Figure 12.5 Uses of sulfuric acid

For the examination you need to be able to state the essential operating conditions for the manufacture of sulfuric acid by the Contact process (Figure 12.6), and to interpret these in terms of reaction kinetics and the position of equilibrium.
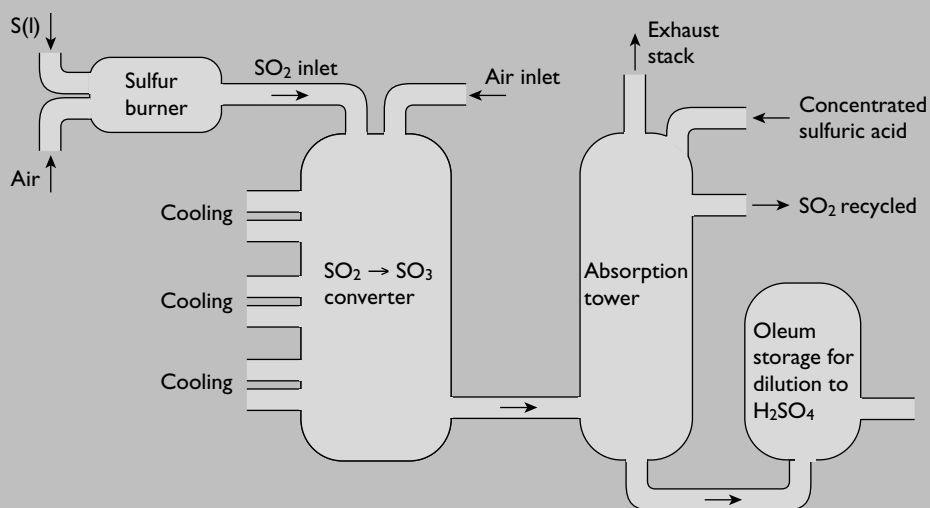

Figure 12.6 The Contact process

The conditions chosen are a compromise:

- pressure — around 100–200 kPa (or 1–2 atm)
- temperature — around 700 K
- catalyst — vanadium(V) oxide (although some plants now use ruthenium which is more expensive)

Formulae

It is important to understand and know when to use the different ways of representing organic molecules. Read the examples carefully so that you are in no doubt.
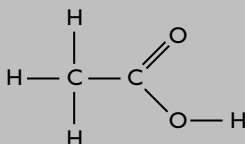
Molecular formula

A molecular formula summarises the numbers and types of atom present in a molecule. The functional group is shown separately from the hydrocarbon chain — for example, C_2H_5OH rather than C_2H_6O.

Structural formula

A structural formula requires the minimum detail to provide an unambiguous structure for a compound. For example, $CH_3CH_2CH_2OH$ is acceptable for propan-1-ol whereas C_3H_7OH is not.

Displayed formula

A displayed formula shows the correct positioning of the atoms and the bonds between them. For example ethanoic acid, which has the structural formula CH_3CO_2H, has the displayed formula:


You may be asked for 'partially displayed formulae'. This means that you have to show the positions of atoms and the bonds between them at the site of a reaction.

Skeletal formula

This is a simplified representation of an organic molecule that concentrates on the carbon 'backbone' of a molecule, together with any functional groups. Bonds to hydrogen atoms are *not* normally shown, unless they form part of a functional group. The skeletal formula for butan-2-ol is shown below:
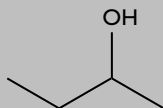

For more complex structures, where the three-dimensional structure of the molecule may be important, a 'partial-skeletal' formula may be used. This shows the geometry of key bonds to hydrogen (and other) atoms in the molecule, as shown below:

Approved: 0777 023 444
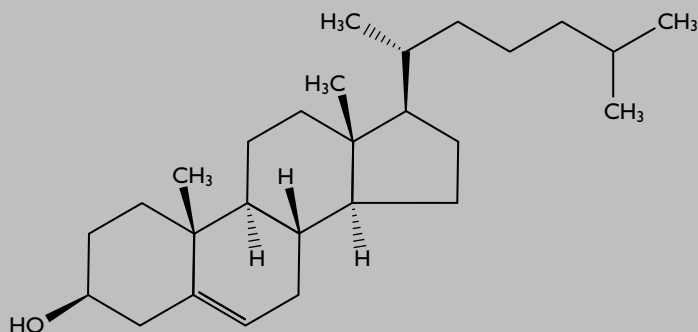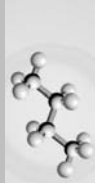
Three-dimensional structures

There are times when you need to be able to show the three-dimensional structures of relatively simple molecules, — for example, showing a pair of optical isomers. The convention of using a solid wedge to represent a bond coming 'out of the paper' and a dashed line for one going 'behind the paper' is used, as shown below:

Mirror plane
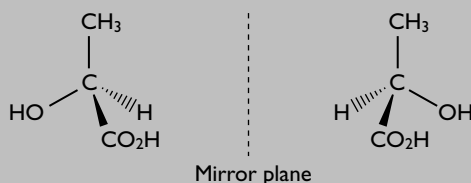
Try this yourself

(30) What is the name of the compound shown in the diagram immediately above?

Names and functional groups

It is important that you know:
- how to name hydrocarbon chains
- how to name the functional groups in organic chemistry
- how to indicate the positions of functional groups in the molecule

There are some simple rules that will help you.
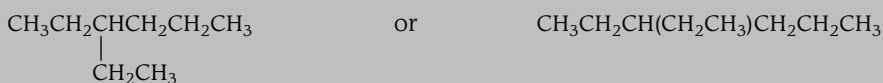
The hydrocarbon chain

The key thing to remember is that the prefix indicates the number of carbon atoms present in the main chain (Table 13.1).
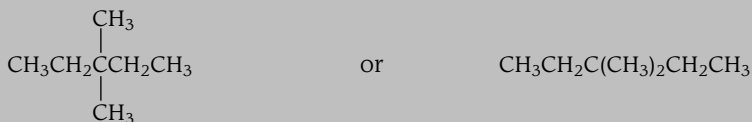
Approved: 0777 023 444

Table 13.1

Number of carbon atoms	Prefix used
1	meth-
2	eth-
3	prop-
4	but-
5	pent-
6	hex-
7	hept-
8	oct-

Hydrocarbon molecules do not have only straight chains, they can be branched. For a branched molecule, look at the number of carbon atoms in the branch and count the number of the carbon to which the branch is joined (remember to count from the end that gives the lower number). Some examples are shown below. Remember to use the *longest continuous* carbon chain as the basic hydrocarbon.

So, $CH_3CH_2CH_2CH_2CH_2CH_3$ is hexane.

$CH_3CH_2CHCH_2CH_2CH_3$ or $CH_3CH_2CH(CH_2CH_3)CH_2CH_2CH_3$
$\quad\quad\quad |$
$\quad\quad\quad CH_2CH_3$

are both 3-ethylhexane (an ethyl group on carbon 3)

$\quad\quad\quad CH_3$
$\quad\quad\quad |$
$CH_3CH_2CCH_2CH_3$ or $CH_3CH_2C(CH_3)_2CH_2CH_3$
$\quad\quad\quad |$
$\quad\quad\quad CH_3$

are both 3,3-dimethylpentane (two methyl groups on carbon 3).

Alkanes

Alkanes are a family of hydrocarbons that contain only C—C single bonds and C—H bonds. Alkanes are relatively unreactive, except to combustion and they form the major fuels that we use. All of the examples given above are alkanes.
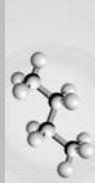
Alkenes

Alkenes are a family of hydrocarbons that have a reactive functional group, the C=C double bond. The double bond makes alkenes more reactive and they are important organic compounds.

In alkenes, it is the position of the C=C double bond that is indicated. So, $CH_3CH_2CH=CHCH_2CH_3$ is called hex-3-ene and $(CH_3)_2C=CHCH_2CH_3$ is called 2-methylpent-2-ene (the double bond is in the second possible position and there is a methyl group branching from carbon atom 2).

Arenes

Arenes are a family of hydrocarbons that contain a benzene ring made up of six carbons.
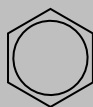
Benzene

In a benzene ring the carbon atoms are numbered clockwise from the uppermost atom. You only need to use this numbering system if there is more than one group attached to the ring.

Tip Arenes are important for the A2 examination. At AS you need to be able to recognise the benzene ring, even though you do not need to know anything about benzene or its compounds.

Other functional groups

Some functional groups are shown in Table 13.2.

Table 13.2

Name of compound	Formula of group
Halogenoalkane/arene	–Hal
Alcohol/phenol	–OH
Aldehyde	–CHO
Ketone	–C=O
Carboxylic acid	$-CO_2H$
Ester	$-CO_2R$ (where R is a hydrocarbon group)
Acyl chloride	–COCl
Amine	$-NH_2$
Nitrile	–CN
Amide	$-CONH_2$

Naming compounds is not too difficult. Some examples are shown in Table 13.3.

Table 13.3

Formula	Name of compound
$CH_3CH_2CH_2Br$	1-bromopropane
CH_3CH_2OH	Ethanol
$CH_3CH_2CH_2CHO$	Butanal
$(CH_3)_2C=O$	Propanone
$CH_3CH_2CO_2H$	Propanoic acid
$CH_3CH_2CO_2CH_3$	Methyl propanoate
CH_3COCl	Ethanoyl chloride
$CH_3CH_2CH_2CH_2NH_2$	1-aminobutane
$CH_3CH_2CH_2CN$	Propanenitrile
CH_3CONH_2	Ethanamide

Approved: 0777 023 444

Try this yourself

(31) Name the following compounds:

    (a) $CH_3CH_2CH_2CH_2Cl$

    (b) $CH_3CHOHCH_3$

    (c) $CH_3CH_2CH_2CH_2CH_2CO_2H$

    (d) $CH_3CH(CH_3)CH_2CH_2NH_2$

(32) Draw structural formulae for the following compounds:

    (a) 2-bromobutane

    (b) propanamide

    (c) methanal

   **(d)** methyl ethanoate

Organic reactions

It is important to be able to remember, and in some cases to predict, what types of reaction a compound containing a particular functional group will take part in. To do this you need to be aware of both the nature of the functional group and of the possible reactions a given reagent may permit.

Fission of bonds

Organic compounds are held together by covalent bonds, so you no longer need to worry about ionic reactions (except in a few rare cases). In organic molecules, a given bond can split in two ways. In **homolytic** fission one electron goes to each fragment:
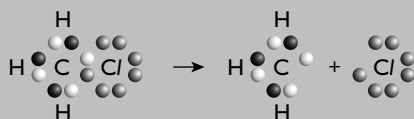

In **heterolytic** fission both electrons go to one fragment and none to the other:
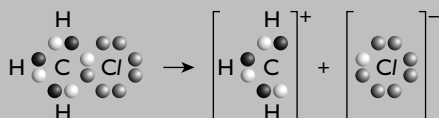
Free radical reactions

Free radicals are usually highly reactive species consisting of an atom or fragment of a molecule with an unpaired electron. In equations, it is usual to show the unpaired electron as a 'dot'. These free radicals may be formed by the action of ultraviolet light (such as in the upper atmosphere) or by the breakdown of a very unstable organic compound.

In general, free radical reactions take place in three distinct steps — initiation, propagation and termination. The reaction you will study is the reaction of methane with chlorine in the presence of ultraviolet light.
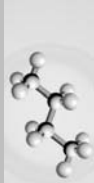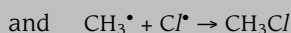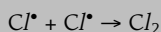
Step 1: initiation Free radicals are formed by the breaking of a bond by homolytic fission:

$Cl–Cl \xrightarrow{\text{UV}} Cl^\bullet + Cl^\bullet$
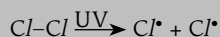
Step 2: propagation The free radicals formed begin a chain reaction in which as each free radical is used another is formed:

$H–CH_3 + Cl^\bullet \rightarrow CH_3{}^\bullet + HCl$

and $\quad CH_3{}^\bullet + Cl–Cl \rightarrow CH_3Cl + Cl^\bullet$
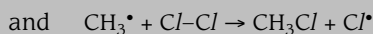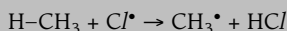
Step 3: termination These are reactions in which free radicals combine and hence end that part of the chain reaction:

$Cl^\bullet + Cl^\bullet \rightarrow Cl_2$

and $\quad CH_3{}^\bullet + Cl^\bullet \rightarrow CH_3Cl$

and $\quad CH_3{}^\bullet + CH_3{}^\bullet \rightarrow CH_3CH_3$

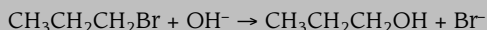## Nucleophilic and electrophilic reactions

Nucleophilic reagents 'like' positive charges and electrophilic reagents 'like' areas of electron density.

> **Tip** Here is a way to remember this — 'nucleo like nucleus, nuclei are positive; electro like electrons, which are negative'.

It follows that the reagents themselves are the opposite of what they seek.

Nucleophiles
Nucleophiles include halide ions, hydroxyl ions, cyanide ions and molecules containing lone pairs, such as water and ammonia, or even ethanol. A typical nucleophilic substitution reaction is:

$CH_3CH_2CH_2Br + OH^- \rightarrow CH_3CH_2CH_2OH + Br^-$

Electrophiles
Electrophiles are electron-deficient species, generally positively charged ions such as H^+, Cl^+, Br^+, I^+, $NO_2{}^+$, $CH_3{}^+$, CH_3CO^+. An example of an electrophilic addition reaction is:

$CH_3CH{=}CH_2 \rightarrow HBr \rightarrow CH_3CHBr\ CH_3$

Other types of reaction
Addition
Addition refers to an increase in saturation, in other words adding a molecule to a $C{=}C$ double bond as in the above reaction. The molecule achieves this by interacting with the π-electrons in the double bond (see the structure of ethene on page 126).

Substitution

Substitution refers to the replacement of one group in an organic molecule by another as in nucleophilic substitution on page 140. Both nucleophiles and electrophiles can take part in substitution reactions.

Elimination

An elimination reaction involves the removal of atoms from two adjacent carbon atoms to leave a double bond. It is the reverse of the electrophilic addition reaction on page 135.

Hydrolysis

This is a reaction, usually in aqueous media, between one organic molecule and water or acid or alkali which leads to the formation of at least two products. Two examples are:

$(CH_3)_3C—Cl + 2H_2O \rightarrow (CH_3)_3C—OH + H_3O^+ + Cl^-$

$CH_3CO_2CH_3 + NaOH \rightarrow CH_3CO_2^-Na^+ + CH_3OH$
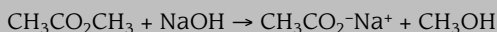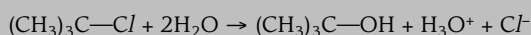
Oxidation

In general, this refers to the oxidation of a C—OH group to form a C=O group in an aldehyde, ketone or carboxylic acid. Such oxidations are often brought about by warming the organic compound with acidified potassium dichromate(VI). This can produce complicated equations, and in organic reactions it is permissible to show the oxidising agent as [O]:

$CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$
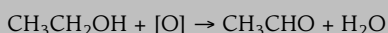
Reduction

This is the opposite of oxidation and, in general, applies to compounds containing a C=O group. Reduction may be brought about by several reducing agents including tin and dilute hydrochloric acid, sodium in ethanol and lithium aluminium hydride. In organic reduction reactions, the reducing agent is usually represented by [H], as shown in the example below:

$CH_3CO_2H + 4[H] \rightarrow CH_3CH_2OH + H_2O$
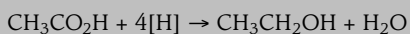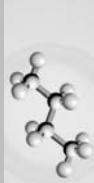
Shapes of molecules

For AS, you need to know the shapes of ethane and ethene. For A2, you also need to know the shape of benzene. Alongside this, you need to be able to work out the shapes of related molecules. The basics of this were covered in Chapter 3, so here are some reminders.

Ethane

An ethane molecule is formed by electrons in hydrogen 1s-orbitals overlapping with electrons in $2sp^3$-orbitals on the carbon atoms to form molecular orbitals in which
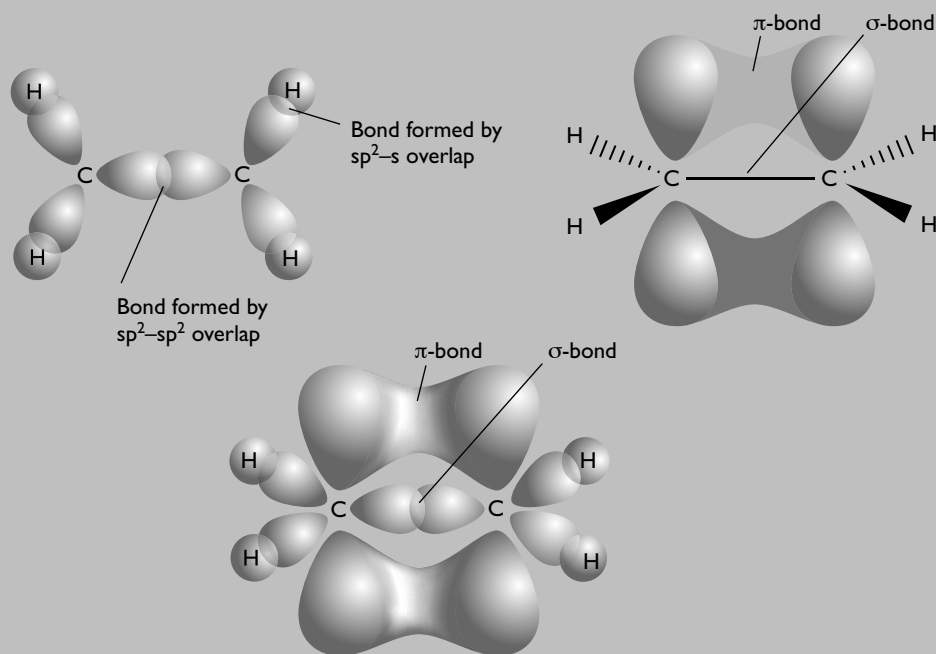
the hydrogen nuclei are embedded. A single C—C σ-bond, formed by the overlapping of one sp³-orbital from each carbon atom, joins the two ends together, but there is no restriction on rotation so the two ends of the molecule can spin relatively freely.

Hydrogen nucleus embedded
in new molecular orbital

Sigma (σ) bond
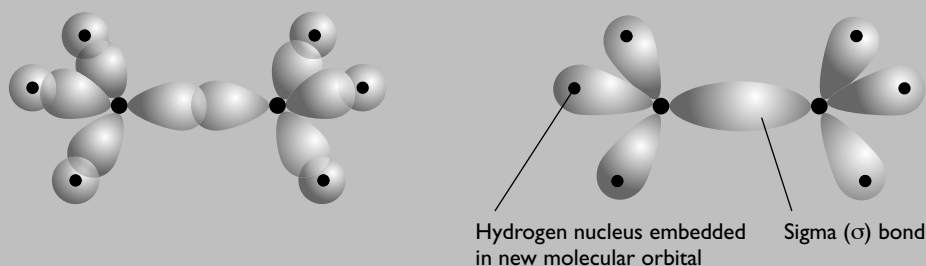
Ethene

In ethene, the carbon atoms form 2sp²-hybrid orbitals for three of the electrons, leaving one electron in a 2p-orbital. An ethene molecule is formed by the overlap of two sp²-orbitals on each carbon with two hydrogen 1s-orbitals, with the third sp²-orbital on each carbon atom overlapping to form a σ-bond. The p-orbitals interact to form an additional π-bond which prevents the rotation of the ends of the molecule about the σ-bond:

Bond formed by
sp²–s overlap

Bond formed by
sp²–sp² overlap

π-bond σ-bond

π-bond σ-bond

Benzene

A molecule of benzene has six carbons arranged in a hexagonal ring. These carbon atoms have hybridised orbitals in the same manner as ethene. However, in benzene, only one $2sp^2$-orbital is bonded to hydrogen, with the other two sp^2-orbitals being bonded to adjacent carbons. The 2p-orbitals interact around the ring producing a π-electron 'cloud' above and below the plane of the ring.

Sigma bonds
sp^2 hybridized orbitals

6 p_z-orbitals

Delocalised π system
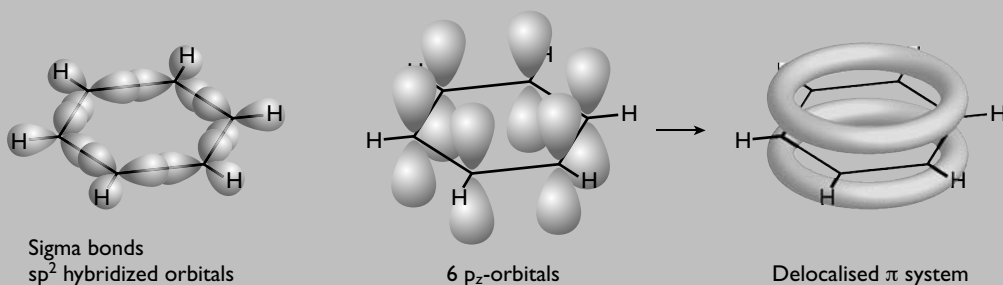
Isomerism

Isomers are compounds that have the same molecular formula (same chemical composition) but different structural formulae. You need to know about three main types of isomerism — structural, geometrical and optical.
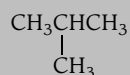
Structural isomerism

Chain isomerism

In **chain isomerism**, the isomers arise due to branching of the carbon chain. So C_4H_{10} can have both a straight chain form and a branched chain form:

$CH_3CH_2CH_2CH_3$ CH_3CHCH_3
                                                    $|$
                                                 CH_3
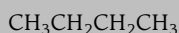
    butane   2-methylpropane

The compounds have different names based on the system described on page 121. The branched chain is three carbons long and has a methyl group on the second carbon atom.

Position isomerism

In **position isomerism**, the carbon chain is fixed, but the position of substituent groups can vary. The alcohols propan-1-ol and propan-2-ol show this:

$CH_3CH_2CH_2OH$ CH_3CHCH_3
                                                    $|$
                                                 OH
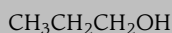
    Propan-1-ol   Propan-2-ol

Approved: 0777 023 444
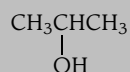
Changing the position of a group can affect how easily it reacts, as well as its physical properties, such as boiling point. Propan-1-ol has a boiling point of 97 °C whereas propan-2-ol has a boiling point of 82 °C.

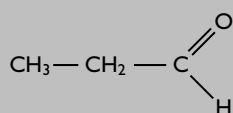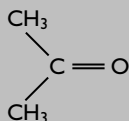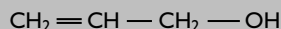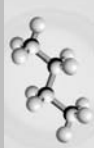### Functional group isomerism

In **functional group isomerism** the nature of the functional group within the molecule is different. This is important because it changes the chemical reactions that the molecule undergoes. The formula C_3H_6O can represent three molecules, each with a different functional group:

| Propanal | Propanone | 2-propen-1-ol |

Geometric or *cis-trans* isomerism

Geometric isomerism occurs where there is restricted rotation around a bond, such as in alkenes. It also needs two groups, one on each end of the double bond, such as in 1,2-dichloroethene:
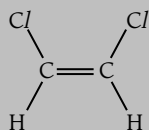
cis-1,2-dichloroethene   *trans*-1,2-dichloroethene
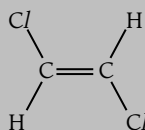
These two forms are different because the double bond prevents the rotation needed to make the two forms identical. Notice that there is another isomer, but this time it is a position isomer, rather than a *cis-trans* isomer.
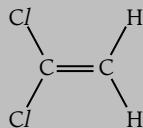
1,1-dichloroethene

To summarise, in *cis-trans* isomerism:
- there is restricted rotation generally involving a carbon-carbon double bond
- there are two different groups on the left-hand end of the bond and two different groups on the right-hand end

Optical isomerism and chiral centres

The final type of isomerism you need to be able to recognise and explain is **optical isomerism**. This gets its name from the effect an optical isomer has on the plane

of plane-polarised light. One isomer rotates the polarised light clockwise, and the other isomer rotates it an equal amount anti-clockwise. This occurs when there is a carbon with four different groups attached to it — this is called a **chiral** carbon. An example was shown on page 120 and another example, butan-2-ol, is shown below:
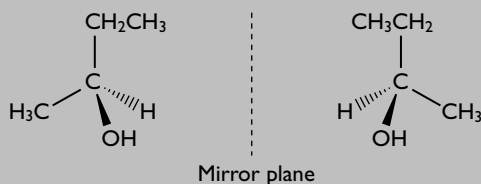
Notice that the two molecules are mirror-images, and that the central carbon atom has four different groups attached. When you draw these structures it is important to check that your diagrams make chemical 'sense'. Take the structure of 2-aminopropanoic acid for example. It is important to show the 'acid' group joined to the central carbon the right way round. (If not, you may be penalised in the exam.) Figure 13.1 shows what you need to do.
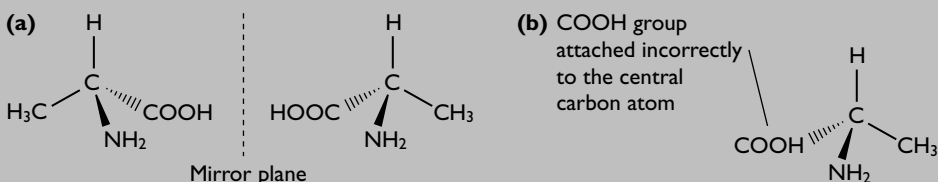
Figure 13.1(a) Optical isomers of 2-aminopropanoic acid
(b) Incorrectly drawn isomer

Identifying chiral carbon atoms can be tricky, particularly in complex or skeletal molecular structures. You have to work out whether or not a given carbon atom has two (or more) identical groups attached to it.

Look at the skeletal structure below:
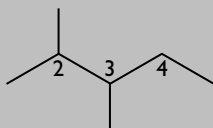
It contains three non-terminal carbon atoms numbered 2, 3 and 4.

Look at each of these in turn. Carbon 2 has two bonds attached to methyl groups, carbon 4 has two bonds attached to hydrogen atoms (not shown), and carbon 3 is attached to four different groups. Therefore, carbon 3 is chiral.

You may be asked to examine a complex molecule and state the number of chiral carbon atoms (or perhaps circle them). An example of such a molecule, the synthetic form of the hormone testosterone, is shown in Figure 13.2.
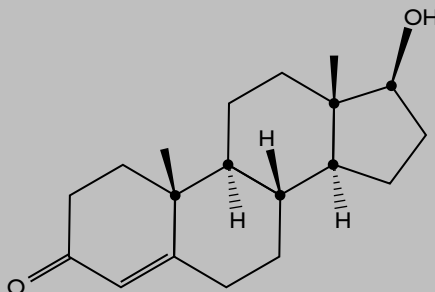
Figure 13.2 Synthetic testosterone

Can you identify the chiral carbon atoms in the structure? There are six, marked ●.

Try this yourself

(33) A compound **P** has the formula C_4H_8O.
    (a) Draw a straight-chain structure for **P**.
    (b) Does **P** have functional group isomers? If so, draw examples.
    (c) How many isomers in total does the straight-chain form of **P** have, incorporating any of the functional groups in Table 13.2?

(34) The compound **Q** has the formula C_4H_7Br and contains a double bond.
    (a) How many non-cyclic isomers exist for **Q**?
    (b) Draw the *cis-trans* isomers of **Q**.

14 Hydrocarbons

Apart from the section on arenes, all this chapter is needed for the AS examination. Some of the content has been covered previously or you may have studied it at IGCSE.

Alkanes

Combustion

Due to their general lack of reactivity, the single most important use of alkanes is as fuels. You may already know about the importance of crude oil, and the 'cracking' of less useful fractions to form more useful products (this is covered on the next pages).

Ethane is used as an example of an alkane, noting that it has the formula C_2H_6 and that the general formula for alkanes is C_nH_{2n+2}.

Ethane reacts differently with oxygen depending on how much oxygen is available.

Plenty of oxygen: $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$

Approved: 0777 023 444

Less oxygen: $2C_2H_6 + 5O_2 \rightarrow 4CO + 6H_2O$

Restricted oxygen: $2C_2H_6 + 3O_2 \rightarrow 4C + 6H_2O$

Restricting the amount of oxygen reduces the amount by which the carbon in ethane is oxidised until it cannot be oxidised at all. The midway point produces poisonous carbon monoxide, which has been known to kill people using faulty gas heaters.

Crude oil as a source of hydrocarbons

The use of oil as a major fuel is less than 150 years old and results from the revolutions in land and air transport brought about by the development of the internal combustion engine. Crude oil is often talked about as if it is a mixture with fixed composition. However, it can vary enormously in the proportions of the various hydrocarbons that make up the mix. This variation affects how much processing the oil requires to yield useful products.

Not all sources of oil have high proportions of the hydrocarbons that are most in demand. However, chemists have developed ways of converting less useful hydrocarbons into more useful ones. The main process for achieving this is 'cracking' — a large molecule hydrocarbon of limited use is broken into smaller molecule hydrocarbons that are in greater demand.

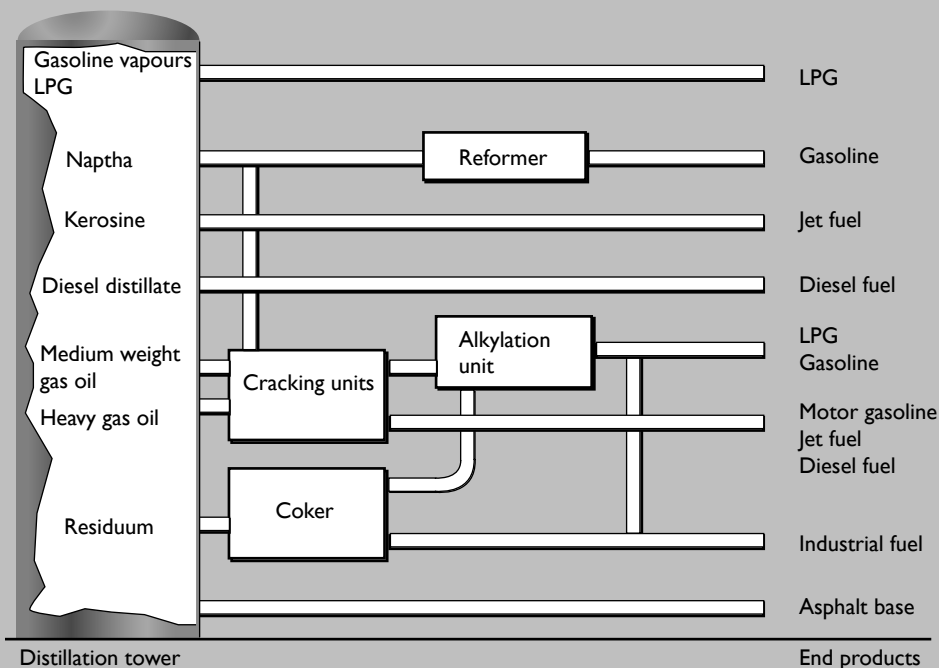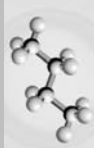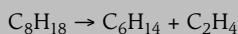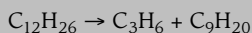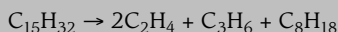Some of the most important processes in an oil refinery are shown in Figure 14.1.

Figure 14.1 Processes in an oil refinery

131

The cracking process involves using either high pressures and temperatures without a catalyst, or lower temperatures and pressures in the presence of a catalyst. The source of the large hydrocarbon molecules is often the 'naphtha' fraction or the 'gas oil' fraction from the fractional distillation of crude oil. Although these fractions are obtained as liquids, they have to be vaporised before cracking can occur.

There is no unique reaction in the cracking process. In general, a large hydrocarbon molecule produces one or more smaller alkane molecules and one or more alkene molecules, for example:

$$C_{15}H_{32} \rightarrow 2C_2H_4 + C_3H_6 + C_8H_{18}$$

$$C_{12}H_{26} \rightarrow C_3H_6 + C_9H_{20}$$

$$C_8H_{18} \rightarrow C_6H_{14} + C_2H_4$$

The alkanes produced are usually used for motor fuel — either petrol (gasoline) or diesel — while the alkenes formed are used in the polymer industry.

Substitution reactions

Alkanes react with difficulty with both chlorine and bromine. In order to react, alkanes need energy from ultraviolet light (sunlight) and, as you might expect, chlorine reacts more easily than bromine. Taking ethane as the example, the hydrogen atoms are replaced one at a time in substitution reactions:

$$C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$$

$$C_2H_5Cl + Cl_2 \rightarrow C_2H_4Cl_2 + HCl$$

$$C_2H_4Cl_2 + Cl_2 \rightarrow C_2H_3Cl_3 + HCl \text{ and so on}$$
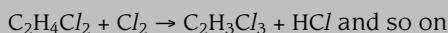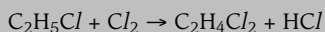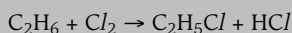
The mechanism for the equivalent reaction with methane was covered on page 124.

Alkenes

Ethene is used as an example of an alkene, noting that it has the formula C_2H_4 and that the general formula for alkenes is C_nH_{2n}.

Addition reactions

Because alkenes have a double bond, it is reasonable to expect addition reactions to be particularly important.

With hydrogen
Ethene reacts with hydrogen at a temperature of about 150 °C in the presence of finely-divided (powdered) nickel. The hydrogen adds across the double bond forming ethane:

$$CH_2{=}CH_2 + H_2 \rightarrow CH_3{-}CH_3$$
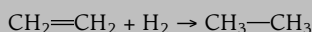
This is not a very useful reaction, but for larger alkenes — such as those found in vegetable oils — the addition of hydrogen across a double bond is more important. These oils are 'hardened', or turned into solid fats, by hydrogenation — a process that is necessary for the manufacture of margarine.

With steam

Water, in the form of steam, can be added across ethene's double bond to form ethanol. This is carried out industrially at a temperature of about 300 °C and a pressure of about 60 atm in the presence of a phosphoric(V) acid catalyst.

For alkenes other than ethene, there is the possibility of adding the hydrogen to two different carbons. In propene, for example, the hydrogen can be added to either the end carbon or to the middle carbon, forming propan-2-ol and propan-1-ol respectively:

$$CH_3—CH{=}CH_2 + H_2O \rightarrow CH_3CHOHCH_3 \text{ or } CH_3CH_2CH_2OH$$
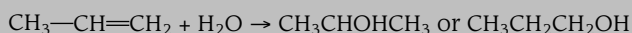
Markovnikoff's rule (worth learning) states that when a molecule of the form HX is added across a double bond, the hydrogen usually becomes attached to the carbon that is already attached to the most hydrogen atoms. This means that in the above reaction, propan-2-ol is favoured.

With hydrogen halides

If a gaseous alkene is bubbled through, or a liquid alkene is shaken with, either a concentrated aqueous solution of hydrogen bromide or hydrogen bromide dissolved in a non-polar solvent, the hydrogen bromide is added across the double bond.

The reaction is similar to the addition of water and follows Markovnikoff's rule:

$$CH_3—CH{=}CH_2 + HBr \rightarrow CH_3CHBrCH_3$$

With halogens

Ethene reacts with halogens by adding across the double bond. Therefore, with bromine at room temperature the reaction forms 1,2-dibromoethane:

$$CH_2{=}CH_2 + Br_2 \rightarrow CH_2BrCH_2Br$$
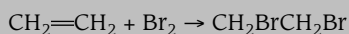
Chlorine, being more reactive, reacts faster than bromine. Iodine reacts more slowly.
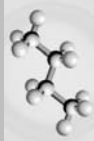
The reaction above refers to ethene reacting with the pure halogen. Often, as in testing for alkenes using bromine water, a competing reaction can take place:

$$CH_2{=}CH_2 + Br_2 + H_2O \rightarrow CH_2BrCH_2OH + HBr$$
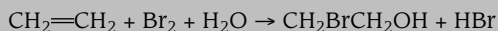
This compound is 1-bromo-2-hydroxyethane (or 2-bromethanol).

Oxidation reactions

Alkenes react with oxidising agents such as acidified manganate(VII) ions. The extent of the reaction, and hence the nature of the products, depends on the concentration of the oxidising agent and the temperature.

With cold, dilute, acidified manganate(VII) ions

Under these conditions ethene is oxidised to the diol 1,2-dihdroxyethane.

$$CH_2\!\!=\!\!CH_2 + [O] + H_2O \rightarrow CH_2OHCH_2OH$$
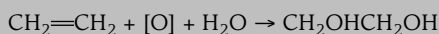
With hot, concentrated, acidified manganate(VII) ions

Acidified manganate(VII) is such a strong oxidising agent that in concentrated solution and with heat the carbon-to-carbon double bond of the alkene is ruptured. You may not think that this is a very useful reaction, but by looking at the products the position of a double bond in an unknown alkene can be determined.

The symbol **R** is used to represent a hydrocarbon group or a hydrogen atom. So, any alkene can be represented by the following formula:

$$\begin{array}{cc} R_1 & R_2 \\ \diagdown & \diagup \\ C\!=\!\!C \\ \diagup & \diagdown \\ R_3 & R_4 \end{array}$$
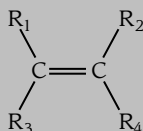
When the acidified manganate(VII) ions oxidise the alkene, two C=O double bonds are formed:

$$\begin{array}{cc} R_1 & R_2 \\ \diagdown & \diagup \\ C\!=\!\!C \\ \diagup & \diagdown \\ R_3 & R_4 \end{array} + 2[O] \rightarrow \begin{array}{c} R_1 \\ \diagdown \\ C\!=\!\!O \\ \diagup \\ R_3 \end{array} + \begin{array}{c} R_2 \\ O\!=\!\!C \\ \diagdown \\ R_4 \end{array}$$
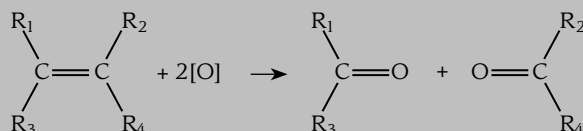
A compound that contains a C=O functional group is known as a **carbonyl compound**. A carbonyl compound with two hydrocarbon groups is called a **ketone**. If one of the **R** groups is hydrogen, the carbonyl compound formed is called an **aldehyde** and this can be oxidised further by acidified manganate(VII) to form a **carboxylic acid**:

$$\begin{array}{cc} R_1 & R_2 \\ \diagdown & \diagup \\ C\!=\!\!C \\ \diagup & \diagdown \\ H & R_4 \end{array} + 2[O] \rightarrow \begin{array}{c} R_1 \\ \diagdown \\ C\!=\!\!O \\ \diagup \\ H \end{array} + \begin{array}{c} R_2 \\ O\!=\!\!C \\ \diagdown \\ R_4 \end{array}$$

$$\begin{array}{c} R_1 \\ \diagdown \\ C\!=\!\!O \\ \diagup \\ H \end{array} + [O] \rightarrow \begin{array}{c} R_1 \\ \diagdown \\ C\!=\!\!O \\ \diagup \\ HO \end{array}$$
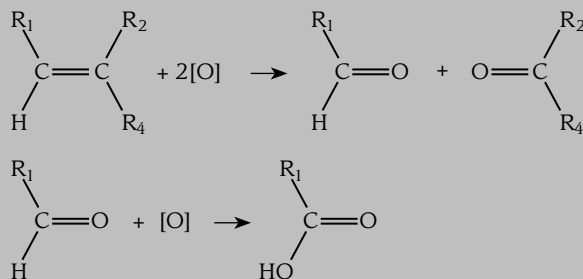
There is one further complication that occurs when there are no **R** groups at one end of the double bond. The carboxylic acid formed under those circumstances (methanoic acid) is itself oxidised by the acidified manganate(VII) ions to form carbon dioxide and water:

$$\begin{array}{c} H \\ \diagdown \\ C=O \\ \diagup \\ H \end{array} + [O] \rightarrow \begin{array}{c} H \\ \diagdown \\ C=O \\ \diagup \\ HO \end{array} + [O] \rightarrow CO_2 + H_2O$$
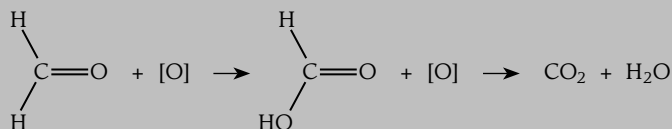
Here are some simple rules that might help you to work out the structure of the original alkene:

- Think about each end of the double bond separately.
- If there are two hydrocarbon groups at one end of the bond, that part of the molecule will give a ketone.
- If there is one hydrocarbon group and one hydrogen atom at one end of the bond, that part of the molecule will give a carboxylic acid.
- If there are two hydrogen atoms at one end of the bond, that part of the molecule will give carbon dioxide and water.
- Combine the information to work back to the structure of the original alkene.

Polymerisation

Carbon is one of the few elements to form rings and extended chains of atoms. Alkenes can join together to form long chains, or polymers. This does not apply only to hydrocarbon alkenes but also to substituted alkenes such as chloroethene ($CH_2=CHCl$) which is used to make PVC. Polymerisation is covered in Chapter 19.

Electrophilic addition
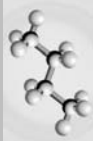
You saw in the previous chapter that halogens behave as electrophiles, and you know that alkenes have a concentration of electrons round the double bond. For the examination, you need to understand the mechanism of electrophilic addition, with the specific example of bromine reacting with ethene. The reaction takes place in two stages.

First, as the bromine molecule approaches the ethene molecule, the π-electrons in ethene induce a dipole on the bromine molecule. A bond is formed between the carbon and the bromine forming a positively charged species called a **carbocation**:
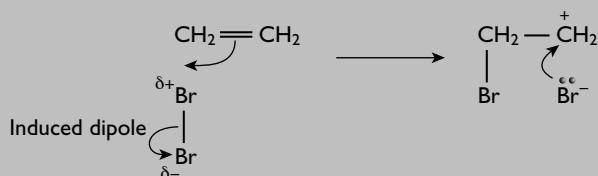
Second, the carbocation is attacked rapidly by the remaining Br^- ion to form the dibromide:

Approved: 0777 023 444

Try this yourself

(35) The reaction between bromine and ethene only occurs so 'cleanly' in a non-aqueous solvent. Explain what other product(s) might be formed if the bromine were dissolved in water.

