Organic chemistry

In this chapter, you will find out about:

- the unique properties of carbon
- hydrocarbons as compounds of carbon and hydrogen only
- the alkanes and their properties
- S isomerism

- the halogen compounds of the alkanes
- the alkenes
- the reactivity of the C=C double bond in alkenes

Carbon's amazing versatility

Carbon is a non-metal in Group IV of the Periodic Table. It forms covalent compounds. The uniqueness of carbon lies in the different ways in which it can form bonds. This shows itself even in the element itself. Carbon exists in several different forms. Two of the forms we have met earlier: diamond and graphite (see page 83). A third form, the fullerenes (Figure 10.1) and carbon nanotubes, have been discovered relatively recently and their exploitation is one of the major features of the exciting new area of research referred to as **nanotechnology**.

The ring structures that carbon can form have been highlighted recently in the revolutionary images G
 addition reactions

- the alcohols as a homologous series
- fermentation as a source of ethanol
- S ◆ comparing the methods of ethanol production
 - the reactions of ethanol
- G carboxylic acids as a homologous series
 - ethanoic acid as a weak acid
- S ◆ esterification.

of pentacene. The bonding in this hydrocarbon molecule has been observed electronically using an atomic force microscope. This microscope is able to probe structures at an atomic level. The images produced are the first to show the bonds in a molecule. It is even possible to see the bonds between the outer carbon atoms and the hydrogen atoms attached to them. This image joins the other iconic visualisations of the atomic world produced by this microscope technology, including the 'IBM logo' (see Chapter 2, Figure 2.22).

The remarkable versatility and complexity of the structures that carbon is able to form is the very basis of the different forms of life here on Earth.



h

Figure 10.1 a A computer image of the structure of carbon-60 (C_{60}) – the first fullerene to be discovered. The structure resembles the panelled structure of a modern soccer ball. **b** The revolutionary image of pentacene from the IBM research laboratory in Zurich (With kind permission of IBM Research - Zurich).

10.1 The unique properties

Amino acids, simple sugar molecules and even fats may be relatively simple molecules but the construction of complex molecules, such as long-chain carbohydrates and proteins, shows the versatility of carbon-containing compounds. The peak of this complexity must be DNA (deoxyribonucleic acid), the molecule that makes life possible (Figure 10.2).

Carbon is unique in the variety of molecules it can form. The chemistry of these molecules is a separate branch of the subject known as **organic** chemistry. Organic chemistry is the chemistry of carbon-containing compounds. There are three special features of **covalent bonding** involving carbon:

- Carbon atoms can join to each other to form long chains. Atoms of other elements can then attach to the chain.
- The carbon atoms in a chain can be linked by single, double or triple covalent bonds.
- Carbon atoms can also arrange themselves in rings.

Only carbon can achieve all these different bonding arrangements to the extent that we see. Indeed, there are more compounds of carbon than of all the other elements put together. Figure 10.3 gives some idea of how these bonding arrangements can produce different types of molecules.



Figure 10.2 Two ways of showing a section of the complex molecule DNA.





Figure 10.3 Carbon is very versatile.

🚱 Questions

- **10.1** What type of bonding do carbon atoms normally participate in?
- **10.2** What is the valency of carbon?
- **10.3** What are the two different structural forms of carbon? What is the name of the new form of carbon, discovered relatively recently?
- **10.4** What are the names of two different carbon-containing molecules that are important for living organisms?

10.2 Alkanes

What is a hydrocarbon?

Around six million compounds of carbon are already known! Because there are so many, it is helpful to pick out those compounds which have similar structures. One of the simplest types of organic compound is the **hydrocarbons**.

Key definition

hydrocarbon – a compound that contains carbon and hydrogen only.

The hydrocarbons that we study at this level can be subdivided into two 'families'. Some hydrocarbons are saturated. These molecules contain only single covalent bonds between carbon atoms. Since carbon has a valency of 4, the bonds not used in making the chain are linked to hydrogen atoms (see Figure 10.3, overleaf). No further atoms can be added to molecules of these compounds. This family of saturated hydrocarbons is known as the **alkanes**.

Key definition

alkanes – saturated hydrocarbons. Molecules of these compounds contain only single bonds between the carbon atoms in the chain and they have the general molecular formula C_nH_{2n+2} . Table 10.1 gives the names and formulae of the first six members of the series of alkanes. The simplest alkane contains one carbon atom and is called methane. Note that the names of this series of hydrocarbons all end in ane. The first part of the name (the prefix) tells you the number of carbon atoms in the chain. These prefixes are used consistently in naming organic compounds.

used contain The formulae given in Table 10.1 are the **molecular** formulae of the compounds. Each molecule increases by a $-CH_2$ — group as the chain gets longer (see Figure 10.3). Indeed, the formulae of long-chain alkanes can be written showing the number of $-CH_2$ — groups in the chain. For example, octane (C_8H_{18}) can be written as CH_3 — (CH_2)₆— CH_3 . The formulae of these molecules all fit the general formula C_nH_{2n+2} (where *n* is the number of carbon atoms present).

In organic chemistry, the structure of a molecule is also very important. Figure 10.4 shows the structural formulae of the first six alkanes in the series. A structural formula shows the bonds between the atoms. As the length of the hydrocarbon chain increases, the strength of the weak forces between the molecules (intermolecular forces or van der Waals' forces) is increased. This shows itself in the increasing boiling points of the members of the series (Table 10.1). The melting points and boiling points of the alkanes increase gradually. Under normal conditions, the first four members of the family are gases, and those between C_5H_{12} and $C_{16}H_{34}$ (which in short are called C_5 to C_{16} alkanes) are liquids. The compounds in the alkane family with 17 or more carbon atoms are waxy solids.

Every organic compound has three different formulae. The first of these is the **empirical formula** (see page 160). This formula is the simplest possible whole-number ratio of the atoms in a compound; thus for methane it is CH_4 , but for ethane it is CH_3 .

The second formula for any compound, and the most crucial, is the **molecular formula**. This represents the actual number of atoms present in the molecule; thus for methane it is CH_4 , for ethane it is C_2H_6 , and so on.

The final formula for any compound, and a highly important one, is the **structural formula** of the molecule of the compound. This formula shows all the atoms in the molecule and how they are bonded together. The structural formulae of the first six alkanes are shown in Figure 10.4 (overleaf).

