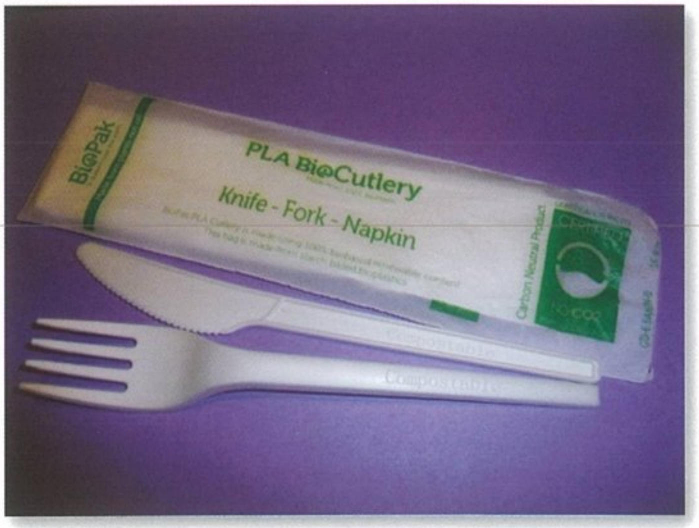


**Figure 58.6** Cutlery made from biobased renewable substances. The bag is made from a starch based polymer.

## Concerns about the manufacture and use of biopolymers

The use of biopolymers brings with it many advantages, however there are also some concerns.

**Resources such as land.** The resources used are grown on farms which could be used to produce food. The use of agricultural land to produce bioplastics and materials, or to produce biofuels, is not defensible in a world where there are millions of people starving. Perhaps this problem could be overcome by the use of waste cellulose (biomass).

**Genetic modification.** Many of the crops used to produce biopolymers have been genetically modified – a process that is causing increasing concern today.

**Use of chemicals such as fertilisers.** In some countries, such as America, corn is used and the growth of corn uses large amounts of nitrogen fertilisers, herbicides and insecticides.

**Degradability.** Although many biopolymers are biodegradable, PLAs apparently will not degrade in landfill conditions – where oxygen is not available. To dispose of them it is necessary to use a controlled environment using microbes or high temperatures.

## QUESTIONS

1. (a) Identify three advantages of polymers.
   (b) Identify three disadvantages of polymers.
   (c) Identify three commercially important monomers.
2. Define the following terms.
   (a) Biomass.
   (b) Biopolymer.
   (c) Biodegradable.
   (d) Biocompatible.
   (e) Renewable.
3. In many applications, polymers have replaced glass, natural textiles (cotton, wool and silk) and also metals. Outline advantages and disadvantages of polymers over the following.
   (a) Glass.
   (b) Textiles made from natural fibres.
   (c) Metals.
4. Polymers are all around us and used in everyday life. Name three types of materials you have studied that are not polymers.
5. Chemistry has played an essential role in the development of civilisation. Use two examples to show how the development of polymers has changed our world.
6. Explain why biopolymers are described as:
   (a) Renewable.
   (b) Biodegradable.
   (c) Biocompatible.
7. Discuss the need for alternative sources of polymers rather than petrochemicals.
8. One problem for society is the disposal of waste.
   (a) Outline a technological development in chemistry that has potential to help reduce this problem.
   (b) Evaluate the value of biopolymers in packaging.

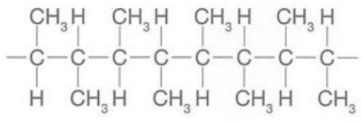
# 59 Revision Of Polymers

Polymers make up a rapidly expanding area of organic chemistry as more uses are found and different polymers are designed to accommodate those uses.

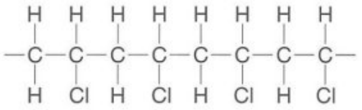
Use these multiple choice questions to help check your knowledge and understanding of concepts about polymers, their production and uses. As you revise this topic think about the advantages of polymers, their uses and the ways they have been beneficial to society. But also consider the harm they can cause and how we can minimise any harmful effects.