Arenes

You need to know about two arenes — benzene and methylbenzene:
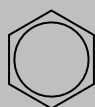
Benzene   Methylbenzene

Although you might not think these molecules are very different, the presence of a side chain in methylbenzene means that it is able to undergo an additional set of reactions compared to benzene.

Substitution reactions

Benzene

Benzene reacts at room temperature with chlorine or bromine in the presence of a catalyst. One of the hydrogen atoms in the ring is replaced by a chlorine or bromine atom. A typical catalyst is the aluminium halide of the halogen being substituted, or iron (which reacts with the halogen to form the iron(III) halide which then acts as the catalyst):

$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$

$C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$
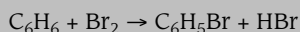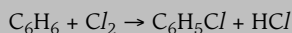
In the presence of ultraviolet light (or sunlight), but without a catalyst, benzene undergoes addition reactions with both chlorine and bromine, with six halogen atoms added to the ring:
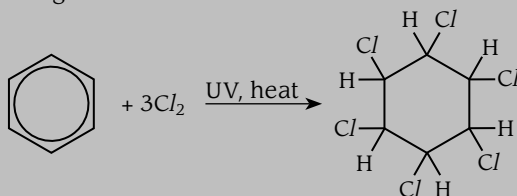
As you might expect, the reaction is faster with chlorine than with bromine.

Approved: 0777 023 444

Methylbenzene

With methylbenzene there are two different types of substitution, depending on whether a ring hydrogen or a methyl hydrogen is substituted.

As with benzene, substitution of a ring hydrogen occurs at room temperature in the presence of an aluminium halide or iron catalyst. There is an additional complication of where the halogen atom goes in relation to the methyl group. Methyl groups direct further substitution to the 2- or 4- positions in the ring (the 1-position is that occupied by the methyl group). This reaction with either chlorine or bromine under these conditions results in the formation of a mixture of 2-halo- and 4-halomethylbenzene:
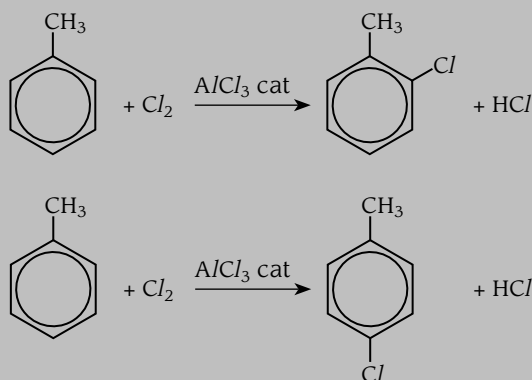
When boiling methylbenzene is reacted with chlorine or bromine in the presence of ultraviolet light, the methyl hydrogen atoms are substituted. Provided sufficient halogen is present, all three hydrogen atoms are eventually substituted:
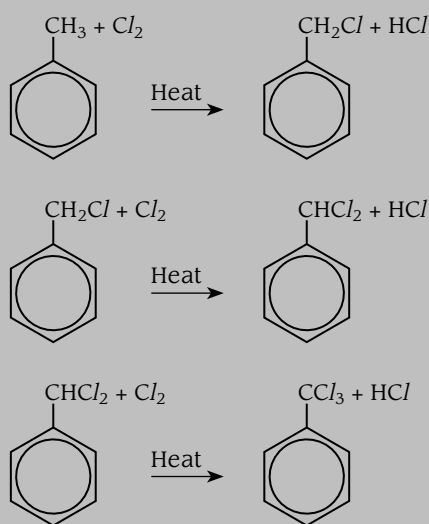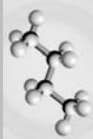
Nitration

This is the only reaction of arenes for which you need to know the mechanism.

Benzene

When benzene is treated with a mixture of concentrated nitric acid and concentrated sulfuric acid at a temperature lower than 50 °C, yellow nitrobenzene is gradually formed. The sulfuric acid acts as a catalyst.

$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$$
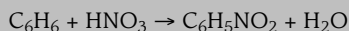
At higher temperatures, or with prolonged reaction even at 50 °C, further nitration occurs with a second nitro group being substituted into the ring. The second nitro group goes into the 3-position:
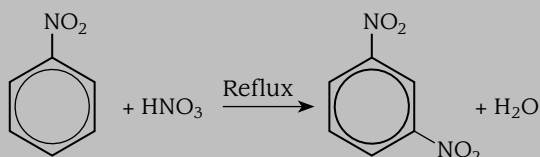
Compare this with the methyl group in methylbenzene (p.137). It *is* possible to get a further nitro group in the 5-position, but the presence of a nitro group 'deactivates' the benzene ring, making it much less likely to react.

The mechanism for the mononitration of benzene is an example of electrophilic substitution. The nitrating mixture of concentrated nitric and concentrated sulfuric acids produces the electrophile — the nitronium ion, NO_2^+:

$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$$

The NO_2^+ ion approaches the delocalised electrons in benzene and two of these form a bond with the positive charge now spread over the rest of the atoms in the ring:
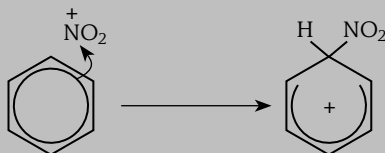
The HSO_4^- ion produced in the nitrating mixture now removes a hydrogen atom, re-forming the sulfuric acid catalyst:
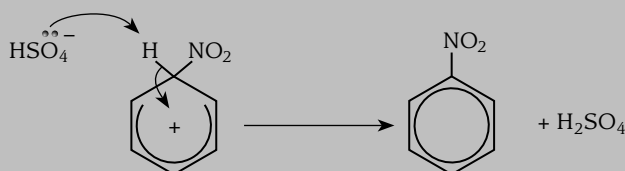
Methylbenzene

In nitration, methylbenzene reacts about 25 times faster than benzene. This means that a lower temperature (around 30 °C rather than 50 °C) has to be used to prevent more than one nitro group being substituted. Apart from that, the reaction is the same and the same nitrating mixture of concentrated sulfuric and nitric acids is used.

As with the halogens, a mixture of the 2- and 4-nitro substituted arenes is formed:
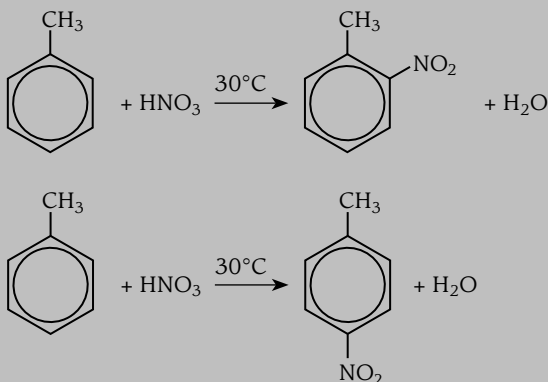
Side-chain oxidation

This applies only to methylbenzene (and other arenes with alkyl side chains). Alkyl groups in alkanes are usually fairly unreactive towards oxidising agents. However, when attached to a benzene ring they are relatively easily oxidised. Heating methylbenzene (or any alkylbenzene) with alkaline potassium manganate(VII) solution, followed by acidification with dilute sulfuric acid, gives benzoic acid:
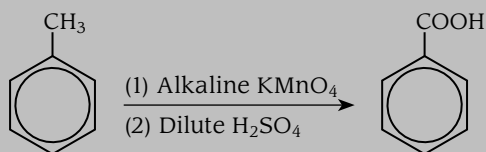
15 Halogen and hydroxy compounds

Most of this chapter, apart from the reactivity of chlorobenzene and the last section on hydroxyl compounds, is needed for the AS examination.
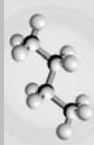
Halogen derivatives

Halogenoalkanes behave differently depending on which other groups are attached to the carbon that the halogen is attached to (you will see this trend with other functional groups).

- If there are only hydrogen atoms attached to the carbon, it is a **primary** (1°) halogenoalkane, for example CH_3CH_2Br.
- If there is one alkyl group attached as well as the halogen, it is a **secondary** (2°) halogenoalkane, for example $(CH_3)_2CHBr$
- If there are *no* hydrogen atoms, only alkyl groups and the halogen, it is a **tertiary** (3°) halogenoalkane, for example $(CH_3)_3CBr$

The C—Hal bond is polar due to the difference in electronegativity between the carbon atom and the halogen atom. Except when bonded to iodine, the carbon atom is relatively positive, making it susceptible to nucleophilic attack by lone pairs of electrons or negative ions.

Nucleophilic substitution

Halogenoalkanes undergo a number of nucleophilic substitution reactions. The syllabus requires you to know about three of these using bromoethane as a starting compound. However, you should be able to recognise this type of reaction with different halogenoalkanes and different nucleophilic reagents.

Hydrolysis

When bromoethane, a primary halogenoalkane, is heated under reflux with sodium hydroxide in a solvent of aqueous ethanol, the bromine is substituted by the hydroxyl group and ethanol is formed:

$$CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$$
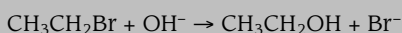
You also need to know the mechanism for this reaction, which can be represented in two ways. The first way is as follows:

$$CH_3 - \overset{\delta+}{CH_2} - Br^{\delta-} \longrightarrow CH_3 - CH_2 - OH \quad + \quad {:}Br^-$$
$${:}\overline{O}H$$
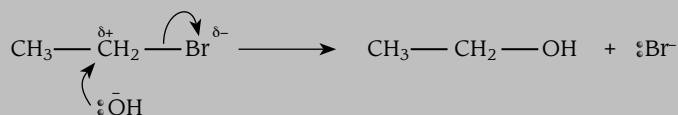
The reaction is described as S_N2, because there are two reactants in the rate-determining or slow step.

> **Tip** Think of S_N2 as 'Substitution Nucleophilic, 2 reactants'.

The other way of representing this reaction is to show it as a two-stage process:

Transition state
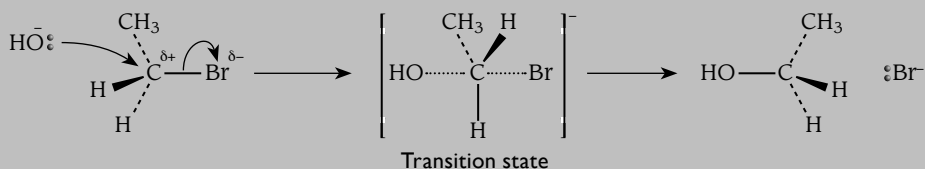
With a tertiary halogenoalkane, the mechanism is still nucleophilic substitution:

$$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$$
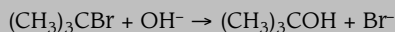
However, in this mechanism, only *one* molecule is present in the rate-determining or slow step. This is an S_N1 mechanism, although there are still two stages:
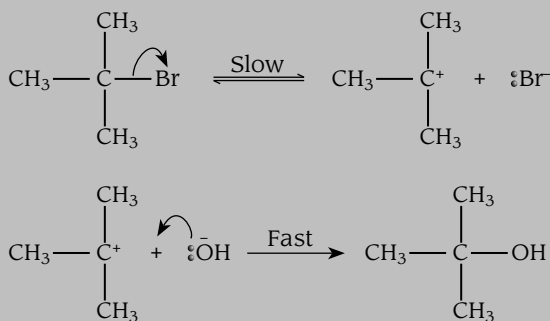
> **Tip** Think of S_N1 as 'Substitution Nucleophilic, 1 reactant'.

For a secondary halogenoalkane, the mechanism is a combination of S_N1 and S_N2.

There is another reaction that can take place when halogenoalkanes react with hydroxide ions. This is covered on page 142.

Formation of nitriles

When a halogenoalkane is heated under reflux with cyanide ions dissolved in ethanol, the cyanide ion is substituted for the halogen and a nitrile is formed:

$$CH_3CH_2Br + CN^- \rightarrow CH_3CH_2CN + Br^-$$
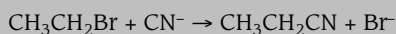
This is an important reaction because a carbon atom has been added to the carbon chain and the nitrile group can be reacted further.

Secondary and tertiary halogenoalkanes react in a similar way, but the mechanism may be different.

Formation of primary amines

When a halogenoalkane is heated with ammonia, a reflux process cannot be used because the ammonia would escape as gas. This reaction has to be carried out in a sealed tube. The reaction takes place in two steps:

$$CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_3^+Br^-$$

$$CH_3CH_2NH_3^+Br^- + NH_3 \rightarrow CH_3CH_2NH_2 + NH_4^+Br^-$$
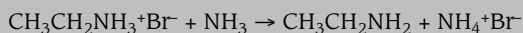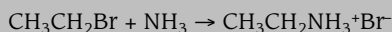
However, in a sealed tube the reaction does not stop with the formation of a primary amine. It continues replacing successive hydrogens on the nitrogen to give secondary and tertiary amines, and finally a quaternary ammonium salt. Note that these reactions are *not* needed for A-level.

Elimination of hydrogen bromide

Under similar conditions to those needed for nucleophilic substitution, it is possible to get an elimination reaction to take place. If, instead of aqueous ethanol, a concentrated hydroxide solution in pure ethanol is used, HBr is eliminated and a double bond is formed:

$$CH_3CH_2Br + OH^- \rightarrow CH{=\!=}CH_2 + H_2O + Br^-$$

It is important to remember that different halogenoalkanes favour one type of reaction over the other (Table 15.1).

Table 15.1

Halogenoalkane	Reaction favoured
Primary	Mainly substitution
Secondary	Both
Tertiary	Mainly elimination

For a given halogenoalkane, to favour **substitution** use:
- lower temperatures
- more dilute solutions of sodium or potassium hydroxide
- more water in the solvent mixture

To favour **elimination** use:
- higher temperatures
- a concentrated solution of sodium or potassium hydroxide
- pure ethanol as the solvent

Different types of halogenoalkane

So far we have used bromoethane as the example of a halogenoalkane and for most purposes that is fine. However, we must not forget that the different halogens have an effect on the halogenoalkanes they form, not least because of the relative strengths of the C—Hal bond (Table 15.2).

Table 15.2

Bond	Bond energy/kJ mol^{-1}
C—F	467
C—Cl	338
C—Br	276
C—I	238

For a halogenoalkane to react, the C—Hal bond has to be broken. From Table 15.2 you can see that this is much more difficult for fluoroalkanes than for the other members of the group.

A number of halogenoalkanes have important uses and in looking at these we need to bear this factor in mind.

Uses

The chemical inertness of chlorofluorocarbons (CFCs) has meant that until recently they were used as propellants in aerosols, as refrigerant gases in refrigerators, as 'blowing agents' for making plastic foams (such as expanded polystyrene) and as solvents. There has been considerable recent evidence of their harmful effects on the atmosphere, which has resulted in a large decrease in their use.

CFCs are largely responsible for destroying the ozone layer. In the high atmosphere, ultraviolet light causes carbon-to-chlorine bonds to break forming chlorine free radicals. It is these free radicals that destroy ozone.

It has also been shown that CFCs can cause global warming. One molecule of CCl_3F, for example, has a global warming potential about 5000 times greater than a molecule of carbon dioxide. Fortunately, there is much less of this compound than carbon dioxide in the atmosphere.

The halogen-containing plastics PVC (poly(chloroethene)) and PTFE (poly(tetrafluoro-ethene)) are commercially important. The plastics themselves are not halogenoal-kanes, but they are made from halogenoalkenes.

As well as these major uses, halogenoalkanes are used as flame retardants and as anaesthetics. These uses once again rely on the relative inertness of halogenoalkanes.

Chlorobenzene is a halogenoarene:
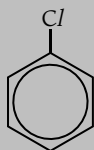
It is much less reactive towards nucleophilic substitution than the halogenoalkanes. The C—Cl bond in the molecule is stronger than you might expect. This is because one of the lone pairs of electrons on the chlorine atom is delocalised with the ring electrons on benzene:

Overlap between lone pair and the ring electrons

Lone pair now delocalised to some extent with the ring electrons

143
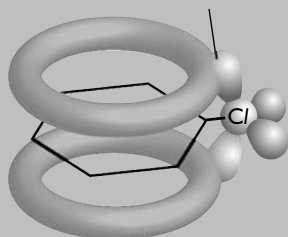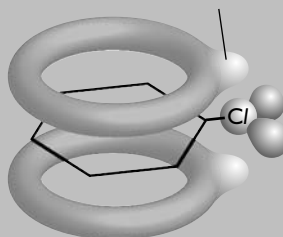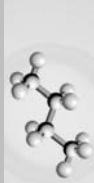
Hydroxy compounds

The first part of this section dealing with alcohols is needed for the AS examination. The second part, dealing with the iodoform reaction, phenol and the relative acidities of water, phenol and ethanol is needed for the A2 examination.

Different types of alcohol

In just the same way as with primary, secondary and tertiary halogenoalkanes, there are primary, secondary and tertiary alcohols.

Ethanol, CH_3CH_2OH, is a primary alcohol.

Propan-2-ol, $CH_3CHOHCH_3$, is a secondary alcohol.

2-methylpropan-2-ol is a tertiary alcohol:

$$CH_3 - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - OH$$
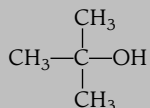
Reactions of alcohols

Combustion

Like most organic compounds, alcohols are flammable. You may remember this from using a spirit burner. The equation for the complete combustion of ethanol is:

$CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$
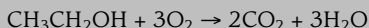
Substitution to form halogenoalkanes

Halogenoalkanes can be hydrolysed to give alcohols, and alcohols can be converted into halogenoalkanes, but by different reagents.

One way of carrying out the substitution is to use the appropriate hydrogen halide. This method works for the bromo- and iodoalkanes if the hydrogen halide is generated in the reaction flask. Sodium bromide with concentrated sulfuric acid can be used for the bromoalkane, but sodium iodide and concentrated phosphoric(V) acid have to be used for the iodoalkane because sulfuric acid would oxidise any HI formed. The equations for the formation of bromoethane and iodoethane are as follows:

$CH_3CH_2OH + HBr \rightarrow CH_3CH_2Br + H_2O$

$CH_3CH_2OH + HI \rightarrow CH_3CH_2I + H_2O$
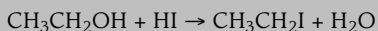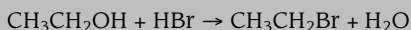
The following method only works with tertiary alcohols, forming the tertiary chloroalkane:

$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - OH \;+\; HCl \;\longrightarrow\; CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - Cl \;+\; H_2O$$
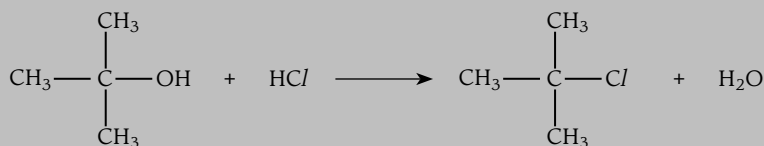
For other chloroalkanes we have to use phosphorus trichloride, PCl_3, phosphorus pentachloride, PCl_5, or thionyl chloride, $SOCl_2$:

$$3CH_3CH_2OH + PCl_3 \rightarrow 3CH_3CH_2Cl + H_3PO_3$$

$$CH_3CH_2OH + PCl_5 \rightarrow CH_3CH_2Cl + POCl_3 + HCl$$

$$CH_3CH_2OH + SOCl_2 \rightarrow CH_3CH_2Cl + SO_2 + HCl$$
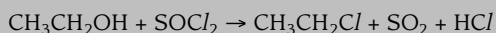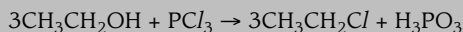
Reaction with sodium

When a small piece of sodium is dropped into ethanol it dissolves, producing bubbles of hydrogen gas. It leaves a colourless solution which, if evaporated to dryness, produces a white solid. This white solid is sodium ethoxide, $CH_3CH_2O^-Na^+$:

$$2CH_3CH_2OH + 2Na \rightarrow 2CH_3CH_2O^-Na^+ + H_2$$
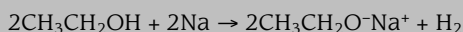
This reaction is sometimes used to dispose of small amounts of old sodium because it is much less violent than reacting sodium with water. It can also be used as a test for an alcohol. The ethoxide ion (like the hydroxide ion) is a strong base and a good nucleophile.
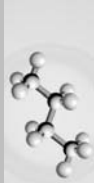
Oxidation reactions

In the presence of an oxidising agent such as acidified dichromate(VI) solution, whether or not an alcohol is oxidised depends on its structure. A positive test for oxidation is that the dichromate(VI) solution turns from orange to blue-green.

- On warming a primary alcohol with acidified dichromate(VI), an aldehyde is first formed. If this is not removed from the reaction vessel it is further oxidised to a carboxylic acid. The mixture turns from orange to blue-green:

$$CH_3 - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - O - H \quad [O] \;\longrightarrow\; CH_3 - \overset{\overset{O}{\|}}{C} \diagdown H \;+\; H_2O$$

$$CH_3 - \overset{\overset{O}{\|}}{C} \diagdown H \;+\; [O] \;\longrightarrow\; CH_3 - \overset{\overset{O}{\|}}{C} \diagdown OH$$
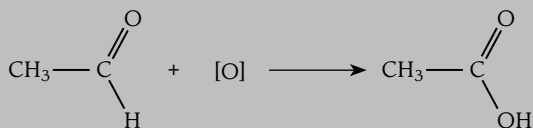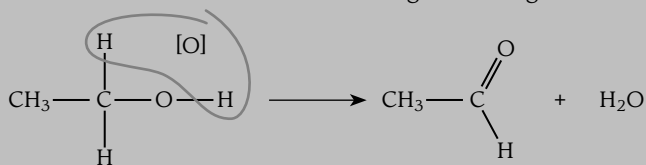
- On refluxing a secondary alcohol with acidified dichromate(VI), a ketone is formed, which is not oxidised further. Again the mixture turns from orange to blue-green:

Propan-2-ol   Propanone
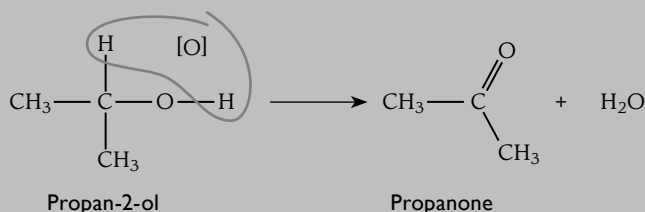
- With a tertiary alcohol, there are no hydrogen atoms on the carbon atoms that can be oxidised, so there is no reaction.

Tertiary alcohol

There is no hydrogen attached to this carbon for the oxygen to remove.
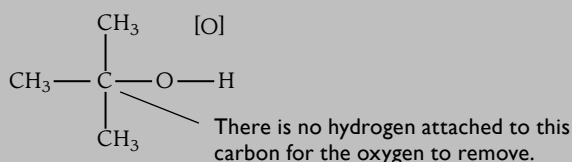
Provided that an aldehyde and a ketone can be distinguished between, these oxidation reactions can be used to detect primary, secondary or tertiary alcohols. There are relatively simple tests for aldehydes that use Fehling's solution or Tollens' reagent (see Chapter 16).

Dehydration

Strong acids such as phosphoric(V) and sulfuric can be used to dehydrate alcohols to form alkenes:

$$CH_3CH_2CH_2OH \rightarrow CH_3CH\!=\!CH_2 + H_2O$$
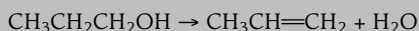
Warming ethanol and passing the vapour over heated aluminium oxide achieves the same reaction:

$$CH_3CH_2OH \rightarrow CH_2\!=\!CH_2 + H_2O$$

Forming esters

If an alcohol is warmed with an organic acid in the presence of H^+ ions, an ester is formed with the elimination of water:
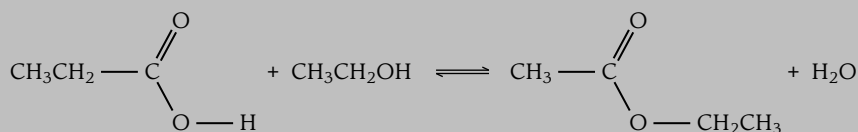
This is an equilibrium reaction and it is often quite slow.

The reaction can be speeded up by using another compound containing the $RC\!=\!O$ group. Suitable compounds include acyl chlorides or acid anhydrides (see Chapter 17).

With ethanoyl chloride and ethanol, the following reaction occurs:

$$CH_3COCl + CH_3CH_2OH \rightarrow CH_3CO_2CH_2CH_3 + HCl$$
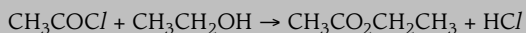
With ethanoic anhydride and ethanol, this reaction takes place:

$$(CH_3CO)_2O + CH_3CH_2OH \rightarrow CH_3CO_2CH_2CH_3 + CH_3CO_2H$$
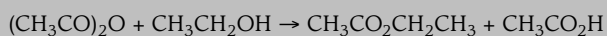
In naming esters the convention is to give the fragment of the alcohol first and then the anion name of the acid. So the esters shown above are all ethyl ethanoate (rather strangely they are usually drawn with the acid fragment first!).

Try this yourself

(36) Name the four esters whose structures are shown below:

(a)

$$CH_3CH_2 - C \overset{O}{\underset{O - CH_2CH_3}{\big\|}}$$

(b)

$$H - C \overset{O}{\underset{O - CH_2CH_2CH_3}{\big\|}}$$

(c)

$$CH_3CH_2CH_2 - C \overset{O}{\underset{O - CH_3}{\big\|}}$$

(d)

$$CH_3 - C \overset{O}{\underset{O - CH_2CH_2CH_3}{\big\|}}$$
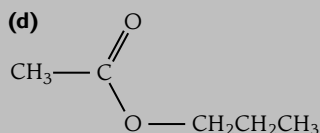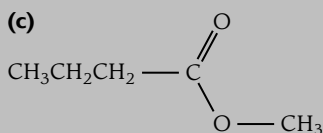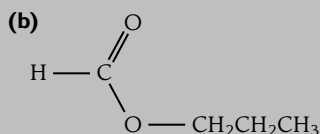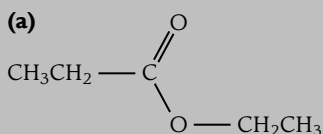
The tri-iodomethane (iodoform) reaction

This reaction is quite specific for a particular structural arrangement in an alcohol. It detects the presence of the $CH_3CH(OH)-$ group. The test is carried out by adding iodine solution to the alcohol and then adding just enough sodium hydroxide to remove the colour of the iodine. On standing, or more usually on warming, a pale yellow precipitate of tri-iodomethane is formed if the group is present.

Phenol

Phenol is an aromatic hydroxyl compound:

OH
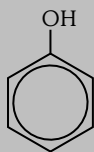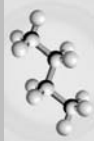
The presence of the benzene ring makes phenol behave differently from alcohols.

Reactions with bases

Phenol is a weakly acidic compound. Its acidity stems from the fact that it ionises in water:

OH $+ H_2O \rightleftharpoons$ O⁻ $+ H_3O^+$

Phenoxide ion

Approved: 0777 023 444
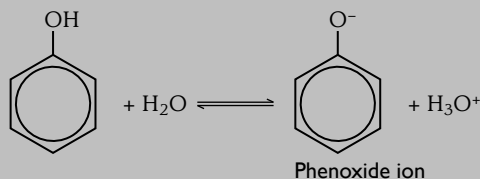
Because phenol is a very weak acid, the equilibrium lies over to the left. It can lose a proton because the remaining negative charge is delocalised over the benzene ring, making the phenoxide ion more stable. There is evidence for this behaviour because phenol reacts with sodium hydroxide to give a colourless product:

Sodium phenoxide
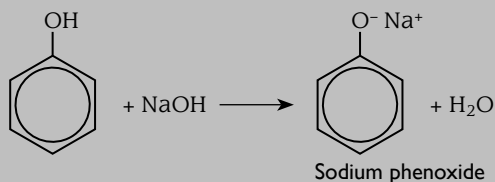
But phenol is neither acidic enough to turn blue litmus paper red, nor to release carbon dioxide from sodium carbonate. It does produce hydrogen when heated with sodium:

Sodium phenoxide
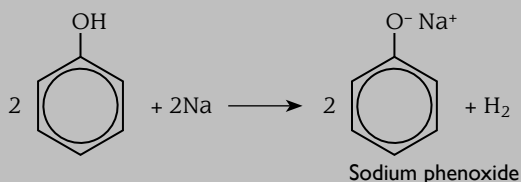
Nitration

Phenol behaves differently from benzene in its reaction with nitric acid. It reacts in the cold with dilute nitric acid, whereas benzene requires a nitrating mixture of concentrated nitric and sulfuric acids. The reason for this is that the presence of the OH group makes the ring much more reactive. It also directs reaction to the 2- and 4-positions on the ring.

With dilute nitric acid, 4-nitrophenol is formed:
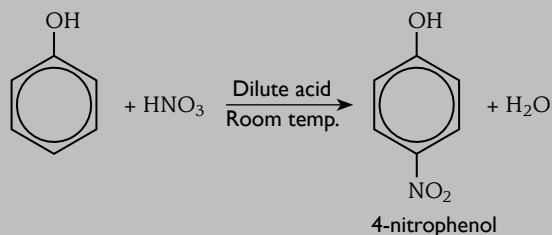
4-nitrophenol

With concentrated nitric acid, 2,4,6-trinitrophenol is formed:

2,4,6-trinitrophenol

Approved: 0777 023 444
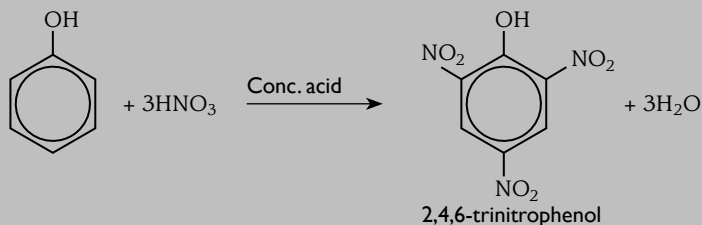
Bromination

When bromine water is added to phenol, there is a similar effect to nitration. The activated ring gives an almost instantaneous white precipitate of 2,4,6-tribromophenol:

2,4,6-tribromophenol
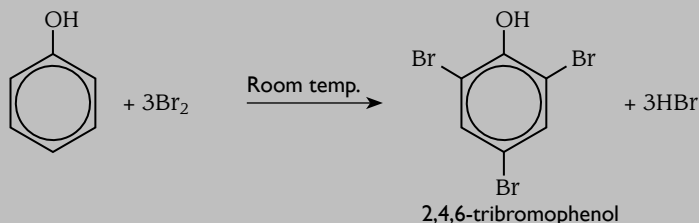
16 Carbonyl compounds

This chapter is needed almost exclusively for the AS examination. Only the very last section is required for the A2 examination. The syllabus treats aldehydes and ketones as two separate classes of organic compound. However, the learning outcomes and this section deal with them together because many of the reactions are similar.

Formation

The oxidation of alcohols by acidified dichromate(VI) was looked at in Chapter 15.

- With a primary alcohol, an aldehyde is first formed. If this is not removed from the reaction vessel, it is further oxidised to give a carboxylic acid:
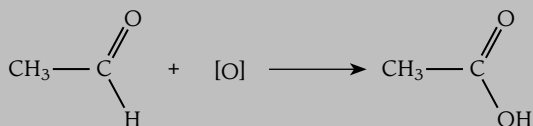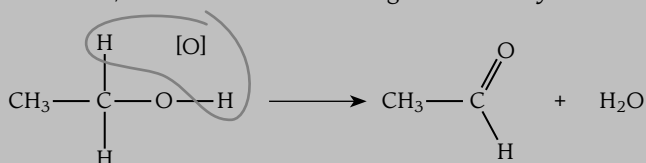
- With a secondary alcohol, a ketone is formed. This is not oxidised further:

Propan-2-ol   Propanone
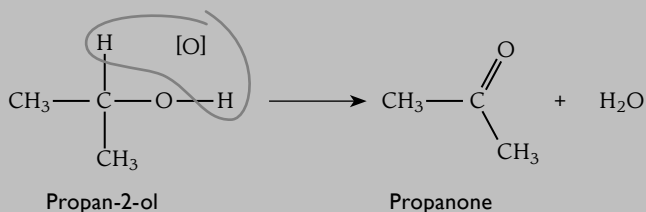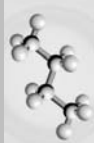
Reactions

Reduction

This is the reverse of the oxidation reactions used in the preparation of carbonyl compounds. It is carried out using sodium tetrahydridoborate (sodium borohydride), $NaBH_4$.

With aldehydes such as ethanal the reaction is as follows, forming a primary alcohol:

$$CH_3-\overset{\displaystyle O}{\underset{\displaystyle H}{C}} \quad + \quad 2[H] \longrightarrow CH_3-\overset{\displaystyle OH}{\underset{\displaystyle H}{C}}-H \quad (CH_3CH_2OH)$$
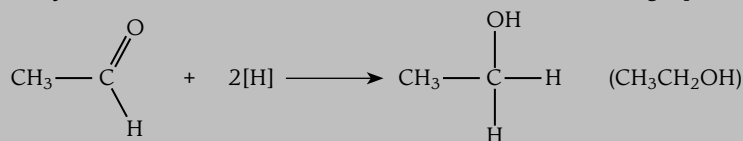
With ketones such as propanone the reaction is very similar. A secondary alcohol is formed:

$$\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}=O \quad + \quad 2[H] \longrightarrow CH_3-\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{C}}-H \quad (CH_3CH_2CH_3) \quad OH$$
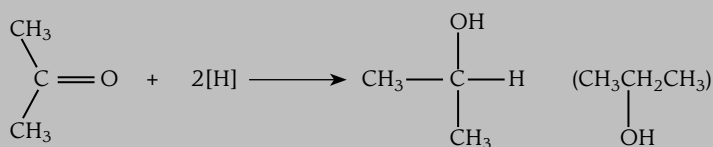
Nucleophilic addition of hydrogen cyanide

In just the same way that alkenes can react by adding a molecule across a C=C double bond, carbonyl compounds can add a molecule across the C=O double bond. At AS you need to know the mechanism for this reaction, using hydrogen cyanide as the nucleophile. You may think that this is a strange reactant, but as we saw earlier it adds a carbon atom to the chain, which is often an important step in a reaction.

The reactions can be summarised in simple equations:

$$CH_3-\overset{\displaystyle O}{\underset{\displaystyle H}{C}} \quad + \quad HCN \longrightarrow CH_3-\overset{\displaystyle OH}{\underset{\displaystyle H}{C}}-CN$$

$$\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}=O \quad + \quad HCN \longrightarrow CH_3-\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{C}}-CN$$
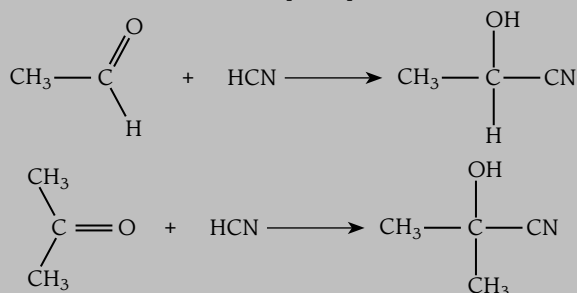
Hydrogen cyanide itself is not used in the reaction because it is a highly toxic gas. Instead, sodium or potassium cyanide is added to the carbonyl compound followed by a small amount of sulfuric acid. This produces hydrogen cyanide in the reaction vessel but also forms cyanide ions, which are important as you will see when we look at the mechanism.

The first thing to remember is that the C=O bond is polarised with a partial positive charge on the carbon and a partial negative charge on the oxygen:
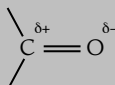
Mechanism of addition of hydrogen cyanide to an aldehyde

The reaction starts with an attack by the nucleophilic cyanide ion on the slightly positive carbon atom:
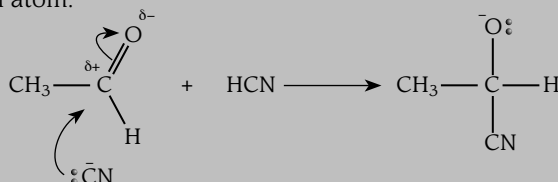
The negative ion formed then picks up a hydrogen ion. It could come from a hydrogen cyanide molecule or from the water or the H_3O^+ ions present in the slightly acidic solution:

Mechanism of addition of hydrogen cyanide to a ketone

The mechanism for ketones is similar to that for aldehydes. The first stage is a nucleophilic attack by the cyanide ion on the slightly positive carbon atom:
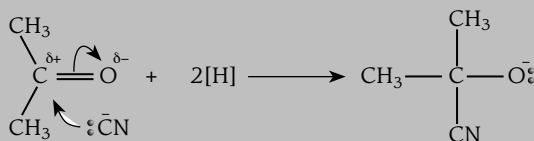
The negative ion formed then picks up a hydrogen ion to give the hydroxynitrile (cyanohydrin as it is sometimes called in older textbooks).
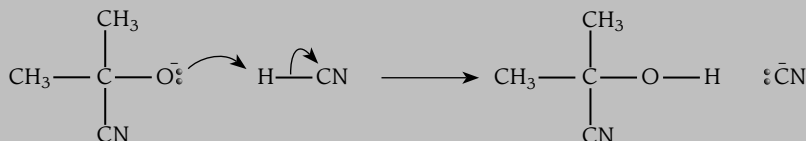
Chirality

You may have noticed that the product formed with the aldhyde has four different groups attached to the central carbon. If you remember the section on isomerism in Chapter 13 you will know that this is therefore a **chiral** carbon atom.

You may also remember that this usually means that the compound exists as a pair of optical isomers that are mirror images of each other. The product of this particular reaction, however, is *not* optically active because ethanal is a planar molecule and the mechanism means that attack by the cyanide ion can occur from both above and below the molecule. This produces a 50:50 mixture of isomers, so the net result is a lack of optical activity.

Reaction with 2,4-dinitrophenylhydrazine (2,4-DNPH)

This rather complicated sounding reagent is used as a simple test for carbonyl compounds. The reaction is called a 'condensation' or sometimes a 'nucleophilic addition–elimination' reaction.

If a few drops of a suspected carbonyl compound (or a solution of the suspected carbonyl compound in methanol) are added to 2,4-DNPH, a distinct orange or yellow precipitate shows a positive result.
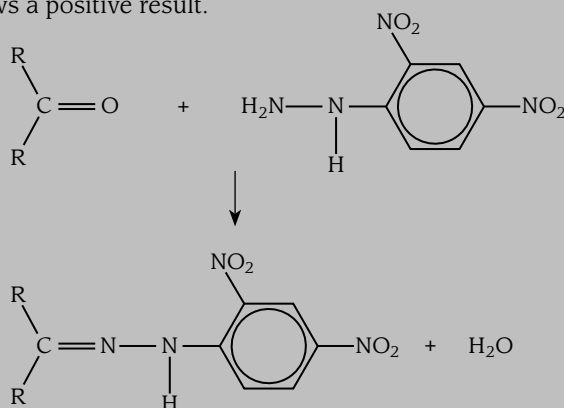
The equation for the reaction is shown above, but it is unlikely that you would be asked to produce this in the examination.

The reaction is rather more useful than just testing for a carbonyl compound. If the precipitate is filtered off, washed and re-crystallised, the melting point of the crystals obtained is characteristic of the particular aldehyde or ketone that reacted, enabling identification to take place.

Distinguishing between aldehydes and ketones

In the section on oxidation reactions of hydroxy compounds in Chapter 15, you saw that primary, secondary and tertiary alcohols can be distinguished between by looking at their oxidation products. These same reactions enable us to distinguish between aldehydes and ketones.

Table 16.1 summarises the behaviour of the two types of carbonyl compound with different reagents.

Table 16.1

Reagent	Aldehydes	Ketones
Acidified dichromate(VI)	Orange solution turns blue-green	No change in the orange solution
Fehling's solution	Blue solution produces an orange-red precipitate of copper(I) oxide	No change in the blue solution
Tollens' reagent	Colourless solution produces a grey precipitate of silver, or a silver mirror is formed on the test tube	No change in the colourless solution

Try this yourself

(37) Compound **K** was produced by the oxidation of an alcohol **J** of molecular formula $C_4H_{10}O$. When **K** is reacted with 2,4-DNPH, a yellow-orange precipitate is formed. **K** also reacts with Fehling's solution forming an orange-red precipitate. When treated with alkaline aqueous iodine, no precipitate is formed.

Study the reactions above and use them to deduce the structural formulae of **J** and **K**.

The tri-iodomethane (iodoform) reaction

We saw in Chapter 15 that this reaction is linked to the $CH_3CH(OH)-$ group in alcohols. It can also be used to identify the CH_3CO- group in carbonyl compounds.

In other words, a positive result — the pale yellow precipitate of tri-iodomethane (iodoform) — is given by an aldehyde or ketone containing the group:
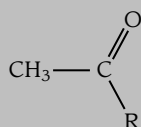
Ethanal is the *only* aldehyde to give a positive reaction. Any methyl ketone will give a positive result.

Approved: 0777 023 444
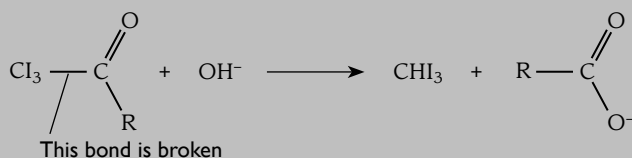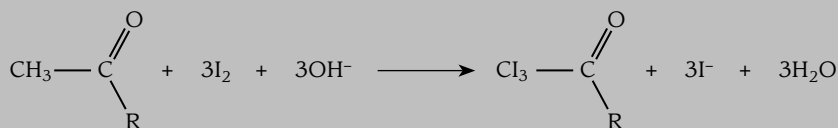
17 Carboxylic acids and their derivatives

This chapter is a mix of material for the AS and A2 examinations. Most of the material on carboxylic acids and esters is for the AS examination; the material related to other derivatives is for A2.

Carboxylic acids

Formation of carboxylic acids

There are three main methods for preparing carboxylic acids (although, strictly, one is a step in another process).