Study tip

It is important to think carefully when you are asked to give the formula of a compound. Make sure you realise whether you are being asked for the molecular formula or the structural formula, and give the correct type.

When giving the structural formula of a compound, make sure you show all the atoms and all the bonds.

Remember, too, to count the bonds around each carbon atom you draw; there can only be four. It is worth practising drawing some of the regular molecules that are asked about.

С _л Н _{2л+2} СН ₄	1	-164	-	
				gas
C_2H_6	2	-87		gas
	3	-42	의 가지 가지 가지 가지 않는다. 	gas
	4	0	Land	gas
	5	+36	l ▼selasi	liquid
$C_{5}H_{12}$		+69	b.p. increasing	liquid
C	$_{4}H_{10}$ $_{5}H_{12}$ $_{6}H_{14}$	$_{4}H_{10}$ 4 $_{5}H_{12}$ 5 6	$_{3}H_{8}$ 5 $_{4}H_{10}$ 4 0 $_{5}H_{12}$ 5 +36 $_{6}$ +69	$_{3}H_{8}$ 5 $_{4}H_{10}$ 4 0 $_{5}H_{12}$ 5 +36 b.p. increasing

 Table 10.1
 Some details of the early members of the alkane series.



Figure 10.4 The structures of the first six alkanes.

Burning alkanes

One chemical property that all these alkanes have in common is that they burn very exothermically (Figure 10.5). They make good fuels. Controlling their availability and cost can have great political consequences. When they burn in a good supply of air, the products are carbon dioxide and water vapour:

methane	+	oxygen	\rightarrow	carbon dioxide	+	water
$CH_4(g)$	+	2O ₂ (g)	\rightarrow	$CO_2(g)$	+	$2H_2O(g)$
				carbon dioxide		
$2C_{0}H_{c}(g)$	+	$7O_{2}(g)$	\rightarrow	$4CO_2(g)$	+	6H ₂ O(g)

Methane forms the major part of natural gas. Propane and butane burn with very hot flames and are sold as liquefied petroleum gas (LPG). They are kept as liquids under pressure, but they vaporise easily when that pressure is released. In areas where there is no mains supply of natural gas, you may have seen propane tanks in gardens, which supply the fuel for heating systems. Cylinders of butane gas are used in portable gas fires in the home. Butane is also used in



Figure 10.5 A spectacular demonstration of methane burning on the hand.

portable camping stoves, blowtorches and gas lighters (Figure 10.6).

A homologous series

The family of alkanes has similar chemical properties. Together they are an example of a **homologous series** of compounds.

Key definition

homologous series – a family of organic compounds that:

- have the same general formula
- have similar chemical properties
- show a gradual increase in physical properties
 such as melting point and boiling point.

Questions

- 10.5 Write down the names and formulae of the first six alkanes.
- **10.6** Draw the structural formulae of methane and butane.
- **10.7** Plot a graph of the boiling points of the first six alkanes against the number of carbon atoms in the molecule. Comment on the shape of the graph.
- 10.8 What is the formula of the first alkane that is:a a liquid at room temperature and pressure?b a solid at room temperature?
- **10.9** Write a word equation for the complete combustion of ethane.
- 10.10 What is the major natural source of methane?
- **10.11** Draw a diagram of the arrangement of the electrons in the bonding of methane, showing just the outer (valency) electrons.



Figure 10.6 A butane portable camping stove.

10.3 Alkenes

Unsaturated hydrocarbons

The ability of carbon atoms to form double bonds gives rise to the **alkenes**. The alkenes are another family of hydrocarbons or homologous series.

Key definition

alkenes – unsaturated hydrocarbons. Molecules of these compounds contain a C=C double bond somewhere in the chain and they have the general formula C_nH_{2n} .

Alkenes have the general formula C_nH_{2n} (where *n* is the number of carbon atoms). Such molecules are unsaturated because it is possible to break this double bond and add extra atoms to the molecule.

The simplest alkene must contain two carbon atoms (needed for one C=C double bond) and is called ethene (Figure 10.7). Table 10.2 shows the molecular



Figure 10.7 The structures of the first three alkenes, and the bonding in ethene.

					Physical state at room temperature
Alkene	Molecular formula C _n H _{2n}	Number of carbon atoms	Boiling point / °C		gas
ethene	C_2H_4	2	-104		gas
propene	C ₃ H ₆	3	_47	•	gas
butene	C ₄ H ₈	4	-6	b.p. increasing	liquid
pentene	C_5H_{10}	5	+30	b.p. mere	

Table 10.2 Details of the first four alkenes.

formulae of the first alkenes. The boiling points of these compounds again show a gradual increase as the molecules get larger. Figure 10.7 also shows the structures of the first three alkenes.

Alkenes are similar to other hydrocarbons when burnt. They give carbon dioxide and water vapour as long as the air supply is sufficient:

ethene + oxygen \rightarrow carbon dioxide + water $+ 2H_{2}O(g)$ $C_2H_4(g) + 3O_2(g) \rightarrow$ $2CO_2(g)$

The presence of the C=C double bond in an alkene molecule makes alkenes much more reactive than alkanes (alkanes contain only C-C single bonds). Other atoms can add on to alkene molecules when the double bond breaks open. This difference produces a simple test for unsaturation.

It is the presence of the C=C double bond in an alkene molecule that gives the homologous series its characteristic properties. For this reason the C=C double bond is known as the functional group of the alkenes. We will meet other functional groups, such as that for the alcohols (-OH), later in the chapter. All the members of a particular homologous series contain the same functional group.

Chemical tests for unsaturation

If an alkene, such as ethene, is shaken with a solution of bromine in water, the bromine loses its colour. Bromine has reacted with ethene, producing a colourless compound:

ethene + bromine \rightarrow 1,2-dibromoethane $C_2H_4(g) + Br_2(aq) \rightarrow$ $C_2H_4Br_2(l)$ colourless orange-brown solution

The double bond in ethene breaks open and forms new bonds to the bromine atoms (Figure 10.8). This

258

type of reaction, where a double bond breaks and adds two new atoms, is known as an addition reaction. An alkane would give no reaction with bromine water; the solution would stay orange-brown (Figure 10.9). In an addition reaction, two substances add together to form

0

a single product. A similar colour reaction occurs between

alkenes and an acidified dilute solution of potassium manganate(VII). This solution is purple, and it turns colourless when shaken with an unsaturated compound. Again, an alkane would produce no change.