## QUESTIONS

1. Which substance is made of many monomers joined together in long chains?
   (A) Monomer.
   (B) Ethanol.
   (C) Polygen.
   (D) Polymer.
2. The process of chemically joining together many small molecules to form one very big chain is called:
   (A) Addition.
   (B) Condensation.
   (C) Polymerisation.
   (D) Distillation.
3. Which characteristic is typical of a thermoplastic polymer?
   (A) The absence of covalent cross-links between chains.
   (B) The presence of chemical cross-links between chains.
   (C) It does not soften or melt when heated.
   (D) It cannot be recycled.
4. The monomer of polyvinyl chloride is:
   (A) Chloroethane.
   (B) Chloroethene.
   (C) Diethylchloride.
   (D) Ethylene dichloride.
5. Which characteristic is typical of low density polyethylene.
   (A) It is tough and inflexible.
   (B) It is hard and rigid.
   (C) Its chains are highly branched.
   (D) It is a biodegradable.
6. Which alternative gives the name of the type of reaction that produced polyethylene from ethene.
   (A) Neutralisation.
   (B) Addition.
   (C) Refluxing.
   (D) Propagation.
7. Plasticisers are added to polymers in order to:
   (A) Give the polymer a solid plastic structure.
   (B) Increase the bulk of the polymer.
   (C) Make the polymer less rigid.
   (D) Prevent UV light making the polymer brittle.
8. This diagram shows part of a polymer chain.

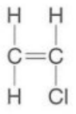


The monomer used to manufacture this polymer was:
   (A) 1,2-Dimethylethene.
   (B) 1,2,3-Trimethylpropene.
   (C) But-1-ene.
   (D) But-2-ene.
9. Naturally-occurring polymers such as cellulose, starch and cotton are called:
   (A) Biopolymers.
   (B) Petrochemicals.
   (C) Addition polymers.
   (D) Biomass.
10. The structure of a small section of a polymer chain can be represented as follows.

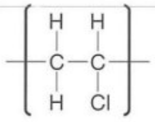


The repeating unit in this polymer is

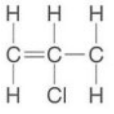
(A)



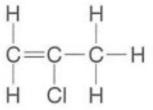
(B)



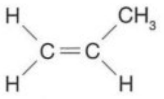
(C)



(D)



**11.** The two cups in the photograph are manufactured from a polymer composed of the monomer illustrated.



What would be the name of the polymer?

(A) Polyethylene.
(B) Polychlorethene.
(C) Polypropene
(D) Polymethylethene.

**12.** Identify the statement that applies to all addition polymers.

(A) They have the same general formula.
(B) They have the same molecular formula.
(C) They are all soluble in water.
(D) They are all formed from monomers with a C=C double bond.

**13.** This diagram represents

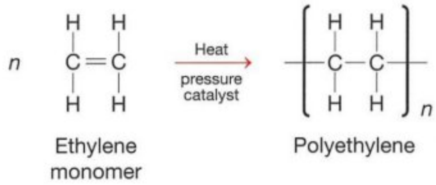
$$-[CH_2-CH_2]_n-$$

(A) A monomer.
(B) A polymer.
(C) The repeating unit in a polymer.
(D) The repeating unit in a monomer.

**14.** The three stages in the formation of an addition polymer are:

(A) Amalgamation, polymerisation, finalisation.
(B) Initiation, propagation, termination.
(C) Cathetisation, formation, completion.
(D) Initiation, catalysis, termination.

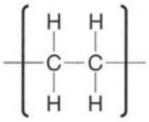
**15.** This equation represents the process of:



(A) Polymerisation of ethene.
(B) Polymerisation of ethane.
(C) Addition of polyethylene.
(D) Addition of polyethylane.

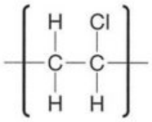
**16.** Which one of the following diagrams represents the repeating unit in PVC?

(A)



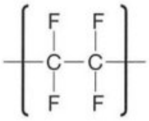
$-[CH_2-CH_2]-$

(B)



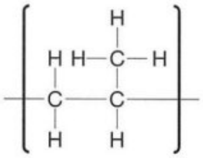
$-[CH_2-CHCl]-$

(C)



$-[CF_2-CF_2]-$

(D)



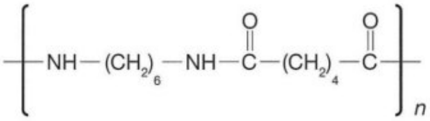
$-[CH_2-CH(CH_3)]-$

**17.** A problem with polymers is:

(A) They are very slow to decompose.
(B) They are difficult to dispose of.
(C) They release toxic substances when burnt.
(D) All of the above.