From an alcohol

You will remember from Chapter 15 that a primary alcohol can be oxidised using acidified dichromate(VI) to give an aldehyde and that if this is not distilled off, it is oxidised further to a carboxylic acid, for example:
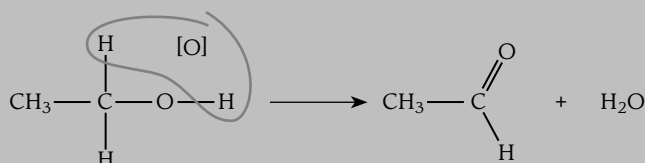
From an aldehyde

We could start with an aldehyde and oxidise it with acidified dichromate(VI) to form the carboxylic acid, for example:
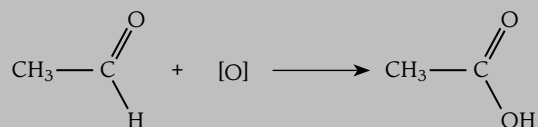
This is rare, since in order to make an aldehyde we have to start with a primary alcohol.

From a nitrile

You saw in Chapter 15 how nitriles can be produced from halogenoalkanes. They can be hydrolysed to form either carboxylic acids or their salts, depending on whether acid or base is used in the hydrolysis.

If the nitrile is heated under reflux with a dilute acid, such as dilute hydrochloric acid, a carboxylic acid is formed, for example:

$$CH_3CN + 2H_2O + H^+ \rightarrow CH_3CO_2H + NH_4^+$$
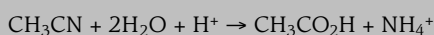
If the nitrile is heated under reflux with an alkali such as sodium hydroxide solution, the sodium salt of the carboxylic acid is formed and ammonia is released, for example:

$CH_3CN + NaOH + H_2O \rightarrow CH_3CO_2^-Na^+ + NH_3$
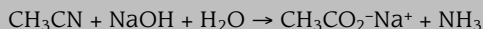
To obtain the carboxylic acid, a strong acid such as hydrochloric acid is added and the carboxylic acid is distilled off.

Reactions of carboxylic acids

Formation of salts

Carboxylic acids are generally relatively weak acids (although there are exceptions). They behave as acids because of their ability to donate protons:

$CH_3CO_2H + H_2O \rightleftharpoons CH_3CO_2^- + H_3O^+$
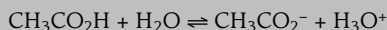
The reaction is reversible with the equilibrium well over to the left. Ethanoic acid is never more than around 1% ionised resulting in solutions with a pH of between 2 and 3.

As a result, carboxylic acids can form salts in a number of ways (although there are some exceptions). Ethanoic acid is used as the example in all the equations shown.

● Aqueous solutions of carboxylic acids react with the more reactive metals such as magnesium to form the salt:

$2CH_3CO_2H + Mg \rightarrow (CH_3CO_2^-)_2Mg^{2+} + H_2$
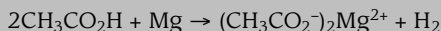
● Aqueous solutions of carboxylic acids react with metal hydroxides such as sodium hydroxide to form the salt:

$CH_3CO_2H + NaOH \rightarrow CH_3CO_2^-Na^+ + H_2O$
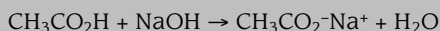
● Aqueous solutions of carboxylic acids react with carbonates and hydrogen carbonates liberating carbon dioxide:

$2CH_3CO_2H + Na_2CO_3 \rightarrow 2CH_3CO_2^-Na^+ + CO_2 + H_2O$

$CH_3CO_2H + NaHCO_3 \rightarrow CH_3CO_2^-Na^+ + CO_2 + H_2O$

There is very little difference between these reactions and those with other acids. If, however, you chose to use a marble chip as the carbonate, the reaction would be noticeably slower.

● Ethanoic acid reacts with ammonia in just the same way as other acids, forming the ammonium salt:

$CH_3CO_2H + NH_3 \rightarrow CH_3CO_2^-NH_4^+$
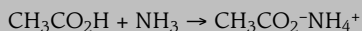
Formation of esters

Making esters from alcohols was covered in Chapter 15, and you learned that a range of reagents can be used to react with the –OH group. Here, we are considering a single reaction — the formation of an ester from a carboxylic acid and an alcohol.
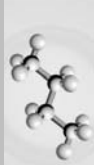
An ester is formed when a carboxylic acid is heated with an alcohol in the presence of an acid catalyst, usually concentrated sulfuric acid. The reaction is slow and reversible, for example:
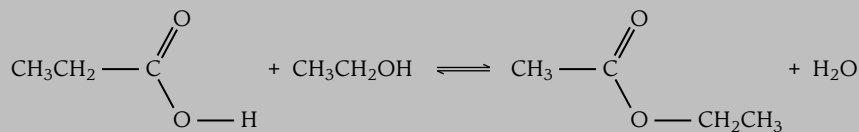
In the laboratory this is achieved by warming the carboxylic acid and alcohol together with a few drops of concentrated sulfuric acid in a water bath for 10–15 minutes and then pouring the contents into a small beaker of cold water. The ester can be detected by its fruity smell. If a sample is required, it can be distilled off from the reaction mixture. Ethyl ethanoate, the most common ester you will come across, can be prepared in this way.

Formation of acyl chlorides

To form an acyl halide from a carboxylic acid, the –OH group in the acid has to be replaced by a –Hal group. You might wonder why this is an important reaction, but acyl chlorides are very reactive and are useful in preparing a range of new materials.

In Chapter 15 we used a group of reagents — phosphorus trichloride, PCl_3, phosphorus pentachloride, PCl_5, and thionyl chloride, $SOCl_2$ — to convert the –OH group of an alcohol to a –Cl group. This same group of reagents can be used to achieve the same outcome here:

$$3CH_3CO_2H + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$$

$$CH_3CO_2H + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$$

$$CH_3CO_2H + SOCl_2 \rightarrow CH_3COCl + SO_2 + HCl$$
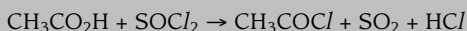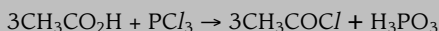
The third reaction is the 'cleanest' because the by-products are gases.

Relative acidity of acids

For the A2 examination it is not enough just to know that carboxylic acids are relatively weak acids because the equilibrium for dissociation lies well to the left. You also need to know what makes some acids stronger or weaker than others.

It helps if you think back to the definition of an acid as a proton donor given in Chapter 7.

> **Tip** It would be a good idea to re-read the section on pK_a and pH on page 73.

Before comparing carboxylic acids, it is useful to look at the ionisation of ethanoic acid in more detail:

Approved: 0777 023 444
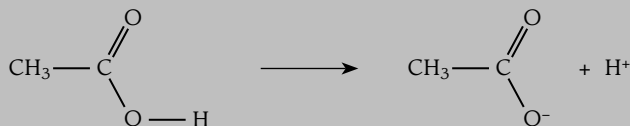
It is helpful to look a little more closely at the ethanoate ion. It has been found that the two carbon–oxygen bond lengths are the same. This means that the usual way of drawing the ion with a C=O and a C—O⁻ cannot be correct. The representation below is more accurate:
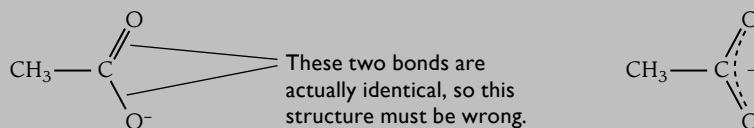
The dashed line represents delocalisation of electrons over the two oxygen atoms and the carbon atom. In general, the more the charge is spread around, the more stable the ion is.

The pK_a values for some carboxylic acids are given in Table 17.1.

Table 17.1

Formula of the acid	pK_a
HCO_2H	3.75
CH_3CO_2H	4.76
$CH_3CH_2CO_2H$	4.87

You might be surprised to see that methanoic acid has a smaller pK_a (stronger acid) than ethanoic acid. Let's think what we know about alkyl groups. They have a tendency to release electrons, which reduces the overall negative charge on the O—C—O group. However, methanoic acid does not have any alkyl groups, so this effect is not present. The addition of an extra CH_2 in propanoic acid makes very little difference to the pK_a.

Now let's see what happens if an **electronegative** atom that pulls electrons away from the O—C—O group is introduced. Chlorine is a good example of an electro-negative atom. The pK_a values for ethanoic acid and its chlorinated derivatives are shown in Table 17.2.

Table 17.2

Formula of the acid	pK_a
CH_3CO_2H	4.76
CH_2ClCO_2H	2.86
$CHCl_2CO_2H$	1.29
CCl_3CO_2H	0.65

You can see how the presence of chlorine atoms makes it easier for the hydrogen to be removed.

Acyl chlorides

We saw earlier how to make acyl chlorides from carboxylic acids. Here, their reactions are covered.

Hydrolysis

Acyl halides react quite violently with water, releasing steamy fumes of HCl and forming the appropriate carboxylic acid:
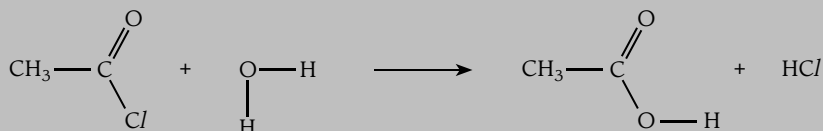
Figure 17.1 The reaction of ethanoyl chloride with water

The equation can also be written as shown below:

$$CH_3COCl + H_2O \rightarrow CH_3CO_2H + HCl$$
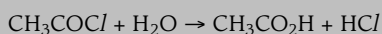
However, when studying the reactions of acyl chlorides with alcohols and phenols, it is useful to think about the form shown in Figure 17.1.

The ease with which acyl chlorides react with water is in contrast with the reactivity of alkyl and aryl chlorides. In Chapter 15 you saw that alkyl halides can be hydrolysed by heating under reflux with sodium hydroxide in aqueous ethanol.

Aryl chlorides are very resistant to hydrolysis. Chlorobenzene shows signs of reaction with OH$^-$ only under extreme conditions of around 500 K and approaching 200 atm pressure. One reason for this lack of reaction is repulsion of the OH$^-$ group by the ring electrons. Perhaps a more significant reason is the interaction between one of the lone pairs of electrons on chlorine and the delocalised ring electrons:

Overlap between lone pair
and the ring electrons
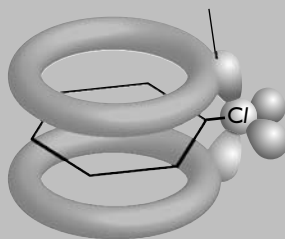
Lone pair now delocalised to some
extent with the ring electrons
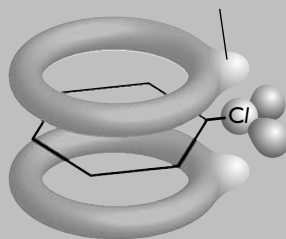
Reaction with alcohols and phenols

With alcohols

The reaction between an acyl chloride and an alcohol is similar to the reaction between an acyl chloride and water, with the release of hydrogen chloride:
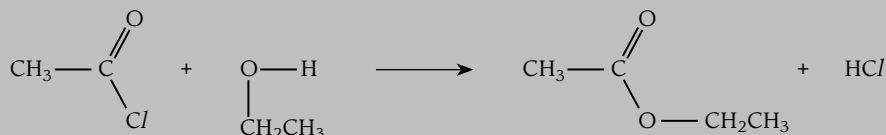
Compare this reaction with the equation shown in Figure 17.1.

From a practical point of view this is a straightforward method for producing an ester because it takes place at room temperature and, because HCl is released, it is not a reversible reaction. This contrasts with the reaction of ethanol with ethanoic acid in the presence of an acid catalyst.

With phenols

In a phenol, the –OH group is attached directly to the benzene ring. The reaction between phenol and ethanoyl chloride is not as vigorous as the reaction with ethanol due to the presence of the benzene ring. Apart from this the reaction is very similar:
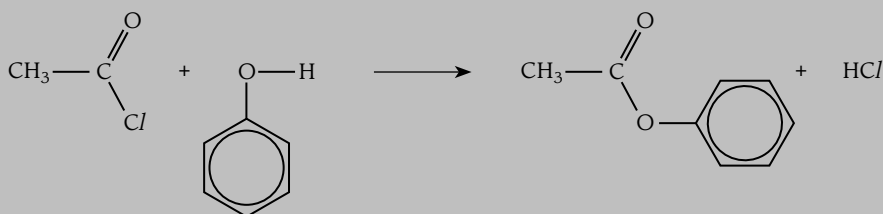
The product is called phenyl ethanoate (remember alcohol/phenol part first, then the carboxylic acid part). The reaction is called **acylation**.

Reaction with primary amines

A primary amine is an ammonia molecule in which one of the hydrogen atoms has been replaced by an alkyl group:

NH_3	CH_3NH_2	$CH_3CH_2NH_2$	
Ammonia	Methylamine	Ethylamine	Phenylamine
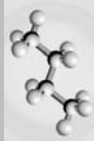
Primary amines react with acyl chlorides by substitution, replacing the chlorine atom and joining via the nitrogen atom, for example:
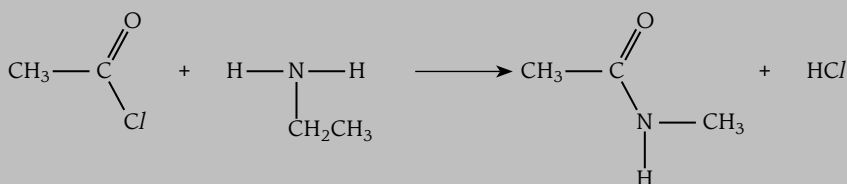
The product is an **N-substituted amide**.

Esters

Most of this section is needed for AS; only polyesters are required for A2.

Hydrolysis

You will remember that to form an ester, an alcohol (or phenol) is reacted with a carboxylic acid and water is formed as a by-product. Hydrolysis is the reverse of this process and can be achieved in either of two ways.

Acid hydrolysis

In acid hydrolysis, the ester is heated under reflux with either dilute hydrochloric or dilute sulfuric acid:

$$CH_3CO_2CH_2CH_3 + H_2O \rightleftharpoons CH_3CO_2H + CH_3CH_2OH$$
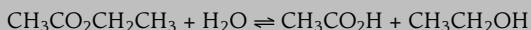
As in the formation of an ester, the reaction is reversible. We try to make the reaction as complete as possible by having an excess of water present.

Base hydrolysis

Base hydrolysis is the more usual way of hydrolysing esters because the reaction goes to completion, rather than forming an equilibrium mixture:

$$CH_3CO_2CH_2CH_3 + NaOH \rightarrow CH_3CO_2^-Na^+ + CH_3CH_2OH$$
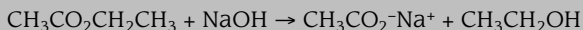
Although this forms the sodium salt of the carboxylic acid, it is still relatively easy to separate the products. First, the alcohol is distilled off and then an excess of a strong acid (dilute hydrochloric or dilute sulfuric acid) is added. This forms the carboxylic acid which is only slightly ionised and can be distilled off.

Commercial uses

Perfumes and flavours

Esters can be formed from a large number of combinations of alcohols with carboxylic acids. They are distributed widely in nature and are responsible for many of the smells and flavours associated with fruits and flowers. This has led to the development of artificial esters for the food industry — for example for ice cream — and for products that need a nice smell, such as detergents and air fresheners. Figure 17.2 shows some of the esters that are used.
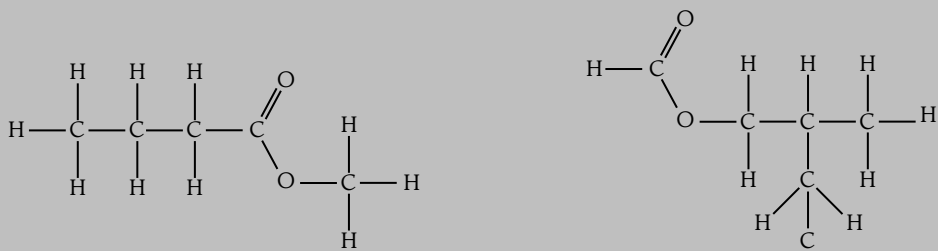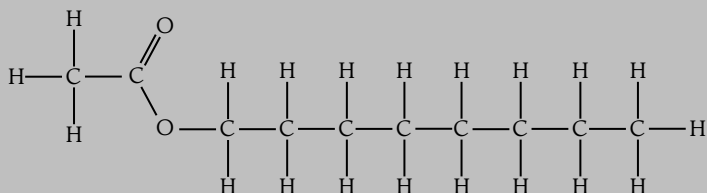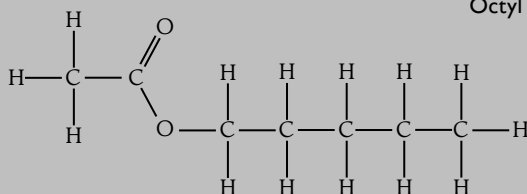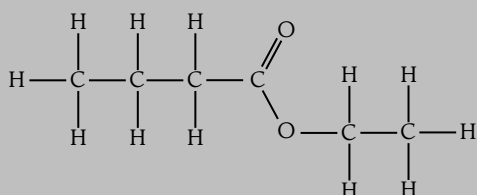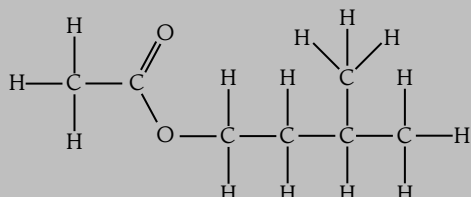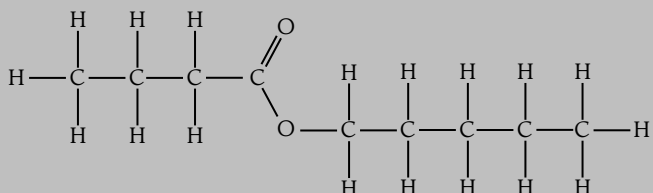
Figure 17.2 Esters used in industry

Natural esters are still used in perfumes.

Margarine production

Most oils and fats are esters of long-chain carboxylic acids with the alcohol glycerol ($CH_2OHCHOHCH_2OH$). Oils often contain carboxylic acids in which the chain has one or more $C=C$ double bonds present. Fats contain mainly carboxylic acids with saturated chains (containing only C—C single bonds) (see Figure 17.3).
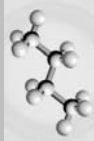
It is this that makes the oils liquid and the fats low-melting solids. These esters are often referred to as glycerides because the common name for the alcohol is glycerol.

$$CH_3(CH_2)_{16}COOCH_2$$
$$|$$
$$CH_3(CH_2)_{16}COOCH$$
$$|$$
$$CH_3(CH_2)_{16}COOCH_2$$
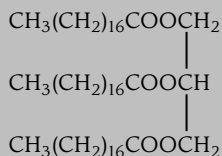
Figure 17.3 A molecule of a fat

In order to make margarine, the vegetable oils have to have some of the double bonds removed. This is achieved by reacting the oils with hydrogen in the presence of a nickel catalyst.

Consumption of saturated fats has been linked to heart disease, so it is important that these do not form a large part of the human diet. Saturated fats are more common in animal fat than in vegetable oils.

Soap making

Animal fats and vegetable oils have been the raw materials for making soaps and some detergents for hundreds of years. The large molecule esters found in oils and fats are heated with concentrated sodium hydroxide solution and undergo base hydrolysis. The sodium salt of the carboxylic acid is formed (and acts as the soap or detergent) along with the alcohol 1,2,3-trihydroxypropane (glycerol):

$$CH_3(CH_2)_{16}COOCH_2 \qquad\qquad\qquad\qquad\qquad\qquad CH_2OH$$
$$| \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$CH_3(CH_2)_{16}COOCH \;+\; 3NaOH \;\longrightarrow\; 3CH_3(CH_2)_{16}COONa \;+\; CHOH$$
$$| \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$CH_3(CH_2)_{16}COOCH_2 \qquad\qquad\qquad\qquad\qquad\qquad CH_2OH$$
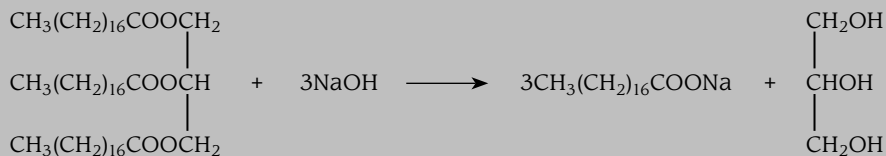
Solvents

The smaller molecule esters are important solvents in, for example, the decaffeination of tea and coffee, and in paints and varnishes (such as nail varnish remover).

Polyesters

A **polyester** is a polymer or chain made up of repeating units joined by an ester linkage. Polymerisation was covered briefly in Chapter 14 where we covered poly-alkenes. The polymerisation is different here because two different molecules are needed, rather than just one.

The most important commercial polyester is known as Terylene® and is produced by reacting a dicarboxylic acid with a dialcohol:

HOOC⟨◯⟩COOH   HO ⸺ CH_2CH_2 ⸺ OH

Benzene-1,4-dicarboxylic acid   Ethane-1,2-diol
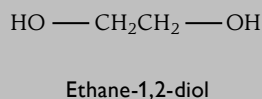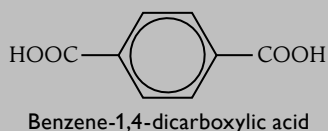
When these molecules react together they form an ester linkage with the loss of a water molecule. The new molecule has a carboxylic acid group at one end and an alcohol group at the other. Therefore, it can continue to react, alternately adding a dialcohol and a dicarboxylic acid as shown below:
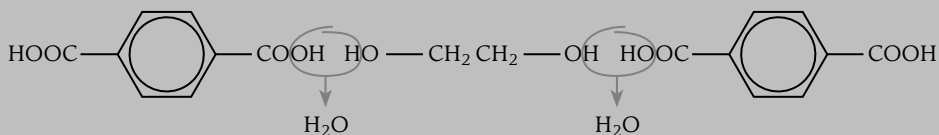
Polymers are covered in more detail in Chapter 19.

18 Nitrogen compounds

This chapter is needed only for the A2 examination.

Primary amines

Formation

Alkyl amines

The reaction to use for the formation of an alkyl amine is the reduction of a nitrile using lithium tetrahydridoaluminate(III) (lithium aluminium hydride). The reaction takes place in ethoxyethane solution and the amine is produced on adding a small amount of dilute acid. This does *not* work with $NaBH_4$:

$$CH_3CN + 4[H] \rightarrow CH_3CH_2NH_2$$
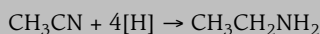
This reaction can also be achieved by heating the nitrile in hydrogen gas in the presence of a platinum, palladium or nickel catalyst:

$$CH_3CN + 2H_2 \rightarrow CH_3CH_2NH_2$$
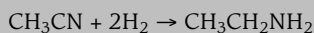
Phenylamine

Phenylamine is prepared from nitrobenzene in a two-stage process. First, nitrobenzene is heated under reflux in a boiling water bath with a mixture of tin and concentrated hydrochloric acid. Because of the acidic conditions, rather than getting phenylamine directly, the nitrobenzene is reduced to phenylammonium ions. The lone pair on the nitrogen in the phenylamine picks up a hydrogen ion from the acid:
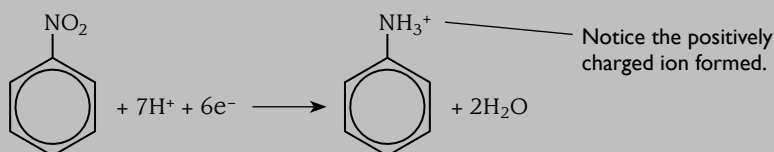
The second stage is to add sodium hydroxide solution to remove the hydrogen ion:
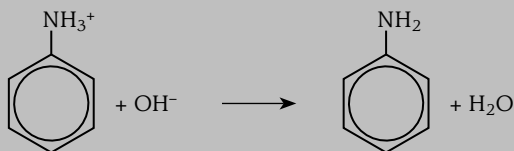
The phenylamine is then extracted by steam distillation.

Basicity

When considering the basic properties of alkyl amines, it is easiest to think of them as substituted ammonia molecules. If you remember that bases are proton acceptors it is not too difficult to make the comparison. Compare the two equations:

$NH_3 + H_3O^+ \rightarrow NH_4^+ + H_2O$

$CH_3CH_2NH_2 + H_3O^+ \rightarrow CH_3CH_2NH_3^+ + H_2O$
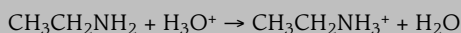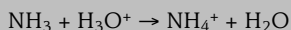
The same rule applies to secondary and tertiary amines, with alkyl groups substituting hydrogen atoms on the nitrogen atom:

$(CH_3CH_2)_2NH + H_3O^+ \rightarrow (CH_3CH_2)_2NH_2^+ + H_2O$

$(CH_3CH_2)_3N + H_3O^+ \rightarrow (CH_3CH_2)_3NH^+ + H_2O$
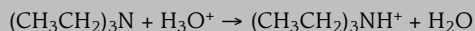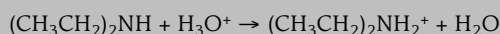
Amines are generally stronger bases than ammonia. This is because alkyl groups are electron donating, pushing negative charge onto the nitrogen atom and strengthening the attraction to the proton. The more alkyl groups there are attached to the nitrogen, the stronger the base formed.

By contrast, phenylamine is a much *weaker* base than ammonia. This is because the lone pair of electrons on the nitrogen atom is delocalised with the π-electrons on the benzene ring and is thus no longer as available to attract hydrogen ions.

Reactions of phenylamine

With aqueous bromine

With bromine water, phenylamine gives a fairly instant white precipitate of 2,4,6-tribromophenylamine at room temperature:
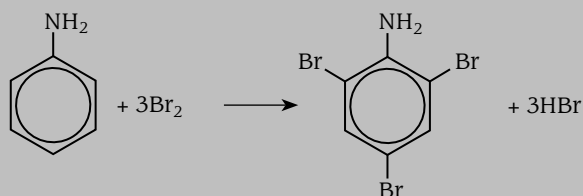
This is an example of electrophilic substitution of the benzene ring.

With nitrous acid

Phenylamine undergoes different reactions with nitrous acid depending on the temperature of the reaction mixture.

At low temperatures (<10 °C) phenylamine is dissolved in cold hydrochloric acid and then a solution of cold sodium nitrite is added slowly. The slow addition is so that the reaction mixture remains around 5 °C. A solution containing benzenediazonium ions is obtained:
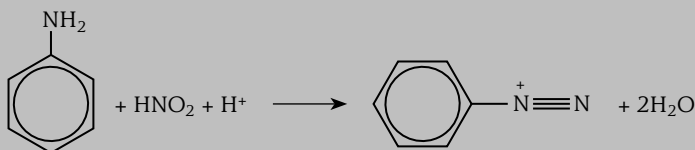
Note that when drawing the structure of a benzenediazonium salt, the positive charge is shown on the nitrogen atom closest to the benzene ring.

The benzenediazonium salt is not isolated, but is often reacted by adding a cold solution of phenol in sodium hydroxide to the mixture:
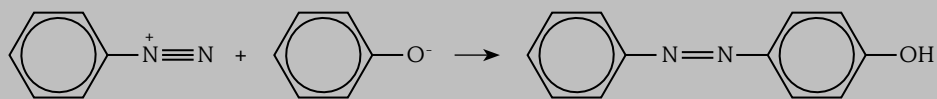
The result is a yellow, orange or red dye, the colour of which depends on the nature of the phenol used. With naphthalen-2-ol (2-naphthol), the following compound is formed:
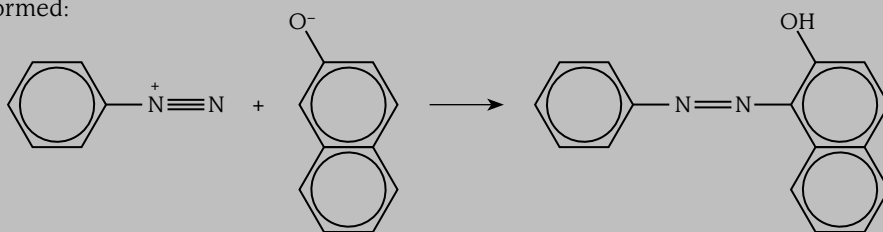
At temperatures above 10 °C, a reaction takes place that produces a complex organic mixture containing mainly phenol. Nitrogen gas is evolved:

$$C_6H_5NH_2 + HNO_2 \rightarrow C_6H_5OH + N_2 + H_2O$$
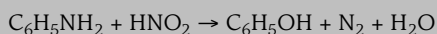
Try this yourself

(38) Explain why phenylamine is a much weaker base than ethylamine.

Amides

Formation from acyl halides

We saw in Chapter 17 how acyl halides react with primary amines. They also react with ammonia to form amides. This is normally carried out by adding the acyl halide to a concentrated solution of ammonia. The reaction is violent, producing clouds of ammonium chloride:

$$CH_3COCl + 2NH_3 \rightarrow CH_3CONH_2 + NH_4Cl$$
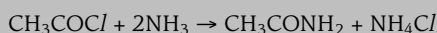
Hydrolysis

Amides are hydrolysed by heating with aqueous acids or aqueous alkalis:

$CH_3CONH_2 + HCl + H_2O \rightarrow CH_3CO_2H + NH_4^+Cl^-$

$CH_3CONH_2 + NaOH \rightarrow CH_3CO_2^-Na^+ + NH_3$
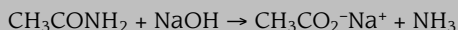
The second reaction is sometimes used as a test for amides, because the ammonia produced is easily detected.

Formation of polyamides

Polyamides are a very important group of polymers that include nylon and Kevlar®. The polymerisation reaction involves two monomers that react by condensation to form an amide bond between them:
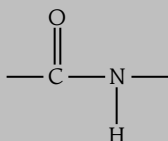
This means that the monomers have to be diamines and dicarboxylic acids.

Nylon-6,6

Nylon is an important polymer used as both a fibre and a bulk solid. It was used originally as a replacement for silk, but was soon being used in strings for musical instruments and in rope. In its solid form it has become a replacement for metal in low–medium stress applications, such as gears. For nylon, the monomers are hexanedioic acid and 1,6-diaminohexane:

$HO_2C(CH_2)_4CO_2H$ $\qquad\qquad$ $H_2N(CH_2)_6NH_2$
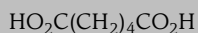
Hexanedioic acid $\qquad$ 1,6-diaminohexane

Each of these molecules has six carbon atoms, so this form of nylon is called nylon-6,6. Water is lost in the formation of each amide bond:
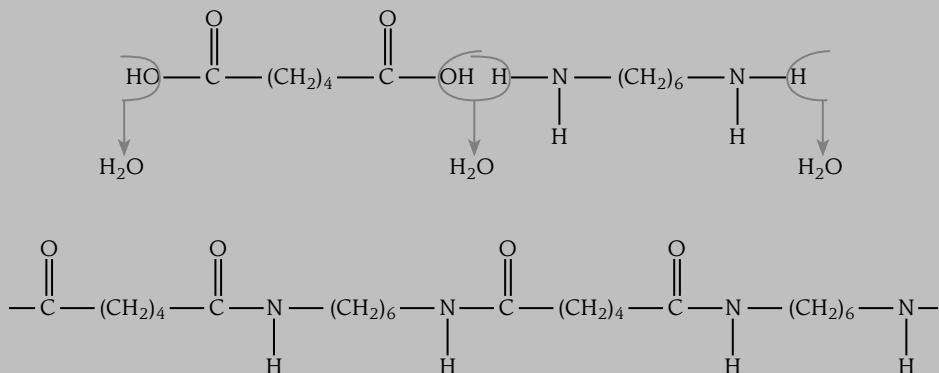
Nylon-6

Another form of nylon can be produced from a single monomer called caprolactam:
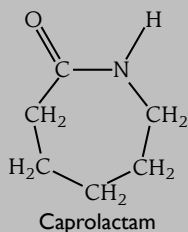
Caprolactam

At first sight, caprolactam does not seem to be a very promising monomer because it exists as a ring. However, when caprolactam is heated in the presence of about 10% water at 250 °C, the ring is broken between the carbon and the nitrogen and an amino acid is formed. The amino acid is then able to polymerise by a condensation reaction with the elimination of water to form nylon-6.
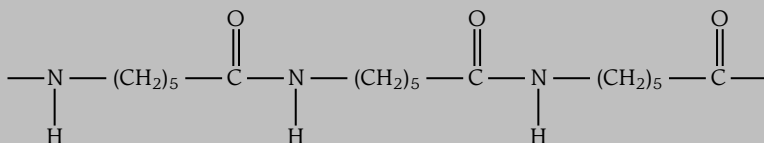
Kevlar®

Kevlar® is a relatively new polymer with exceptional strength-to-weight properties. It is used in body armour such as bulletproof vests. It is also used in sporting applications such as bicycle tyres, sails and racing cars.

The monomers for Kevlar® are the aryl equivalents of those used for nylon:

Benzene-1,4-dicarboxylic acid   1,4-diaminobenzene
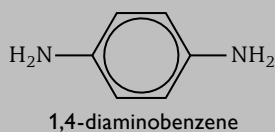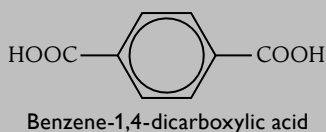
A similar condensation reaction takes place:
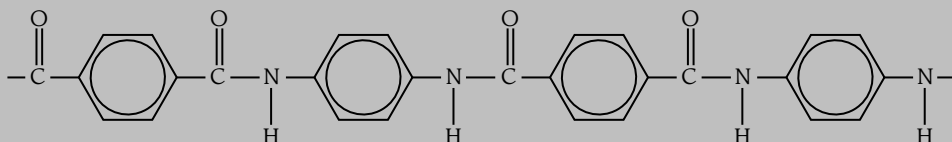
One disadvantage of polyamides is that they are hydrolysed by strong acids (although Kevlar® is more resistant).

> **Try this yourself**
>
> **(39)** Describe two main differences between *condensation* polymerisation as described here and *addition* polymerisation as described in Chapter 19.
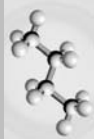
Amino acids and proteins

Acid–base properties of amino acids

As the name suggests, amino acids are organic compounds that contain both a carboxylic acid group and an amine group. The amino acids that are important biologically have the amine group attached to the *same* carbon atom as the carboxylic acid group. They are known as 2-aminoacids (or alpha-amino acids). Glycine (2-aminoethanoic acid) is the simplest:

$H_2N—CH_2—CO_2H$
Glycine (2-aminoethanoic acid)
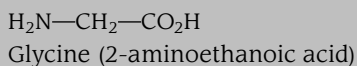
Amino acids are crystalline, high melting point (>200 °C) solids. Such high melting points are unusual for a substance with molecules of this size; they are a result of internal ionisation. Even in the solid state, amino acids exist as **zwitterions** in which a proton has been lost from the carboxyl group and accepted by the nitrogen of the amine group:

$H_3N^+—CH_2—CO_2^-$
Zwitterion of glycine
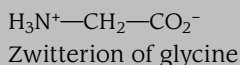
Hence, instead of hydrogen bonds between the amino acid molecules there are stronger ionic (electrovalent) bonds. This is reflected in the relative lack of solubility of amino acids in non-aqueous solvents compared with their solubility in water.

The zwitterions exhibit acid–base behaviour since they can accept and donate protons.

In acid, a proton is accepted onto the carboxylic acid anion forming a unit with an overall positive charge:

$H_3N^+—CH_2—CO_2^- + H_3O^+ \rightarrow H_3N^+—CH_2—CO_2H + H_2O$
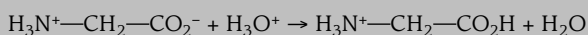
In alkali, the reverse occurs with the loss of a proton from the nitrogen atom:

$H_3N^+—CH_2—CO_2^- + OH^- \rightarrow H_2N—CH_2—CO_2^- + H_2O$
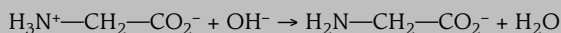
The species present in a given solution depends on the pH of the solution.

Formation of peptide bonds

If we consider amino acids in their non-ionic form, it is easy to see that they have the potential to react together to form a polymer (in a similar way to nylon). The carboxylic acid and amine groups will react to form an amide linkage (this is called a **peptide bond** in biological systems) with the elimination of a water molecule. This reaction is of immense biological significance because the polymers formed are polypeptides or proteins, and form part of the chemistry of all living organisms.

There are 20 amino acids of significance in biological systems and since each possesses a carboxylic acid and an amine group, the possibilities for constructing polypeptides and proteins are enormous.

Approved: 0777 023 444

Consider two simple amino acids, glycine (2-aminoethanoic acid) and alanine (2-aminopropanoic acid). These can be joined in two ways:
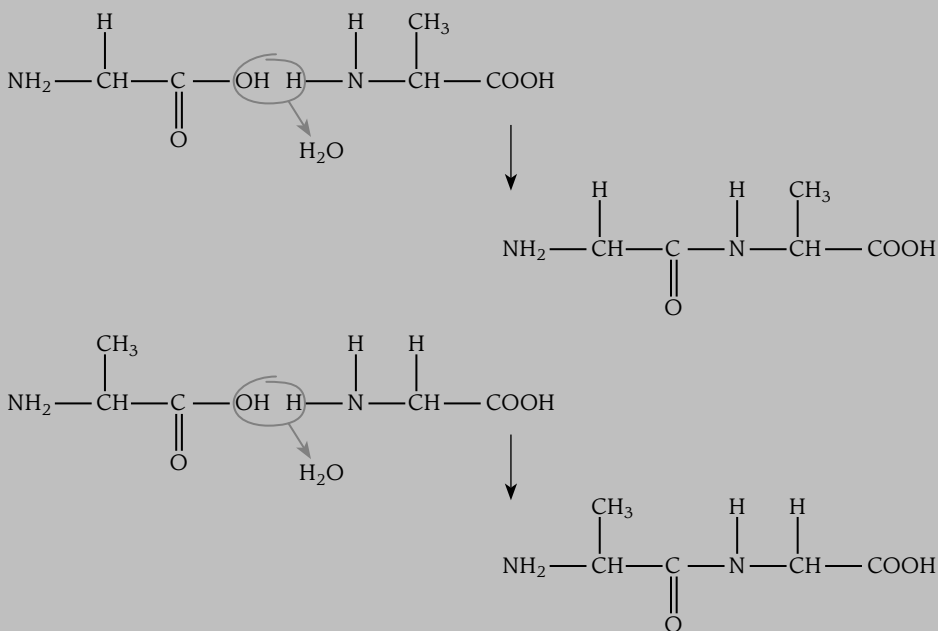
The two dipeptides formed have different structures. A typical protein is formed from between 50 and 200 amino acids joined in a variety of sequences, so you can see how complex protein chemistry can be!

Hydrolysis of proteins

Because proteins contain amide (or peptide) bonds, they can be hydrolysed. This can help us to analyse the amino acids that make up a given protein (or polypeptide).

The traditional way of doing this was to heat the protein in $6 \, mol \, dm^{-3}$ hydrochloric acid at around $100\,°C$ for 24 hours. It has recently been discovered that this process can be speeded up considerably. The protein is now placed in $6 \, mol \, dm^{-3}$ hydrochloric acid under an atmosphere of nitrogen and microwaved for up to 30 minutes.

The amide (peptide) bonds are broken leaving the amino acids in their protonated form, for example:

Approved: 0777 023 444
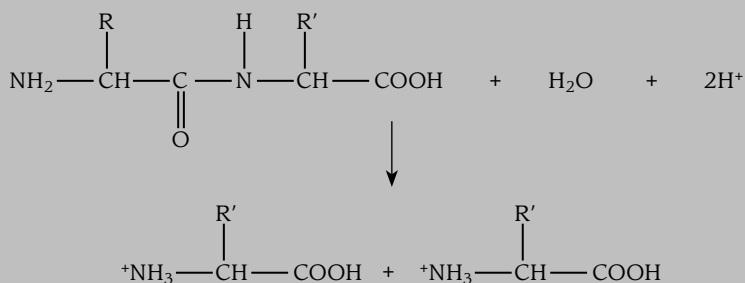
19 Polymerisation

This chapter is needed for both the AS and A2 examinations. Addition polymerisation may be tested at AS; condensation polymerisation is needed for A2.

Addition polymerisation

Poly(ethene)

Addition polymerisation takes place when molecules containing a C$=$C double bond are joined together to form a long chain. The simplest of these reactions is the polymerisation of ethene:

$$n\text{CH}_2\!\!=\!\!\text{CH}_2 \rightarrow (\text{---CH}_2\text{---CH}_2\text{---})_n$$
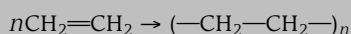
In this reaction, the conditions needed are a temperature of around 200 °C, a pressure of around 2000 atmospheres and a small amount of oxygen to initiate the reaction. Under these conditions the chain could be made up of anything between 2000 and 20 000 molecules. This reaction produces a form of poly(ethene) called **low-density poly(ethene)** due to the fact that the chains are branching and do not allow close packing. This polymer is used to make plastic bags and for other low-strength sheet applications.

Another form of poly(ethene), **high-density poly(ethene)**, can be produced but the conditions used are very different. The temperature is much lower at around 60 °C, the pressure is only a few atmospheres and a catalyst is required. These conditions cause the chains to grow in a much more ordered way enabling them to pack together much more closely, hence increasing the density of the bulk polymer. This polymer is used to make plastic containers, washing-up bowls and some plastic pipes.

Poly(chloroethene)

Chloroethene is similar to ethene, but has one hydrogen atom replaced by a chlorine atom. The double bond is still present and so the molecule can be polymerised:

$$n\text{CH}_2\!\!=\!\!\text{CH}Cl \rightarrow (\text{---CH}_2\text{---CH}Cl\text{---})_n$$
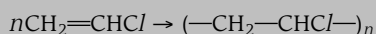
This polymer is still called after the old name for chloroethene — vinyl chloride — so you will see it referred to as polyvinylchloride or PVC. Although the reaction is the same, it is usual to draw the molecules showing the chlorines to one side of the chain as below:
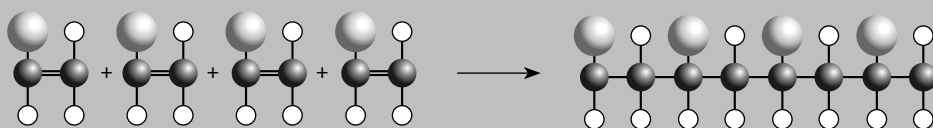
The equation to show this is as follows:
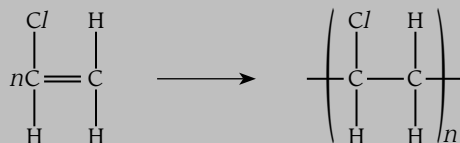
Poly(chloroethene) is used to make a wide range of products including guttering and plastic window frames. It can be rather hard and rigid. Chemicals called plasticisers can be added to increase the flexibility. This increases the range of uses — for example, electrical cable insulation, sheet materials for flooring, footwear and clothing.