Figure 10.8 The addition of bromine to ethene.



Figure 10.9 The test for unsaturation: bromine water with a an alkane an b an alkene added and then shaken. The bromine water is decolorised by the alkene. There is no reaction with the alkane.

Activity 10.1 Testing alkanes and alkenes

Skills

- A03.1 Demonstrate knowledge of how to safely use techniques, apparatus and materials (including following a sequence of instructions where appropriate)
- A03.3 Make and record observations, measurements and estimates
- A03.4 Interpret and evaluate experimental observations and data

This activity compares the reaction with bromine water of several liquid alkanes and alkenes. The test for unsaturation is demonstrated. Small samples of the liquids are also ignited and the appearance of the flames compared.

A worksheet is included on the CD-ROM.

Questions

- **10.12** Write down the names and molecular formulae of the first four alkenes.
- 10.13 Draw the structures of ethene and propene.
- **10.14** What is the common empirical formula of the first four alkenes?
- **10.15** What do you observe if ethene is bubbled through bromine water?
- **10.16** Write a word equation for the reaction between ethene and bromine water.
- **10.17** Draw a diagram showing the arrangement of electrons in the bonding of ethene. Show just the outer (valency) electrons.

10.4 Hydrocarbon structure and isomerism

Naming organic compounds

101

The alkanes are a 'family' (or homologous series) of saturated hydrocarbons. Their names all end in *-ane*; Figure 10.10 shows a model of tetradecane ($C_{14}H_{30}$). The names of the first six alkanes were given in Figure 10.4 (page 256).

The prefixes to the names of the alkanes are standard and indicate the number of carbon atoms in the chain (see Table 10.1, page 255). So a compound in any homologous series with just one carbon atom will always have a name beginning with *meth*-, one with two carbon atoms *eth*-, and so on. Hence the names of the alcohols and carboxylic acids are as shown in Tables 10.4 and 10.6 (pages 265 and 270). When a halogen atom is introduced into a chain, the name of the compound contains a prefix indicating which halogen is present.

The different homologous series all have particular endings to their names (Table 10.3).

Many different organic compounds are formed when a hydrogen in the original alkane 'backbone' is replaced by another group. The product formed when ethene reacts with bromine in solution (Figure 10.8) illustrates the system of naming organic compounds.



- The product has two carbon atoms joined by a single bond. So it is named after ethane.
- The molecule contains two bromine atoms. It is called dibromoethane.



Figure 10.10 A model of a straight-chain alkane $(C_{14}H_{30})$.

Homologous series		
alkane	-ane	propane
alkene	-ene	propene
alcohol	-ol	propanol
carboxylic acid	-oic acid	propanoic acid

Table 10.3 The naming of the different homologous series.

The bromine atoms are not both attached to the same carbon atom. One bromine atom is bonded to each carbon atom. The carbon atoms are numbered 1 and 2. The full name of the compound is 1,2-dibromoethane.

Branched-chain alkanes exist where a hydrocarbon sidechain has replaced a hydrogen to produce a more complex molecule. In order to show where this side-chain is attached, we number the carbon atoms in the chain. This means that we can indicate where the side-chain is, in the name. The numbering always starts at one end of the chain. The counting starts at the end which keeps the number of the side-chain position as low as possible. You will see some examples of this numbering in the next section.

lsomerism

G

The system of naming compounds emphasises the importance of structure. Molecules with the same molecular formula can have different structures. The same number of atoms can be connected together in different ways. This is known as **isomerism**.

There are two different compounds with the molecular formula C_4H_{10} :

butane	H	Н	н	н	
	н — с —	_ c _	_ c _	_ c _	- н
	ļ	1	1	1	

burns in air to form CO_2 and H_2O liquefies at 0 °C

2-methylpropane



colourless gas burns in air to form CO_2 and H_2O liquefies at -12 °C

liquenes at -12 In butane, all four carbon atoms are arranged in one 'straight' main chain. However, the atoms do not have 'straight' main chain. However, the atoms do not have to be arranged in this way. The fourth carbon atom can to be arranged in this way. The fourth carbon atom can go off from the main chain to give the 'Y-shaped' or go off from the main chain to give the 'Y-shaped' or such as tructure of 2-methylpropane. Compounds branched structure of 2-methylpropane. Compounds such as these are known as **isomers**. The properties of such as these are known as **isomers**. The properties of these particular isomers are quite similar; the difference these particular isomers are quite similar; the difference shows itself mainly in their melting points and boiling shows itself mainly in their melting branched chains have points. Hydrocarbons containing branched chains have lower melting points and lower boiling points than lower melting points and lower boiling points than straight-chain compounds with the same number of carbon atoms.

All the alkane molecules with four or more carbon atoms possess isomers. For example, there are three isomers with the formula C_5H_{12} . The alkenes with four or more carbon atoms can show a different kind of isomerism. In this, the position of the C=C double bond is moved along the chain. There are two molecules with a 'straight' chain of four carbon atoms and the molecular formula C_4H_8 :

but-1-ene



The structures are different. Again, the carbon atoms are numbered. The number added to the formula indicates the position of the double bond. In but-1-ene the double bond is between carbon atoms 1 and 2, whereas in but-2-ene it is between carbon atoms 2 and 3.

Key definition

isomers – compounds that have the same molecular formula but different structural formulae.

Alkynes are a third family of hydrocarbons. In alkynes, the molecules contain a $C \equiv C$ triple bond. The simplest member is ethyne (C_2H_2) . This highly reactive gas used to be known as acetylene. It is used in oxy-acetylene welding torches. We do not study the alkynes any further at this level.

0

Activity 10.2 Modelling the structures of hydrocarbon isomers

Skills

- A03.3 Make and record observations, measurements and estimates
- A03.4 Interpret and evaluate experimental observations and data

The purpose of this activity is to use molecular models to explore the differences in structure between isomers.

Questions

E

10.18 Give the names of the first member of each of these homologous series:

- **a** the alkenes **b** the alcohols
- **c** the carboxylic acids.
- **10.19** Define the term isomer.
- **10.20** Draw the structures of but-1-ene and but-2-ene.
- **10.21** Draw the structures of the two isomers having the formula C_4H_{10} .
- **10.22** Draw two isomers of an alkane with five carbon atoms.

Models are built to answer questions as to how many isomers there are for certain given molecular formulae and to visualise the structural differences between certain isomers. The basis of different types of isomerism is modelled.