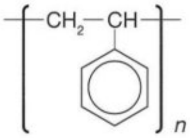
**18.** The diagram that represents nylon is:

(A)

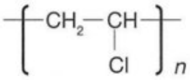


$-[NH-(CH_2)_6-NH-C(=O)-(CH_2)_4-C(=O)]_n-$

(B)

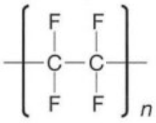


(C)



$-[CH_2-CH(Cl)]_n-$

(D)



$-[CF_2-CF_2]_n-$

**19.** Two examples of condensation polymers are:

(A) Nylon and polyester.
(B) Polyethylene and polyvinyl chloride.
(C) Teflon and polyester.
(D) Polystyrene and nylon.

**20.** Ethylene (ethene) is an important raw material for polymer production because it:

(A) Readily undergoes addition reactions.
(B) Is readily hydrogenated.
(C) Is less reactive then ethane.
(D) Occurs naturally in abundant reserves.

**INQUIRY QUESTION**

Polymers have been developed with a wide variety of properties and uses. Research the beneficial and harmful effects of this development on society and on the environment.

# 60 Revision Of Organic Chemistry

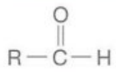
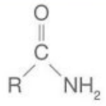
You have reached the end of Module 7 on organic chemistry. Well done. This chapter contains quick quiz questions on the work covered in this book. These questions can help you check that you know the basic facts about organic chemistry. It does not attempt to cover every fact you need to know. Use it as an indication of where your knowledge or understanding of concepts is weak and needs more revision, or perhaps help from your teacher.

Of course, chemistry is not just about facts. You should continue to discuss the issues that have come up during this section of your course and be aware of new developments in organic chemistry.

## QUESTIONS

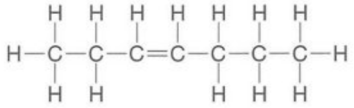
### Nomenclature

1. Carbon has an atomic number of 6 because its atoms contain 6 .......................... .
2. The electron configuration of carbon is .......................... .
3. In a double bond the number of electrons shared is .......................... .
4. The chemistry of carbon and its compounds is called .......................... chemistry.
5. A specific group of atoms, within a molecule, that is responsible for the chemical reactions of that molecule is called a .......................... group.
6. A series of compounds that all share a functional group is called a .......................... series.
7. Identify the functional group for each of the following homologous series.
   (a) Alcohols.
   (b) Carboxylic acids.
   (c) Alkenes.
   (d) Alkynes.
   (e) Amines.
   (f) Amides.
   (g) Alkanes.
   (h) Aldehydes.
   (i) Ketones.
8. A hydrocarbon series in which all the compounds have the general formula $C_nH_{2n+2}$ is called .......................... .
9. Write the general formula for the following homologous series.
   (a) Alkenes.
   (b) Alkynes.
   (c) Haloalkanes.
10. Fill in the table to match general formulas with the names of their homologous series.

| | |
|---|---|
|  $R-\overset{\overset{\displaystyle O}{\|}}{C}-H$ | |
| | Ketone |
|  | |
| | Amine |
| | Carboxylic acid |
| | Alcohol |

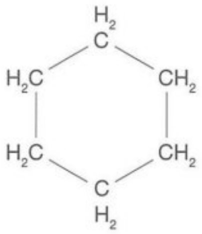
11. Name the following compounds.

(a)

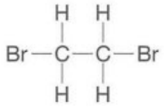


$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$

(b)

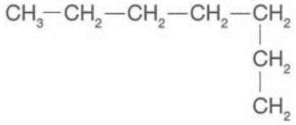


(c)

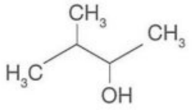


$Br-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-Br$

(d)

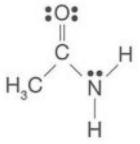


(e)

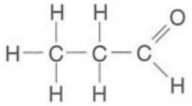


(f) $CH_3NH_2$

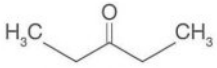
(g)



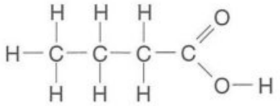
(h)