Disposal of polyalkenes

The use of polyalkenes has become so widespread that we are now faced with the disposal of thousands of tonnes of waste polyalkenes each year. This causes a number of problems:

- In general, polyalkenes are not biodegradable, so burying them in landfill sites is useless. Plastic bags and bottles can prove harmful to wildlife. Even fish have been found to have tiny particles of plastic in their stomachs. New biodegradable polymers have been developed for use in some types of packaging, such as plastic bags.
- There is a large amount of hydrocarbons locked in the polyalkenes that are thrown away. This is wasting a precious resource — crude oil. In some parts of the world, some plastics are sorted and some used to fuel power generation plants. It is important that this use is seen as a replacement for oil because simply incinerating the polyalkenes to dispose of them would add to the carbon dioxide put into the atmosphere.
- There are so many different types of polymer used that it is not easy to sort them quickly for future use, either for recycling or as a fuel. Indeed some polyalkenes, such as PVC, produce toxic gases such as hydrogen chloride and dioxins when they are burned.

Condensation polymerisation

This section is only tested in the A2 examination.

Characteristics of condensation polymerisation

The points to remember about condensation polymerisation are as follows:

- A small molecule, such as water, is eliminated as each monomer is added.
- You need two different monomers (usually but *not* always, e.g. nylon-6)
- The properties of the polymer depend on the monomer molecules used.

Polyamides

We saw in Chapter 18 how the polyamides nylon-6, nylon-6,6 and polypeptides and proteins are formed by condensation polymerisation. There is nothing new to learn
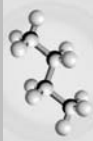
here — simply remember that in condensation polymerisation small molecules (often, but not necessarily, water) are eliminated as the polymer grows.

Polyesters

We saw in Chapter 17 how another group of condensation polymers — polyesters in the form of Terylene® — could be formed by condensation polymerisation. There is nothing new to learn here.

Identifying polymers

The last part of this section of the syllabus outlines what you might be asked to deduce about a given polymer. You may be asked to:

- predict the type of polymerisation reaction for a given monomer or pair of monomers
- deduce the repeat unit of a polymer obtained from a given monomer or pair of monomers
- deduce the type of polymerisation reaction that produces a given section of a polymer molecule
- identify the monomer(s) present in a given section of a polymer molecule

It is perhaps easiest to see what you need to be able to do by looking at some examples. Let's look at each of the four points in turn.

Example 1

Predict what type of polymerisation would take place with each of the following monomers, explaining your answers:

(a) ethene and propene

(b) 1,2-dihydroxyethane and 1,4-benzenedicarboxylic acid

(c) aminoethanoic acid (glycine)

Answer

(a) Both ethene and propene contain double bonds, so they react by addition polymerisation to produce a mixed polyalkene.

(b) The key here is recognising that there is a hydroxy compound and a carboxylic acid and remembering that they react to form an ester. Each monomer has two identical functional groups, so together they can form a polymer. When a carboxylic acid reacts with a hydroxyl compound to form an ester, water is eliminated. Therefore, this is condensation polymerisation.

(c) Here there is only one monomer. It has an amine group at one end and a carboxylic acid group at the other. These two groups (on different molecules) react together to form an amide, and since the monomer

---

has a functional group at each end, polymerisation can take place. When an amide is formed a condensation reaction takes place and water is eliminated, so this is condensation polymerisation.

Example 2

Draw the repeat unit for the polymer formed when the following monomers react together:

(a) 1,6-diaminohexane, $H_2N(CH_2)_6NH_2$, and hexanedioic acid, $HO_2C(CH_2)_4CO_2H$

(b) caprolactam
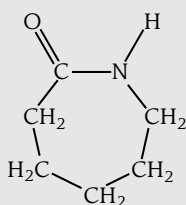
Answer

(a) In order to tackle these questions you must think about the way the monomers combine. In this case they react with the elimination of water:
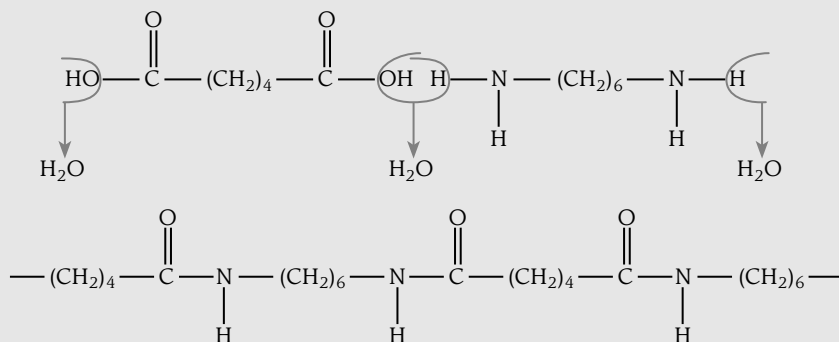
Once you have drawn the polymer, the repeat unit is formed from each *pair* of monomers. In this case, it is the part indicated between the lines:
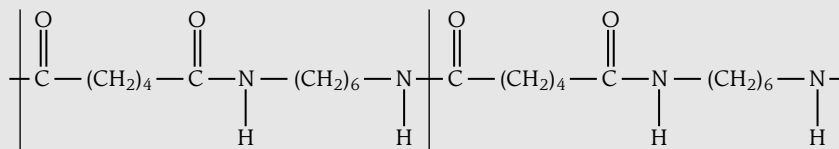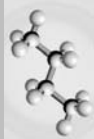
(b) The first thing to notice here is that, as it stands, caprolactam is not really a monomer. To become a monomer, the ring has to break between the carbon and nitrogen. The molecule formed is:
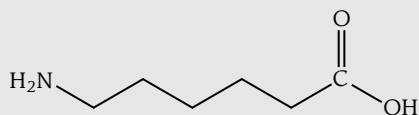
These molecules then polymerise. Starting from only one monomer, the repeat unit has to include most of it! The repeat unit is indicated between the lines:
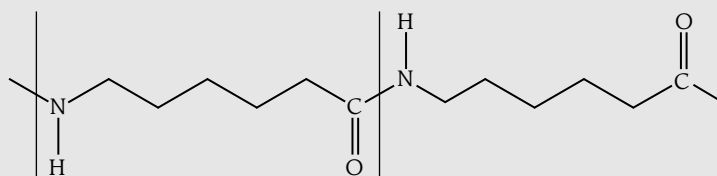
Example 3

The diagrams below show parts of two polymers:

(a)
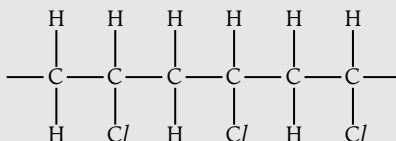
(b)
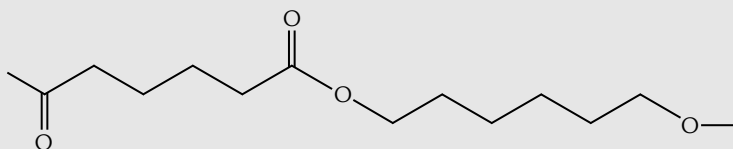
Deduce what type of polymerisation produced each polymer, explaining your answers.

Answer

(a) In this polymer the bonds within the chain are all carbon–carbon single bonds. This can only have resulted from addition polymerisation, because in condensation polymerisation there are *always* other atoms in the polymer chain.

(b) This polymer contains an ester linkage denoted by the —O—C=O group. This can only have been formed from two monomers by condensation polymerisation with the loss of water.

Example 4

The diagram shows a length of polymer containing the residues of a monomer(s). Draw the structure of the original monomer(s).
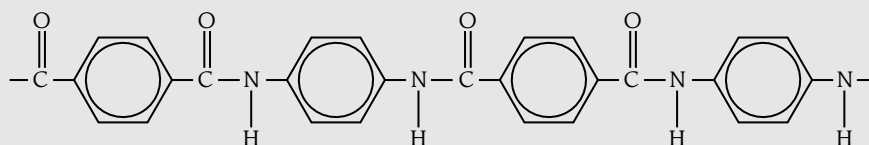
Answer

When tackling this sort of question you need to work out where the monomer residue starts and ends, and to decide whether the polymer was made by addition or condensation polymerisation.

If you think it was made by addition, then the monomer will contain a C=C double bond. If you think it was made by condensation polymerisation you need to think about the functional groups that were at either end of the monomer.

The structure of the polymer shows two types of monomer, as shown by the lines in the diagram below:
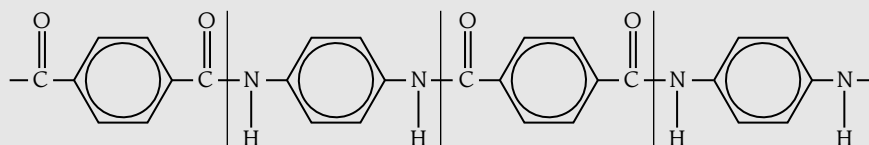
You can also identify an amide linkage, which should tell you that the monomers were probably a dicarboxylic acid and a diamine:

Benzene-1,4-dicarboxylic acid   1,4-diaminobenzene

20 Applications of chemistry

This chapter is only needed for the A2 examination. It is important to realise that although the three sections of this part of the syllabus have both content and learning outcomes, the purpose of this chapter is for students to apply their knowledge of chemistry in new contexts. Here the contexts are spelled out in terms of areas of chemistry in which modern developments are important.

Approved: 0777 023 444
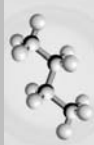
There may be questions in the exam paper where the specific application has not been covered in the syllabus, but the chemistry behind it has. You need to be able to recognise and apply this chemistry in the context of the question.

The chemistry of life

This section covers a number of biochemical topics. Note the advice in the syllabus that you will *not* be asked to recall specific proteins.

Protein chemistry

The first part of this section is based on work covered in Chapter 18. You should know that proteins are polymers formed by the condensation of amino acids (Figure 20.1). You also need to remember that there are 20 different biologically active amino acids.
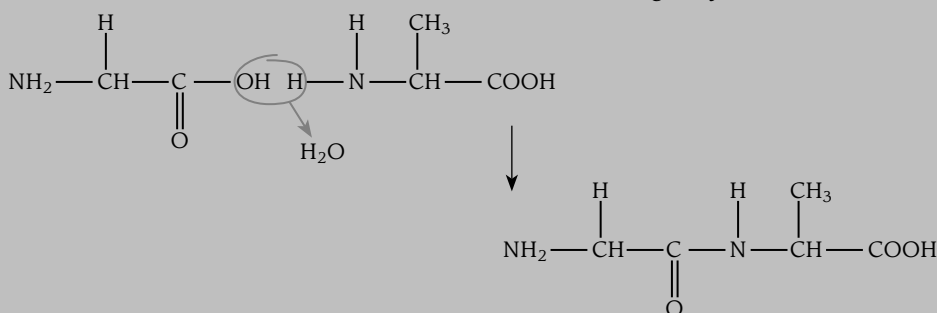
Figure 20.1 Condensation of amino acids

Figure 20.1 is a reminder of how amino acids react together. You need to remember that there may be up to 200 amino acids in a protein chain, and that they can be arranged in any sequence using any of the 20 different 2-amino acids (alpha-amino acids).

If you think about a polypeptide containing just four amino acids, there are lots of ways of putting them in a sequence. Even if the possibility of amino acid repeats — for example AABC — is ignored, there are still a lot of combinations. How many do you think there are?

ABCD, ABDC, ADBC, ACBD... etc.

The sequence of amino acids is called the **primary structure** of a protein. Polypeptides have a 'backbone' to their structure that runs the length of the chain. If you look at Figure 20.1 you can see that the only difference from one amino acid to the next is in the side chains, the backbone is the same and has the pattern —C—C—N—C—C—N— etc. The chain can be rotated about carbon-to-carbon bonds to make it twist or fold, and this gives the protein its **secondary structure.** Hydrogen bonds between peptide bonds in different sections of the chain lead to two main types of structure — the α-helix (Figure 20.2(a)) and the β-pleated sheet (Figure 20.2(b)).
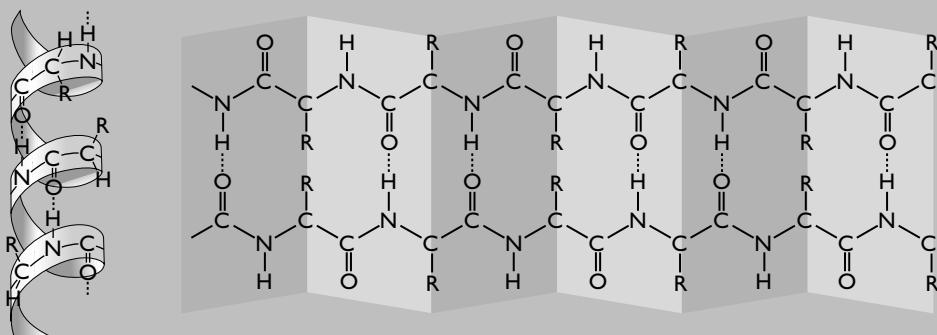
Figure 20.2 Secondary structure of a protein (a) α-helix (b) β-pleated sheet

The sequence of amino acids is important because the groups that form side chains in a polypeptide or protein can interact with other side chains further along the chain as it bends. This is known as the **tertiary structure** of a protein. Some examples of side chains of the different amino acids and the bonds that can form between them are shown in Table 20.1.

Table 20.1

Amino acid	Structure	Type of bond formed
Alanine	$H_2NC(CH_3)HCO_2H$	van der Waals
Serine	$H_2NC(CH_2OH)HCO_2H$	Hydrogen bonds
Aspartic acid	$H_2NC(CH_2CO_2H)HCO_2H$	Ionic (electrovalent)
Lysine	$H_2NC((CH_2)_4NH_2)HCO_2H$	Ionic (electrovalent)
Cysteine	$H_2NC(CH_2SH)HCO_2H$	Disulfide bridges

Things to remember

- Proteins are polymers formed from 2-amino acids (alpha-amino acids) by condensation polymerisation.
- 2-amino acids have different side-chains, which gives them their polar or non-polar nature; 20 different 2-amino acids are used in the body.
- 2-amino acids exist as **zwitterions** in both the solid state and in aqueous solution.
- The **primary structure** of a protein is the sequence of 2-amino acids in the polypeptide chain.
- The polypeptide chain has direction, with one end (N-terminal) an amine group and the other end (C-terminal) a carboxylic acid.
- The **secondary structure** of a protein results from hydrogen bonds formed between different parts of the folded chain. The most stable of these structures are in the form of α-helices and β-pleated sheets.
- The **tertiary structure** of a protein arises from the folding of the polypeptide chain due to interactions between the side chains of the amino acids. These interactions include van der Waals forces, hydrogen bonds and ionic (electrovalent) bonds, together with covalent disulfide bridges.
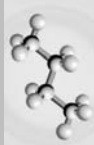
- The functioning of a protein is linked directly to its three-dimensional structure.
- Proteins can be hydrolysed back to amino acids (see Chapter 18).

Proteins as enzymes

Enzymes are particular types of protein that behave as catalysts enabling chemical reactions to take place efficiently at body temperature. Unlike inorganic catalysts that are often able to catalyse a range of reactions with similar substances, enzymes are specific in their behaviour, generally catalysing one particular reaction.

Most enzymes are water-soluble (the body is an aqueous environment), globular (ball-shaped) proteins. The complex folding that gives the tertiary structure to these proteins creates channels and grooves in the surface of the enzyme. It is the precise shape of these features that fit a given substrate molecule when it reacts. This is known as the **active site** of the enzyme.

You may be asked to draw a diagram to help explain this, so think about the important parts of the process (Figure 20.3).

Enzyme Enzyme–substrate complex

Active site

Bonds in substrate are weakened

Substrate Products
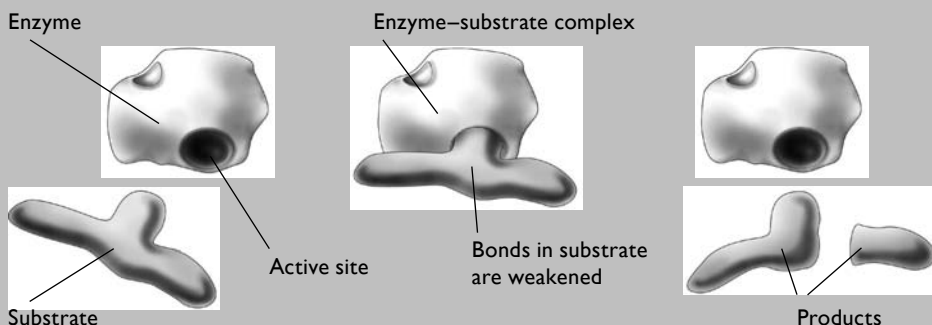
Figure 20.3 Reaction between an enzyme molecule and a substrate molecule

Enzymes, like other catalysts, work by providing an alternative reaction pathway of lower activation energy, E_{cat}, as shown in Figure 20.4.

Energy

E_a

E_{cat}

Reactants

Products

Time

Key
— Uncatalysed reaction
— Catalysed reaction
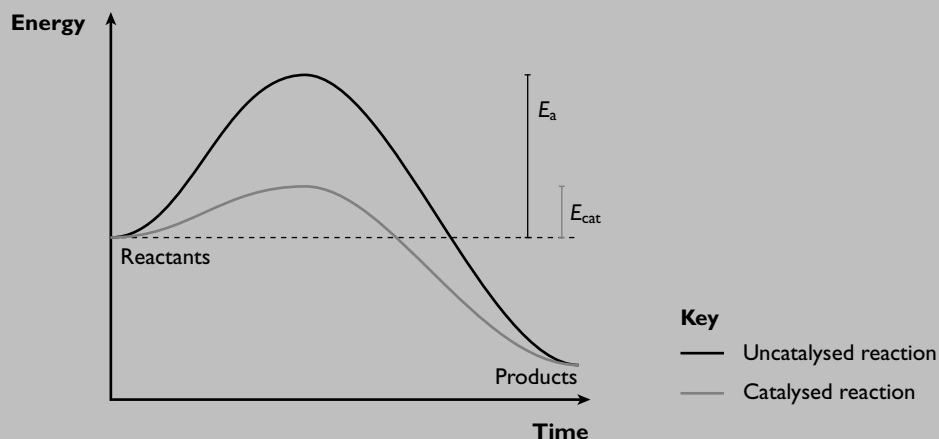
Figure 20.4 A reaction with and without an enzyme catalyst

Approved: 0777 023 444

The catalysed reaction requires less energy than the uncatalysed reaction. It is usual to describe the reaction as follows:

enzyme + substrate $\rightleftharpoons$ enzyme–substrate complex $\rightarrow$ enzyme + products
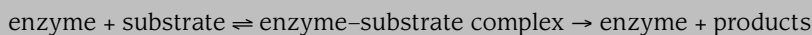
The first step is reversible because unless the available energy is greater than E_{cat}, the complex may break down with no product being formed. Once the products have been formed they leave the active site of the enzyme, making way for a new substrate molecule to bind.

Factors affecting enzyme activity

The activity of an enzyme in catalysing a given reaction is dependent on the weak interactions that maintain the tertiary structure of the protein. As a result, even small changes in conditions can disrupt enzyme activity. The two most obvious changes are the temperature and pH of the solution in which the reaction takes place.

The effect of temperature

Temperature is the more complex of the two factors because it influences:
- the speed of the molecules
- the thermal stability of the enzyme and of the substrate
- the activation energy, E_{cat}, of the catalysed reaction

Given that most enzyme-catalysed reactions occur at temperatures close to Earth's ambient temperature, we do not expect a significant reaction rate at around 0 °C (in aqueous solutions this would be approaching freezing point). High temperatures disrupt the relatively weak bonds that maintain the tertiary structure of the protein. This leaves a range of approximately 0 °C to 60 °C for enzyme-catalysed reactions with a peak of activity around 40 °C (Figure 20.5).
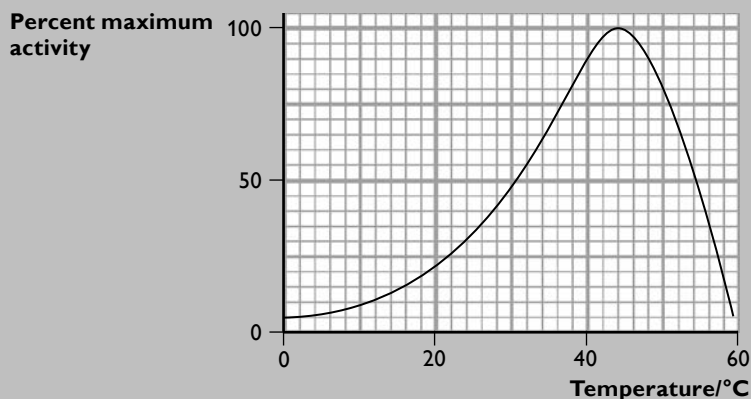
Figure 20.5 The effect of temperature on enzyme activity

One of the reasons why a high fever can be so dangerous is that at temperatures much above 40 °C some enzyme-catalysed processes no longer take place.

The effect of changing pH

Enzyme activity is dependent on the pH of the environment for two main reasons:

- Small changes in pH can affect the ionisation of amino acid side-chains, which can alter the ability of a substrate to bind to the active site.
- Extremes of pH can cause proteins to denature (lose the three-dimensional arrangement of the protein chains), which can also affect their solubility.

Most enzymes operate over a fairly narrow pH range around an optimum pH. These can be quite different, depending on the enzyme (Figure 20.6).
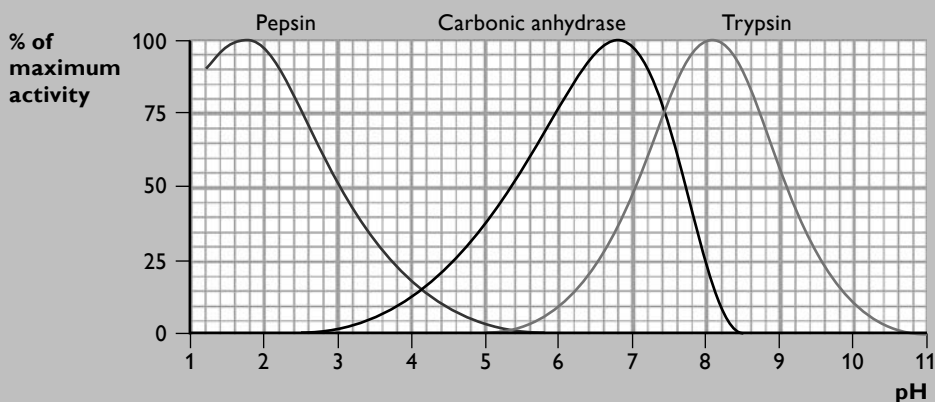
Figure 20.6 The effect of pH on the activity of three different enzymes

As you can see in Figure 20.6, pepsin, which acts on proteins in the acid conditions of the stomach, has an optimum pH of around 2; carbonic anhydrase, which operates in red blood cells, has an optimum pH of around 7; trypsin, which acts on peptides in the slightly alkaline conditions of the small intestine, has an optimum pH of around 8.

Inhibition of enzyme activity
As well as changes in the structure of the enzyme brought about by changes in temperature or pH, enzyme activity can be affected by the presence of other molecules. These molecules are known as **inhibitors** and can affect the enzyme in one of two ways.

Competitive inhibition
Enzyme activity may be reduced in the presence of a molecule that has a similar structure to the substrate. This enables it to bind to the active site of the enzyme, competing with the substrate molecule. The result of such competition on the effectiveness of the enzyme depends on the relative concentrations of the substrate and inhibitor molecules. Unlike the changes in temperature or pH, the ability of the enzyme to function is not changed, it's just that the active site can be blocked by the inhibitor (Figure 20.7).
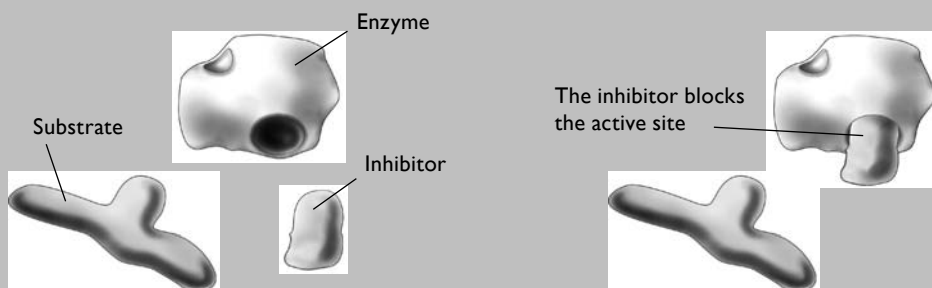
Figure 20.7 Competitive inhibition

The extent to which competitive inhibition affects the rate of the enzyme-catalysed reaction depends on:
- the concentration of substrate
- the concentration of inhibitor
- the relative strengths of bonds formed between the active site and the substrate, and active site and the inhibitor

The effects of this are shown in Figure 20.8.
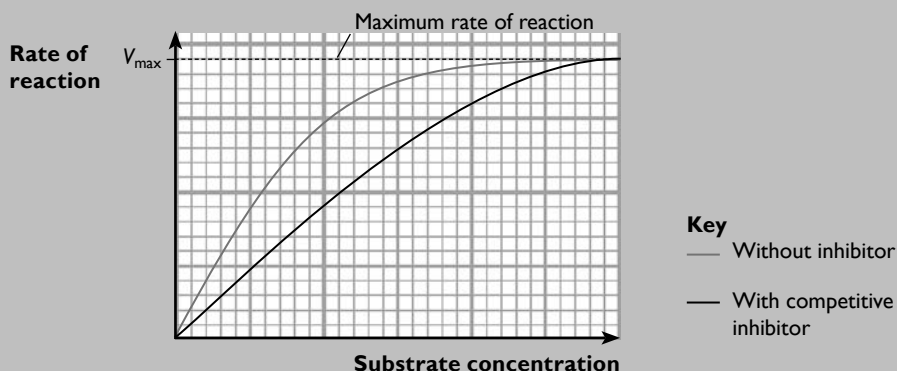
Figure 20.8 The effect of a competitive inhibitor on the rate of an enzyme-catalysed reaction

If there is a high enough substrate concentration it is possible to reach the maximum rate, V_{max}.

Non-competitive inhibition of enzyme activity
The activity of an enzyme can also be reduced, or even stopped, by a molecule binding to an area other than the active site. This can change the shape of the active site making it impossible for the substrate to bind to it (Figure 20.9). This type of inhibitor molecule does not need to resemble the substrate and can be quite small.

Inhibitor Enzyme
Substrate
Conformation change
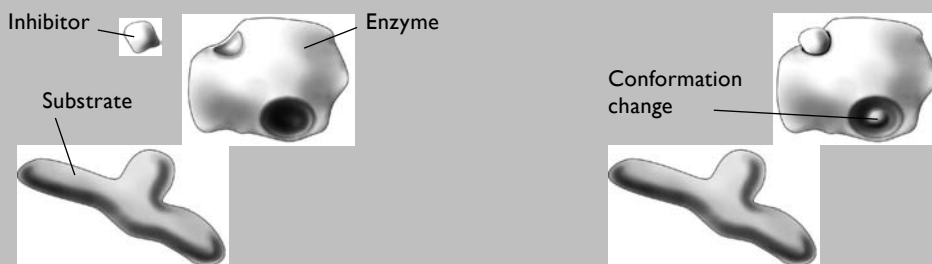
Figure 20.9 Non-competitive inhibition

The extent to which non-competitive inhibition affects the rate of the enzyme-catalysed reaction depends on:
- the concentration of the inhibitor
- the affinity of the enzyme for the inhibitor

The effects are shown in Figure 20.10, which is a graph of rate of reaction against substrate concentration. Competitive inhibition is included in Figure 20.10 for comparative purposes. K_m is the concentration of substrate at which the rate has reached half the maximum rate, V_{max}.

Rate of reaction V_{max}

Key
— Without inhibitor
— Competitive inhibitor same V_{max} different K_m
---- Non-competitive inhibitor same K_m different V_{max}

K_m **Substrate concentration**
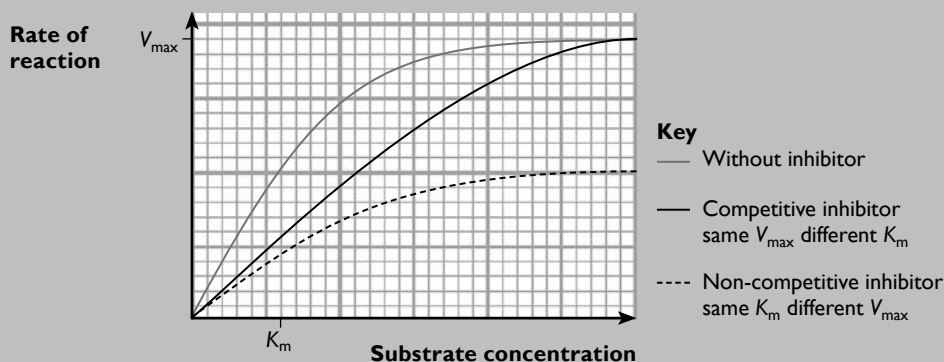
Figure 20.10 Comparison of the effects of non-competitive and competitive inhibitors on the rate of an enzyme-catalysed reaction

Cofactors

Many enzymes need an ion or a group to be present in order for them to work effectively. Some of these, such as metal ions — for example Zn^{2+} in carbonic anhydrase — are built into the structure of the enzyme itself. Others might be large organic molecules, often provided by a vitamin. These bind temporarily to the enzyme and assist with the transfer of groups or electrons not available within the active site itself (see p. 191).

Things to remember
- Enzymes act as biological catalysts by providing an alternative pathway with lower activation energy, E_{cat}, than the uncatalysed reaction.
- Enzymes are proteins that catalyse reactions in aqueous solutions at low temperatures and a specific pH.

Approved: 0777 023 444

- As a catalyst, an enzyme works with a specific substrate (unlike inorganic catalysts).
- The ability of an enzyme to function is dependent on its three-dimensional shape, specifically the precise shape of the active site.
- The substrate not only fits the active site, it binds to it to enable the reaction to take place.
- Enzyme-catalysed reactions may be reduced in their effectiveness by two types of inhibition:
  – in competitive inhibition, the inhibitor has a similar shape to the substrate and competes with it to occupy the active site
  – in non-competitive inhibition, the inhibitor does not bind to the active site, but binds elsewhere on the enzyme. This changes the shape of the enzyme and prevents the normal catalysed reaction from taking place.

Genetic information

You need to know about the role that DNA plays in cells, particularly with respect to protein synthesis. Some detailed chemistry of the processes within the cell is needed.

The structure of DNA

DNA (deoxyribonucleic acid) controls the passing of genetic information from one generation to the next. It also plays an important role in the synthesis of proteins.

The structure of DNA was discovered by Watson and Crick in 1953. It has enabled our understanding of heredity, plant and animal breeding, genetic diseases and the identification of individuals by their DNA 'fingerprint'.

DNA consists of a double strand of a macromolecule formed by condensation polymerisation. The monomers in the chain are called **nucleotides.** They are assembled into the chain by linking sugar (deoxyribose) and phosphate groups to form the backbone with bases attached as side chains. You can see this in block diagram form (the only form you will be asked to deal with in the exam) in Figure 20.11.
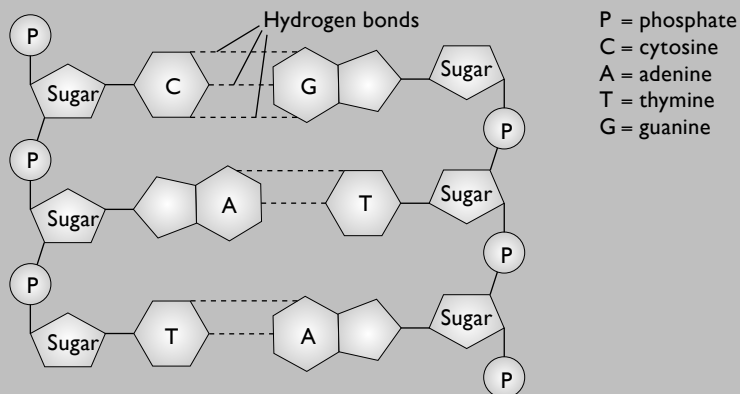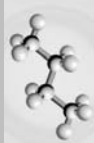
Figure 20.11 Block diagram to illustrate DNA structure

The sugar molecule is in the form of a five-membered ring and is joined to the phosphate group via an ester link. It is also joined to one of four bases:

- adenine (A)
- cytosine (C)
- guanine (G)
- thymine (T)

Within the double strand of DNA the bases are always paired in the same way — adenine with thymine and cytosine with guanine.

> **Tip** A way to remember the base pairs is: All Things Come Good.

You do not need to learn the structures of the bases, which are complex. If you need more detail it will be given in the question.

DNA consists of two strands each made up as described, but running in opposite directions (anti-parallel). The strands coil around one another to form a double helix which is held together by hydrogen bonds between the pairs of bases. Two hydrogen bonds form between adenine and thymine, and three hydrogen bonds form between cytosine and guanine. The sugar–phosphate backbone is on the outside of the double helix, with the bases in the middle, as shown in Figure 20.12.
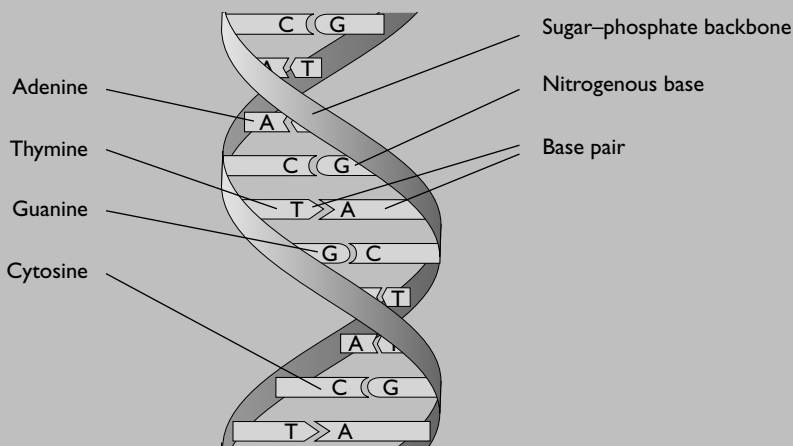
Figure 20.12 The structure of DNA

It is important to remember that the DNA in a cell codes for lots of different proteins. The section of DNA that codes for a particular protein is called a **gene.**

The structure of RNA

There is another nucleic acid, RNA, which is found in cells. The structure of RNA is similar to that of DNA, with a number of significant differences (Table 20.2).

Approved: 0777 023 444

Table 20.2

Factor	Deoxyribonucleic acid, DNA	Ribonucleic acid, RNA
Sugar	Pentose sugar is deoxyribose	Pentose sugar is ribose
Bases	Adenine Cytosine Guanine Thymine	Adenine Cytosine Guanine Uracil
Structure	Double helix with two anti-parallel strands	Single strand that can be folded to produce helical sections

There are three different types of RNA, each with a role to play in protein synthesis.

Messenger RNA (mRNA)
mRNA is complementary to a portion of one of the DNA strands and is copied from the DNA gene sequence for a particular polypeptide chain. The 'message' encoded in the mRNA is translated into the sequence of amino acids in the polypeptide. The mRNA travels out of the cell nucleus into the cytoplasm of the cell where it bonds to a ribosome.

Transfer RNA (tRNA)
Transfer RNA is a much smaller molecule than mRNA. Each tRNA molecule acts as a 'carrier' for an amino acid to a ribosome during protein synthesis. Each tRNA recognises the coding sequence for a particular amino acid in the mRNA.

Ribosomal RNA (rRNA)
There are a number of different rRNAs that form the major structural components of ribosomes. Ribosomes are found in the cell cytoplasm and are where protein synthesis occurs. It is the largest of the three forms of RNA with an M_r of up to 1 000 000.

The relationships between the different types of RNA can be seen in Figure 20.13.
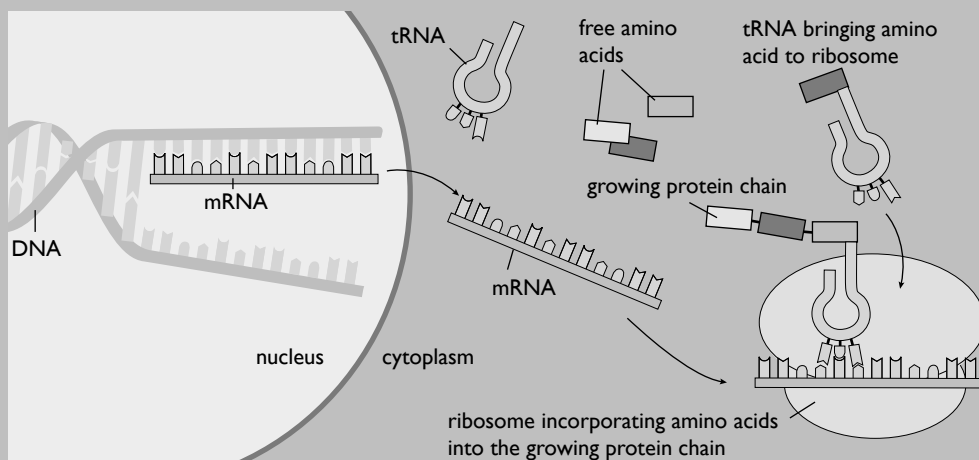
Figure 20.13 Relationships between the different types of RNA
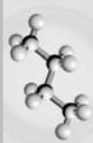
Protein synthesis

As we have seen, the ribosomes are the cellular 'factories' that synthesise proteins, and we have looked at the roles the different types of RNA play in this process. In order to understand protein synthesis fully we need to take a step or two back.

Both DNA and RNA each contain four bases. However, there are 20 amino acids used to make proteins. Therefore, more than one base is needed to code for a particular amino acid. If one pair of bases coded for a given amino acid there would only be 4^2 or 16 possible amino acids. As there are 20 amino acids, this means that three bases (a triplet) must be needed to code for every amino acid. This gives 4^3 or 64 possibilities.

Figure 20.14 shows how each of the 20 amino acids is coded, together with codes to stop the sequence — UGA, UAG and UAA — and one code AUG (Met) to start the sequence.

In Figure 20.14, the codes are read from the centre outwards.
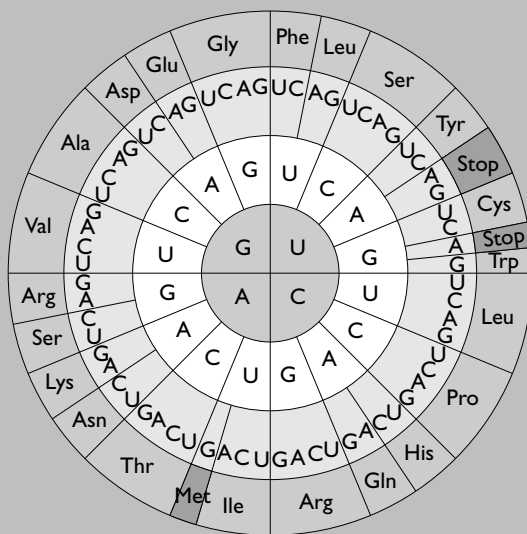
Figure 20.14 The genetic code

Try this yourself

(40) Which amino acid does each of the following base triplets code for? You can use the abbreviations in your answer.
    (a) GAU
    (b) CCA
    (c) AAA

(41) Give one triplet code for each of the following amino acids:
    (a) Ser (serine)
    (b) Cys (cysteine)
    (c) Tyr (tyrosine)

Approved: 0777 023 444

Amino acids cannot bind directly to mRNA. Transfer RNA molecules act as 'carriers', binding to a specific amino acid at one end of the tRNA molecule. At the other end of the tRNA molecule there is a triplet of bases (the anti-codon) that binds to the triplet of bases (the codon) on the mRNA. Each tRNA molecule interacts with the ribosome, enabling the amino acids to be joined to the growing chain by peptide bonds. This is summarised in Figure 20.15.
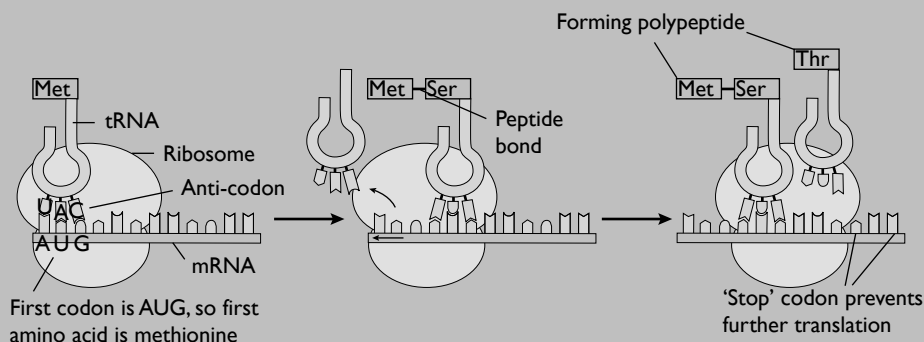
Figure 20.15 Process of synthesising a polypeptide in a ribosome

Mutations

Errors can occur during DNA replication and protein synthesis. However, it is relatively rare for these not to be corrected by mechanisms within the cell. Changes to the original DNA are known as **mutations**. They can occur naturally or can be caused by physical or chemical factors that damage DNA. These include ultraviolet light, ionising radiation, cigarette smoke and a range of other chemicals.

In many cases a single change to the base sequence will have little effect because most amino acids are coded for by a number of codons — for example, a change from GUA to GUG would still code for the amino acid valine (Val). However, if the mutation deleted a base from the sequence, this would produce an entirely different sequence of codons and hence a new amino acid sequence and a different protein. Mutation can result in genetic conditions such as sickle-cell anaemia and cystic fibrosis.