The approach can be extended by looking at computer-generated images of hydrocarbons at certain websites such as 'Molecule of the Month' (www.chm.bris.ac.uk/motm/motm.htm).

A worksheet is included on the CD-ROM.

- **10.23** Draw the structure of 1,2-dibromoethane.
- **10.24** Structures A to H are the structural formulae of some organic compounds.
 - **a** Give the letters that represent:
 - i two alkanes
 - ii two compounds which are not hydrocarbons
 - iii the molecule that is ethene.
 - **b** What is the name of **H**?



10.5 Chemical reactions of the alkanes

The alkanes are rather unreactive compounds. They are saturated, so they cannot take part in addition reactions. They are unaffected by acids or alkalis. However, they can take part in substitution reactions, particularly with the halogens.

Combustion

We have seen earlier that, when a hydrocarbon burns in a good supply of air or oxygen, the two products are carbon dioxide and water. The word equation for the burning of butane, for instance, is:

butane + oxygen \rightarrow carbon dioxide +water $2C_4H_{10}(g) + 13O_2(g) \rightarrow$ $8CO_2(g)$ $+ 10H_2O(g)$

The same products are obtained whichever alkane is burnt, so long as there is a sufficient oxygen supply.

However, if the air supply is limited, then the poisonous gas carbon monoxide can also be formed. Carbon monoxide is the product of incomplete combustion of a hydrocarbon. For example:

water methane + oxygen \rightarrow carbon monoxide + $+ 4H_{2}O(g)$ $2CH_4(g) + 3O_2(g) \rightarrow$ 2CO(g)

Carbon monoxide (CO) is toxic because it interferes with the transport of oxygen around our bodies by our red blood cells. Every year a number of people die accidentally from carbon monoxide poisoning because of poorly serviced gas fires in their homes. If the flues to the fire are blocked, insufficient air is supplied to the fire and carbon monoxide is produced. Simple carbon monoxide detectors can be bought in supermarkets, or electronic detectors fitted in homes (Figure 10.11).

Incomplete combustion can also produce fine particles of carbon itself. These have not even reacted to produce carbon monoxide. It is these fine carbon particles (or soot) which can glow yellow in the heat of a flame. They give a candle flame or the 'safety' flame of a Bunsen burner its characteristic yellow colour (Figure 10.12).

Study tip

Exam questions very frequently ask about the combustion products of organic fuels and hydrocarbons, in both the presence of sufficient and insufficient air. It is useful to make sure you know the word equations.

Questions on the combustion of hydrocarbons are also quite often asked in the form of equations that you have to complete by balancing them.



Figure 10.11 An electronic carbon monoxide detector.



Figure 10.12 The 'safety' flame of the Bunsen burner. The air supply to the flame is restricted.

substitution reactions with the halogens substitution reaction with chlorine is interesting the substitution reaction with chlorine is interesting

the sure it is a photochemical reaction:

methane + chlorine sunlight chloromethane + hydrogen chloride $CH_4(g) + Cl_2(g) \xrightarrow{\text{sunlight}} CH_3Cl(g) + HCl(g)$

Nethane and chlorine react in the presence of Methane and Methane and Presence of sunlight. Ultraviolet light splits chlorine molecules sunlight separate energised atoms. These atoms then react with methane. So the overall result is that react when a tom replaces (substitutes for) a hydrogen achlorine in a methane molecule to give chloromethane (CH₃Cl). The reaction can continue further as more hydrogen atoms are substituted. Compounds such h_{as} dichloromethane (CH₂Cl₂), trichloromethane $_{(CHCl_3)}$ and tetrachloromethane (CCl₄) are formed in this way.

Questions

- 10.25 Write a word equation for the incomplete combustion of methane.
- 10.26 What is the formula of carbon monoxide?
- 10.27 What causes a candle flame to be yellow?
- 10.28 Why is carbon monoxide toxic?
- 10.29 What are the name and formula of the first substitution product of the reaction between methane and chlorine?
- 10.30 The hydrocarbon propane is an important constituent of the fuel liquid petroleum gas (LPG). For the burning of propane in an excess of air, give:
 - **a** a word equation
 - **b** a balanced symbol equation.

Trichloromethane (CHCl3), or chloroform, was an early anaesthetic. However, the dose which can kill a patient is not much higher than the amount needed to anaesthetise a patient! So it was very easy to make mistakes. Something else was needed. Investigations were carried out on the anaesthetic effect of other substituted alkanes. In 1956, halothane was discovered. It is a more useful anaesthetic. Its formula is CF₃CHBrCl, and its structure is:

G

G





Substituted alkanes are also good organic solvents. 1,1,1-trichloroethane is one solvent that is used frequently, in dry-cleaning, for example.

- 10.31 What source of energy is required for the substitution reaction between methane and chlorine to take place?
- **10.32** Bromine reacts with alkanes in a similar way to chlorine. Hydrogen bromide is made in the substitution reaction between propane and bromine:

propane + bromine

- \rightarrow bromopropane + hydrogen bromide
- **a** Draw the structure of propane.
- **b** Draw the structure of a form of bromopropane.
- **c** The reaction between propane and bromine is a photochemical reaction. Suggest what is meant by photochemical.

10.6 Chemical reactions of the alkenes

Alkenes are much more reactive than alkanes. Under suitable conditions, molecules such as bromine, hydrogen and water (steam) will add across the C=Cdouble bond.

Bromination

This reaction is used as the chemical test for an unsaturated hydrocarbon (see Figure 10.9, page 258). Bromine water is decolorised when shaken with an alkene. The reaction will also work with the bromine dissolved in an organic solvent such as hexane.

G Hydrogenation

The addition of hydrogen across a C=C double bond is known as hydrogenation. Ethene reacts with hydrogen if the heated gases are passed together over a catalyst. The unsaturated ethane is the product:

ethene + hydrogen 150-300°C ethane C,H₄(g) + $H_2(g)$ $C_2H_6(g)$

Hydrogenation reactions similar to the reaction with ethene are used in the manufacture of margarine from vegetable oils.

The vegetable oils of interest include corn oil and sunflower oil. They are edible oils and contain long-chain organic acids (fatty acids). The hydrocarbon chains of these acids contain one or more C=C double bonds; they are unsaturated molecules (Figure 10.13). Oils such as sunflower oil are rich in polyunsaturated molecules. This means that the melting point is relatively low and the oil remains liquid at normal temperatures (and even with refrigeration). By hydrogenating some, but not all, of the C=C double bonds, the liquid vegetable oil can be made into a solid but spreadable fat (margarine).