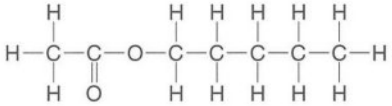
(i)



(j)



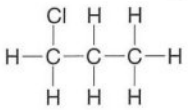
(k)



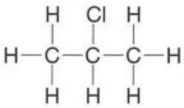
$H-\underset{H}{\overset{H}{C}}-\underset{\underset{\displaystyle O}{\|}}{C}-O-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$

12. Name the following pair of isomers.

(a)

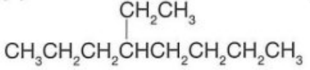


(b)



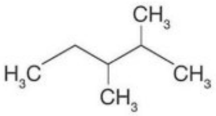
13. Name the simplest ketone and state the number of carbon atoms in its formula.
14. Name and state the formula for the simplest alkene.
15. Name and state the formula for the simplest alkane.
16. What series of organic compounds contains an $NH_2$ functional group attached to the end of a hydrocarbon chain?
17. Name the following compounds.

(a)

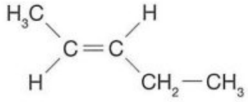


$CH_3CH_2CH_2\overset{CH_2CH_3}{\overset{|}{C}}HCH_2CH_2CH_2CH_3$

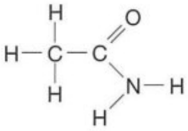
(b)



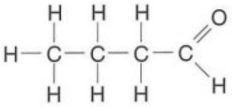
(c)



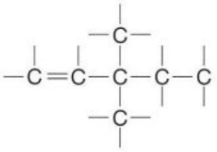
(d)



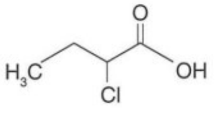
(e)



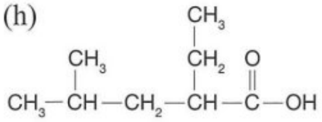
(f)



(g)



(h)



$CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2-\overset{CH_3}{\overset{|}{\overset{CH_2}{\overset{|}{C}H}}}-\overset{O}{\overset{\|}{C}}-OH$

18. Write structural formulas for the following compounds.
    - (a) Hex-2-ene.
    - (b) Pentan-2-one.
    - (c) Methylamine.
    - (d) Propanal.
    - (e) Propan-1-ol.
    - (f) 2-Methyl-propan-1-ol.
    - (g) 1-Bromo-2-chlorobutane.
19. Name the homologous series which have a carbonyl functional group.
20. To which homologous series does 3-chloropentane belong?

## Hydrocarbons

1. Name the bonds that hold atoms together in hydrocarbons.
2. How many electrons are shared in a triple bond?
3. Which type of model provides the most accurate information about the three-dimensional structure of molecules?
4. Name the three types of intermolecular forces between molecules of carbon compounds.
5. Of those three types of intermolecular forces, which type is strongest?
6. The shape of a propyne molecule with a triple bond is …………………… .
7. The shape of an ethane molecule is

……………………………………………………………………… .

8. The shape of an ethene molecule, with its double bond, is ……………………………………………… .
9. Do alkanes, alkenes and alkynes have polar or non-polar molecules?
10. The melting and boiling points of hydrocarbons are (high/low) because their intermolecular forces consist of only weak …………………… forces.
11. Are alkanes soluble in water or organic solvents?
12. Name two products of the complete combustion of hydrocarbons.
13. Identify three properties of hydrocarbons that mean care has to be taken in their use.
14. Name the process used to extract hydrocarbons from petroleum.
15. Which hydrocarbon would you expect to have the higher boiling point, one with four carbon atoms, or one with 10 carbon atoms?
16. Identify two physical properties of hydrocarbons.
17. In a non-polar bond, the difference in electronegativity of the bonded atoms is (small/large).
18. Carbon atoms form (polar/non-polar) bonds with oxygen, nitrogen, phosphorus, sulfur and the halogens.
19. What is the process of separating chemicals based on their different boiling points called?
20. Name three homologous series of hydrocarbons.