Sickle-cell anaemia

Sickle-cell anaemia is a condition that affects red blood cells making them crescent-shaped, rather than disc-shaped. The condition affects the haemoglobin and results in small blood vessels being blocked, preventing a good oxygen supply to some tissues. It is caused by a single mutation resulting in a change at the position of the sixth amino acid out of 146 in one of the protein chains in haemoglobin:

Normal chain   Val   His   Leu   Thr   Pro   Glu   Glu…

Sickle chain   Val   His   Leu   Thr   Pro   Val   Glu…
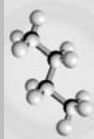
Cystic fibrosis

Cystic fibrosis is a relatively common genetic disorder. In some parts of the world it occurs in 1 in every 2000 live births. It has been estimated that around 1 in 22 Caucasians are carriers of the gene that causes it.

In cystic fibrosis, the normal fluid secretions in the lungs and gut are replaced by sticky mucus. It also affects the pancreas and restricts the supply of digestive enzymes. The sweat glands produce abnormally salty sweat. The reason for this condition is that a particular membrane protein responsible for the passage of chloride ions out of cells is either missing or faulty, thus preventing the release of chloride ions from cells.

It has been found that this is often the result of a particular triplet being deleted, resulting in a missing amino acid and hence a different sequence:

Normal chain   Ile   Ile   Phe   His   Lys...

Fibrosis chain   Ile   Ile   His   Lys...

Things to remember

- There are two types of nucleic acid, DNA and RNA. They are formed from nucleotide monomers, each consisting of a sugar, a phosphate and a base.
- Both nucleic acids are condensation polymers with a sugar–phosphate backbone and the bases attached to the sugars forming side chains.
- DNA consists of a double stranded helix with the sugar–phosphate backbone on the outside and the bases pointing inwards towards each other. The two strands run in opposite directions and are held together by hydrogen bonds between the bases.
- There are four different bases in DNA, always paired in the same way: adenine–thymine and cytosine–guanine.
- RNA differs from DNA in that it:
  - contains the sugar ribose rather than deoxyribose
  - has a single strand
  - contains the base uracil rather than thymine
- DNA carries the genetic code for the production of proteins.
- Protein synthesis involves three types of RNA: messenger RNA (mRNA), transfer RNA (tRNA) and ribosomal RNA (rRNA).
- mRNA molecules contain a codon (triplet code) in which three bases in the RNA sequence code for one amino acid in the polypeptide chain.
- tRNA brings specific amino acids to the ribosome and binds to specific codons in the mRNA to allow the peptide bonds to form, extending the polypeptide chain.

Energy

You don't need to know a great deal about energy in biological systems for the A2 chemistry examinations. The syllabus focuses on adenosine triphosphate, ATP, which has an important role as a short-term energy source for metabolic reactions in living organisms.

The structure of ATP is shown in Figure 20.16. It is based on parts of molecules that you already know about:

- adenine — the base in DNA and RNA
- ribose — the sugar in RNA
- phosphate — the group found in the backbone of both DNA and RNA
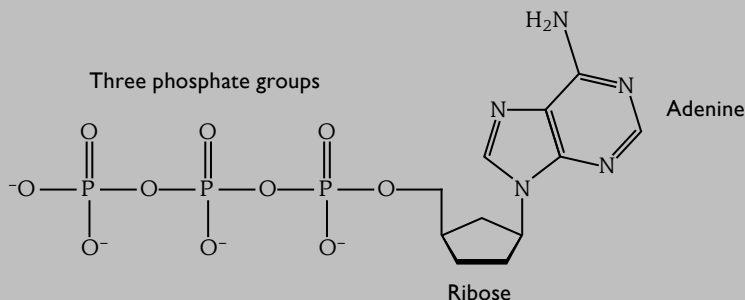
Figure 20.16 Structure of ATP

The hydrolysis of ATP is an exothermic reaction. The energy released is used by enzymes to drive catalysed reactions. The products of the reaction are ADP (adenosine diphosphate) and an inorganic phosphate ion, usually shown as P_i:

$$\text{ATP} + H_2O \rightarrow \text{ADP} + P_i \qquad \Delta H = -30\,\text{kJ}\,\text{mol}^{-1}$$

Metabolism uses ATP constantly, so its synthesis in the mitochondria of cells is a vital process. Each release of energy generates ADP, and ATP is re-formed from this. Figure 20.17 shows how this can happen.
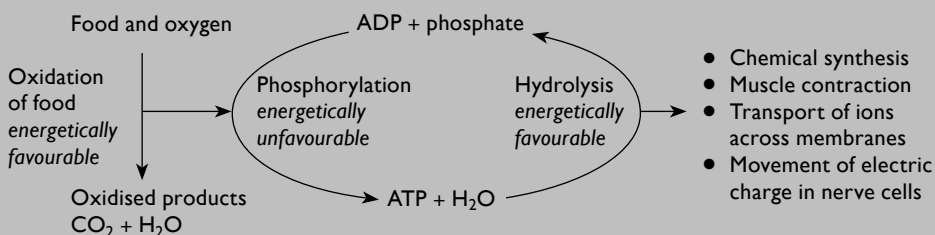
Figure 20.17 Regeneration of ATP

The oxidation of one molecule of glucose produces up to 38 molecules of ATP. The breakdown products of fats and proteins in our diet also feed into the respiratory pathway providing energy for cells via ATP. It is important to remember that while the hydrolysis of ATP is energetically favourable, the activation energy is normally high. It is only in the presence of the appropriate enzyme that the reaction occurs, enabling cellular processes to be controlled.

Things to remember

- All the chemical reactions involved in the function of cells and tissues are linked via metabolic pathways.
- ATP is a short-term energy source for metabolic reactions.
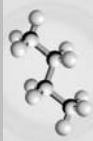
- Energy is released when ATP is hydrolysed to ADP and inorganic phosphate.
- The synthesis of ATP from ADP requires energy, which usually comes from the oxidation of food, and takes place in the mitochondria.

Metals in biological systems

Iron in haemoglobin

You are probably aware of the most well-known of the proteins that contain iron — haemoglobin. It is this protein complex that is responsible for carrying oxygen around the body in red blood cells. Haemoglobin consists of four protein chains, each bound to a non-protein haem group containing an iron(II), Fe^{2+}, ion. It is these Fe^{2+} ions that bind to the oxygen molecules. Each haem group can bind to one oxygen molecule, so each haemoglobin complex can carry four oxygen molecules (Figure 20.18). The arrangement is octahedral, and similar to the complexes with other transition metals (Chapter 11).
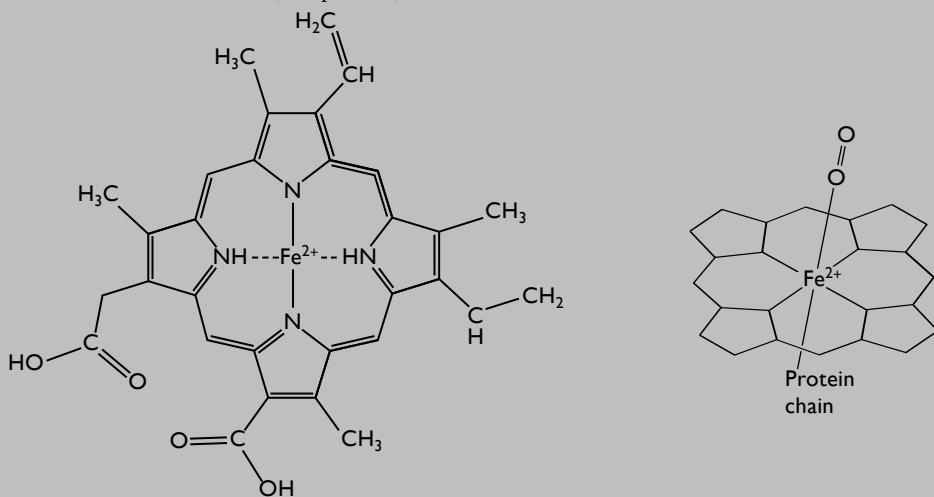
Figure 20.18 Haemoglobin

As with other transition metal complexes, the oxygen ligand can be replaced by other ligands. In the case of carbon monoxide this can prove fatal. Carbon monoxide binds to haemoglobin around 200 times more strongly than oxygen. This binding is effectively irreversible and results in haemoglobin being unable to exchange oxygen.

Sodium and potassium ions in membrane channels

The balance of ions within living cells is different from that of their surroundings. An example of this can be seen with sodium ions (Na^+) and potassium ions (K^+). The concentration of sodium ions within a cell is lower, and the concentration of potassium ions higher, than in the surrounding liquid. This is of particular importance in nerve cells. When a nerve is stimulated, sodium ions flood into the cell. When the 'signal' has passed it is vital to restore the original balance ready for another nerve impulse.

The energy for these changes comes from the hydrolysis of ATP. This change is accomplished by the use of an ion-transporting enzyme known as 'Na$^+$, K$^+$-ATPase'. This is not a very helpful name and so it is often referred to as the 'sodium–potassium pump'. These enzyme molecules are found bridging cell membranes and control the flow of ions in and out of the cells.

Zinc as an enzyme cofactor

The enzyme carbonic anhydrase is one of the most efficient enzymes in the human body. It is responsible for the removal of carbon dioxide from the blood within the red blood cells by producing hydrogencarbonate ions. Cofactors act by enabling the substrate to react at the active site (Figure 20.19).

Apoenzyme
(protein portion)

+

Cofactor
(non-protein portion)

Substrate

Whole enzyme
(protein portion)
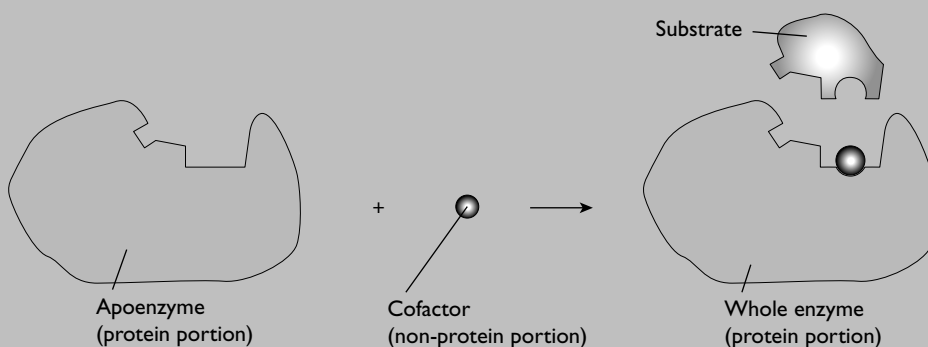
Figure 20.19 Action of a cofactor

In the case of carbonic anhydrase, the presence of a high charge density from the Zn^{2+} ions at the active site assists in the breakdown of a water molecule into H$^+$ and OH$^-$ ions. The OH$^-$ ions then attack the carbon dioxide forming hydrogencarbonate ions:

$$CO_2 + OH^- \rightarrow HCO_3^-$$
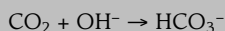
Once the hydrogencarbonate is released, another water molecule binds to the zinc ion allowing the cycle to begin again.

Toxic metals

A number of metals, particularly 'heavy metals' (lead, mercury, cadmium and arsenic) can have serious effects on health even though they may be present in only small amounts in the environment. One of the reasons for this is that they can accumulate in the food chain and, therefore, may be ingested at significantly higher levels than those found in the environment.

For example, mercury can disrupt disulfide bridges and other 'heavy metals' have been shown to disrupt van der Waals forces. Lead is known to cause mental health problems in children, and mercury can cause major failure of the nervous system. The effects of mercury are sometimes referred to as 'Minamata disease' after the Japanese city in which over 1700 people died after methyl mercury was released in

waste water. The mercury accumulated in the food chain via shellfish and fish which were then consumed by the local population.

Things to remember
- Metals have key roles in the functioning of biological systems.
- Iron is important in proteins that use the haem group; the balance of sodium and potassium ions is vital for maintaining cell structure and the transmission of nerve impulses; zinc is important as a cofactor in the key enzyme carbonic anhydrase.
- Metals such as lead and mercury are toxic due to the effects they have on the tertiary structure of proteins, particularly van der Waals forces and disulfide bridges.
- The effects of heavy metals are made worse because they can accumulate in the food chain even if within the environment their concentrations are small.

Applications of analytical chemistry

The examination of this part of the syllabus generally focuses on the use of the different analytical techniques, particularly in terms of analysing data to provide structural information about compounds. Your knowledge of core chemistry will help you to do this.

Methods of detection and analysis

There are five main areas of analysis that you need to be familiar with:
- electrophoresis and DNA fingerprinting
- proton-NMR spectroscopy
- X-ray crystallography
- chromatography
- mass spectrometry

In each case you need to be able to explain how the technique works and what information it provides. You may be expected to interpret data from one or more of these techniques to solve a problem.

Electrophoresis and DNA fingerprinting
We saw in Chapter 18 that amino acids form zwitterions in aqueous solution, and that the exact nature of a zwitterion depends on the pH of the solution:

H_3N^+—CH_2—CO_2^-

zwitterion

Low pH: $\qquad H_3N^+$—CH_2—$CO_2^- + H_3O^+ \rightarrow H_3N^+$—$CH_2$—$CO_2H + H_2O$

High pH: $\qquad H_3N^+$—CH_2—$CO_2^- + OH^- \rightarrow H_2N$—$CH_2$—$CO_2^- + H_2O$
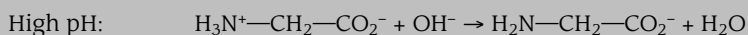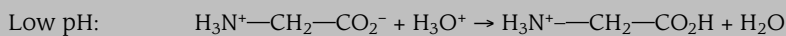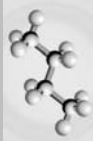
The same process can be used to separate protein fragments (peptides).

The velocity of the amino acids is related directly to the voltage applied across the plate. Other factors can affect the relative velocities of samples:
- Smaller molecules move faster than larger molecules carrying the same charge.
- A molecule with large side chains moves more slowly than a straight-chain molecule with the same charge and M_r.
- The pH of the buffer influences the extent of ionisation, and hence movement and direction.

DNA fingerprinting

This has become a 'high-profile' analytical technique due largely to its use in forensic science to screen crime suspects. It uses the same technique as electrophoresis, but rather than relying on filter paper as the medium, a gel is used. In recent years the technique has been refined so that only a tiny amount of DNA is needed. This can be extracted from material such as blood, hair, cheek cells, semen or skin.

The DNA is treated with enzymes to break it into fragments that can be analysed by electrophoresis. If the amount of DNA is very small, a technique called the polymerase chain reaction (PCR) can be used to produce more copies of the DNA. It is possible to start the analysis with as little as 0.2 nanograms (2×10^{-10} grams) of DNA.
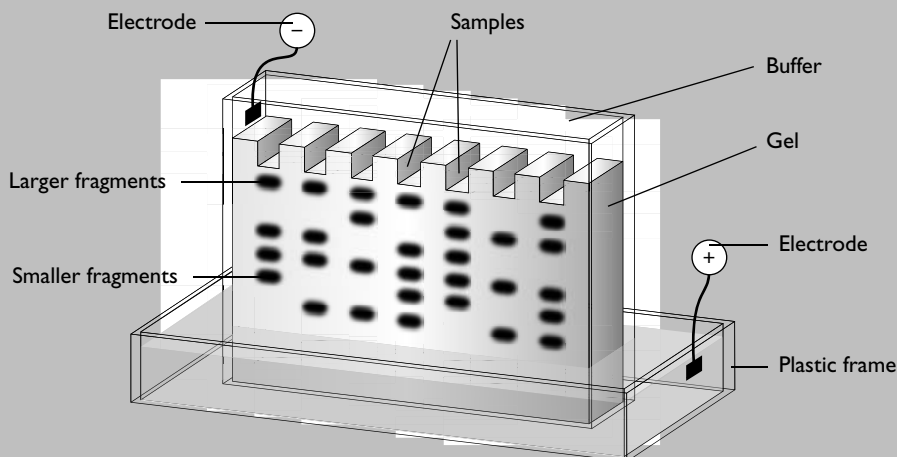
Figure 20.22 Gel electrophoresis

Figure 20.22 shows the apparatus for carrying out gel electrophoresis. Samples of the DNA fragments are put into small 'wells' in the gel near the cathode. The phosphate groups on the DNA fragments are negatively charged and are attracted to the anode, with smaller fragments moving faster than larger ones. The results can be stained to help them show up or, if the DNA fragments are treated with radioactive phosphorus, a photographic print can be obtained. A typical example is shown in Figure 20.23.
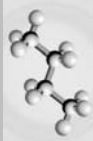
Proton-NMR spectroscopy

The nucleus of a hydrogen atom spins about an axis. Since the nucleus is positively charged, this spinning produces a magnetic field giving each nucleus a magnetic moment. If an external magnetic field is applied, the nuclei align their magnetic moments parallel to the applied field (Figure 20.24 (a)). Another possible state exists where the magnetic moments are aligned against the applied field, but this requires extra energy (Figure 20.24(b)).
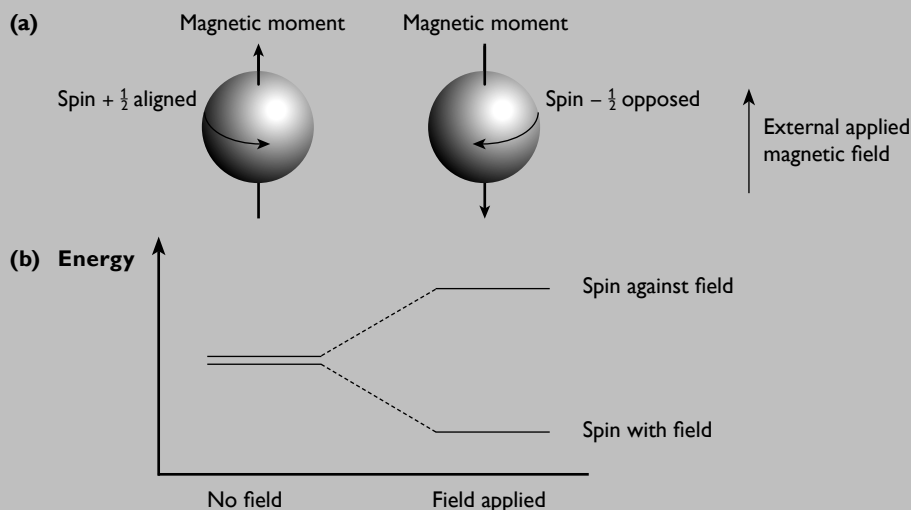
Figure 20.24 Magnetic moments

Just looking at hydrogen atoms is not particularly useful, but hydrogen atoms in organic molecules are influenced by the atoms adjacent to them. Not all protons absorb energy at the same frequency when 'flipping' their magnetic moment to oppose the applied magnetic field. The external magnetic field applied is modified by the different chemical environments in the molecule. For example, the presence of an electronegative atom causes the bonding electrons to be attracted towards it, leaving any protons less shielded from the external field. This causes the energy change for 'flipping' the proton magnetic moment to be at a higher frequency.

To obtain the NMR spectrum of a compound, it is first dissolved in a solvent that does not absorb in the proton-NMR region and then placed in a magnetic field. Energy is supplied at radio frequency by scanning over a range. Carrying out this procedure on ethanol at low resolution results in three distinct absorptions due to the three protons in different environments (Figure 20.25). A small amount of tetramethylsilane (TMS) is added to give a marker at 0.05.
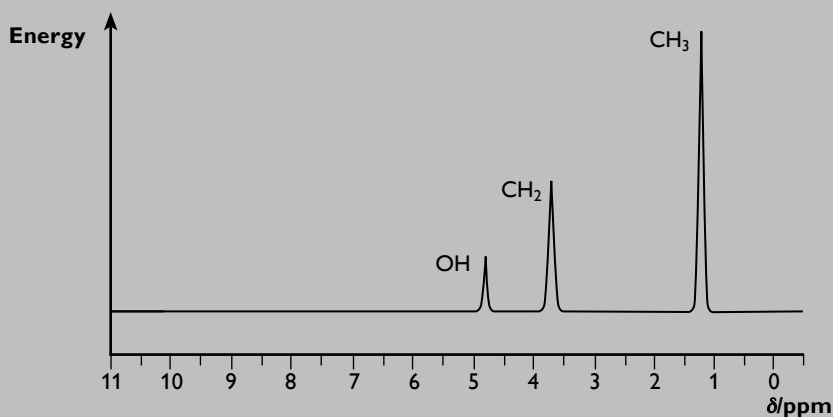
Figure 20.25 Low resolution NMR spectrum of ethanol

Note that the peaks are not only in different positions, but that the areas under the peaks are different. The proton attached to the electronegative oxygen atom is less shielded and so absorbs at higher frequency, which in an NMR spectrum is to the *left*. The scale, given the symbol δ, is measured in parts per million. The protons affected least by the oxygen are the three protons in the methyl group at the other end of the molecule and are shown by the peak furthest to the right. This is also the peak of greatest area, since it is produced by three protons in an identical chemical environment.

The spectrum for ethanol at high resolution (Figure 20.26) is a little different. Two of the peaks are now split into smaller peaks. This occurs because protons are not only influenced by their chemical environment, but also by the magnetic moments of adjacent protons. This is called **spin–spin splitting**.
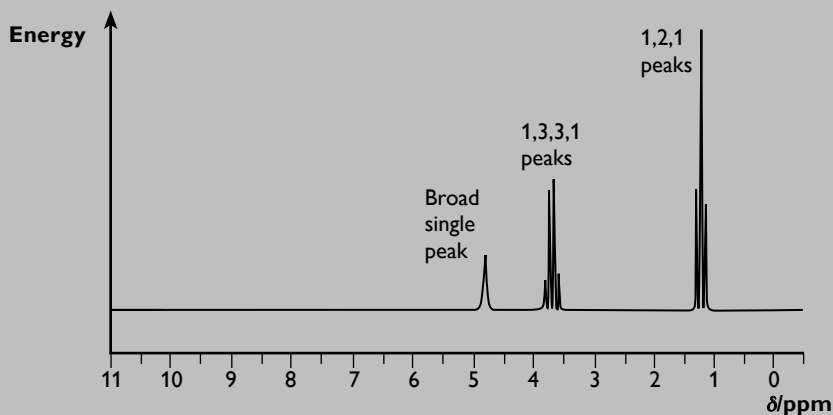
Figure 20.26 High resolution NMR spectrum of ethanol

Consider the protons in the methyl, $-CH_3$, group. They are influenced by the protons on the adjacent methylene, $-CH_2-$, group. These two protons could both align with the applied field, both against the applied field, or one with and one against the

applied field — and there are two ways of doing this! This results in the methyl absorption being split into three peaks in the ratio 1:2:1:

↑↑ ↑↓ ↓↓

↓↑

The absorption due to the methylene protons is split into four peaks in the ratio 1:3:3:1 by the adjacent methyl protons. You might expect that the –OH proton peak would also be split by the methylene protons. However, this does not happen because these protons exchange rapidly with other –OH protons present. A useful test for –OH protons is to add D_2O (deuterium oxide) to the sample. Deuterium nuclei do not absorb in the same range as normal protons, so if an –OH group is present, its peak disappears when D_2O is added.

Table 20.3 shows possible splitting patterns produced by protons adjacent to the one being considered.

Table 20.3

Number of protons adjacent to given proton	Number of lines in multiplet	Relative intensities of lines
1	2	1:1
2	3	1:2:1
3	4	1:3:3:1
4	5	1:4:6:4:1

Things to remember
- The nuclei of hydrogen atoms spin about an axis producing a magnetic moment.
- In an external magnetic field there are two energy states — aligned with and against the external field. If energy is supplied in the radio frequency range the protons can 'flip' to the higher energy state (aligned against the external field).
- The field experienced by a given proton is modified by fields produced by different chemical environments (chemical shift). Protons adjacent to electronegative atoms have absorptions moved to higher frequency (δ).
- The field is further modified by the magnetic moments of adjacent protons (spin-spin splitting). These splitting patterns are characteristic of alkyl groups e.g. –CH gives 1:1, –CH_2 gives 1:2:1 and –CH_3 gives 1:3:3:1.
- Protons in –OH groups usually show only one peak because they exchange with other –OH protons present. Adding D_2O makes this peak disappear.

X-ray crystallography

X-rays are very short wavelength electromagnetic radiation. The wavelengths are similar to the interatomic distances in solids. If a beam of monochromatic X-rays (i.e. rays with a single wavelength) is directed at a crystal, some of the X-rays are diffracted by the planes of atoms in the crystal. This produces a pattern of intensities that can be interpreted to give electron density maps of the crystal. The most

concentrated electron density is around the largest atoms (the ones with the most electrons).

This technique allows us to measure bond lengths and bond angles of molecules, but does *not* show up hydrogen atoms since they only possess one electron and are swamped by other larger atoms.

Things to remember

- X-rays are diffracted by planes of atoms in a crystal because they have similar wavelengths to the separation of the atoms in molecules.
- The intensity of the interaction depends on the electron density around a given atom. Due to this, hydrogen does not show up.
- Using X-ray crystallography, bond lengths and bond angles in molecules can be measured.

Chromatography

Partition

In order to understand how chromatography works, you first need to understand what is meant by **partition**. You are familiar with water as a solvent, but many other liquids also act as solvents. In general, substances dissolve when the energy of the solute–solvent system is lower when the solute is dissolved than when the solute is not dissolved. This is usually the case if the interactions between the solute and the solvent molecules are similar to those between the solvent molecules themselves.

Molecules can attract one another in a variety of ways:

- ionic attractions
- ion–dipole attractions
- hydrogen bonding
- van der Waals forces

As a rule:

- polar solvents are more likely to dissolve ions, substances that form hydrogen bonds and molecules with dipoles
- non-polar solvents dissolve solutes whose molecules are attracted to each other by only van der Waals forces

Iodine is a molecular solid and is unlikely to be as soluble in water, a polar solvent, as it is in hexane, a non-polar solvent. If some iodine crystals are shaken with a mixture of water and hexane until no further change occurs, the iodine distributes itself between the two solvents according to its solubility in each. On measuring the amount of iodine dissolved in each solvent, we find that the ratio of the concentrations is constant, no matter how much iodine is used. This constant is known as the **partition coefficient, K_{pc}.**

$$K_{pc} = \frac{[I_{2(hexane)}]}{[I_{2(water)}]}$$

Here, K_{pc} is an equilibrium constant for the dissolving of iodine in the two solvents. Partition coefficients generally have no units.
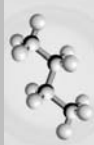
Paper chromatography

You may wonder what this has to do with chromatography, but paper chromatography works because the solutes partition themselves between water held on the fibres of the paper and the solvent that is being used. This means that solutes which are more soluble in the solvent are carried further.

Components in a mixture can be identified by running reference samples alongside the mixture or by calculating the **retardation factor, R_f**. This is the ratio of the distance travelled by the spot to the distance travelled by the solvent (Figure 20.27).

Start to solvent front   Start to centre of spot
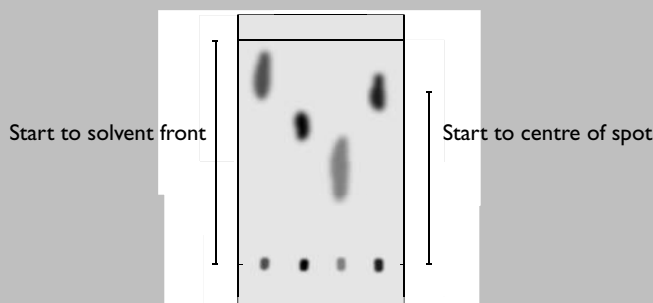
Figure 20.27 Data needed to calculate R_f

You are probably familiar with using paper chromatography to separate the dyes in different inks, and have perhaps obtained a chromatogram like the one shown in Figure 20.28.

Start   **Intermediate**   **Finish**

Paper strip

Water level

Water level

Ink spot

Water level
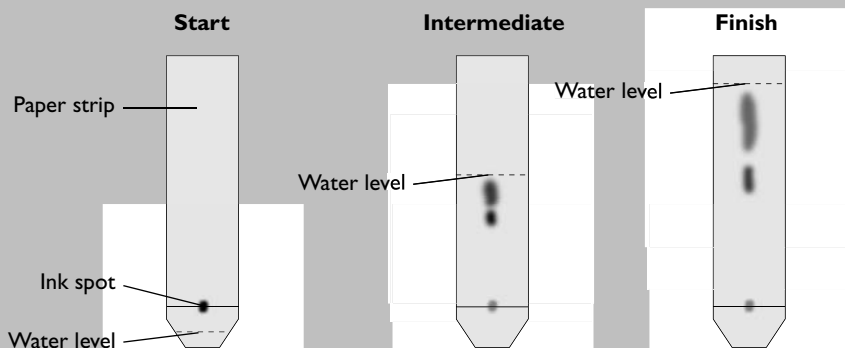
Figure 20.28 Paper chromatography of black ink

Some mixtures may not give coloured spots. For example, if we try to separate a mixture of amino acids by chromatography the individual amino acids are invisible. To reveal the separation we have to use a 'locating agent', in this case ninhydrin, which turns the spots purple-pink (Figure 20.29).

Approved: 0777 023 444

Before spraying with ninhydrin

M 1 2 3 4 5

After spraying with ninhydrin

M 1 2 3 4 5
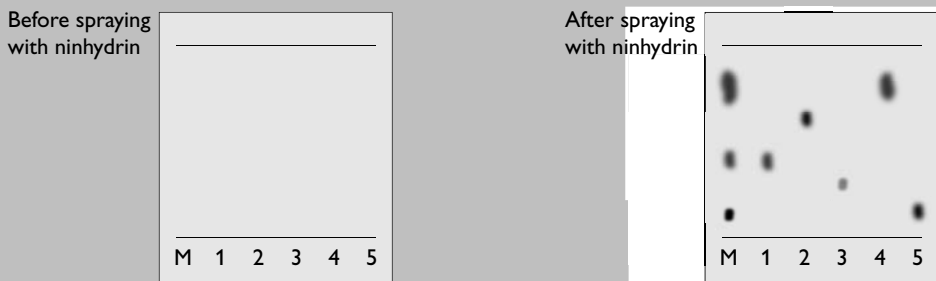
Figure 20.29 Use of a locating agent in paper chromatography

In Figure 20.29, reference samples of amino acids (1–5) have been run alongside the mixture so there is no need to calculate R_f values.

Thin-layer chromatography

This method relies on the adsorption of the solute onto the particles of the thin layer, rather than partition between water trapped on the cellulose and the solvent. Figure 20.30 highlights the differences.

Solute molecules dissolved in the stationary liquid phase

Solute molecules adsorbed on the surface of the stationary phase

Stationary liquid phase   Solid support

Polar solid surface
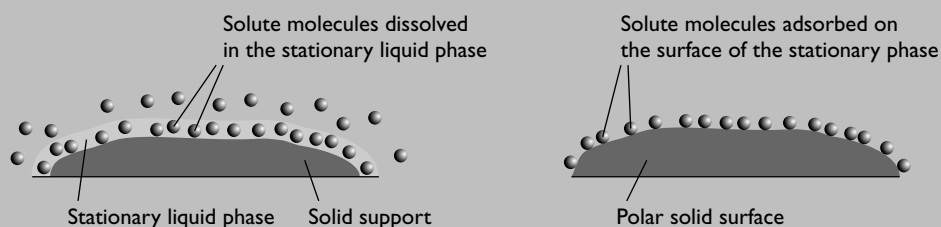
Figure 20.30 Separation by (a) partition and (b) adsorption

Gas-liquid chromatography (GLC)

In GLC, a gas is used as the mobile phase and a non-volatile liquid held on small inert particles is the stationary phase. These particles are packed into a long column a few millimetres in diameter and up to 3 metres long. The column is coiled and mounted in an oven whose temperature can be controlled. This technique works for samples that are gases or which have significant vapour pressure at the temperature of the oven.

The sample is injected into the column and vaporised if necessary. The separation takes place in the column and the individual components emerge from the end of the column and are detected. Sometimes the GLC column is connected to a mass spectrometer (see next section). Different components take different times to flow through the columns. These are known as **retention times** and depend on the following factors:

- the dimensions (length and diameter) of the column
- the temperature of the column
- the flow rate of the carrier gas
- the volatility of the sample
- the interactions between the components of the sample with both the mobile and stationary phases

The retention times may help to identify individual components. By measuring the area under each peak, the proportions of the different components in the sample can be determined.

High performance liquid chromatography (HPLC)
This technique is similar to GLC. The main differences are:
- the mobile phase is a liquid rather than a gas
- the liquid is forced through the column at pressures up to 400 atm
- the columns are much shorter (10–30 cm)
- the components are usually detected by measuring the absorbance of ultraviolet radiation through a cell at the end of the column

As with GLC, the retention times of different substances depend on a number of factors:
- the temperature of the column
- the pressure used (because that affects the flow rate of the solvent)
- the nature of the stationary phase (not only what material it is made of, but also particle size)
- the exact composition of the solvent

Things to remember
- When a solute is shaken with two immiscible solvents, it will dissolve in both. The ratio of the concentration of the solute in each is called the 'partition coefficient'.
- Chromatography is based on the ability of a solute to dissolve preferentially in one of two solvents.
- Components in a chromatogram can be identified by their retardation factor, R_f — the ratio of the distance travelled by the substance compared with the distance travelled by the solvent. Reference samples can also be used to aid identification.
- For colourless samples, such as amino acids, a locating agent is used to make the spots visible.
- In GLC, compounds can be identified by their retention times. Measuring the area under the peaks enables the proportions of each substance in a mixture to be determined.

Mass spectrometry
The principles on which mass spectrometry is based are simple, and modern mass spectrometers (Figure 20.31) are highly accurate having an accuracy greater than 1 part in 100 000.

Approved: 0777 023 444
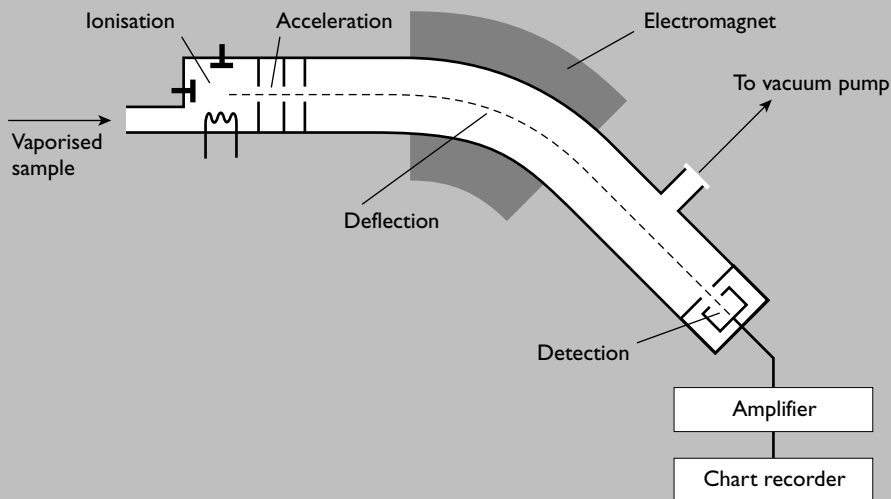
Figure 20.31 A mass spectrometer

In the mass spectrometer the following processes occur:
- If it is not already a gas, the compound is vaporised.
- It is bombarded with electrons, which knock other electrons off some of the atoms or molecules forming positive ions: $M + e^- \rightarrow M^+ + 2e^-$
- Gaseous ions are accelerated in an electric field and then pass through an electrostatic analyser forming a tightly focused beam.
- The ions pass between the poles of an electromagnet, which deflects the beam. Lighter ions are deflected more than heavier ions.
- The strength of the magnetic field is adjusted to allow ions to pass through a slit and be detected.

We saw in Chapter 1 how mass spectrometry can be used to determine accurate atomic masses. It can also be used to give useful information about organic molecules. Mass spectrometry can give three different types of information:
- Measurement of the relative heights of the M and M + 1 peaks allows us to determine the number of carbon atoms in a molecule. Examination of the M and M + 2 peaks can identify the presence of chlorine or bromine.
- Measurement of the accurate mass of the molecular ion (the M peak) enables us to determine the molecular formula.
- Identification of fragment ions produced in the mass spectrometer may allow the piecing together of the structure of the parent molecule.

Use of the M + 1 peak
Naturally-occurring carbon consists almost entirely of ^{12}C and ^{13}C in the ratio 98.9% ^{12}C to 1.1% ^{13}C. We can use this information, together with the abundance of the M and M + 1 peaks, to calculate the number of carbon atoms, n, in a molecule.

$$n = \frac{100\ (A_{M+1})}{1.1\ (A_M)}$$
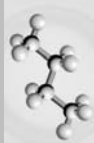
where n is the number of carbon atoms and A_M and A_{M+1} are the abundances of the M and M + 1 peaks.

Use of the M and M + 2 peaks

The halogens chlorine and bromine occur naturally as mixtures of two predominant isotopes. This is shown in Table 20.4.

Table 20.4

Element	Isotope	Relative abundance	Approximate. ratio
Chlorine	^{35}Cl	75.8%	3:1
	^{37}Cl	22.4%	
Bromine	^{79}Br	50.5%	1:1
	^{81}Br	49.5%	

You can see that if the ratio of the abundance (height) of the M and M + 2 peaks is 3:1 it indicates the presence of a chlorine atom in the molecule. If the ratio is 1:1 it indicates the presence of a bromine atom. If more than one atom of halogen is present there would also be an M + 4 peak and we would be able to determine which halogen atoms are present from the ratios.

Using accurate molecular masses

With high resolution mass spectrometers we can measure m/e ratios to five significant figures (at least 1 part in 100 000). This means that it is not only possible to accurately measure the M_r of a compound, but also to determine its molecular formula.

The two compounds below have the same M_r to the nearest whole number:

Pent-1-ene C_5H_{10} $CH_3CH_2CH_2CH{=}CH_2$
But-1-ene-3-one C_4H_6O $CH_2{=}CHOCH_3$

Using the accurate relative atomic masses for hydrogen, carbon and oxygen — H = 1.0078, C = 12.000, O = 15.995 — we can determine the accurate relative molecular masses of the two compounds.

$C_5H_{10} = 5 \times 12.000 + 10 \times 1.0078 = 70.078$
$C_4H_6O = 4 \times 12.000 + 6 \times 1.0078 + 15.995 = 70.0418$

Using fragmentation patterns

The electron beam that produces ionisation in the mass spectrometer can also break bonds, producing fragments of the parent molecule. Some of these fragments will have a positive charge and produce further peaks in the mass spectrum. The fragmentation pattern can help to distinguish between structural isomers because they form different fragments. The two mass spectra shown in Figure 20.32 were obtained from propan-1-ol (Figure 20.32(a)) and propan-2-ol (Figure 20.32(b))
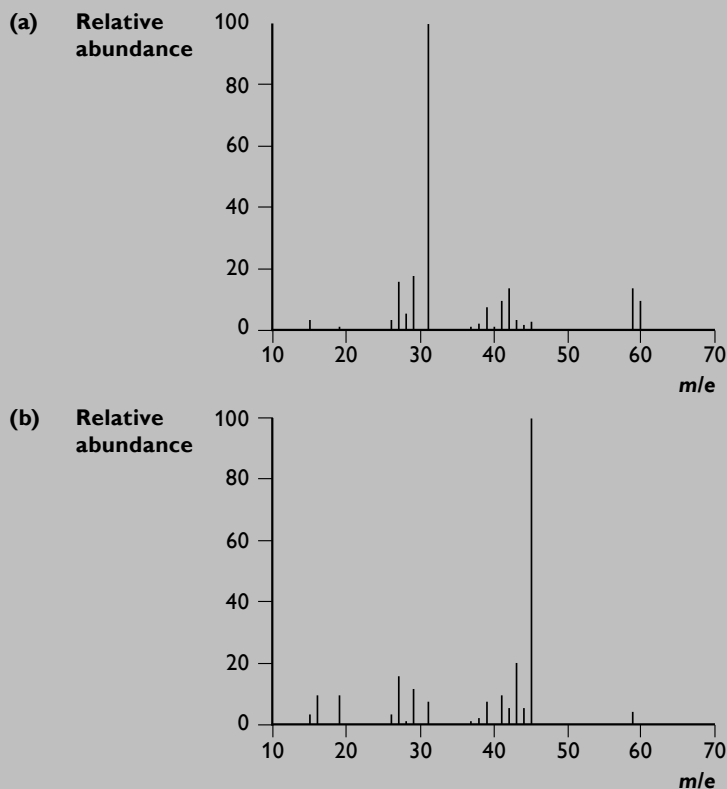
Figure 20.32 Mass spectrum of (a) propan-1-ol and (b) propan-2-ol

The mass spectra have very different fragmentations. In propan-1-ol the largest peak is at m/e 31, whereas in propan-2-ol the largest peak is at m/e 45. What are the fragments that cause these two peaks and how are they formed from the parent molecules? Let's start by looking at the two isomers:
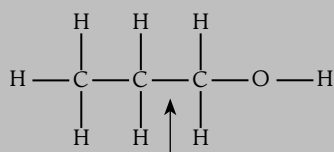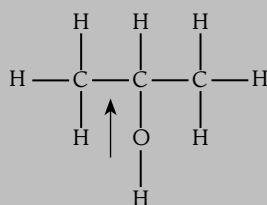
Look at the spectrum of propan-1-ol. A break in the middle of the molecule (where the arrow is) produces either $CH_3CH_2^+$ and $\bullet CH_2OH$ or $^+CH_2OH$ and $CH_3CH_2\bullet$. The uncharged species do not appear in the mass spectrum; the charged species have peaks at m/e values of 29 and 31.

In propan-2-ol, fragmentation between the first two carbon atoms produces either CH_3^+ (m/e = 15) or $^+CH(OH)CH_3$ (m/e = 45) as the charged species.

The fragments in each case can be found in the relevant spectrum in Figure 20.32. For the examination you do not need to be able to explain *why* particular fragments form, just to be able to identify *what* their formula might be.

Things to remember

- In a mass spectrometer, compounds are vaporised, turned into positive ions by bombardment with electrons, accelerated by an electric field and separated by mass using a magnetic field.
- In organic compounds, the ratio of the abundances of the M and M + 1 peaks can be used to determine the number of carbon atoms present, since 1.1% of naturally-occurring carbon is ^{13}C. The expression used is:

  $$n = \frac{100 \ (A_{M + 1})}{1.1 \ (A_M)}$$

- If the mass spectrum contains an M + 2 peak, either chlorine or bromine is present in the molecule. If the ratio is 3:1 chlorine is present; 1:1 indicates that bromine is present.
- A highly accurate mass spectrum can identify the molecular formula of a compound.
- The fragmentation pattern of a molecule can help determine the structure of a compound.