Animal fats tend to be more saturated than vegetable oils and fats. The animal fats in cream can be made into butter. Many doctors now believe that unsaturated fats are healthier than saturated ones.





This is why margarines are left partially unsaturated: not all the C=C double bonds are hydrogenated. Olive oil is distinctive in having a high content of oleic acid, which is a monounsaturated fatty acid. Margarine can be made from olive oil without any hydrogenation.

0

Another important addition reaction is the one used in the manufacture of ethanol. Ethanol is an important industrial chemical and solvent. It is formed when a mixture of steam and ethene is passed over a catalyst of immobilised phosphoric(v) acid (the acid is adsorbed on silica pellets) at a temperature of 300 °C and a pressure of 60 atmospheres:

300 °C, 60 atmospheres ethanol steam phosphoric acid ethene + $C_2H_5OH(g)$ $C_2H_4(g) + H_2O(g)$

This reaction produces the ethanol of high purity needed in industrial organic chemistry.

😱 Questions ،

- 10.33 What are the molecular and structural formulae of 1,2-dibromoethane?
- 10.34 Write the word and chemical equations for the hydrogenation of ethene.
- 10.35 What is the catalyst used in hydrogenation reactions?
- 10.36 Unsaturated hydrocarbons take part in addition reactions.
 - **a** Write a word equation for the reaction between propene and hydrogen.
 - **b** Write a symbol equation for the reaction between butene and steam.
- **10.37** a Chloroethane is one of the chemicals manufactured from ethene.
 - İ. Name the compound that reacts with ethene in an addition reaction to give chloroethane.
 - ii Draw the structural formula of chloroethane.
 - **b** Chloroethane can also be made by a substitution reaction. What are the reagents and reaction conditions for this reaction?

10.7 Alcohols

IV. Ethanol is one of the best-known organic compounds. It is just one of a whole family of compounds – the alcohols. The alcohols are a homologous series of compounds that contain —OH as the functional group (Figure 10.14). A functional group is a group of atoms in a structure that determines the characteristic reactions of a compound.

reactions of Table 10.4 shows the molecular formulae of the early members of the series. The simplest alcohol contains one carbon atom and is called methanol. Note that the names all have the same ending (-ol). The general formula of the alcohols is $C_nH_{2n+1}OH$, and they can be referred to as the alkanols. The structural formulae of the first four alcohols are as shown in Figure 10.15. The early alcohols are all neutral, colourless liquids that do not conduct electricity.

Key definition

alcohols – a series of organic compounds containing the functional group –OH and with the general formula $C_nH_{2n+1}OH$



Figure 10.14 The structure of ethanol.

Alcohol	Molecular formula C _n H _{2n+1} OH	Boiling point / °C	
methanol	CH₃OH	65	
ethanol	C₂H₅OH	78	
propan-1-ol	C ₃ H ₇ OH	97	
butan-1-ol	C₄H ₉ OH	117	▼ I in grossing
pentan-1-ol	C ₅ H ₁₁ OH	137	b.p. increasing

Table 10.4 Some alcohols.





Making ethanol

Hydration of ethene

The industrial method of making ethanol involves the addition reaction that we saw at the end of Section 10.6. In this, ethene and steam are compressed to 60 atmospheres and passed over a catalyst (immobilised phosphoric(v) acid) at 300 °C:

ethene	+	steam	300°C, 60 atmospheres	ethanol
$C_2H_4(g)$	+	$H_2O(g)$	\rightarrow	$C_2H_5OH(g)$

Ethanol is an important solvent and a raw material for making other organic chemicals. Many everyday items use ethanol as a solvent. These include paints, glues, perfumes, aftershave, etc.

Fermentation

Ethanol and carbon dioxide are the natural waste products of yeasts when they ferment sugar. Sugar is present in all fruit and grains, and in the sap and nectar of all plants. Yeasts are found everywhere. The ancient Babylonians and Egyptians found that, if they crushed grapes or germinated grain, the paste would bubble

Activity 10.3 The fermentation of glucose using yeast

Skills

 A03.1 Demonstrate knowledge of how to safely use techniques, apparatus and materials (including following a sequence of instructions where appropriate)
 A03.3 Make and record observations, measurements and estimates

Beer and wine are produced by fermenting glucose with yeast. Yeast contains enzymes that catalyse the breakdown of glucose to ethanol and carbon dioxide. In this experiment, a glucose solution is left to ferment. The products of fermentation are then tested. The solutions generated by the class may be retained for a demonstration of distillation (see Activity 2.3).

A worksheet is included on the CD-ROM.

and produce an intoxicating drink. Pasteur discovered that yeasts are single-cell, living fungi. They ferment sugar to gain energy – by anaerobic respiration. As ethanol is toxic to yeast, fermentation is self-limiting. Once the ethanol concentration has reached about 14%, or the sugar runs out, the multiplying yeast die and fermentation ends. The best temperature for carrying out the process is 37 °C. The reaction is catalysed by enzymes in the yeast:

glucose $\xrightarrow{\text{yeast}}$ ethanol + carbon dioxide $C_6H_{12}O_6(aq) \xrightarrow{\text{enzymes}} 2C_2H_5OH(aq) + 2CO_2(g)$

Alcoholic drinks such as beer and wine are made on a large scale in vast quantities in copper or steel fermentation vats. Beer is made from barley, with hops and other ingredients added to produce distinctive flavours. Wine is made by fermenting grape juice. Beer contains about 4% by volume of ethanol, whereas wine contains between 8% and 14%. Stronger, more alcoholic, drinks are made in one of two ways. Fortified wines, such as sherry and port, have pure ethanol added to them. Spirits, such as whisky, brandy and vodka, are made by distillation (see page 30). Fermentation can be carried out in the laboratory using the apparatus in Figure 10.16. The air-lock allows gas to escape from the vessel but prevents airborne bacteria entering.

Study tip

Fermentation is an anaerobic process. It takes place under conditions where there is no air or oxygen available.

oxygen available. Therefore, there is no oxygen (O_2) present in the equation for the reaction taking place.

Carbon dioxide is the gas produced in the reaction.

Comparing the methods of ethanol production

The two different methods of producing ethanol have their respective advantages and disadvantages. The method chosen will depend on the availability of resources and the main purpose for producing the ethanol. A comparison of the methods is summarised in Table 10.5.