## Products Of Reactions Involving Hydrocarbons

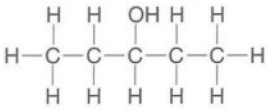
1. Name a substance produced by both complete and incomplete combustion of organic compounds.
2. A substance that undergoes complete combustion will burn (more/less) cleanly than one that undergoes incomplete combustion.
3. Substitution reactions occur in (saturated/unsaturated) compounds.
4. Alkenes takes part in (substitution/addition) reactions.
5. Identify four types of chemicals that can take part in addition reactions with unsaturated hydrocarbons.
6. Name any products you would expect to produce from the following substitution reactions in UV light.
    - (a) Propane and bromine water.
    - (b) Chlorine and butane.
    - (c) Cyclohexane and bromine water.
    - (d) Ethane and chlorine.
7. What precautions should you take when using bromine water?

8. State the products for addition reactions between the following chemicals.
   (a) Ethene and chlorine.
   (b) Ethene and water.
   (c) Ethene and bromine water.
   (d) Ethene and hydrogen iodide.
   (e) Propene and bromine water.
9. Only one product is formed from (addition/substitution) reactions.
10. Which halogen is most reactive and forms the most stable compounds – chlorine, bromine, fluorine or iodine?

## Alcohols

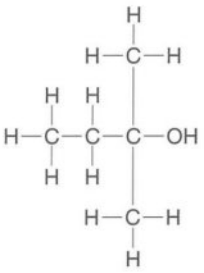
1. Name the following alcohols and state whether each is primary, secondary or tertiary.

(a)

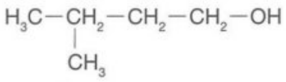


$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$

(b)



(c)



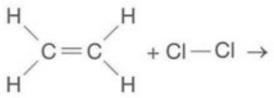
$H_3C-\underset{CH_3}{CH}-CH_2-CH_2-OH$

2. Alcohol molecules are (polar/non-polar).
3. State the functional group and general formula of an alcohol.
4. Identify the types of intermolecular forces in alcohols.
5. Identify the effect of hydrocarbon chain length on the solubility of an alcohol.
6. Identify the effect of hydrocarbon length on the boiling point of an alcohol.
7. Which has the higher boiling point, an alkane or an alcohol of similar size?
8. State the products formed by complete combustion of an alcohol.
9. To measure the enthalpy of combustion of an alcohol, you would use a (calorimeter/spirit burner).
10. Identify products for the following reactions.
    (a) Dehydration of ethanol.
    (b) Dehydration of propanol.
    (c) Substitution of hydrogen chloride into ethanol.
    (d) Oxidation of ethanol.
11. Primary alcohols are oxidised to ........................ and then to ........................ .
12. Secondary alcohols are oxidised to ........................ .
13. Tertiary alcohols (are/are not) oxidised.
14. Identify two ways you could make an alcohol.
15. Name three types of biofuels.
16. Name an organism that can be used to produce ethanol by fermentation.
17. What could you use to bring about the oxidation of a primary alcohol such as ethanol?
18. Is ethanol used in Australia as a supplement to or a replacement for fossil fuels such as petrol and diesel?
19. Which is a renewable fuel, ethanol or petrol?
20. Write an equation for the production of ethanol from ethene.

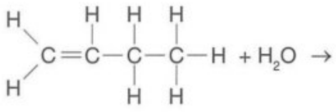
## Reactions Of Organic Acids And Bases

1. List the following series of carbon compounds in order of increasing melting and boiling points. (Assume you are comparing molecules of similar size.)
   Haloalkanes, carboxylic acids, alkanes, alcohols, esters.
2. Write the general formula for an ester.
3. Esters are (less/more) polar than alcohols.
4. The production of an ester from an alcohol and a carboxylic acid is called ........................ .
5. Name a technique used in the process of esterification to help prevent the escape of volatile reactants and products.
6. Complete the equations to show substitution reactions.
   (a) $CH_3-CH_2-CH_3 + Br_2 \rightarrow$
   (b) $CH_3-CH_2-Cl + NaOH(aq) \rightarrow$
7. Complete the equations to show addition reactions.

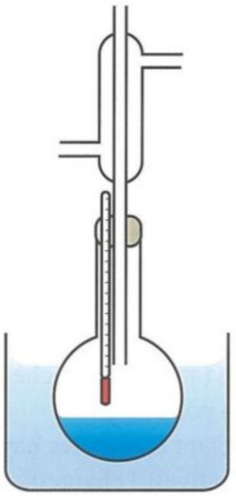
(a)



(b)



8. When bromine water is added to an alkane and an alkene, which reacts more rapidly? Explain.
9. Label the condenser in the esterification apparatus illustrated.