Applications in chemistry and society

In this section we have looked at a range of modern analytical techniques and the ways in which they may be used. The syllabus refers to another area in which analytical techniques play an important role — that of monitoring the environment. The two examples below illustrate this.

Monitoring PCBs in the atmosphere

PCBs (polychlorinated biphenyls) are a group of man-made chemicals that have been used in a variety of manufactured goods since the late 1920s. They can persist in the environment and accumulate in the food chain. PCBs can be found around waste sites, particularly incinerators, where they can be converted into similarly dangerous dioxins. Many countries have banned or severely restricted the production of PCBs.

Humans may be exposed to PCBs by consuming contaminated food, drinking contaminated water or breathing contaminated air. Mothers exposed to PCBs may transmit them to their unborn child or to breast-feeding infants. Effects of PCBs include an increased risk of some forms of cancer, reduced fertility in men and some neurological effects.

PCBs can be monitored by taking air samples remotely, separating the chemicals found using GLC and then analysing them by mass spectrometry. They can also be monitored in water and in soil samples.

Measuring isotope ratios in ice cores

Oxygen is one of the key markers when studying past climates. Natural oxygen exists as two main isotopes — ^{16}O and a tiny amount of ^{18}O, which contains two

extra neutrons. These two isotopes can be detected and the ratio measured using mass spectrometry.

The ratio of these isotopes of oxygen in water changes with the climate. By determining the ratio of ^{16}O and ^{18}O oxygen in marine sediments, ice cores and fossils and comparing this with a universally accepted standard, scientists can study climate changes that have occurred in the past. The standard used for comparison is based on the ratio of oxygen isotopes in ocean water at a depth of between 200 and 500 metres.

Evaporation and condensation are the two processes that most influence the ratio of ^{16}O and ^{18}O oxygen in the oceans. Water molecules containing ^{16}O evaporate slightly more readily than water molecules containing ^{18}O. Similarly, water vapour molecules containing ^{18}O condense more readily.

During ice ages, cooler temperatures extend toward the equator, so the water vapour containing ^{18}O rains out of the atmosphere at lower latitudes than it does under milder conditions. The water vapour containing ^{16}O moves toward the poles, eventually condenses, and falls onto the ice sheets where it stays. The water remaining in the ocean develops an increasingly higher concentration of ^{18}O compared with the universal standard, and the ice develops a higher concentration of ^{16}O. Thus, high concentrations of ^{18}O in the ocean tell scientists that ^{16}O was trapped in the ice sheets. The exact oxygen ratios can indicate how much ice covered the Earth. This work can also provide pointers to any current change in climate by examining the isotopic ratio in recent ice cores.

Design and materials

You may be asked to use your knowledge of core chemistry in discussing new materials and chemical techniques. This section focuses on modern developments in the areas of drug design and delivery, new materials, manipulation of materials on a molecular scale (nanotechnology), environmental problems and extending the useful life of both materials and energy sources.

Medicinal chemistry and drug delivery

Drug design

Huge quantities of money are invested each year by pharmaceutical companies on research into new drugs and treatments for major diseases. The cost is often the result of promising candidates that prove to be unsatisfactory at the clinical trial stage after many months or years of development.

In modern research, careful preparation and analysis is carried out so that the range of possible molecules to be tested is limited and that unsuitable ones are screened out at an early stage. However, sometimes only tiny structural differences can make a huge difference to the effect of the drug. One such example is the drug thalidomide,

which was produced by researchers seeking an alternative sedative to Valium® for women during pregnancy. Like many organic compounds, thalidomide exists in the form of two optical isomers:
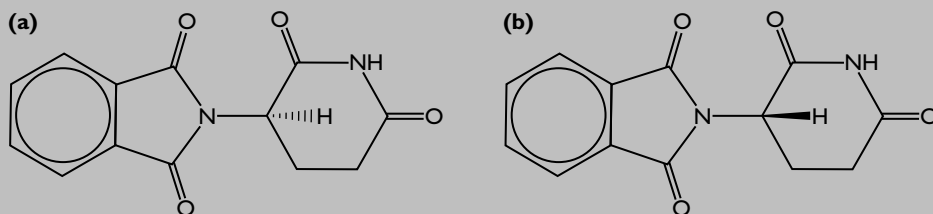
Figure 20.33(a) R-thalidomide and (b) S-thalidomide

The difference in the two forms is slight, but it was sufficient for the S-form to cause serious birth defects, whereas the R-form had the desired properties of being a sedative and anti-nausea drug.

Drug molecules act by binding to receptors, which are often enzymes. You will remember how only particular substrate molecules fit into the active site and bind to it. Molecules that do not have the precise shape and binding sites are either inactive or have different effects. A simple example of this is the compound carvone. This is an optically active compound that binds to sites in the olfactory system (the region responsible for detecting smells). The two isomers (Figure 20.34) have quite different smells:

(R)-(−)-carvone from spearmint oil

(R)-(+)-carvone from caraway seed oil
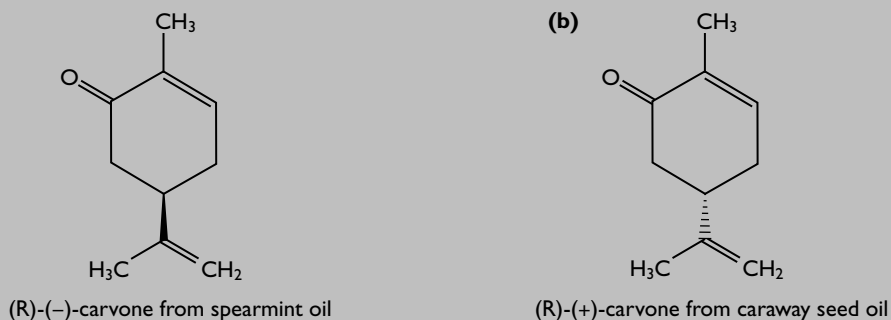
Figure 20.34 Isomers of carvone

In modern drug research, chemists use computer models to see how a particular drug might interact with the active site on the receptor. They also have access to online databases to check on interactions with other enzymes in the body. These techniques, while not cheap in themselves, have refined drug design and research making new powerful treatments for major diseases available in a shorter time.

The drug Taxol® is based on a natural substance found in yew trees. It is used to treat some forms of cancer. If you study its structure (Figure 20.35) you will recognise that it contains a number of amide and ester linkages, all of which can be hydrolysed in acid. Based on this it would not be sensible to give the drug orally without protecting it in some way.
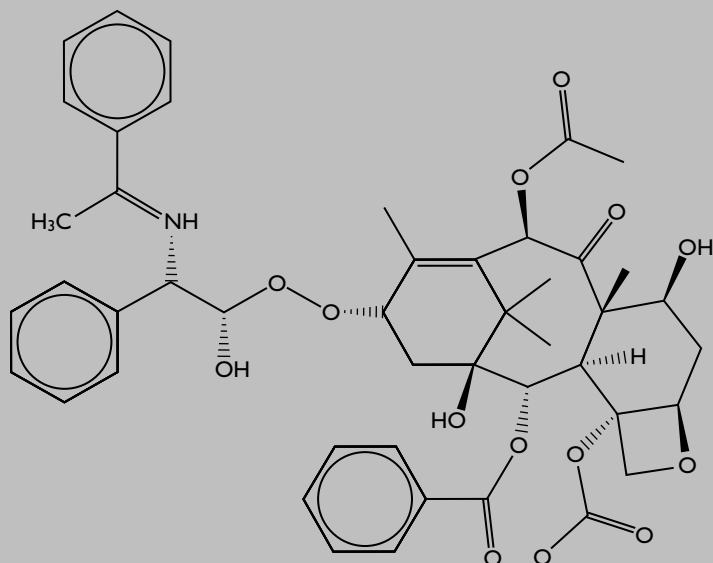
Figure 20.35 The structure of Taxol®

One successful method of delivery that has become widespread is to use artificial liposomes (Figure 20.36). These are tiny spheres made from one or more phospholipid bilayers. They contain an aqueous core that houses the drug.
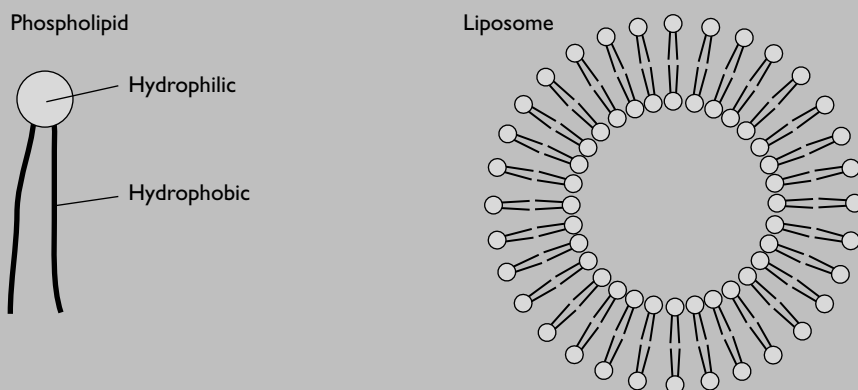
Figure 20.36 Structure of a liposome

Another method for protecting a drug when it is in the bloodstream is to attach it to a polymer the body will tolerate. One of the most commonly used is 'polyethylene glycol' or PEG:

$$HO—(CH_2—CH_2—O)_n—H$$
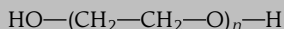
If the length of the chain is not too long, PEG is soluble in water (and hence in blood). It does have the disadvantage that a molecule of PEG can carry only two drug molecules.

Drug delivery

Although the synthesis of new drugs is a major challenge, an equally challenging aspect of medicinal chemistry is to make sure the drug is delivered to its target. Many drugs are swallowed and so have to pass through the body's digestive system in order to get into the bloodstream and be carried to the target site. Acid conditions in the stomach, mildly alkaline ones in the small intestine and the presence of a range of enzymes to digest food can potentially break down or change the structure of a drug.

Things to remember

- Drugs have to be designed to be effective and to have minimal side effects.
- Drugs act by having the right shape to fit onto the receptor and the correct binding sites.
- Many drug molecules are chiral (exist as optical isomers) and only one of the forms is likely to have the desired effect.
- If only one of these forms can be synthesised (asymmetric synthesis) it saves time and resources.
- Natural products are often useful starting materials for new drugs.
- Liposomes and polymers (such as PEG) can be used to protect drugs from being broken down and deliver them to their target.

Properties of polymers

We have already covered a number of aspects of polymers in Chapter 19. This section is more concerned with the properties of polymers and how they might be modified for particular purposes.

Addition polymers

The properties of addition polymers can be modified in number of ways, based on their structure and the bonds between the polymer strands. Addition polymers containing only carbon and hydrogen have only temporary dipoles between the strands, and as such are easily deformed. The longer the chain, the stronger are the van der Waals forces between adjacent chains. The presence of side chains also affects the bulk properties of an addition polymer. Unbranched polymers pack closer together than polymers with lots of side chains and this increases the bulk density of the polymer. These differences lead to two distinct forms of poly(ethene) — LDPE (low density poly(ethene)) that has lots of side chains (Figure 20.37(a)), and HDPE (high density poly(ethene)) in which the polymer strands are packed more closely together (Figure 20.37(b)).

(a)   **(b)**
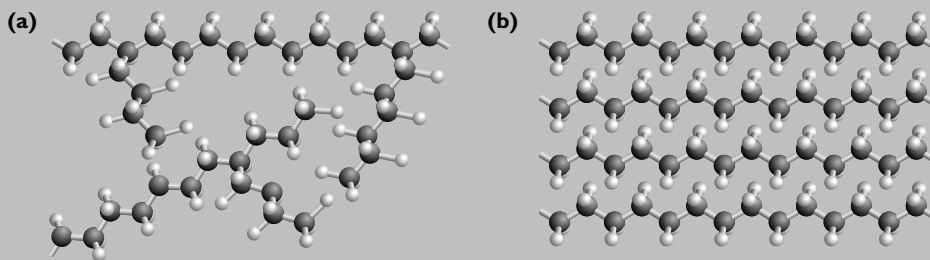
Figure 20.37(a) Structure of (a) LDPE and (b) HDPE

Condensation polymers

In condensation polymerisation the nature of the monomers can vary (in proteins for example) with only the bonds formed between the monomers being constant. This means that the properties of a polymer can be varied by changing one or both of the monomers. Nylon-6,6, proteins and Kevlar® are all polyamides, yet they have very different properties:

- Nylon-6,6 is made from two monomers with a similar hydrocarbon chain. It consists of long chains suitable for use in textiles.
- Proteins are made from a variety of amino acids and have a huge range of properties depending on the amino acid sequence. Some, for example enzymes, are water soluble; others, for example collagen, are tough and water-resistant.
- Kevlar® is made from two monomers with similar hydrocarbons in the chain (but much bulkier than in nylon-6,6). It is extremely tough and is used in the construction of bulletproof vests, and in high performance tyres.

Other polymers have been developed that conduct electricity or emit light, opening up the possibilities of 'wearable' MP3 players, mobile phones and computers.

Things to remember

- Addition polymers formed from hydrocarbons tend to deform because they are held together by van der Waals forces between the chains. These are dependent on chain length.
- Bulk properties of addition polymers depend on the packing of the chains, which in turn depends on how branched they are. Those with more branching have lower density and are generally weaker.
- Addition polymers that contain conjugated double bonds have the ability to conduct electricity, or emit light.
- Condensation polymers have a wide variety of properties, depending on the structure of their monomer(s).
- Most natural polymers, such as proteins, are condensation polymers.

Nanotechnology

A basic definition of **nanotechnology** is the engineering of functional systems on the molecular scale. It is a science that had its beginnings in the late 1970s and early
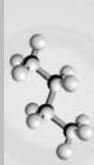
1980s and, in general, it refers to systems on a scale of 1 to 100 nanometres (1×10^{-9} to 1×10^{-7} metres) — the average human hair is about 25 000 nanometres wide.

Some of the early work on nanotechnology centred on a form of carbon known as 'buckminsterfullerene' or a 'buckyball' (Figure 20.38), discovered in 1985.
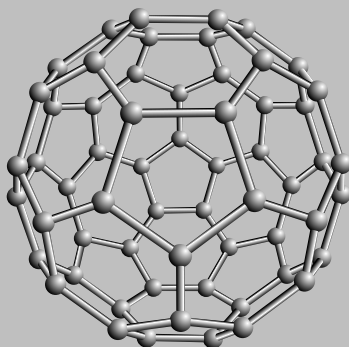
Figure 20.38 A 'buckyball'

The discovery of a new form of a pure element is a rather rare occurrence, particularly for a common element. Therefore, reports of such discoveries generate an unusual amount of excitement among scientists. A whole new chemistry has developed in which fullerene molecules are manipulated to form compounds. Since the C_{60} sphere is hollow, other atoms can be trapped within it.

Linked to this discovery was the fact that single sheets of carbon atoms could be isolated from graphite. This substance, known as 'graphene', consists of one-atom-thick layers of carbon atoms arranged in hexagons (Figure 20.39).
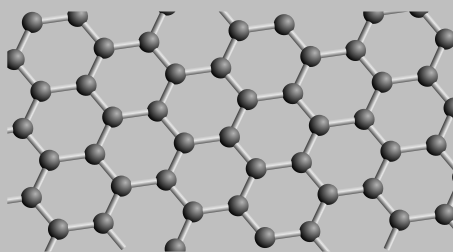
Figure 20.39 Structure of graphene

Transistors made from such samples have been shown to operate at gigahertz frequencies — comparable to the speed of modern computers. The material could theoretically operate near terahertz frequencies, hundreds of times faster.

In addition to this, these sheets can be rolled into cylinders known as **nanotubes** (Figure 20.40) and even combined with half a buckyball to produce nanoscale test tubes.

Approved: 0777 023 444

Pollution

Oil

One of the major environmental problems in recent years has been pollution due to oil spillages. These have been caused by oil tankers sinking or running aground or by leakages from oil wells and pipelines. They are usually problems of the marine and coastal environments. The oil floats on the surface of the water and is washed ashore where it causes immediate and longer-term damage to aquatic bird and fish populations. If the oil can be prevented from reaching shore, the damage is likely to be much reduced.

One method of trying to prevent oil slicks from spreading is to use booms made of porous materials called 'sorbents' that are able to soak up the oil. Traditional booms also absorb water and soon sink as they become waterlogged. More recently, new materials have been developed to act as sorbents. These are able to absorb more than 200 times their own mass of oil without sinking. The key has been the creation of a fibreglass sorbent that has fluorinated hydrocarbons trapped in the structure. The hydrocarbon is hydrophobic ('water-hating') and so repels the water while allowing the oil to be absorbed.

Polluted soil

Land that has been used for industrial activity may become polluted with materials related to the industry. There is a huge variety of these pollutants, including heavy metals. The removal of harmful contaminants from soil is known as **soil remediation**. There are a number of methods that can be used, the choice of which depends on the nature of the contaminants.

Excavation and dredging are the most common processes used in soil remediation. These processes involve extracting soil that is contaminated and judged to be unrecoverable using current technology, and transporting it to a landfill site set aside for this purpose. Purified soil may be used to fill in the area where the extraction took place.

Soil remediation is sometimes accomplished using a process known as pump and treat. This approach involves the removal of contaminated groundwater, followed by various methods to purify the extracted liquid. The soil is also extracted and treated to remove various contaminants. It is then returned to its original position. The purified water is pumped back into the purified soil, effectively restoring the ecological balance of the area.

Where a high concentration of contaminants is present in groundwater, a process known as **solidification** is used. Chemical reagents that will combine with the materials in contaminated water and sludge are added to make solid compounds that can be separated from, or filtered out of, the water. This way the water is left in the natural ecosystem but the contaminant chemicals are removed.

Bioremediation involves the addition of specific bacteria or plants that feed on the contaminated particles and create harmless by-products. These organisms must be chosen carefully as they may multiply rapidly with no natural predators.

Approved: 0777 023 444

Bioremediation is more common in contaminated water, but can work in soils. Naturally-occurring microorganisms in soil can break down some organic contaminants into carbon dioxide and water, providing that other nutrients are supplied. These can be pumped deep into the soil in calculated amounts. This technique has been used successfully to treat contamination by a wide range of organic compounds.

The use of plants in removing contaminants is sometimes referred to as **phytoremediation** and is not a new process. Certain plants (**hyperaccumulators**) are able to accumulate, degrade or make harmless some contaminants in soils, water or air. Metals, pesticides, solvents, explosives, crude oil and its derivatives have been treated in this way. Mustard plants, alpine pennycress and pigweed have proven to be successful at removing contaminants. Water hyacinth is highly successful at removing both heavy metals and cyanide from water supplies.

Pollution in the atmosphere
We saw in Chapter 15 that chlorofluorocarbons pose a significant threat to the Earth's ozone layer and contribute to global warming. As a result, they have been largely phased out of commercial (and some industrial) use by the finding of alternatives. CFCs are not the only compounds that threaten the ozone layer or contribute to global warming, but you will not be required to remember specific details of others.

In the past, vehicle exhausts have caused considerable pollution of the air at street level. The phasing out of lead additives and the increasing use of catalytic converters has largely solved this problem in developed countries. However, large amounts of carbon dioxide are still being produced that add to global warming.

Recent developments in the use of electricity and hydrogen to power vehicles may help to solve this problem (see 'New forms of energy') but at present the technology is expensive.

Extending the life of resources
Increasing awareness of both pollution and the limited resources on Earth has led to innovation in chemical research and the introduction of the phrase **green chemistry**.

Among the changes in outlook of research, the following principles are now widely adopted:
- prevention of waste (cheaper than cleaning up afterwards)
- energy efficiency is maximised
- feedstocks for processes should be sustainable
- chemical products should break down naturally
- hazardous solvents should be avoided

Copper mining
Examples of this in practice include copper mining. At the beginning of the twentieth century the world's annual demand for copper was around half a million tonnes, and ores containing about 4% copper were the limit of what was regarded as profitable. Today, the demand for copper is approaching 5 million tonnes per year and ores

once regarded as worthless, and containing less than 1% copper, are now being used for extraction. Not only are companies mining new ores, but they are also re-working 'spoil heaps' from previous extractions.

A new, energy-efficient technology called **bioleaching** has been developed to enable this. Most copper minerals are sulfides, with chalcopyrite ($CuFeS_2$) being the most abundant and thus the most important economically. Sulfide minerals are insoluble in water and acid solutions unless they are first oxidised. While exposure to air is sufficient to oxidise these minerals, the process is slow and inefficient. The kinetics of the oxidation process are vastly improved by the introduction of *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* bacteria to the system.

The overall chemical reactions for chalcopyrite are:

$$4CuFeS_2 + 11O_2 + 6H_2O \xrightarrow{\textit{Thiobacillus ferrooxidans}} 4CuSO_4 + 4Fe(OH)_3 + 4S$$

$$2S + 3O_2 + 2H_2O \xrightarrow{\textit{Thiobacillus thiooxidans}} 2H_2SO_4$$
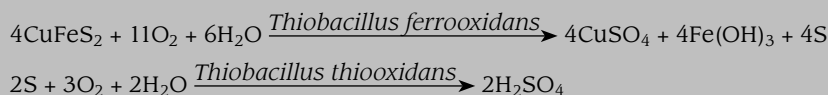
Similar technology is being used to extract other metals — for example gold, nickel and zinc.

Supercritical carbon dioxide as a solvent
A supercritical fluid is a gas that is compressed and heated to have both the properties of a liquid and a gas at the same time. Carbon dioxide becomes supercritical at a pressure of about 7300 kPa and a temperature of 31 °C.

Supercritical carbon dioxide is well established as a solvent for use in extraction processes. There are number of reasons for this. It can penetrate a solid sample faster than liquid solvents because of its high diffusion rate, and can rapidly transport dissolved solutes from the sample matrix because of its low viscosity. There are also fewer solvent residues present in the products.

One of the commonest uses of supercritical carbon dioxide is decaffeination of coffee and tea, which is now an established industrial process. Other examples have been developed, including the extraction of hops, natural products, high-value pharmaceutical chemicals, essential oils and environmental pollutants. The recovery of the solvent is straightforward and it can be re-used.

New forms of energy
Traditional forms of energy have relied on fossil fuels either directly or indirectly (as in electricity generation). These are generally inefficient (rarely better than 35–40%) and are also a source of carbon dioxide (and possibly other pollutants). In addition, a number of the materials used for fuels also have important uses as feedstocks — for example crude oil for polymers and raw materials for the organic chemistry industry. Converting from coal-burning to gas-powered power stations increases the efficiency of energy conversion to electricity, and if a 'combined heat-and-power' system is used conversion rates approaching 80% can be achieved.

There are, however, alternatives to burning valuable resources such as oil.

Biofuels

Bioethanol produced by fermenting agricultural products can be used to supplement petrol and/or gasoline. This has been used for a number of years in parts of Africa and South America. More recently developments have begun in the USA and Europe. Another biofuel is biodiesel, which has been developed from a number of oilseed crops. Biofuels are potentially a useful replacement for fuels based on crude oil, but their production needs careful analysis in terms of the overall energy balance — for example, does the production of the crop need more fertiliser produced using fossil fuels?

Batteries and fuel cells

Battery technology has undergone a revolution in recent years with the development of alternatives to traditional alkaline cells and of small rechargeable batteries that can be recharged more than 1000 times. This saves waste and pollution since batteries are no longer thrown away once their power has been used. Many stores now collect used batteries. Rechargeable lead–acid batteries have been used in cars for many years and are still in use. Recharging the batteries still requires electricity generated by conventional means, although solar rechargers are now available.

Fuel cells are an alternative to batteries, although for large-scale uses the technology is still in its infancy. In a fuel cell, a fuel (such as hydrogen or a hydrocarbon gas) and oxygen are passed over electrodes. This generates electrical power. Such systems were developed originally for spacecraft, but more recently car manufacturers have shown interest in this technology with a number of prototypes being developed.

Hydrogen

Hydrogen is a useful fuel in that the product of combustion, water, is non-polluting. However, hydrogen is not a naturally-occurring fuel. It has to be produced from either existing feedstocks, such as natural gas, oil and coal, or from renewable sources such as water by electrolysis. Even if this could be achieved using renewable energy such as solar energy there are still practical problems to be overcome.

One of these problems is storage of the hydrogen. It has to be compressed so that it can be stored in a small enough space to fit a vehicle, and this presents the risk of an explosion in an accident. Two solutions to this problem are being researched:
- absorbing the hydrogen onto a solid material that can then be released chemically as needed
- using nanotechnology to produce a material with molecular-sized holes to absorb the hydrogen and release it as required

In the last few years, work on buckyballs has led to hopes that they might be useful as a hydrogen-storage medium. Two strategies are under development — one involving

coating the surface with Group I or Group II metal atoms and the other by creating buckyball cages to contain hydrogen (Figure 20.41).
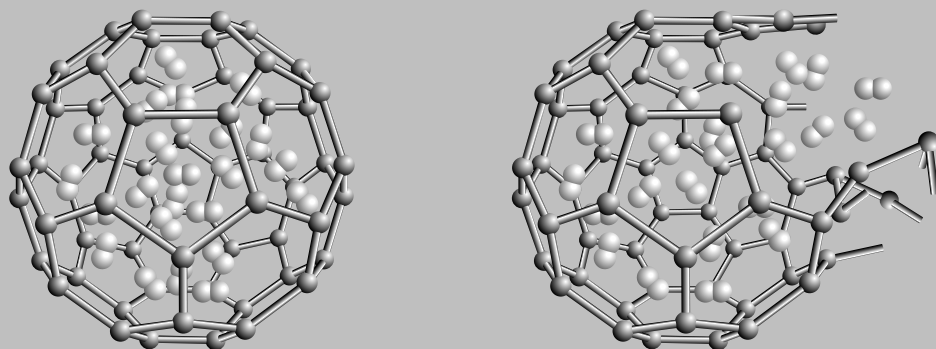
Figure 20.41 Buckyball cages

Things to remember

- The development of efficient and affordable solutions to environmental pollution depends on knowledge of the physical and chemical properties of the pollutants.
- It is better to reduce waste by efficient chemical processes than to clean up pollution afterwards.
- There are limited resources on Earth and efficient use of these, including recycling, is critical to our consumer economy.
- Chemistry has a vital part to play in the development of new energy supply and the more efficient use of existing fossil fuels.

Approved: 0777 023 444

Experimental skills and investigations

This section is needed for both the AS and the A2 examinations. The AS practical component Paper 3 and the A2 practical component Paper 5 are covered separately.

Paper 3: AS practical paper

Skills tested on this paper are:
- manipulation of apparatus
- presentation of data
- analysis and evaluation

Almost one-quarter of the total marks for the AS examination are for experimental skills and investigations. These are assessed on Paper 3, which is a practical examination worth 40 marks. Although the questions are different each year, the number of marks assigned to each skill is always approximately the same. This is shown in the table below.

Skill	Minimum mark allocation*	Breakdown of marks	Minimum mark allocation*
Manipulation, measurement and observation, MMO	12 marks	Successfully collecting data and observations	8 marks
		Quality of measurements or observations	2 mark
		Making decisions relating to measurements or observations	2 marks
Presentation of data and observations, PDO	6 marks	Recording data and observations	2 marks
		Displaying calculations and reasoning	2 marks
		Data layout	2 marks
Analysis, conclusions and evaluation, ACE	10 marks	Interpreting data or observations and identifying sources of error	4 marks
		Drawing conclusions	5 marks
		Suggesting improvements	1 mark

*The remaining 12 marks will be allocated across the skills in this grid, and their allocation may vary from session to session.

The examination consists of two or three questions. One question is an observational problem. You will be asked to carry out particular experiments to investigate one or more unknown substances. These substances may be elements, compounds or mixtures. You could be asked to construct tables to record your observations, analyse your results and draw appropriate conclusions.
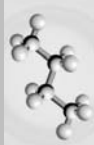
The other question or questions are quantitative — in other words, involve meas-
urement. These could include titrations (volumetric analysis) or measurement of a
quantity such as enthalpy of reaction or reaction rate. You will be expected to:
- construct tables, draw graphs or use other appropriate ways of presenting data
- analyse the data
- perform calculations
- draw conclusions

One or more of the questions will ask you to identify sources of error and make
suggestions for reducing these.

A detailed breakdown of examiners' expectations for each mark category is given in
the syllabus and it is important that you read through this.

Manipulation, measurement and observation

In the examination, unless you are told differently by your teacher or supervisor,
you can tackle the questions in any order. It makes sense to attempt the question
carrying the most marks first, in case you run out of time. However, with some
thought and careful planning this should not happen.

Manipulation and measurement

It is important to think about the accuracy of the different readings you are asked
to make. For example, an electronic stopwatch might measure to the nearest one-
hundredth of a second, but accuracy to the nearest second is more appropriate in
any time measurement you are likely to make. You need to think about the number
of decimal places or significant figures to use when you are recording data. It is
important to remember that different pieces of apparatus will give measurements
with different degrees of accuracy. Overall, any experimental data are only as accu-
rate as the *least* accurate measurement. It is important to understand the difference
between accuracy and precision. The diagrams below may help.

	Accurate	Inaccurate (systematic error)
Precise		
Imprecise (scattered results)		

You may be asked to use a burette to add a liquid reagent and measure the quantity
used. You should have had lots of practice during your AS course at using a burette
and reading the scale.

Approved: 0777 023 444

Tip You should read a burette to the nearest $0.05\,cm^3$, in other words halfway between two of the smallest divisions. You cannot estimate more precisely than this because the smallest drop a burette can deliver is approximately $0.05\,cm^3$.

A common mistake students make is in calculating the average burette reading used in a titration. This cannot have a greater degree of accuracy than the burette can produce. Therefore, the average burette reading has to end in $.00\,cm^3$ or $.05\,cm^3$. Anything else is wrong and will be penalised.

23

23.45 cm³
(not 24.55)

24
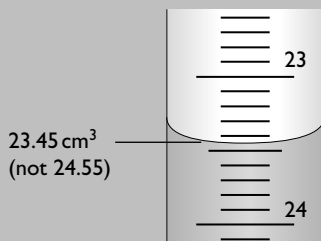
In a titration you need to carry out sufficient repeat titres to establish the 'correct' end point. For a titration with a sharp end point this should be within $0.10\,cm^3$.

Tip Once you have established the approximate end point, say $22.60\,cm^3$, for the accurate titrations, you can run in $20\,cm^3$, swirling the mixture, before adding a few drops at a time. This will save time.

It is important that you always try to pick the same point for determining the end point. If it is a potassium manganate(VII) titration this is when the mixture just has a permanent pale pink colour. If it is an acid–base titration, the end point is when the indicator just remains in its acid state on swirling.

Tip Do not add more than two or three drops of indicator unless instructed otherwise. Using more indicator does not give a more precise end point because all of the indicator has to change to its acid form.

If you are asked to perform a kinetics experiment, read carefully through the instructions before you start. Make sure that you have everything ready before you start the reaction — reagents measured out, stopwatch ready, thermometer in place (if relevant). Being organised is the best way to get good results and to avoid wasting time.

Tip In a kinetics experiment, if you are adding a quantity of one reagent to another, make sure that you start the stopwatch at the same point each time. This could be halfway through adding the reagent, or at the point when the last of the reagent has been added.

If you are carrying out an enthalpy of reaction experiment you will probably be asked to measure the temperature of the reaction mixture every 30 seconds or every minute. It is important that you are organised and ready to do so.

Approved: 0777 023 444

Tip Stir the mixture continuously with the thermometer to make sure that you are measuring the temperature of the whole mixture (this is particularly important if the mixture contains a solid). Get ready by checking the position of the mercury in the thermometer as you are coming up to the next timed reading.

Observations

In most examinations one specific question involves making careful observations, recording them and then drawing conclusions from these observations. If you are to score good marks on this question it is *vital* that you make good observations and record these accurately.

To make sure your observations are correct you must be certain that you follow the instructions completely.

Tip Examples where students make errors include the following:
- adding excess reagent when told to add a few drops *followed* by an excess — this often means that an observation which carries marks is missed
- adding reagents in the wrong sequence — this can mean that changes which should be observed do not happen
- using too much of the 'unknown' or too much reagent — this can mask observations
- using a solid 'unknown' rather than a solution of the substance —observations may be different or masked
- failing to test for a gas produced (lighted splint, glowing splint, indicator paper, smell) — marks will be lost because of observations missed

Presentation of data and observations

It is important that, having carried out a practical task, the results are recorded systematically and logically. In some cases, such as observational exercises, there may be a table printed on the exam paper for you to fill in. In other exercises, such as titrations, you may need to draw your own table for the data.

You may also be asked to draw a graph to display the results of an experiment. Here are some tips on what is needed to score high marks when drawing a graph.

Tip There are a number of key features on a graph that examiners look for:
- a title describing what the graph represents
- both axes labelled, including the correct units
- the independent variable plotted on the *x*-axis and the dependent variable on the *y*-axis
- use of a sharp pencil for plotting the points and sketching the graph
- a sensible scale chosen to make the most of the graph paper (at least half in both dimensions)
- drawing a line of best fit for data that vary continuously
- identifying anomalous results (outliers) and not giving these undue weight

The diagram below shows how to draw a 'line of best fit'. The line is placed so that points are equidistant from the line with equal numbers of points on each side.
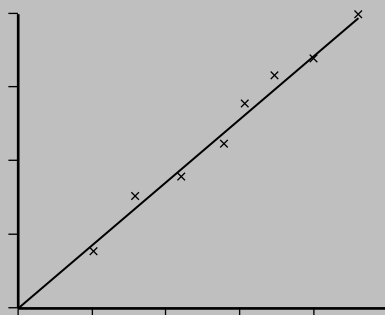
The diagram below shows what is meant by an 'outlier' — a result which, for some reason, is clearly not part of the data set we want to use.
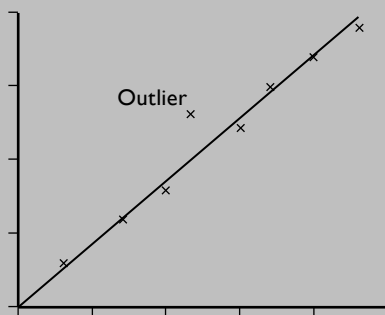
When an experiment produces qualitative data, it is just as important to represent the data accurately. Accurate recording of what happened at different stages of an experiment — for example when a few drops of reagent were added, when more reagent was added and when the reagent was present in an excess — will help you explain what is happening and score the available marks.

Try to use accurate and unambiguous language when describing colours or colour changes. Make sure that it is clear whether you are referring to a solution or a precipitate in the solution.

> **Tip** The words you use must be clear to the examiner as well as to yourself.
> - Do *not* use words such as 'see-through' or 'transparent' when you mean 'colour-less'. It is perfectly possible to 'see through' potassium chromate(VI) solution but it is not colourless, and copper(II) sulfate solution is 'transparent', but it is not colourless.
> - Try to be as precise as possible about colours. A simple word like 'blue' is rarely enough to describe colour changes such as those that take place when aqueous ammonia is progressively added to a solution of copper(II) ions.
> - If a gas is given off remember that the observation is that 'bubbles are produced' or 'effervescence takes place', *not* just that 'carbon dioxide is evolved'. If the gas

is carbon dioxide you also need to say how you tested for it — for example 'it turned limewater milky/cloudy'.

Analysis, conclusions and evaluation

Analysis and conclusions

In order to draw conclusions and evaluate the procedures you have carried out, you first need to analyse the results of any practical you complete, and then explain what they show. Before reaching a conclusion you may need to carry out a calculation. If this is the case, you should show the key steps in the calculation so that it can be followed by the examiner who can then check the accuracy. For example, in a titration a series of repeats is undertaken to ensure accuracy and to identify any anomalous results. When the average titre is calculated, an anomalous result should be excluded from the calculation.

You may be asked to draw a graph to display results because this is an excellent way to show trends or relationships. A straight-line graph passing through the origin shows a directly proportional relationship between the dependent and independent variables. Sometimes the graph will be a curve and you may need to measure the gradient of the curve at different points. When doing this, use large triangles to calculate the gradient as this gives a more accurate calculation. Remember that a graph provides evidence to support a conclusion.

Evaluation

This is one of the hardest skills to develop. It relies on your ability to think critically about the reliability of the data you have collected and the conclusions drawn.

One way to do this is to think about the errors that affect results. In any experiment there are two types of error:

- Random errors cause results to fluctuate around a mean value. The results are made more reliable by taking a number of readings and averaging them.
- Systematic errors affect all measurements in the same way, giving values higher or lower than the true result. Hence, systematic errors cannot be averaged out. An example of this is the heat loss in an enthalpy change experiment.

Remind yourself of these differences by looking back at the diagram on p. 220.

Tip When you evaluate an experiment you should be able to do the following:
- suggest improvements to the procedures you used
- compare repeated results to judge their reliability
- identify any anomalous results (outliers)
- identify variables you need to control
- estimate uncertainty in measurements
- distinguish between random and systematic errors

Paper 5: A2 assessment

Skills tested on Paper 5 are:
- planning
- analysis and evaluation

Practical skills and investigations are examined on Paper 5, which is worth 30 marks. This is *not* a laboratory-based examination, but it tests the practical skills that you will have developed during your A-level course. The table below shows the breakdown of marks.

Skill	Total marks	Approximate breakdown of marks	
Planning	15 marks	Defining the problem	5 marks
		Methods	10 marks
Analysis, conclusions and evaluation	15 marks	Dealing with data	8 marks
		Evaluation	4 marks
		Conclusion	3 marks

It is expected that you will know how to:
- plan how to carry out an experiment
- perform the experiment according to your plan
- evaluate what you have done

The examination consists of two or more questions. One of these will ask you to design an experimental investigation of a given problem. This question is *not* structured. It requires you to answer using diagrams, extended writing, flow charts, tables and equations. You may also be asked to express a prediction in the form of a written hypothesis that links the independent and dependent variables or in the form of a graph showing the expected outcome.

There may be questions that contain some experimental data and which ask you to analyse, evaluate and draw conclusions from those data. Once again this type of question is *not* highly structured and you will need to decide for yourself the methods you use to tackle the question.

One or more questions may be on areas of chemistry that are difficult to investigate experimentally in a school laboratory. Such questions will *not* require knowledge of equipment or theory beyond that in the A-level syllabus. Any information you need that you would not be expected to know will be given in the question.

A detailed breakdown of examiners' expectations for each mark category is given in the syllabus, and it is important that you read through this.

experimental skills & investigations
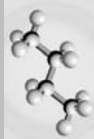
Planning

Planning can be a difficult practical skill to master. It depends on thinking carefully about the practical problem set. It also relies on a good understanding of the practical experience you have gained during the course. The following may make it easier for you to gain marks.

Tip The writing of a plan is best tackled in stages. Practical exercises vary greatly in their demands, so it is probably best to consider two types of plan — one for quantitative exercises and another for qualitative exercises.

(1) Quantitative exercises

- You should be able to identify the independent and dependent variables from the information given.
- You should be able to identify other key variables and propose measures to control these.
- You should be able to make a quantitative prediction of the likely outcome of the experiment (if required).
- The plan needs to be able to test any prediction/hypothesis in a reliable, unambiguous and reproducible way.
- Even if the question does not ask for a formal prediction/hypothesis, you should have a clear idea of what you expect the results to show.
- The data provided in the question will need processing in some way to enable analysis and evaluation (see later). This also means that some discussion of how this processing is to be carried out needs to go into the plan.
- Any recording, graphical and numerical processes should be stated.
- The steps by which the experimental procedure and analysed data will be evaluated should be included.

(2) Qualitative exercises

This type of exercise might involve planning the preparation of a given mass of a compound or an analysis scheme for an unknown compound. The plan should be sufficiently detailed that, if the experiment were performed by a competent chemist, it would produce the anticipated outcomes. Many students lose marks at this stage by not producing a sufficiently detailed plan and relying on the examiner to 'fill in the gaps'.

- The suggested plan must be workable given the apparatus available, and the scale required (e.g. for producing a known mass of compound).
- The quantities of reagents to be used should be specified.
- The heating or cooling of the reaction mixture and the method chosen to do so should be included.
- The sequence of carrying out tests on an unknown compound should be stated so that false results can be excluded.
- Any purification techniques employed in the production of a compound should be included.

Analysis, conclusions and evaluation

Analysing data

In analysing data, you will need to be able to use your understanding of the theory behind a given experiment. Some people find it difficult to put together a clear, reasoned and justified argument to support this. The stages in the argument must be clear and easy for the examiner to follow.

> **Tip** When analysing numerical data you need to be proficient in handling the mathematics involved and confident in carrying out the calculations needed — including the correct use of significant figures. Remember, the number of significant figures to which an answer is expressed shows the precision of the measured quantities. The general rule is that you should use the same number of significant figures as are found in the *least precise* measurement.

You also need to be able to analyse errors in the experiment. These fall into two groups — those associated with the use of a particular piece of apparatus and those linked to the level of competence of the operator or flaws in the procedure. One way to start thinking about apparatus errors is to compare the use of a burette in measuring different volumes of a liquid. If you use it to measure out $5\,cm^3$, the error in measurement will be five times greater than if you use it to measure $25\,cm^3$.

Evaluation

This is one of the harder skills to develop because to be successful in evaluating an experiment or procedure you need to have a clear idea of the aims, objectives and predicted outcome.