The ethanol produced by fermentation comes from a renewable resource. When used as a fuel, the ethanol produced in this way is potentially 'carbon neutral'. The carbon dioxide released during fermentation and by burning the fuel is balanced by that absorbed from the atmosphere by the crop, usually sugar cane, as it grows.



Figure 10.16 A laboratory fermentation vessel.

Questions

- 10.38 Name the first three members of the alcohol homologous series.
- 10.39 Write the word and chemical equations for the hydration of ethene by steam.
- 10.40 What are the essentials needed for the production of ethanol by fermentation?
- 10.41 Ethanol can be made by the addition of water to ethene. Ethanol can also be made by the fermentation of sugars using the apparatus shown here.



- **a** Name the gas produced during the fermentation shown above.
- **b** This gas escapes through the piece of apparatus labelled A. What is the main purpose of this piece of apparatus?
- **c** What must be added to a sugar solution to make it ferment?
- **d** At about what temperature does fermentation take place at its fastest rate?
- e Explain your choice of temperature given in **d**.
- **10.42** Methanol and ethanol are members of a homologous series.
 - **a** Draw the molecular structures of methanol and ethanol.
 - **b** Explain what the term homologous series means.

10.43 What are the names and structures of the two isomers of propanol?

Ethanol by the hydration of ethene	Ethanol by fermentation
originates from a non- renewable resource – petroleum	made from readily renewable resources
small-scale equipment capable of withstanding pressure	relatively simple, large vessels
a continuous process	a batch process – need to start process again each time
a fast reaction rate	a relatively slow process
yields highly pure ethanol	ethanol must be purified by subsequent distillation – though fermented product can be used as it is for some purposes
a sophisticated, complex method	a simple, straightforward method

 Table 10.5
 A comparison of the methods of ethanol production.

10.8 The reactions of ethanol

Ethanol as a fuel

Ethanol burns with a clear flame, giving out quite a lot of heat:

ethanol	+	oxygen	\rightarrow	carbon dioxide	+	water
C,H ₅ OH(l)					+	$3H_2O(g)$

On a small scale, ethanol can be used as methylated spirit (ethanol mixed with methanol or other compounds) in spirit lamps and stoves. However, ethanol is such a useful fuel that some countries have developed it as a fuel for cars.

Brazil, whose climate is suitable for growing sugar cane, started producing ethanol fuel in 1973. It has one of the largest ethanol fuel programmes in the world (Figure 10.17). The ethanol is produced by fermenting crop residues, and as such is considered a biofuel. Ethanol and other biofuels are used in motor vehicles as an alternative to fuel obtained from oil deposits. Ethanol produced by fermentation of sugar from sugar cane has been used as an alternative fuel to gasoline (petrol), or mixed with gasoline to produce 'gasohol'. It



Figure 10.17 An ethanol and petrol station in Sao Paulo, Brazil.

is a renewable resource and has the potential to reduce petroleum imports. 'Gasohol' now accounts for 10% of the gasoline sales in the USA. 'Gasohol' and other 'oxygenated fuels' have the advantage of reducing the emissions of carbon monoxide from cars. It is thought that biofuels can reduce environmental damage if developed and controlled properly, but overuse of biofuels could be harmful if it leads to more deforestation to grow biofuel crops.

Study tip

G

Exam questions often ask you to balance the equations for the combustion reactions of either hydrocarbons or alcohols.

Make sure you balance the oxygen (O) atoms in the equation. Remember, with alcohols, that there is an oxygen atom in the alcohol molecule itself.

Oxidation

Vinegar is a weak solution of ethanoic acid (previously called acetic acid). It is produced commercially from wine by biochemical oxidation using bacteria (Acetobacter). Wine can also become 'vinegary' if it is left open to the air. The same oxidation can be achieved quickly by powerful oxidising agents such as warm acidified potassium manganate(vII):

+ oxygen \rightarrow ethanoic acid + water ethanol from oxidising agent

 $H_{2}O$

2[O] \rightarrow CH₃COOH C₂H₅OH +

The colour of the potassium manganate(VII) solution turns from purple to colourless.



Ethanol can be dehydrated to produce ethene. This is one way of preparing ethene in the laboratory. Ethanol vapour is passed over a heated catalyst. The catalyst can be aluminium oxide or broken pieces of porous pot. Ethene is not soluble in water, so it can be collected as shown in Figure 10.18.

Esterification

Alcohols react with organic acids (see Section 10.9) to form sweet-smelling oily liquids known as esters. For example:

ethanoic acid + ethanol \rightarrow ethyl ethanoate + water $CH_3COOH(l) + C_2H_5OH(l)$ \rightarrow CH₃COOC₂H₅(l) + H₂O(l)

Concentrated sulfuric acid is added as a catalyst for this esterification reaction.

Alcohol and health

Ethanol is the only alcohol that is safe to drink. It must only be drunk in moderation, if at all. Methanol is very toxic and even in small amounts can cause blindness and death.

Ethanol mixes totally with water, which takes it everywhere in the body that water goes. The amount of alcohol that a person may drink varies with age, sex, weight and drinking history.

Heavy drinking can cause a healthy liver to become fatty and enlarged. Eventually scarring (cirrhosis) can cause liver failure and death. Prolonged heavy drinking can eventually damage the muscle tissue of the heart. It may also lead to some long-term damage to the brain. Alcohol is a depressive drug and can be addictive. Drinking heavily on a particular occasion produces drunkenness, during which speech becomes slurred, vision is blurred and reaction times are slowed. Some cultures forbid its use.

Questions

- 10.44 Sugar cane grows quickly in tropical areas. Sugar can be fermented to make ethanol. Either ethanol or mixtures of petrol and ethanol (gasohol) can be used as the fuel for cars. a Ethanol consists of organic molecules.
 - - What type of compound is ethanol?
 - Ethanol has the formula C_2H_5OH . ii Draw its structure.
 - **b** Gasohol boils over a temperature range of 40–150 °C in the laboratory. Ethanol has a boiling point of 78 °C. Draw a labelled diagram to show how a sample of ethanol may be obtained from gasohol.
- 10.45 Ethanol is a fuel. In laboratories that do not have a gas supply, it may be used in a spirit burner.
 - a The diagram shows a spirit burner being used to heat a beaker of water. A black solid is formed on the bottom of the beaker.
 - Name the black substance formed on the beaker.
 - Suggest why the black substance is ii formed when the ethanol is burnt.
 - **b** Both methanol and ethanol burn in an excess of air to form the same products.