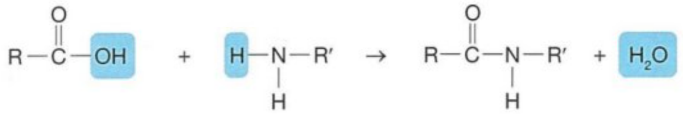


10 Write a general equation to show the hydrolysis of an ester.

11. The synthesis of soap by hydrolysis is called .........................

12. A chemical reaction which releases a small molecule such as water is referred to as .........................

13. Name two types of products from the following reaction.


$R-C(=O)-OH + H-N(H)-R' \rightarrow R-C(=O)-N(H)-R' + H_2O$

14. What group of compounds consists of an $NH_2$ functional group attached to the end of a hydrocarbon chain?

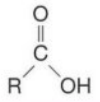
15. Name an acid and an alcohol that could be used to synthesise butyl hexanoate.

16. Amides are (more/less) polar than carboxylic acids.

17. Amines are (more/less) polar than alcohols.

18. Which homologous series of organic compounds has members which can act as a base?

19. Complete the table to compare amines, amides and carboxylic acids.

| Feature | Amine | Amide | Carboxylic acid |
|---|---|---|---|
| Functional group | $-NH_2$ | | |
| General formula | | |  |
| Polarity | Slightly polar | | |
| Melting and boiling points | | Highest | |
| Effect on indicators | | | |
| Reduced to | | | |

20. Which are stronger acids, carboxylic acids or halocarboxylic acids?

21. Hydrolysis reactions involve reactions with .........................

22. Identify two products of the hydrolysis of esters.

23. A soap is the salt of a long chain fatty ......................... with a ......................... ion attached.

24. Soaps and detergents reduce surface tension so we call them .........................

25. Soaps and detergents keep dirt and grease suspended in water, so we call them .........................

26. The polar head of a soap molecule is (hydrophilic/ hydrophobic).

27. These days, most detergents are made from molecules with (straight/branched) chains as these are (more/less) polluting.

28. Cationic surfactant molecules have a head that is (positively/negatively) charged.

29. Outline two-step reaction pathway you could use to convert propene to bromopropane.

30. Proteins are synthesised in our bodies from .........................

## Polymers

1. A small molecule that can bond in long chains is called a .........................

2. A large molecule made of many small monomers is called a .........................

3. Another name for ethene is .........................

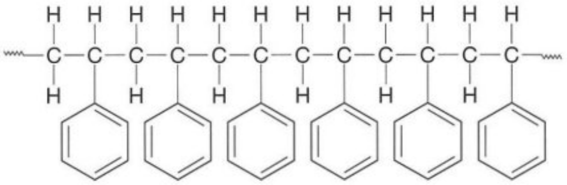
4. Polyethylene and polypropylene are (addition/ condensation) polymers.

5. What do we call the catalysts used to make polyethylene?

6. Branched chains occur in (low/high) density polyethylene.

7. PVC is made from the monomer .........................

8. This formula represents the structure of which common polymer?



9. A polymer that is mostly linear rather than branched, and can be recycled would be called a (thermoplastic/thermosetting) polymer.

10. Nylon, polycarbonates and polyurethanes are made by (addition/condensation) reactions.

11. Polymers that are biodegradable, renewable and biocompatible are called .........................

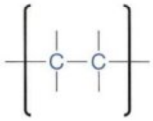
12. When two different monomers are used, a ......................... is produced.

13. The substance added to increase flexibility and ease of handling of a polymer is called a .........................

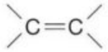
14. Additives used to bulk out a polymer are called .........................

15. Name an additive sometimes added to a polymer and state its function.

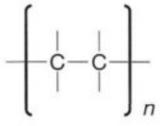
16. This structure is called the (repeating unit/ monomer) in polyethylene.



17. This structure is called a (monomer/polymer).



18. This structure is called a (monomer/polymer).



19. The monomer of PTFE is .........................

20. Polyester and nylon are (condensation/addition) polymers.