Evaluation can include:
- identifying anomalous results (or outliers)
- deducing possible causes for the anomalous results and suggesting ways of avoiding them
- a view of the adequacy of the range of data used
- commenting on the effectiveness of measures taken to control variables
- an argued judgement on the confidence you have in the conclusions reached

It goes without saying that if anomalous results are to be identified then the expected pattern of results must be known. This could be from a prediction as part of a hypothesis about the experiment, or because an experimentally determined point does not fit the trend of other data. Having identified the anomaly you should suggest what might have caused it, and have a strategy for dealing with it (which might involve excluding it or repeating the measurement). The effect of including and excluding an outlier in drawing a line of best fit is shown in the diagram on the next page.

experimental skills & investigations
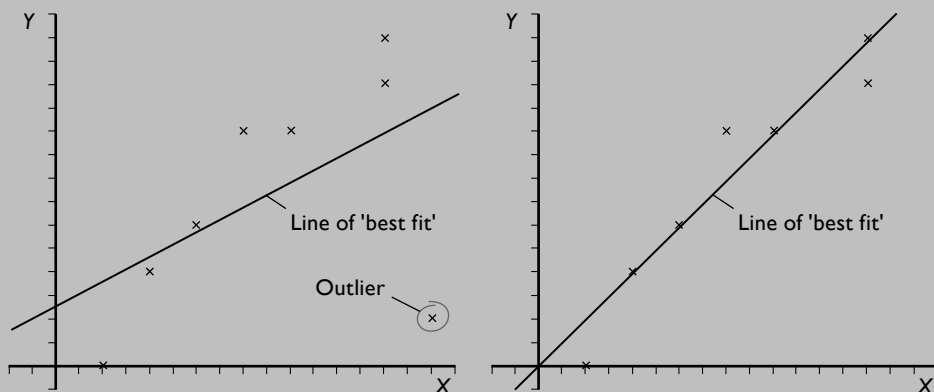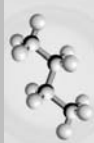
Tip So what should you do if the results of a quantitative experiment are inaccurate? The first thing is to establish whether the errors are due to the apparatus used or to the data collected.

If the errors in the data collected exceed the apparatus errors then it is important to identify the flaws in the procedure which led to these errors and to suggest a more reliable procedure. If the error is a result of a temperature fluctuation in the laboratory, you might suggest using a water bath with a thermostat to reduce this fluctuation. If the errors in the data do not exceed those due to the apparatus used, you need to suggest how to reduce the apparatus errors. If one of the sources of error is in weighing a solid, it is not sufficient to say 'use a better balance'; you must quantify this — for example, 'use a balance accurate to ±0.01 g'.

Remember that there is no credit for saying that the experiment went well or gave good results. You *must* say why, and give evidence to support this.

Drawing conclusions

This is usually the final stage in commenting on an experiment or procedure. It relies on you having a thorough knowledge of the chemistry involved.

The conclusion you draw must be based on how well the data collected matches the original hypothesis or prediction, or is supported by the results of qualitative tests. You will be expected to use your knowledge of the theoretical background to the experiment or procedure and to make judgements about the data or results based on this knowledge.
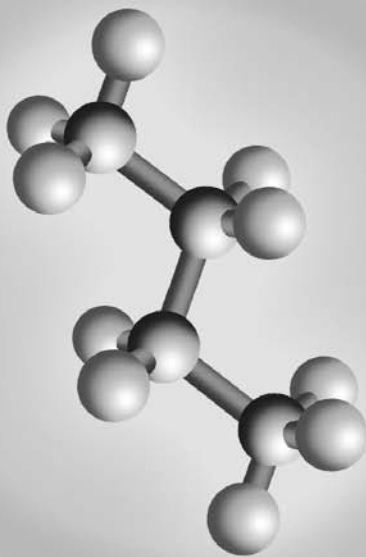
Questions
&
Answers

In this section are two sample examination papers — one similar to the Cambridge International Examinations (CIE) AS Chemistry Paper 2, and the other similar to the CIE A2 Chemistry Paper 4. All of the questions are based on the topic areas described in the previous parts of the book.

You have 1 hour and 15 minutes to do the AS paper. There are 60 marks, so you can spend just over one minute per mark. You have 2 hours for the A2 paper. There are 100 marks, so again you can spend just over one minute per mark. The A2 paper also contains questions on the applications part of the syllabus, and these may take you a little longer. If you find you are spending too long on one question, then move on to another that you can answer more quickly. If you have time at the end, then come back to the difficult one.

It is important to remember that when you take an A2 paper it is assumed that you already know the AS material. Although the questions in the paper are focused on the A2 content from the syllabus, the underlying chemistry may be based on work covered at AS.

Some of the questions require you to recall information that you have learned. Be guided by the number of marks awarded to suggest how much detail you should give in your answer. The more marks there are, the more information you need to give.

Some of the questions require you to use your knowledge and understanding in new situations. Don't be surprised to find something completely new in a question — something you have not seen before. Just think carefully about it, and find something that you do know that will help you to answer it. Make sure that you look carefully at the information provided in the question — it will have been included for a reason!

Do think carefully before you begin to write. The best answers are short and relevant — if you target your answer well, you can get a lot of marks for a small amount of writing. Don't say the same thing several times over, or wander off into answers that have nothing to do with the question. As a general rule, there will be twice as many answer lines as marks. So you should try to answer a 3-mark question in no more than six lines of writing. If you are writing much more than that, you almost certainly haven't focused your answer tightly enough.

Look carefully at exactly what each question wants you to do. For example, if it asks you to 'Explain', then you need to say *how* or *why* something happens, not just *describe* what happens. Many students lose large numbers of marks by not reading questions carefully.

Following each question in this part, there is an answer from Candidate A, who might achieve a C or D grade, and an answer from Candidate B who might achieve an A or B grade. The candidates' answers are followed by an examiner's comments. You might like to try answering the questions yourself first before looking at these.

AS exemplar paper
Question 1

The first six ionisation energies of an element X are given in the table.

Ionisation energy/kJ mol^{-1}					
First	Second	Third	Fourth	Fifth	Sixth
550	1064	4210	5500	6908	8761

(a) Define the term *first ionisation energy*. (3 marks)

(b) Write an equation, with state symbols, for the *third* ionisation energy of element X. (2 marks)

(c) Use the data provided to deduce in which group of the periodic table element X is placed. Explain your answer. (3 marks)

The first ionisation energies of the Group IV elements are given below.
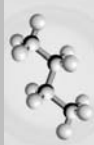
Element	C	Si	Ge	Sn	Pb
1st I.E./kJ mol^{-1}	1086	789	762	709	716

(d) Use your knowledge of the atomic structure of these elements to explain the *trend* in ionisation energies. (3 marks)

Total: 11 marks

Candidate A
(a) It is the energy required to convert a mole of atoms ✗ of an element into a mole of cations, ✗ with each atom losing one electron ✓.

e There are two errors in this definition. The candidate fails to refer to the gaseous state of both the atoms and cations.

(b) X(g) – 3e$^-$ → X^{3+}(g) ✗ ✓

e The candidate has confused the 3rd ionisation energy with the loss of three electrons. The state symbols are correct, for **1 mark**.

(c) X is in Group II of the periodic table ✓.

e This correctly states that X is in Group II. However, the candidate has not explained the evidence and therefore loses 2 of the 3 available marks.

(d) The atoms are getting bigger so the electrons are further from the nucleus making them easier to remove ✓. The outer electrons are screened from the nuclear charge ✓.

e This is a fairly good answer. However, there is no mention of the increasing nuclear charge.

Approved: 0777 023 444

Candidate B

(a) This is the energy needed to remove one electron from each ✓ of 1 mol of gaseous atoms ✓ of an element to form 1 mol of gaseous cations ✓.

e This good answer gives all three points in the mark scheme.

(b) $X^{2+}(g) - e^- \rightarrow X^{3+}(g)$ ✓ ✓

e The equation is correct, as are the state symbols.

(c) **X** is in Group II of the periodic table ✓. There is a large jump in energy to remove the 3rd electron ✓, which is from a full shell ✓.

e This very good answer uses the data in the table and the candidate's own knowledge of the arrangement of electrons in atoms.

(d) There are two effects here. First, the atoms are getting bigger so the electrons are further from the nucleus making them easier to remove ✓. Second, the outer electrons are screened from the nuclear charge reducing its pull on them ✓.

e This is a good answer. However, the candidate has not mentioned that these two effects outweigh the increasing nuclear charge and so fails to score the third mark.

Question 2

The modern periodic table is based on one proposed by Mendeleev following his observations of patterns in the chemical properties of the elements.

The diagram shows the first ionisation energies of the first 20 elements in the periodic table.

Ionisation energies of the first 20 elements
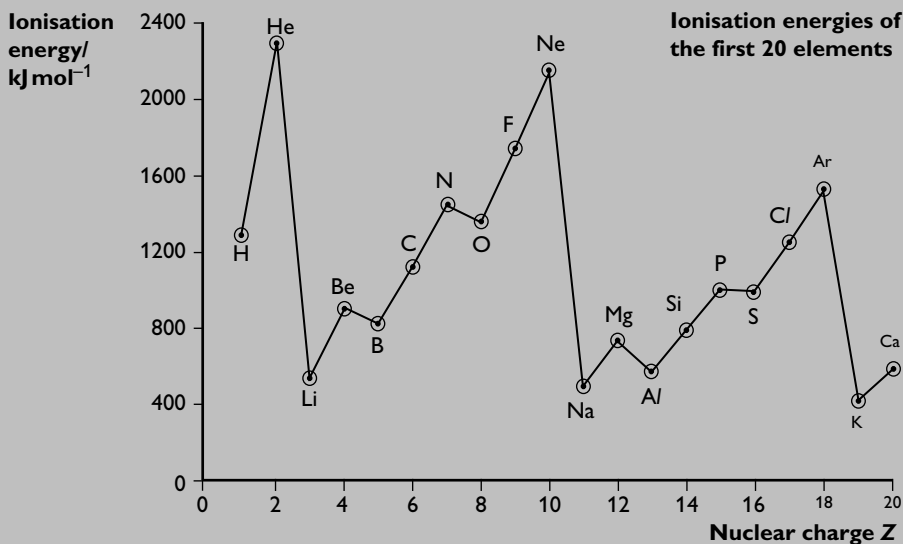
(a) Look at the section of the diagram from Li to Ne. Explain why there is a general increase in first ionisation energy. (3 marks)

(b) Explain why the first ionisation energy of the third element in each period (B and A*l*) is lower than that of the second elements (Be and Mg). (2 marks)

(c) Explain why the first ionisation energy of oxygen is lower than that of nitrogen. (2 marks)

(d) (i) Explain why the first ionisation energy of potassium is lower than that of sodium. (1 mark)

   (ii) Describe a chemical reaction that illustrates the effect this has on the reactivity of the two elements. (2 marks)

(e) When Mendeleev produced his table, he did not include the noble gases (Group 0 elements). Suggest why. (1 mark)

Total: 11 marks

Candidate A

(a) For each element an extra proton is added in the nucleus ✓.

   e It is important to look at the number of marks available for each question. Here there are 3 marks, suggesting you need to make three points. However, this candidate has made only one point and so can gain only 1 mark.

(b) The third elements have electrons in p-orbitals ✓ but the second elements only use s-orbitals ✗.

   e This answer is partially correct. However, the important point is that electrons in p-orbitals are held less strongly because they are, on average, further from the nucleus.

(c) Nitrogen has one electron in each p-orbital but oxygen has one p-orbital with a pair of electrons ✓.

   e Again, this is partially correct. The other point is that the paired electrons in oxygen repel one another, making it easier to remove one of them.

(d) (i) The outer electron of potassium is not held as tightly as that in sodium ✗.

   e This answer is really re-stating the question. The point is that potassium has an extra shell of electrons between the nucleus and the outermost electron.

   (ii) With water, sodium fizzes ✓ but potassium burns ✗.

   e This gives a correct observation for sodium and suggests that the potassium reaction is more vigorous. However, it isn't the potassium that burns, but the hydrogen that is produced.

(e) He didn't know how to make them react ✗.

   e The answer is that Mendeleev did not know that these elements existed.

Candidate B

(a) As we go from Li to Ne we are adding an extra proton and an extra electron ✓. All the protons go into the nucleus, increasing the attraction for all of the electrons ✓, and making them more difficult to remove ✓.

> *e* A very good and complete answer with three distinct and relevant points made.

(b) In the third element, an electron has to go into a p-orbital ✓. These are on average further from the nucleus and the electrons are not held so tightly as electrons in s-orbitals. This makes them easier to remove ✓.

> *e* Good! The candidate recognises that electrons in p-orbitals are, on average, further from the nucleus and so it requires less energy to remove them.

(c) Oxygen has a pair of electrons in the 2p-orbital. These repel one another making it easier to remove one of them ✓. In nitrogen, there is one electron in each 2p-orbital ✓.

> *e* The candidate makes two distinct, correct points, one explaining the situation in oxygen, and one relating this to the electron arrangement in nitrogen.

(d) (i) Potassium has an extra shell of electrons between the outer electron and the nucleus making it easier to remove the electron ✓.

> *e* This is correct, no further explanation is needed.

(ii) When they react with water, sodium fizzes and dissolves ✓, but potassium burns with a lilac-pink flame ✗.

> *e* This is a pity. If the candidate had mentioned that it is the hydrogen that burns there would have been two correct and linked observations here.
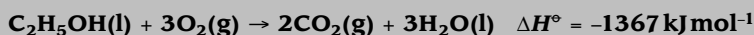
(e) These elements hadn't been discovered when Mendeleev wrote his table ✓.

> *e* This is correct.

Question 3

Ethanol is considered as an important replacement fuel for petrol in a number of countries.

(a) When ethanol is used as a fuel, combustion takes place as shown in the equation below. The table shows values for standard enthalpy changes of formation, ΔH_f°.

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \quad \Delta H^{\circ} = -1367 \, kJ \, mol^{-1}$$

Approved: 0777 023 444

Compound	$\Delta H_f^{\ominus}$/kJ mol^{-1}
$CO_2(g)$	−394
$H_2O(l)$	−286

(i) **Define the term *standard enthalpy change of formation*.** (3 marks)

(ii) **Calculate the standard enthalpy change of formation of ethanol.** (3 marks)

(iii) **On the axes provided, sketch the enthalpy profile diagram for the combustion of ethanol. Label $\Delta H^{\ominus}$ and E_a on your sketch.** (3 marks)
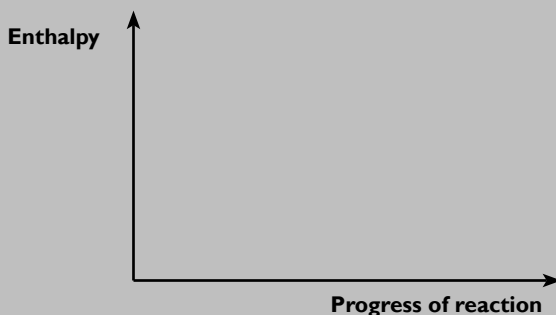
(b) Ethanol can be produced from ethene by reacting it with steam in the presence of a catalyst. The reaction is reversible.

$C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g)$
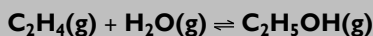
The table shows the percentage conversion of ethene using excess steam under different conditions.

Pressure/atm	Temperature/°C	Conversion/%
40	200	37
40	300	25
75	200	55
75	300	40

(i) **Explain the effect of increasing the pressure on the percentage conversion.** (2 marks)

(ii) **Deduce the sign of the enthalpy change for this reaction, explaining how you arrived at your conclusion.** (2 marks)

(iii) **The equation shown for the reaction shows one mole of ethene reacting with one mole of steam. Why is excess steam used in the industrial process?** (1 mark)

Total: 14 marks

Candidate A
**(a) (i)** This is the enthalpy change when 1 mol of substance ✓ is formed from its elements ✓.
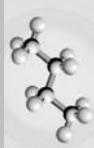
e This definition is not quite complete. The candidate has omitted to mention that it has to be under standard conditions.

(ii) To calculate this, I need to reverse the equation and add the equations for the formation of CO_2 and H_2O ✗.

+1367 – 394 – 286 = 687 kJ mol⁻¹ ✓ ✓ (ecf)

e This is an unfortunate mistake. The candidate has forgotten that the equations for the formation of CO_2 and H_2O need to be multiplied by 2 and 3 respectively to match the combustion of ethanol equation when reversed. The maths based on this faulty logic is, however, correct and so scores 'ecf' (error carried forward) marks.

(iii)
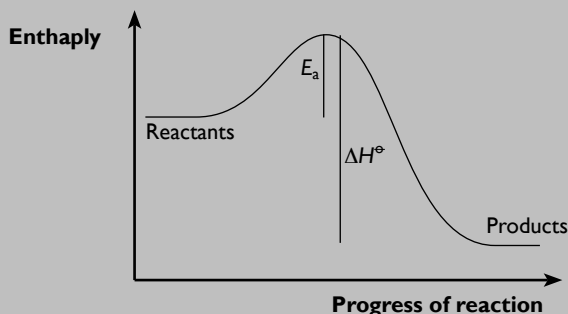
Shape ✓, E_a ✓, $\Delta H^\ominus$ ✗

e This is a good attempt, with the shape and E_a both shown correctly.

(b) (i) Higher pressure means better conversion ✓.

e While this is a correct statement about the effect of higher pressure, it does not explain why it occurs, so only scores 1 mark.

(ii) It's an exothermic reaction.

e The candidate has made a correct statement but does not gain any marks. This is because the question has not been answered. This is an easy and costly error to make. In each examination many candidates lose marks by not reading the question, or by giving an answer to a slightly different question.

(iii) It pushes the equilibrium to the right ✓.

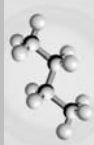*e* This question can be answered in a number of different but equally acceptable ways. This is perfectly correct.

Candidate B

(a) (i) This is the enthalpy change when 1 mol of substance ✓ is formed from its elements ✓ under standard conditions ✓.

Approved: 0777 023 444

e This candidate has learnt the definition thoroughly and given a complete answer.

(ii) Reverse the equation for the formation of ethanol, then add $2 \times \Delta H^{\ominus}_f$ for CO_2 and $3 \times \Delta H^{\ominus}_f$ for H_2O ✓.

+1367 – 2 × 394 – 3 × 286 = –279 kJ mol^{-1} ✓ ✓

e In this calculation, the candidate explains what is being done and why. As a result, the calculation of $\Delta H^{\ominus}_f$ for ethanol is correct.

(iii)
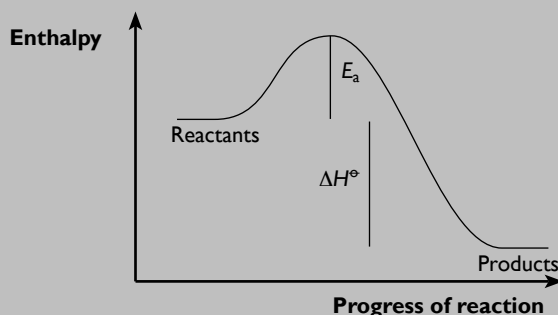
Shape ✓, E_a ✓, $\Delta H^{\ominus}$ ✓

e Although the candidate gains all 3 marks, the answer is not quite perfect. It would have been better to show arrowheads on the lines for E_a and $\Delta H^{\ominus}$.

(b) (i) A higher percentage of ethene is converted at higher pressure ✓ because there are fewer gas particles on the right-hand side of the equilibrium ✗.

e The first statement here is true, but the second statement does not go quite far enough. There are fewer gas particles on the right-hand side of the equilibrium, but the point is that this shifts the equilibrium to the right, yielding more ethanol.

(ii) The forward reaction is exothermic so the sign is negative ✓. Less ethene is converted at higher temperatures because the equilibrium moves to the left to try to reduce the temperature ✓.

e A good, full answer showing that this candidate understands Le Chatelier's principle. However, it is a pity that the answer to part (i) did not include this detail.

(iii) To make sure as much ethene as possible reacts ✓.

e This is a different answer from that given by Candidate A, but it is still correct.

Question 4

Group VII is the only group in the periodic table that has elements that are in gaseous, liquid and solid states at room temperature. In this question you need to consider the three elements, chlorine, bromine and iodine.

(a) All three elements exist as diatomic molecules with the atoms linked by a single covalent bond. Explain the differences in their volatility. (2 marks)

(b) The table shows the bond energies for the three hydrogen halides.

Bond energy /kJ mol^{-1}		
HCl	HBr	HI
432	366	298

   (i) Explain the trend in bond energies shown. (2 marks)

   (ii) Describe the effect of plunging a red-hot wire into tubes containing each of the hydrogen halides. (2 marks)

(c) Chlorine reacts with hot aqueous sodium hydroxide according to the following equation:

$3Cl_2(aq) + 6OH^-(aq) \rightarrow 5Cl^-(aq) + ClO_3^-(aq) + 3H_2O(l)$

State the oxidation number of chlorine in each chlorine-containing compound formed. (2 marks)

Total: 8 marks

Candidate A

(a) Down the group the charge on the nucleus increases.

> *e* No marks can be awarded here because, although this is a true statement, it does not answer the question. Beware of just writing 'snippets' of chemistry from this area of the syllabus. Think what you need to say in order to answer the question.

(b) (i) As the halogen atoms get bigger ✓, the overlap between orbitals with hydrogen gets less. This weakens the H–X bond ✓.

> *e* This good answer is complete and to the point.

   (ii) HCl no effect, HBr some decomposition, HI lots of decomposition ✓.

> *e* Although the candidate has indicated the correct consequences, for 1 mark, there is no real description of what would be observed.

(c) –1 in Cl^- ✓ and +5 in ClO_3^- ✓

> *e* In this correct answer, the candidate does not just state the oxidation number, but relates it to the correct ion.

Candidate B

(a) The molecules are held together by van der Waals forces ✓.

The larger the atoms, the greater the van der Waals forces and hence the higher the boiling point ✓.

e This is a very good descriptive answer that links the type of force/bonding involved with the reason for the increasing boiling points.

(b) (i) As we descend the group the halogen atoms increase in size ✓. This reduces the overlap between orbitals on the hydrogen atom and the halogen atom, weakening the H–X bond ✓.

e This is another good and full answer. It is expressed differently from the answer given by Candidate A, but both answers are correct.

(ii) HCl no effect, HBr some decomposition with a yellow-orange tinge, HI lots of decomposition with violet vapour ✓ ✓.

*e* Here the candidate describes both the degree of reaction and what would be observed to support this trend.

(c) 1 in Cl^- ✗ and +5 in ClO_3^- ✓

e This is a pity. The minus sign is missing from in front of the 1 for Cl^- making the answer incorrect. The response for ClO_3^- is correct.

Question 5

Two of the forms of isomerism found in organic compounds are structural isomerism and *cis–trans* isomerism.

(a) Two of the structural isomers of $C_3H_4Cl_2$ are shown below.

Isomer 1   Isomer 2
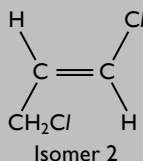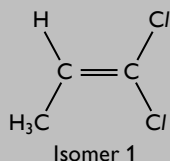
(i) Draw the two other structural isomers of $C_3H_4Cl_2$ that are chloroalkenes and that contain a methyl group. (2 marks)

(ii) Draw another structural isomer of $C_3H_4Cl_2$ that is *not* a chloroalkene. (1 mark)

(iii) How many isomers of $C_3H_4Cl_2$ in total contain the –CH_2Cl group? (1 mark)
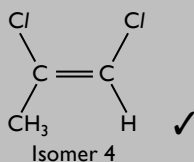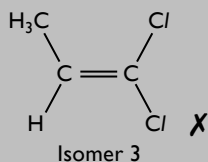
(b) (i) **Which, if any, of the structural isomers, including isomers 1 and 2 and those that you have drawn, are *cis–trans* isomers?** (1 mark)

(ii) **Draw the two possible products you could get if the *cis*-isomer was reacted with HBr.** (2 marks)
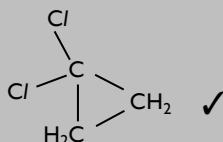
Total: 7 marks

Candidate A

(a) (i)

Isomer 3 ✗   Isomer 4 ✓

ℯ Isomer 3 is the same as isomer 1, but rotated 180° around the double bond.

(ii)

 ✓

ℯ This is correct. The candidate did well to spot that this has to be a cyclic compound if it isn't an alkene!

(iii) Two ✗

ℯ This candidate is not sure about isomers of compounds that contain a double bond. The candidate has also not been logical since both isomers 3 and 4 contain a methyl group, as does isomer 1.

(b) (i) 3 and 4 ✗

ℯ The candidate once more shows confusion about *cis–trans* isomerism. For this to exist, the atoms or groups have to be at opposite ends of the double bond.

(ii) $CH_3CClBr–CH_2Cl$ ✓ and $CH_3CHCl–CHClBr$ ✓

ℯ Apparently the candidate does know what *cis*- means! These are good answers, but would have been clearer if the formulae had been displayed.
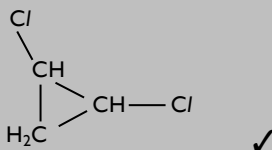
Candidate B

(a) (i)

Isomer 4 ✓   Isomer 5 ✓
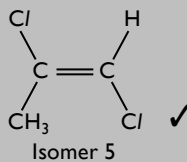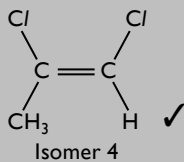
ℯ Both isomers are correct.

Approved: 0777 023 444

(ii)

✓

e This is a different cyclic isomer from that given by Candidate A, but is still correct.
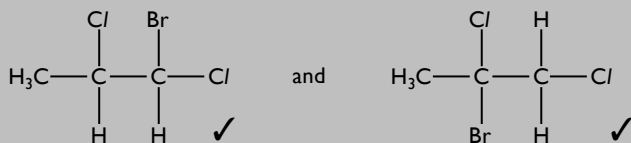
(iii) Three ✓

e This leads from a sound understanding of isomerism and the correct answer in (a)(i).

(b) (i) 4 and 5 ✓

e Good! This is once more made simple after a correct answer to (a)(i). This candidate's answers illustrate how a good grasp of the basic principles can lead to much better marks.
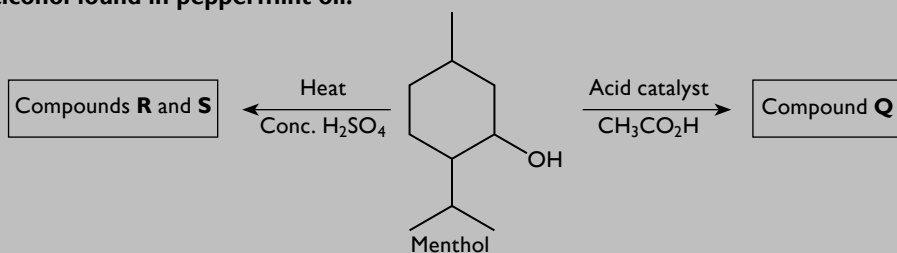
(ii)

and

✓   ✓

e This is a well thought out answer.

Question 6

The diagram shows some of the reactions of menthol, a naturally-occurring alcohol found in peppermint oil.

Compounds **R** and **S**   ←   Heat / Conc. H_2SO_4 —   [menthol structure]   —   Acid catalyst / CH_3CO_2H →   Compound **Q**

Menthol

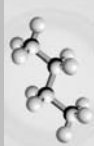**(a) (i)** The structure of menthol is shown in skeletal form. What is its molecular formula?   (1 mark)

(ii) Is menthol a primary, secondary or tertiary alcohol?   (1 mark)

(b) (i) What type of reaction forms compound Q?   (1 mark)

(ii) Compounds R and S have the same molecular formula. Draw their structures.   (2 marks)

(iii) Compound R is treated with aqueous bromine. State what you would observe. (1 mark)

(c) Menthol can be oxidised to form compound T, which forms an orange-yellow precipitate with 2,4-dinitrophenylhydrazine.

(i) Give the reagents and conditions for the formation of T. (2 marks)

(ii) What would you observe during the oxidation? (1 mark)

Total: 9 marks

Candidate A

(a) (i) $C_{10}H_{17}O$ ✗

e The candidate seems to have assumed that the cyclohexane ring is a benzene ring and has miscalculated the number of hydrogen atoms.
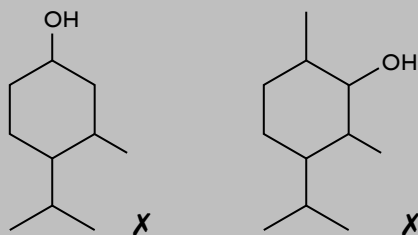
(ii) Secondary ✓

e This is correct.

(b) (i) Making an ester ✓

e Good, the candidate recognises that the reaction is between an organic acid and an alcohol.

(ii)

e There is confusion here. The candidate seems to think that the –OH group is not removed but can migrate to different ring positions.

(iii) The bromine would turn colourless ✓

e This is not a perfect answer, but it is close enough to earn the mark.

(c) (i) Heat ✓ with potassium manganate(VII) ✗

e The candidate uses the correct substance but to earn both marks acidified aqueous managanate(VII) should be specified.

(ii) The purple solution would turn pink ✗.

e This is not sufficiently accurate. The correct answer is 'very pale pink' or 'colourless'.

Approved: 0777 023 444

Candidate B

(a) (i) $C_{10}H_{20}O$ ✓
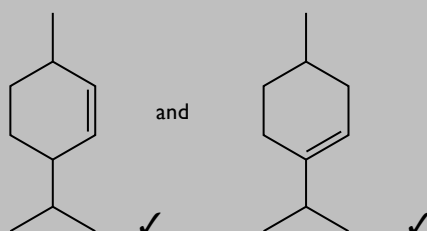
e This is correct.

(ii) Secondary ✓

e This is correct.

(b) (i) Esterification ✓

e Good, this candidate also recognises that the reaction is between an organic acid and with an alcohol to form an ester.

(ii)

and

e This is a very good answer. Not only has the candidate worked out that an elimination reaction takes place giving a double bond in the ring, but that it could involve one of two different hydrogen atoms and the –OH group.

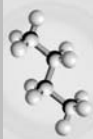**(iii)** The orange colour of the bromine would disappear ✓.

e This is a full and correct answer. Compare it with that of Candidate A.

(c) (i) Heat with acidified ✓ potassium dichromate(VI) solution ✓.

e Both the correct reagent and conditions are given, for 2 marks.

(ii) The dichromate solution would be decolorised ✗.

e To earn the mark, the initial colour and the change should both be given. The orange dichromate solution is not decolorised — it turns green.

A2 exemplar paper
Question 1

(a) Define the term *standard electrode potential*. (3 marks)

(b) Draw a labelled diagram to show how you would measure the electrode potential of Pb/Pb^{2+}. (4 marks)

(c) Using relevant $E^\ominus$ data from the *Data Booklet*, explain how these data relate to the relative reactivity of chlorine, bromine and iodine as oxidising agents. (2 marks)

(d) Use relevant $E^\ominus$ data from the *Data Booklet* to construct redox equations, and calculate the standard cell potentials for the reactions between:

(i) SO_2(aq) and Br_2(aq)

(ii) acidified H_2O_2(aq) and MnO_4^-(aq) (4 marks)

Total: 13 marks

Candidate A

(a) The standard electrode potential is the potential of the electrode measured under standard conditions ✓ using molar solutions ✓.

e This definition is almost correct, for 2 marks. It does not mention that the potential is measured against a standard hydrogen electrode, so the third mark is lost.
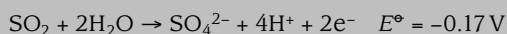
(b)

✓✓✗✗
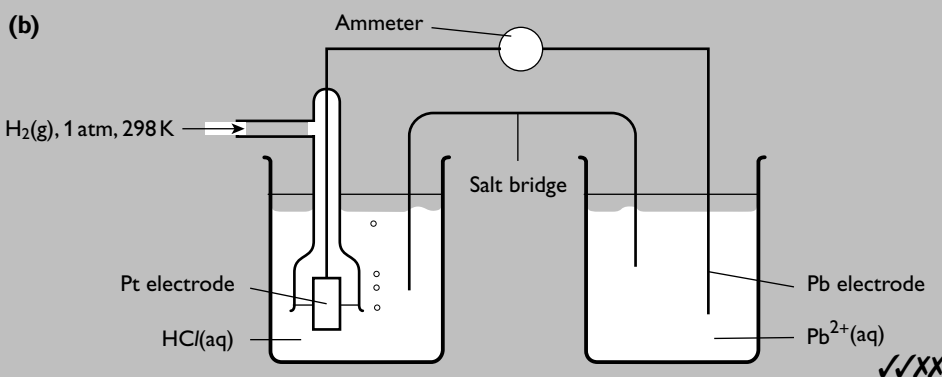
e This is a nice clear diagram with just two mistakes — the ammeter should be a voltmeter, and there is no concentration (1.0 mol dm^{-3}) given for the solutions.
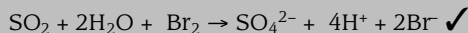
(c) The *Data Booklet* gives the $E^\ominus$ data for chlorine, bromine and iodine as +1.36 V, +1.07 V and +0.54 V respectively. The positive sign shows that the elements are oxidising agents ✓. The larger the value of $E^\ominus$ the better the oxidising agent ✓.

e This is a well-reasoned answer.

Approved: 0777 023 444

(d) (i) The two half-equations are:

$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$ $E^\ominus = -0.17\,V$
$Br_2 + 2e^- \rightarrow 2Br^-$ $E^\ominus = +1.07\,V$

To work out the equation I need to add these:

$SO_2 + 2H_2O + Br_2 \rightarrow SO_4^{2-} + 4H^+ + 2Br^-$ ✓

$E^\ominus_{cell} = -0.17 + 1.07 = +0.90\,V$ ✓

e This is a good, well laid out and easy to follow answer.

(ii) The two half-equations are:

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ $E^\ominus = +1.52\,V$
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ $E^\ominus = +1.77\,V$ ✗
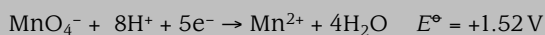
To work out the equation I need to reverse the second equation and multiply by 5, then add this to twice the first equation:

$2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$
        $10H_2O \rightarrow 5H_2O_2 + 10H^+ + 10e^-$

$2MnO_4^- + 16H^+ + 2H_2O \rightarrow 2Mn^{2+} + 5H_2O_2$
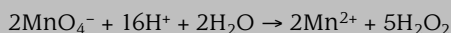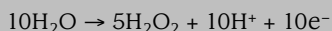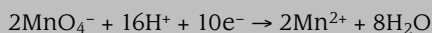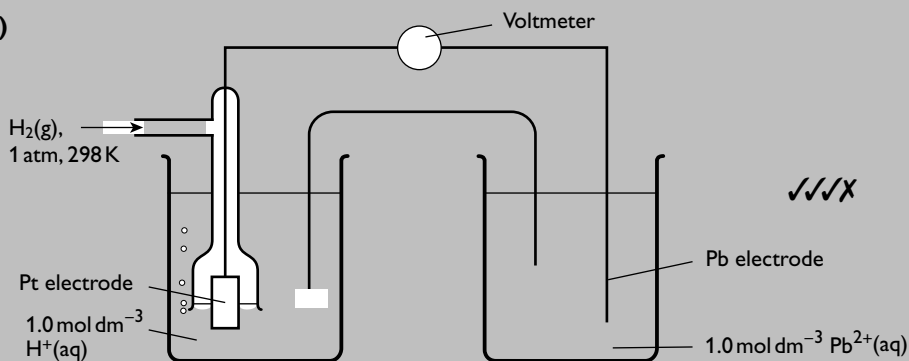
$E^\ominus_{cell} = 1.52 - 1.77 = -0.25\,V$ ✓ (ecf)

e The answers are again well laid out and easy to follow, but the candidate has chosen an incorrect half-equation for hydrogen peroxide, where hydrogen peroxide is reduced, not oxidised. The value for $E^\ominus_{cell}$ has been calculated correctly, so there is an 'error carried forward' mark here.
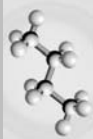
Candidate B

(a) The standard electrode potential is the potential of the electrode measured under standard conditions ✓ against a standard hydrogen electrode ✓.

e This definition is almost correct, but does not mention that the solutions need to be molar. Perhaps the candidate assumed this under 'standard conditions' because it is shown in the diagram in part (b). However, you must not assume that the examiner will understand what is in your mind!

(b)

H$_2$(g), 1 atm, 298 K
Voltmeter
Pt electrode
1.0 mol dm^{-3} H$^+$(aq)
Pb electrode
1.0 mol dm^{-3} Pb^{2+}(aq)
✓✓✓✗

Approved: 0777 023 444

e This is a nice clear diagram with just one mistake — the salt bridge is not labelled.

(c) The *Data Booklet* shows that the $E^{\ominus}$ data for chlorine, bromine and iodine are all positive, indicating that they are oxidising agents ✓. The values +1.36 V, +1.07 V and +0.54 V respectively tell us that the larger the value of $E^{\ominus}$ the stronger the oxidising agent ✓.

e This is a well-reasoned answer that uses slightly more precise language than Candidate A.

(d) (i) The two half-equations are:

$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$ $E^{\ominus} = -0.17\,V$
$Br_2 + 2e^- \rightarrow 2Br^-$ $E^{\ominus} = +1.07\,V$
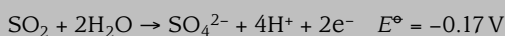
Since the electrons balance, to work out the equation I need to just add the half-equations:

$SO_2 + 2H_2O + Br_2 \rightarrow SO_4^{2-} + 4H^+ + 2Br^-$ ✓
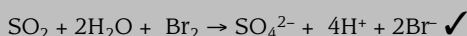
$E^{\ominus}_{cell} = -0.17 + 1.07 = +0.90\,V$ ✓

e This is a good answer that is well laid out and easy to follow.

(ii) The two half-equations are:

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ $E^{\ominus} = +1.52\,V$
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ $E^{\ominus} = +0.68\,V$

To make the electrons balance and hence work out the equation I need to reverse the second equation and multiply it by 5, and double the first equation. Then add the two equations together.

$2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$
$5H_2O_2 \rightarrow 5O_2 + 10H^+ + 10e^-$

$2MnO_4^- + 16H^+ + 5H_2O_2 \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$
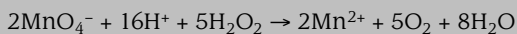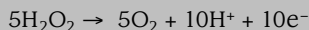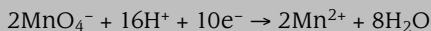
$E^{\ominus}_{cell} = 1.52 - 0.68 = +0.84\,V$ ✓

e This is very good. The answers are again well laid out and easy to follow, even though this is a harder reaction to work with.

Question 2

Both silver chloride and silver bromide have been used in photographic film for many years. The compounds form a thin emulsion on the film and when exposed to light, the halide ion absorbs a photon and releases an electron. This electron then reduces the silver ion to metallic silver.

Approved: 0777 023 444

$$Br^- + h\upsilon \rightarrow Br + e^-$$
$$Ag^+ + e^- \rightarrow Ag$$
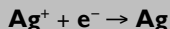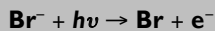
(a) Predict whether it would need more energy or less energy for this process for **AgCl** than **AgBr**. Explain your answer. (1 mark)

(b) Write a chemical equation to represent the lattice energy of **AgCl**. (1 mark)

(c) Using the following data, calculate the lattice energy of **AgCl(s)**.

First ionisation energy of silver	$+731\,kJ\,mol^{-1}$
Electron affinity of chlorine	$-349\,kJ\,mol^{-1}$
Enthalpy change of atomisation of silver	$+285\,kJ\,mol^{-1}$
Enthalpy change of atomisation of chlorine	$+121\,kJ\,mol^{-1}$
Enthalpy change of formation of AgCl(s)	$-127\,kJ\,mol^{-1}$

(3 marks)

(d) How might the lattice energy of **AgBr(s)** compare with that of **AgCl(s)**? Explain your answer. (2 marks)

(e) Silver chloride is not very soluble in water. This makes the formation of a white precipitate on addition of silver ions to a solution containing chloride ions a useful analytical test. The solubility of silver chloride is $1.3 \times 10^{-5}\,mol\,dm^{-3}$.

    (i) Write an expression for the solubility product of silver chloride. (1 mark)

    (ii) Calculate the value of the solubility product and give its units. (2 marks)

(f) If ammonia solution is added to a freshly formed precipitate of silver chloride, the precipitate dissolves to give a colourless solution. Write a balanced equation for this reaction. (2 marks)

Total: 12 marks

Candidate A

(a) Chlorine is more reactive than bromine so will be harder to change from Cl^- to Cl ✓.

    e   The logic here is fine, even if it is not precise.

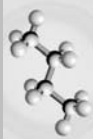**(b)** $Ag^+(g) + Cl^-(g) \rightarrow AgCl(s)$ ✓

    e   Although the AgCl is ionic, charges do not have to be shown since it is a solid.

(c) To find the lattice energy use a Born–Haber cycle:

$+285 + 121 + 731 + 349$ ✗ $+ \Delta H^{\ominus}_{L} = -127$

$\Delta H^{\ominus}_{L} = -127 - 285 - 121 - 731 - 349$ ✓

    $= -1613\,kJ\,mol^{-1}$ ✓ (ecf)

> *e* There is one error in the Born–Haber calculation — the sign of the electron affinity of chlorine has been copied incorrectly. The remainder of the calculation is correct scoring two 'error carried forward' marks.

(d) The value of the lattice energy of AgBr differs from that of AgC*l* because of two factors — the enthalpy change of atomisation and electron affinity of bromine and chlorine are different. For bromine the energy change of atomisation is less positive; the electron affinity is less negative. Together these make the lattice energy less positive because the electron affinity has the greater difference ✓.

> *e* This is a good try for 1 mark. However, there is another term that affects the value of the lattice energy. This is the enthalpy of formation of silver bromide compared with that of silver chloride.

(e) (i) K_{sp} = [Ag⁺(aq)][C*l*⁻(aq)] ✓

> *e* This is correct.

(ii) K_{sp}(AgC*l*) = $1.3 \times 10^{-5} \times 1.3 \times 10^{-5}$ = 1.69×10^{-10} mol dm⁻³ ✓ ✗

> *e* The calculation is correct but the units are wrong.

(f) Ag⁺C*l*⁻ + 2NH₃ ⇌ [Ag(NH₃)₂]⁺ + C*l*⁻ ✓

> *e* This is correct.

Candidate B

(a) Bromine forms Br⁻ less easily than chlorine forms C*l*⁻, so the reverse reaction should be easier ✓.

> *e* This is correct.

(b) Ag⁺(g) + C*l*⁻(g) → Ag⁺(s)C*l*⁻(s) ✗

> *e* This is incorrect. It is the AgC*l* that is a solid, not the individual ions.

(c) To find the lattice energy I need to use a Born–Haber cycle.