- Name these products. i
- Suggest why it is not possible to set fire ii to the contents of a bottle of wine.
- 10.46 Write the word and chemical equations for the oxidation of ethanol to ethanoic acid (use [O] for the oxidising agent).
- 10.47 What alkene is produced when propan-1-ol is dehydrated?
- 10.48 Name the ester produced when ethanol reacts with ethanoic acid. Write the word equation for the reaction. What is the catalyst for the reaction?

Ø 10.9 Organic acids and esters

Carboxylic acids

The carboxylic acids are another homologous series of organic compounds. All these acids have the functional group —COOH attached to a hydrocarbon chain. Table 10.6 (overleaf) shows the molecular formulae of the first two members of the series. The compounds have the general formula $C_n H_{2n+1} COOH$ (or $C_n H_{2n+1} CO_2 H$). Figure 10.19 shows the structural formulae of the first four acids in the series.

The first two acids in the series are liquids at room temperature, although ethanoic acid will solidify if the temperature falls only slightly. The acids dissolve in water to produce solutions that are weakly acidic. Methanoic acid is present in nettle stings and ant stings, while ethanoic acid (once called acetic acid) is well known as the acid in vinegar.

Study tip

When naming a carboxylic acid, remember that the carbon atom of the acid group is part of the chain. It is counted as the first carbon in the chain.

That is why CH₃COOH is the formula of ethanoic acid: there are two carbon atoms in the molecule.

Ethanoic acid as a weak acid

Whereas a strong acid such as hydrochloric acid is completely split into ions, ethanoic acid only partially dissociates into ions in water. A dynamic equilibrium is set up in the solution. The solution does contain an excess of hydrogen ions (H⁺) over hydroxide ions (OH⁻), so the solution is weakly acidic (see page 143):

ethanoic acid \rightleftharpoons ethanoate ions + hydrogen ions $CH_3COOH(aq) \rightleftharpoons CH_3COO^{-}(aq) +$ $H^+(aq)$

G

			Boiling point	
Carboxylic acid	Molecular formula C _n H _{2n+1} COOH	Melting point / °C	/°C	L
methanoic acid	нсоон	9	101	m.p. and b.p. increasing
ethanoic acid	СН₃СООН	17	118	I m.p. and

Table 10.6 The first two carboxylic acids.



Figure 10.19 The structures of methanoic, ethanoic, propanoic and butanoic acids.

A solution of the acid will show the characteristic reactions of an acid. For example, it will react with bases to form salts:

ethanoic acid + sodium hydroxide

 \rightarrow sodium ethanoate + water

CH3COOH(aq) + NaOH(aq) \rightarrow CH₃COONa(aq) + H₂O(l)

Vinegar can be used as a 'descaler' in hard water areas. The ethanoic acid in vinegar reacts with limescale (calcium carbonate), producing carbon dioxide and dissolving the scale:

calcium carbonate + ethanoic acid

 \rightarrow calcium ethanoate + water + carbon dioxide $CaCO_3(s) + 2CH_3COOH(aq)$

 \rightarrow (CH₃COO)₂Ca(aq) + H₂O(l) + CO₂(g)

Commercial descalers are often based on weak acids, methanoic acid for instance, or on moderately strong acids such as sulfamic acid.

C

Activity 10.4 The acidic reactions of ethanoic acid

Skills

- A03.1 Demonstrate knowledge of how to safely use techniques, apparatus and materials (including following a sequence of instructions where appropriate) A03.2 Plan experiments and investigations
- A03.3 Make and record observations, measurements and estimates
- A03.4 Interpret and evaluate experimental observations and data

This activity tests ethanoic acid with Universal Indicator solution, magnesium, sodium hydroxide solution and sodium carbonate solution. These reactions are then compared with those of a hydrochloric acid solution of the same concentration. The comparison shows that ethanoic acid is a weak acid.

A worksheet is included on the CD-ROM.

Esterification

Ethanoic acid will react with ethanol, in the presence of a few drops of concentrated sulfuric acid, to produce ethyl ethanoate. The concentrated sulfuric acid is a catalyst for the reaction:

ethanoic acid + ethanol $\xrightarrow{\text{conc. H}_2SO_4}$ ethyl ethanoate + water $CH_{3}COOH(l) + C_{2}H_{5}OH(l) \rightarrow CH_{3}COOC_{2}H_{5}(l) + H_{2}O(l)$ This type of reaction is known as esterification. The structure of ethyl ethanoate is shown below:



Ethyl ethanoate is just one example of an ester. This family of compounds have strong and pleasant smells. Many of these compounds occur naturally. They are responsible for the flavours in fruits and for the scents of flowers (Table 10.7). We use them as food flavourings and in perfumes. The ester group or linkage is also found in complex molecules such as natural fats and oils, and in man-made fibres such as Terylene (see page 288).

Ester	Smell or flavour
ethyl 2-methylbutanoate	apple
3-methylbutyl ethanoate	pear
1-methylbutyl ethanoate	banana
butyl butanoate	pineapple
octyl ethanoate	orange
methylpropyl methanoate	raspberry
pentyl butanoate	strawberry

Table 10.7 The smells of esters.

Activity 10.5 Making esters from alcohols and acids

Skills

9

- A03.1 Demonstrate knowledge of how to safely use techniques, apparatus and materials (including following a sequence of instructions where appropriate)
- A03.3 Make and record observations, measurements and estimates
- A03.4 Interpret and evaluate experimental observations and data

In this activity, the reactions between a range of alcohols and acids are carried out on a test-tube scale, to produce small quantities of a variety of esters quickly. The characteristic odours of the different esters are then tested.

A worksheet is included on the CD-ROM.

Questions

G

- **10.49** Ethanol is a product of many fermentation reactions. The molecular formula of ethanol is C_2H_5OH .
 - a Draw the structural formula for ethanol.
 - **b** When ethanol is heated with an excess of acidified potassium dichromate, it is converted to ethanoic acid:

 $\begin{array}{c} C_2H_5OH \rightarrow CH_3COOH \\ {}_{ethanol} \qquad ethanoic \ acid \end{array}$

- What type of chemical reaction is this?
 C Some synthetic flavourings are made by reacting an alcohol with a carboxylic acid: alcohol + carboxylic acid → ester + water What other substance and conditions are needed to carry out this reaction?
- **d** The structure of the ester propyl butanoate is shown here.



Draw the structural formula of the carboxylic acid from which this ester is made.

- **10.50** The flavour and smell of foods are partly due to esters. An ester can be made from ethanol and ethanoic acid.
 - **a** Name this ester.
 - **b** Write a word equation for the reaction between ethanol and ethanoic acid.

10.51 The diagram below shows a method used in France to change wine into vinegar. Living organisms (*Acetobacter*) bringing about a chemical change and producing a marketable product is an example of traditional biotechnology.

0



- a What type of reaction has occurred in the vat?
- **b** Name a chemical reagent, other than oxygen, that can change ethanol into ethanoic acid.
- **c** Name a technique that could be used to separate ethanoic acid from the other liquids in vinegar.
- **d** Describe a chemical test that would distinguish between wine and vinegar.

Summary

You should know:

- that carbon forms a vast range of compounds and that the study of their properties is known as organic chemistry
- that hydrocarbons are the simplest of the many types of organic compound
- about the different 'families' (or homologous series) of hydrocarbons: the alkanes are saturated hydrocarbons, while the alkenes are a second series of unsaturated hydrocarbons
- how the alkanes are important fuels and that the simplest, methane, is the main component of natural gas
- that the simple test for unsaturated hydrocarbons is the fact that they decolorise bromine water
- that there are many more different series of organic compounds, each with a different functional group attached to a hydrocarbon backbone

that the alcohols are a separate series of compounds, the most important of which is ethanol
that ethanol has major uses as a fuel and as a solvent
that hydrocarbons and alcohols burn in excess air to produce carbon dioxide and water vapour
they can be isomers of each other
how alkanes undergo substitution reactions with the halogens, but alkenes are more reactive and take
that oxidation of alcohols produces a further series of compounds, the carboxylic acids
how alcohols and carboxylic acids react to produce esters in reactions known as esterification.

End-of-chapter questions

There are very many more compounds of the element carbon than there are of any other element. Why are these compounds particularly important to us?

2 These three compounds, A, B and C, belong to three different homologous series.

C_2H_4	C_2H_6	C_2H_5OH
Α	В	С

a	What is meant by the term homologous series ?	[1]
b	To which homologous series does each compound belong?	[3]
с	Give a chemical test which could distinguish between compound A and compound B. Describe the	
	test and give the result for compounds A and B.	[3]
d	How could compound A be chemically converted to compound C?	[2]
e	What is the name of the process which forms compound C from sugar?	[1]

But-1-ene is a typical alkene. It has the structural formula shown below.

CH₃-CH₂-CH=CH₂

The structural formula of cyclobutane is given below.



a	The	se two hydrocarbons are isomers.	[2]
		1 + 1 = 100 MPr	[1]
	1	Define the termula of another isomer of out a supply and eveloputane Name	
	ii	Define the term <i>isomer</i> . Draw the structural formula of another isomer of but-1-ene and cyclobutane. Name	[3]
	iii	Define the term <i>isomer</i> . Draw the structural formula of another isomer of but-1-ene and cyclobutane. Name Describe a test which would distinguish between but-1-ene and cyclobutane. Name	
		Describe a test which would distinguish the reagent used and give the result for both isomers. Chapter 10: Organic chemistry	273

- **b** Describe how alkenes, such as but-1-ene, can be made from alkanes. c Name the product formed when but-1-ene reacts with each of the following:
- - i bromine
 - hydrogen ii
 - iii steam.

Ь

[Cambridge IGCSE® Chemistry 0620/32, Question 4, June 2010]

Butane is an alkane. It has the following structural formula. 4



The equation for the complete combustion of butane is given below. Insert the two missing volumes. a $2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(g)$ volume of gas / cm³ 40 Butane reacts with chlorine to form two isomers of chlorobutane. i What type of reaction is this? ii Explain the term isomer. iii Draw the structural formulae of these two chlorobutanes. c One of the chlorobutanes reacts with sodium hydroxide to form butan-1-ol. Butan-1-ol can be oxidised to a carboxylic acid.

- State a reagent, other than oxygen, which will oxidise butan-1-ol to a carboxylic acid. i
- ii Name the carboxylic acid formed.
- iii Butan-1-ol reacts with ethanoic acid to form an ester. Name this ester and give its structural formula, showing all the individual bonds.

[Cambridge IGCSE® Chemistry 0620/31, Question 6, June 2012]

5 Propenoic acid is an unsaturated carboxylic acid. The structural formula of propenoic acid is given below.



i	Describe how you could show that propenoic acid is an unsaturated compound. Give details	
	of the test and the result.	[2]
ii	Without using an indicator, describe how you could show that a compound is an acid.	(-)
	Give details of the test and the result.	[2]
Pro	openoic acid reacts with ethanol to form an ester. Deduce the name of this ester. Draw its	L
stru	uctural formula, showing all bonds.	[3]
An	organic compound has a molecular formula $C_6H_8O_4$. It is an unsaturated carboxylic acid	LJ.
One	e mole of the compound reacts with two moles of sodium hydroxide.	
	Explain the phrase molecular formula.	[0]
	One mole of this carboxylic acid reacts with two moles of sodium hydroxide	[2]
l	How many moles of -COOH groups are there in one mole of this compound?	[-]
i 1	What is the formula of another functional group in this compound?	[1]
I	Deduce a structural formula of this compound	[1]
	[Cambridge ICCSE@ Charriet a sector	[1]
	ii Pro stru An Ono	 of the test and the result. ii Without using an indicator, describe how you could show that a compound is an acid. Give details of the test and the result. Propenoic acid reacts with ethanol to form an ester. Deduce the name of this ester. Draw its structural formula, showing all bonds. An organic compound has a molecular formula C₆H₈O₄. It is an unsaturated carboxylic acid. Due mole of the compound reacts with two moles of sodium hydroxide. Explain the phrase molecular formula. One mole of this carboxylic acid reacts with two moles of sodium hydroxide. How many moles of -COOH groups are there in one mole of this compound? What is the formula of another functional group in this compound? Deduce a structural formula of this compound.

ambridge IGCSE® Chemistry 0620/33, Question 5, November 2012]

[2]

[1] [1]

[1]

[2]

[1]

[2]

[2]

[1]

[1]

[3]