E_a(Ag) + E_a(C*l*) + 1st IE(Ag) + EA(C*l*) + LE(AgC*l*) = E_f(AgC*l*)

+285 + 121 + 731 – 349 + $\Delta H^{\oplus}_L$ = –127

$\Delta H^{\oplus}_L$ = –127 – 285 – 121 – 731 + 349

= –915 kJ mol⁻¹ ✓ ✓ ✓

> *e* This is completely correct. The answer is well laid-out and easy for an examiner to follow.
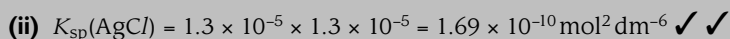
(d) When we consider AgBr rather than AgC*l*, three values in the Born–Haber cycle change — E_a(C*l*), EA(C*l*) and E_f(AgC*l*). The electron affinity of bromine is less negative than that of chlorine, the energy of atomisation of bromine is less positive than that of chlorine, and the enthalpy of formation of silver bromide will

be less negative than that of silver chloride. Overall this suggests that the lattice energy of silver bromide will be less negative ✓ ✓.
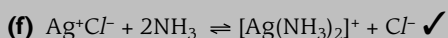
e This very good complete answer scores both marks.
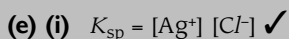
(e) (i) $K_{sp} = [Ag^+] [Cl^-]$ ✓

e This is correct.

(ii) $K_{sp}(AgCl) = 1.3 \times 10^{-5} \times 1.3 \times 10^{-5} = 1.69 \times 10^{-10} \, mol^2 \, dm^{-6}$ ✓ ✓

e Both the calculation and the units are correct.

(f) $Ag^+Cl^- + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + Cl^-$ ✓
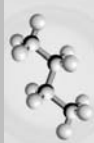
e This is correct.

Question 3

(a) Nitric acid reacts with bases such as aqueous ammonia, NH$_3$(aq), to form salts. A 25.0 cm^3 sample of nitric acid was pipetted into a conical flask. Aqueous ammonia was added from a burette until little further change in pH of the solution was observed. The resulting pH curve for the titration is shown below.
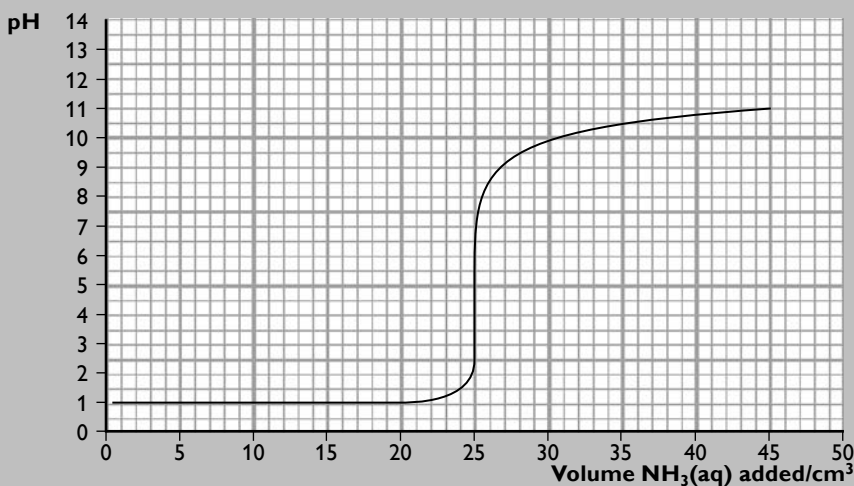
(i) Estimate the pH at the end point of this titration. (1 mark)

(ii) How can you tell from the pH curve that aqueous ammonia is a weak base? (1 mark)

**(iii) What was the concentration of the nitric acid?** (1 mark)

The pH ranges of four indicators are given in the table.

Indicator	pH range
Gentian violet	0.1–2.0
Methyl red	4.4–6.2
Cresol red	7.2–8.8
Alizarin yellow R	10.1–12.0

   (iv) Explain which of these indicators would be most suitable to use for this titration. (1 mark)

(b) A buffer solution was made by mixing 50 cm³ of 0.100 mol dm⁻³ sodium ethanoate solution with 50 cm³ of 0.100 mol dm⁻³ ethanoic acid solution. K_a for ethanoic acid is 1.8×10^{-5} mol dm⁻³. Calculate the pH of the buffer solution. Show your working. (2 marks)

(c) The equation shows the dissociation of ethanoic acid:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons CH_3CO_2^-(aq) + H_3O^+(aq)$$
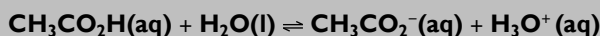
Explain the effect of adding the following to this solution:

   (i) H₃O⁺ ions (1 mark)

   (ii) OH⁻ ions (1 mark)

                                      Total: 8 marks

Candidate A

(a) (i) pH 5 ✓

   e This is correct.

   (ii) The curve ends below pH 14 ✓.

   e Although this is true, it does not provide evidence that ammonia is a weak base.

   (iii) 1.0 mol dm⁻³ ✗

   e This is incorrect. If the pH = 1, then [H⁺] = 1 × 10⁻¹ = 0.1 mol dm⁻³

   (iv) Methyl red, because it changes colour during the vertical portion of the curve ✓.

   e This is a good answer.

(b) pH = –log (1.8 × 10⁻⁵) + log $\frac{(0.100)}{(0.100)}$ ✗
    = –log (1.8 × 10⁻⁵) + log 1
    = –log (1.8 × 10⁻⁵) because log 1 = 0
    = 4.7 ✓

   e This is perhaps a little harsh. However, the concentrations of the two solutions need to be halved to 0.050 mol dm⁻³ — they happen to cancel out here.

(c) (i) On adding H_3O^+ ions these will combine with $CH_3CO_2^-$ ions shifting the equilibrium to the left ✓.

e This is a good answer.

(ii) On adding OH^- ions these will react with H_3O^+ ions shifting the equilibrium to the right ✓.

e This is another good answer.

Candidate B

(a) (i) pH 5 ✓

e This is correct.

(ii) The curve does not reach pH 14. It flattens out around pH 11.5 ✓.

e A correct statement based on the data from the titration curve.

(iii) Since the starting pH is 1, $-\log[H^+] = 1$ and hence the concentration of the acid must be $1 \times 10^{-1} = 0.1 \, \text{mol} \, \text{dm}^{-3}$ ✓.

e This is correct and well explained.

(iv) Methyl red because the mid-point of its pH range is close to the mid-point of the vertical portion of the curve ✓.

e This is another correct, well explained answer.

(b)
$$pH = -\log(1.8 \times 10^{-5}) + \log\frac{(0.050)}{(0.050)}$$
$$= -\log(1.8 \times 10^{-5}) + \log 1$$
$$= -\log(1.8 \times 10^{-5}) \text{ because } \log 1 = 0$$
$$= 4.7 \checkmark \checkmark$$

e Both the calculation and the units are correct.

(c) (i) When H_3O^+ ions are added, they will combine with $CH_3CO_2^-$ ions, thus shifting the equilibrium to the left ✓.

e This is a good answer.

(ii) When OH^- ions are added, they will react with H_3O^+, thus shifting the equilibrium to the right ✓.
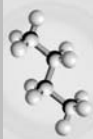
e This is another good answer.

Question 4

The metals of Group II and the transition metals show very different properties.

(a) Give *three* examples of differences in *chemical* properties between these two groups of metals. (3 marks)

(b) Anhydrous copper(II) ions, Cu^{2+}, are colourless. Aqueous copper(II) ions, $[Cu(H_2O)_6]^{2+}$, are pale blue. Copper(II) ions complexed with ammonia, $[Cu(NH_3)_4(H_2O)_2]^{2+}$, are deep blue-purple. Explain these observations in terms of your knowledge of copper(II) and its d-orbitals. (3 marks)

(c) Copy the axes below. Sketch the visible spectrum of A, $[Cu(H_2O)_6]^{2+}$, and B, $[Cu(NH_3)_4(H_2O)_2]^{2+}$, on the axes, labelling clearly which is which. (2 marks)

(d) Which of the d-orbitals are used in forming octahedral complexes such as $[Cu(H_2O)_6]^{2+}$? (1 mark)

(e) When the manganate(VII) ion, MnO_4^-, reacts with sulfur dioxide, SO_2, in acid solution, the deep purple solution turns almost colourless.

(i) Write a balanced equation for this reaction. (2 marks)

(ii) Suggest a reason why the new solution has little colour. (1 mark)

Total: 12 marks

Candidate A

(a) Transition metals form coloured compounds ✓, they behave as catalysts ✓ and they have high melting points ✗.

> *e* The first two properties are chemical in nature, but the third is physical.

(b) Colours are due to splitting of the d-orbitals into groups of higher and lower energy because of ligands. In anhydrous copper(II) no ligands are present, so there is no colour ✓. In $[Cu(H_2O)_6]^{2+}$ the complex emits ✗ blue because there is a small energy gap between the two sets of orbitals. In $[Cu(NH_3)_4(H_2O)_2]^{2+}$ the gap is bigger, so it emits violet ✓. (ecf)

> *e* The candidate points out correctly that colour in transition metal compounds is a result of the d-orbitals splitting into two groups of different energy. The mistake made is in believing that energy is emitted when electrons move from high to low energy, rather than energy being absorbed in promoting electrons. Hence the second mark is lost. The third mark has been awarded consequentially.

(c)
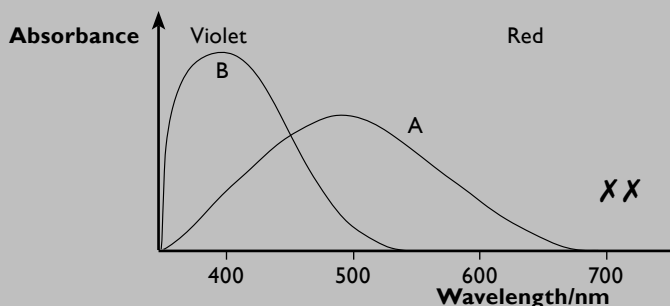
> *e* The candidate has drawn two emission spectra rather than absorption spectra.

(d) $3d_{x^2-y^2}$ and $3d_{z^2}$ ✓

> *e* This is correct.

(e) (i) $2MnO_4^- + 3SO_2 + 2H_2O \rightarrow 2MnO_2 + 3SO_4^{2-} + 4H^+$ ✗ ✓ (ecf)

> *e* The candidate has used a wrong half-equation for manganate(VII). However, the overall equation is balanced correctly and so scores the second mark as an 'error carried forward'.

(ii) The manganese is all precipitated as MnO_2 ✗.

> *e* This is an unfortunate consequence of the incorrect equation. No mark can be awarded here because the candidate has ignored data given in the question about the colour change.
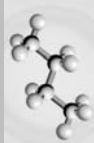
Candidate B

(a) Transition metals behave as catalysts ✓, they form complexes with ligands ✓ and many of their compounds are coloured in aqueous solution ✓.

> *e* Three correct differences in chemical properties are given.

(b) Colours are due to splitting of the d-orbitals into groups of higher and lower energy because of ligands. In anhydrous copper(II) there are no ligands, so there is no colour ✓. In $[Cu(H_2O)_6]^{2+}$ the complex absorbs orange and red light because there is a small energy gap between the two sets of orbitals ✓. In $[Cu(NH_3)_4(H_2O)_2]^{2+}$ the gap is bigger, so it transmits violet ✗.

> *e* The candidate points out correctly that colour in transition metal compounds is a result of the d-orbitals splitting into two groups of different energy and that the complex $[Cu(H_2O)_6]^{2+}$ absorbs orange and red light (and by implication transmits the rest). The statement 'in $[Cu(NH_3)_4(H_2O)_2]^{2+}$ the gap is bigger' is correct, but the third mark is lost because of failure to refer to the colour of light absorbed.

(c)

✓✓
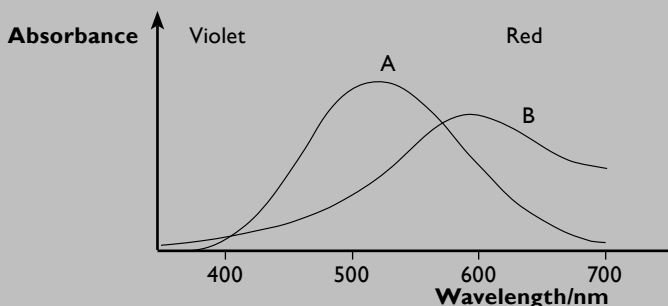
e The candidate has correctly drawn two absorption spectra. In questions like this the examiners are looking for correct principles being illustrated rather than perfect representations.

(d) $3d_{x^2-y^2}$ and $3d_{z^2}$ ✓

e This is correct.

(e) (i) $2MnO_4^- + 5SO_2 + 2H_2O \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$ ✓ ✓

e This is the correct equation, correctly balanced.

(ii) Mn^{2+} has one electron in each of its 3d-orbitals. To promote an electron would require energy to overcome the repulsion of putting two electrons in the same orbital. This does not occur readily, making Mn^{2+} almost colourless ✓.

e This is a good answer. The candidate recognises the critical point that the manganese is present as Mn^{2+} at the end of the reaction.

Question 5

The common analgesic drug paracetamol can be made from phenol in three steps.
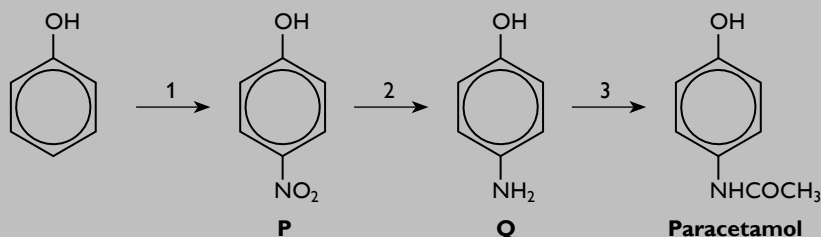
(a) (i) Suggest the reagents and conditions for step 1. (2 marks)

(ii) What type of reaction is step 2? (1 mark)

**(iii) What reagents and conditions would you use for step 2?** (2 marks)

(iv) Name a reagent that could be used for step 3. (1 mark)

Approved: 0777 023 444

    (v) What *two* functional groups are present in *paracetamol*? (2 marks)

**(b) (i) State what you would see if aqueous bromine was added to
compound Q.** (2 marks)

    (ii) Draw the product from the reaction of Q with aqueous HC*l*. (1 mark)

    (iii) What sort of reaction is this? (1 mark)

Total: 12 marks

Candidate A

(a) (i) Concentrated nitric and sulfuric acids ✗

e The candidate has given the reagents for nitration of benzene. Nitration of
phenol takes place under milder conditions (see Candidate B).

(ii) Hydrogenation ✓

e Although most textbooks would refer to this as a reduction reaction, hydro-
genation would probably be allowed here.

(iii) Tin and concentrated hydrochloric acid, ✓ heat ✓

e The correct reagents and conditions are given, for 2 marks.

(iv) CH_3CO_2H ✗

e The candidate does not seem to have recognised that an amide has been
formed.

(v) Alcohol ✗ and amide ✓

e The candidate has forgotten that the –OH group is attached to a benzene ring
and is, therefore, a phenol group, not an alcohol.

(b) (i) A white precipitate forms ✓.

e The candidate has remembered that a white precipitate is formed with phenols
and bromine, but has omitted to mention that the bromine loses its colour as
it reacts. Therefore, the candidate scores only 1 of the 2 marks.

(ii)
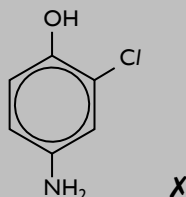
e This is incorrect. HC*l* does not react to give substitution in the ring.

(iii) Substitution ✓ (ecf)

e Although this is an incorrect answer, it describes correctly what the candidate
believed to be true in (ii) and so scores an 'error carried forward' mark.

Approved: 0777 023 444

Candidate B

(a) (i) Dilute nitric acid ✓ on warming ✓.

e This is a good answer with reagent and conditions correct.

(ii) Reduction ✓

e This is correct.

(iii) Lithium aluminium hydride ✓ in ether ✓.

e This is another good answer with both reagents and conditions correct.

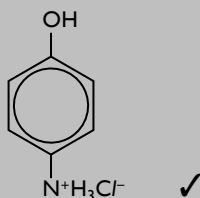**(iv)** Ethanoyl chloride ✓.

e This is correct.

(v) Phenol ✓ and amide ✓.

e Both groups are correct.

(b) (i) Bromine is decolourised ✓ and a white precipitate is formed ✓.

e Both observations are correct.

(ii)

OH

N⁺H₃Cl⁻   ✓

e This is correct.

(iii) Neutralisation ✓

e Yet another correct answer.

Question 6

Man-made polymers play an important part in the manufacture of a wide range of products. Contact lenses are made using hydrophilic polymers with structures such as the two examples shown below.
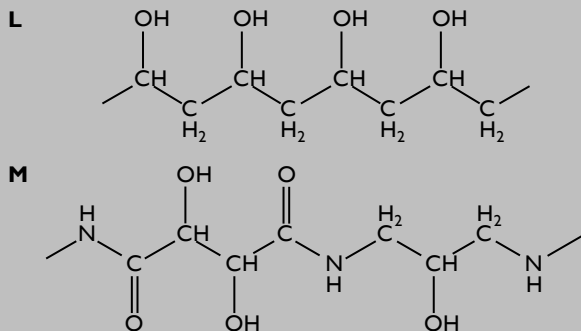
(a) What does the term *hydrophilic* mean? (1 mark)

(b) Draw the monomer units for each of the two polymers, **L** and **M**. (3 marks)

(c) (i) The polymer chains in **L** can be cross-linked using a small molecule containing two functional groups. Draw the structure of such a molecule. (1 mark)

(ii) What type of bond would be formed between **L** and the molecule you have drawn? (1 mark)

Proteins and polypeptides are natural polymers found in living organisms. They are formed by linking different types of amino acid. Two amino acids are shown below.

$H_2NCH_2CO_2H$ H_2NCHCO_2H

CH_3
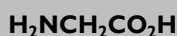
   Glycine (gly) Alanine (ala)

(d) (i) Draw the structure of the dipeptide gly–ala formed from these two amino acids. You should show the peptide bond in displayed form. (2 marks)

(ii) What is unusual about the structure of glycine compared with other amino acids? (1 mark)

(e) A small polypeptide **T** was broken down into its constituent amino acids with the following outcome:

$T \rightarrow 2H_2NCH_2CO_2H + 3H_2NCHCO_2H + 2H_2NCHCO_2H$

CH_3 CH_2CSH
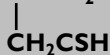
$M_r = 75$ $M_r = 89$ $M_r = 133$

(i) How many peptide bonds were broken in this reaction? (1 mark)

(ii) Calculate the M_r of **T**. (1 mark)

(iii) Describe how the polypeptide could be broken down in the laboratory without the use of enzymes. (2 marks)

Total: 13 marks

Candidate A
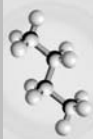
(a) Liking water ✗.

e This is too vague an answer to score the mark.

(b) Monomer of L: $H_2C=CHOH$ ✓

Monomers of M: $CO_2HCH(OH)CH(OH)CO_2H$ ✗

$NH_2CH_2CH(OH)CH_2NH_2$ ✓

> *e* This is quite a good answer. The candidate has examined the two polymers carefully and deduced the three monomers correctly. However, the functional group at the left-hand end of the first monomer of M is not shown correctly. The $-CO_2H$ group in the first monomer is written as if it is at the right-hand end of the molecule. It should be written as HO_2C-.

(c) (i) $CH_2=CH_2$ ✗

> *e* This is incorrect and ignores the point in the question that the molecule has to have two functional groups.

(ii) Covalent bond ✗

> *e* This is not sufficient to score the mark — see Candidate B's answer.

(d) (i) $H_2NCH_2COHNCHCO_2H$ ✓
$\qquad\qquad\quad CH_3$

> *e* This is the correct formula for the dipeptide gly–ala. However, it does not show the peptide bond in a displayed form, so the second mark is lost.

(ii) It is not optically active ✓.

> *e* This is correct.

(e) (i) Seven ✗

> *e* No. Seven amino acids are linked by six peptide bonds.

(ii) 575 ✓

> *e* This is correct.

(iii) Refluxed with acid ✓.

> *e* This is partly correct, for 1 mark. The process is refluxing with acid, but it matters which acid. The candidate should have mentioned concentrated hydrochloric acid.

Candidate B
(a) Attracted to water ✓.

> *e* This is correct.

(b) Monomer of L: $H_2C=CHOH$ ✓

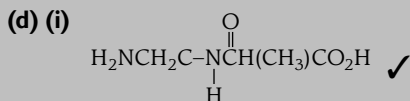Monomers of M: $HO_2CCH(OH)CH(OH)CO_2H$ ✓
and $H_2NCH_2CH(OH)CH_2NH_2$ ✓

> *e* This is a very good answer. All the monomers are identified correctly and their structures shown accurately.

(c) (i) $HO_2C-CH_2-CO_2H$ ✓

> *e* This is correct.

(ii) Covalent ester linkage ✓

e This is correct.

(d) (i)

$$H_2NCH_2C-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{N}}CH(CH_3)CO_2H \quad ✓$$

e This good answer shows both the dipeptide gly–ala and the peptide bond in displayed form.

(ii) Glycine is not chiral ✓

e This is correct.

(e) (i) Six ✓

e This is another correct answer.

(ii) 565 ✗

e This is an unfortunate miscalculation.

(iii) Reflux ✓ with concentrated hydrochloric acid ✓.

e The answer is correct and complete.

Question 7

Chemical reactions in the body take place below 40°C. They are able to do so because of the wide range of enzymes — biological catalysts — present in the body.
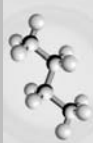
(a) What sort of macromolecules are enzymes? (1 mark)

(b) Fever, when the body temperature exceeds 40°C, can be very dangerous because many enzyme reactions are no longer effective. Explain why this is the case. (2 marks)

(c) The diagram shows the reaction pathway of a reaction that is normally catalysed by an enzyme, but when the enzyme is *not* present. Sketch on the diagram the pathway when the enzyme is present.

Energy

Reactants

Products
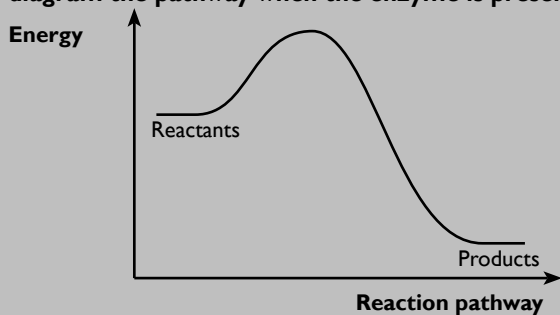
Reaction pathway (2 marks)

(d) The effectiveness of enzyme-catalysed reactions can be reduced by substances known as *inhibitors*. Explain the difference between a competitive and a non-competitive inhibitor. (2 marks)

(e) The graph below shows how the rate of an enzyme-catalysed reaction varies with substrate concentration at a given temperature.
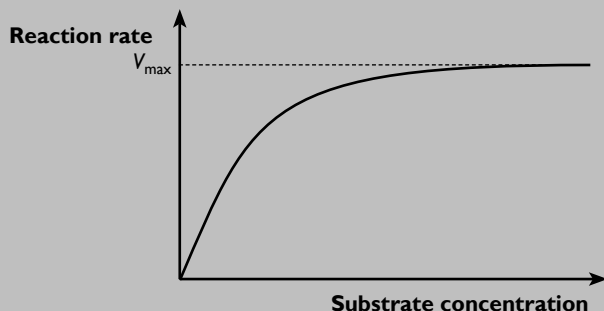
On the diagram sketch curves to show the effect on this reaction of:

(i) a competitive inhibitor, labelled C

(ii) a non-competitive inhibitor, labelled N. (4 marks)

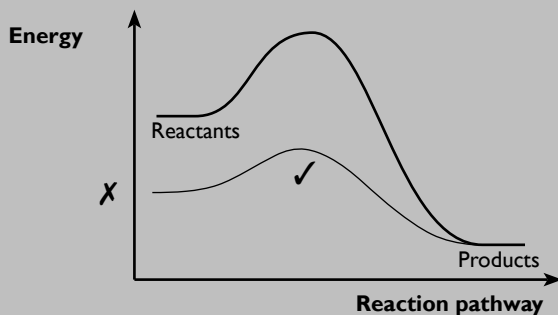**Total: 11 marks**

Candidate A

(a) Proteins ✓

   e Correct, enzymes are usually polypeptide or protein molecules.

(b) Proteins break down easily at low temperatures ✗ ✗.

   e No. A protein molecule does not break down at temperatures in the low 40s. Some of the weaker bonds present are disrupted, which changes the overall structure.

(c)

   e This answer is partly correct — the activation energy is shown correctly as lowered. However, the energy of the reactants should be the same as in the uncatalysed reaction.

Approved: 0777 023 444

(d) A competitive inhibitor binds temporarily to the active site ✗ but a non-competitive inhibitor binds permanently ✗.

   🄴 Although the candidate clearly knows something about competitive and non-competitive inhibitors, the thinking is a little muddled. 'Competitive' means that the inhibitor is competing with the substrate for the active site. 'Non-competitive' means that there is no competition, so the effect must be different.
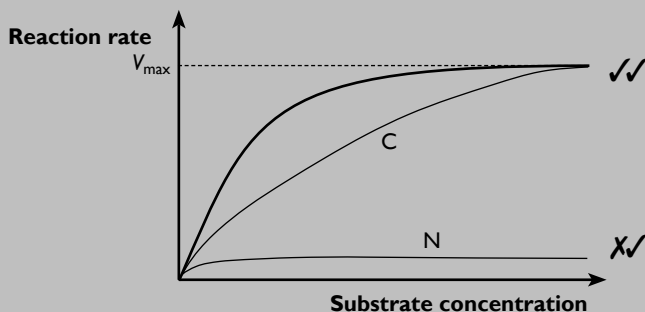
(e)

   🄴 The graph for a competitive inhibitor is completely correct, i.e. with the same V_{max} and a different slope (K_m). However, the graph for a non-competitive inhibitor should show the same slope (K_m), but a different V_{max}. Only one of these conditions is met.
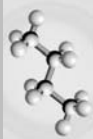
Candidate B
(a) Protein molecules ✓.

   🄴 The answer is correct.

(b) At temperatures around 40 °C, the bonds forming the tertiary structure of proteins are disrupted ✓. This means that the 3-dimensional structure of the enzymes changes and the substrate no longer fits the active site ✓.

   🄴 This is a very good answer. the reason for the change in activity of enzymes above 40 °C is explained well.

(c)
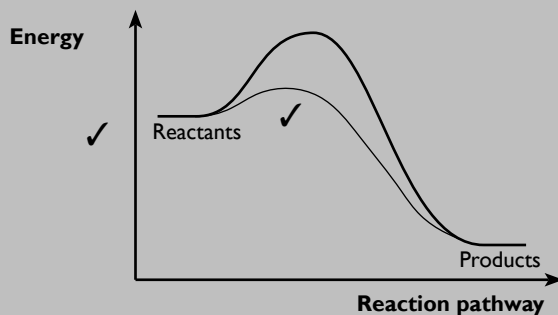
e This good sketch shows that although the activation energy is reduced by the presence of the enzyme, the energy of both the reactants and products is not changed.

(d) A competitive inhibitor competes with the substrate to bind to the active site ✓. A non-competitive inhibitor binds elsewhere in the molecule but changes the shape of the active site making it harder for the substrate to bind there ✓.

e This very good answer highlights accurately the differences between competitive and non-competitive inhibitors.

(e)
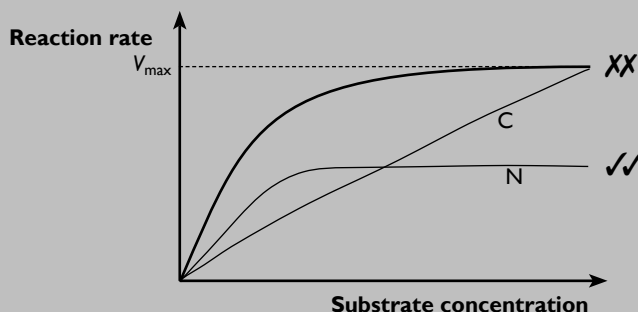
e This is a pity. The candidate has remembered the effect of a non-competitive inhibitor, but has not thought through the line for the competitive inhibitor. It cannot be a straight line that stops suddenly.

Question 8

Modern instrumental techniques play an increasingly important role in determining the structures of organic compounds.

(a) An aromatic compound R has a mass spectrum in which the M and M + 1 peaks are in the ratio 10:0.9. The M peak is at *m/e* 122. Analysis of the compound gave the following composition by mass: C, 78.7%; H, 8.2%; O, 13.1%.

Showing your working:

(i)   use the data to determine the empirical and molecular formulae of compound R   (3 marks)

(ii) use the M and M + 1 data to confirm how many carbon atoms are present in compound R.   (2 marks)

(b) The NMR spectrum of compound R is shown below.
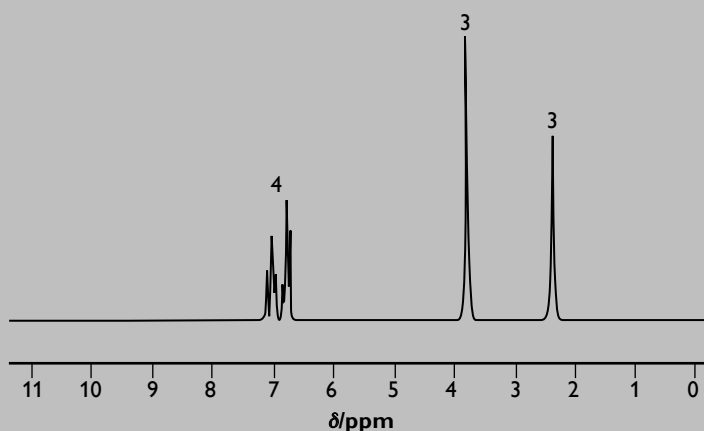
Use the *Data Booklet* to identify the types of proton present in compound R and hence deduce its structure. You should explain how you reach your conclusion. (4 marks)

(c) Compound S, an isomer of R, gave the NMR spectrum below.
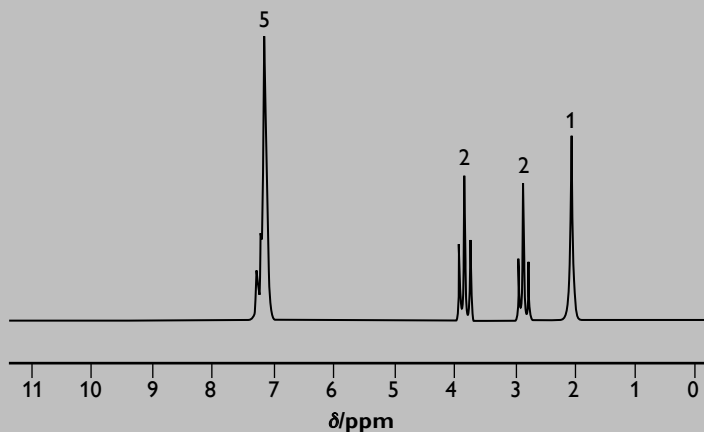
On adding D_2O to a sample of S and re-examining the NMR spectrum, the peak at $\delta = 2.0$ was found to have disappeared.

(i) Suggest a structure for compound S. (2 marks)

(ii) Explain why the peak at $\delta = 2.0$ disappears when D_2O is added. (1 mark)

Total: 12 marks

Candidate A

(a) (i)

Element	C	H	O
%	78.7	8.2	13.1
A_r	12	1	8 ✗
%/A_r	6.6	8.2	1.6
Ratio	4 ✓	5	1

Based on the above, this compound would have an M_r of 69 and the empirical formula of C_4H_5O, but we know that R has a mass peak at 122. This suggests we need to double the ratio to give $C_8H_{10}O_2$. ✓ (ecf)

e It is a pity that the candidate made the mistake of using the proton number rather than A_r for oxygen. This will have a knock-on effect in other parts because there should only be one oxygen in the formula.

(ii) If the heights of the M and M + 1 peaks are in the ratio 10:0.9, then the number of carbon atoms is

$n = \dfrac{100 \times 0.9}{1.1 \times 10}$ ✓ = 8.2 or 8 carbons ✓

e The candidate has correctly used the M:(M + 1) ratio to calculate the number of carbons. This confirms the number obtained in the empirical formula calculation.

(b) δ = 2.4: single peak, 3 protons — methyl group attached to benzene ring ✓

δ = 3.9: single peak, 3 protons — methyl group attached to oxygen ✓

δ = 7.0: complex peaks, 4 protons — hydrogens joined to benzene ring ✓

The structure of compound R is:

$$CH_3 - O - \text{(benzene ring)} - CH_2 - OH \quad ✗$$
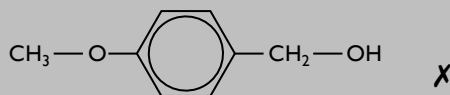
e The assignment of the δ values to correct proton types is correct, but now does not correspond to the structure shown for R. This is a result of the incorrect calculation of the number of oxygen atoms present.

(c) (i) The structure of S is:

$$HO - \text{(benzene ring)} - O - CH_2 - CH_3 \quad ✗✗$$
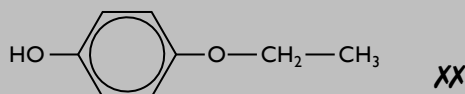
e This structure is an isomer of R, but the arrangement of protons does not match the NMR spectrum of S, and no explanation is given.

Approved: 0777 023 444

(ii) This proton must be an –OH proton that exchanges with D, which does not show in an NMR spectrum ✓.

e This is correct.

Candidate B

(a) (i)

Element	C	H	O
%	78.7	8.2	13.1
A_r	12	1	16
$\% / A_r$	6.6	8.2	0.81
Ratio	8 ✓	10	1 ✓

The empirical formula is $C_8H_{10}O$, and since this has an M_r of 122, this must also be the molecular formula ✓.

e This calculation has been carried out correctly. The empirical formula matches M_r and hence the empirical and molecular formulae are the same.

(ii) Number of carbon atoms (n) is

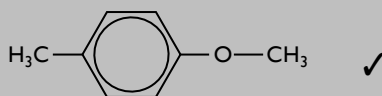$n = \dfrac{100 \times 0.9}{1.1 \times 10}$ ✓ = 8.2 or 8 carbons ✓

e The calculation of the number of carbon atoms from the M:(M + 1) peaks confirms that deduced in part (i).

(b) δ = 2.4: single peak, 3 protons — methyl group attached to benzene ring ✓

δ = 3.9: single peak, 3 protons — methyl group attached to oxygen ✓
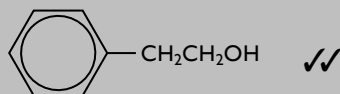
δ = 6.9: complex peaks, 4 protons — hydrogens joined to benzene ring ✓

The structure of compound R is:

H_3C—⬡—O—CH_3 ✓

e The assignment of δ values to correct hydrogen atoms means that the structure shown for R matches the NMR spectrum.

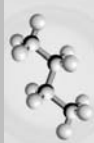**(c) (i)**

⬡—CH_2CH_2OH ✓✓

δ = 2.0 — single proton attached to –OH (exchanges with D_2O)

δ = 2.9 — 1:2:1 triplet, so adjacent to $-CH_2-$ (similar to $-CH_3$ attached to benzene)

δ = 3.8 — 1:2:1 triplet, so adjacent to $-CH_2-$

δ = 7.2 — five identical protons attached to benzene ring

Approved: 0777 023 444

  e   The structure shown for S is an isomer of R, and the explanation of the NMR spectrum is consistent with this structure.

(ii) This proton must be an –OH proton that exchanges with D, which does not show in an NMR spectrum ✓.

  e   This is correct.

Question 9

A great deal of money is spent researching new drugs to combat diseases and medical conditions such as cancer. One of the challenges is to target drugs better so that they do not affect healthy cells, and also so that smaller doses can be given. Another challenge is to improve delivery of a drug to the site of the disease so that less drug is broken down on its way around the body.

(a) Drugs taken by mouth pass through the body's digestive system. In particular, the acid conditions in the stomach mean that drugs may be broken down there. The compound EPCG extracted from green tea shows promising anti-cancer properties when given by injection.

EPCG
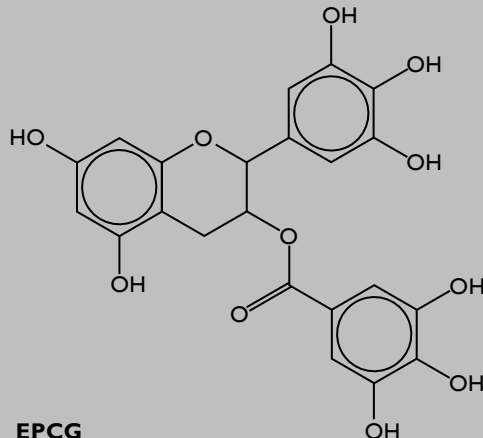
    (i)   Circle *the functional group* that would be hydrolysed on passage through the stomach. (1 mark)

    (ii) This compound is very soluble in aqueous solutions. Explain why this is the case. (2 marks)

    (iii) Suggest another functional group that would be hydrolysed easily on passage through the stomach. (1 mark)

(b) Another way of ensuring that drugs reach their target is to protect them on their passage through the body. One way to do this is to

enclose the drugs in liposomes. These are tiny spheres made up of phospholipids, compounds which are naturally found in cell membranes.
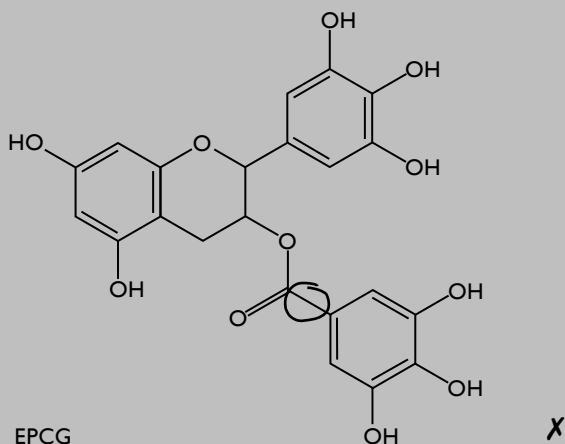

Liposome

Phospholipid

Phosphate head

Lipid tails

A O═B O═ C
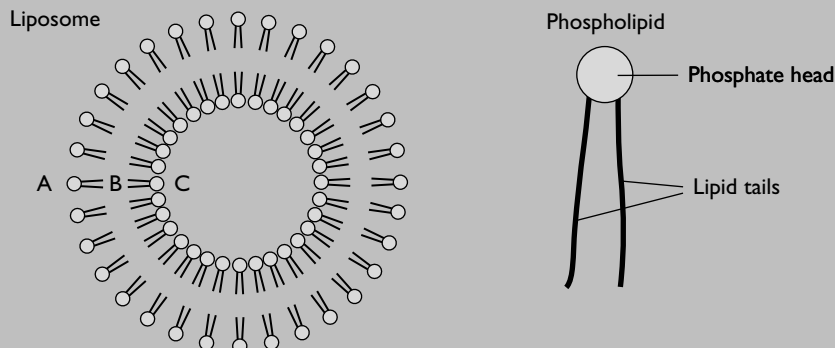
(i) **Identify where on the liposome the drug EPCG would be carried, explaining your answer.** (2 marks)

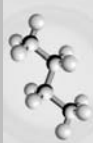(ii) **Suggest why there is so much interest in liposomes in the drug industry.** (1 mark)

Total: 7 marks

Candidate A

(a) (i)

OH

OH

HO

O

OH

OH

OH

O

OH

OH

OH

EPCG

X

e The candidate has not circled the ester linkage, which is the only group in EPCG that can be hydrolysed.

(ii) It contains lots of –OH groups ✓.

e The statement is correct, for 1 mark. However, there is no explanation given. It is important to remember that 2 marks in a question means that two points are needed in the answer.

(iii) A peptide ✓

> *e* Although this is not strictly correct (peptide bonds are only usually referred to in protein chemistry) a peptide bond is effectively the same as an amide bond and thus the mark is awarded.

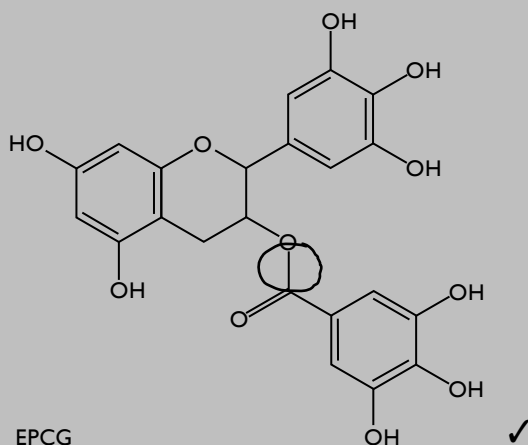**(b) (i)** It would be carried at point **A** ✗ linked to the phosphate group.

> *e* Although the candidate has recognised that the compound would be linked to the phosphate group, at point A the drug would be exposed to reaction as it passed through the body.

(ii) They can carry drugs to where they are needed ✗.

> *e* This is too vague to gain a mark.

Candidate B

(a) (i)

EPCG ✓

> *e* The ester linkage is circled, which is correct.

(ii) It contains many –OH groups ✓ which can hydrogen bond with water ✓.

> *e* This is a correct statement about the structure and a correct reason for its solubility.

(iii) An amide ✓

> *e* This is correct.

(b) (i) It would be carried at point **C** linked to the phosphate group ✓. Here it would be protected from attack during its passage through the body ✓.

> *e* This good answer shows an understanding of the bonding and the reason for enclosing the drug in the liposome.

(ii) They can carry both hydrophilic and hydrophobic drugs ✓.

> *e* The candidate understands the nature of liposomes and the different environments that they contain — a good answer.

268

'Try this yourself' answers

(1) **(a)** $^{23}_{11}Na$ **(b)** $^{19}_{9}F$ **(c)** $^{32}_{16}S$ **(d)** $^{52}_{24}Cr$ **(e)** $^{39}_{19}K^+$

(2) **(a)** 0.5 mol **(b)** 1.5 mol **(c)** 0.25 mol

(3) **(a)** 4 g **(b)** 14 g **(c)** 7 g **(d)** 11 g

(4) **(a)** RbO **(b)** $C_3O_3H_8$

(5) 1.3 g

(6) 3.7 g

(7) 9.0 g

(8) 125 cm³ of O_2; 75 cm³ CO_2

(9) 1.59 g of PbO_2

(10) 1200 cm³ of CO_2

(11) 0.110 mol dm⁻³ and 6.19 g dm⁻³

(12) 0.15 mol dm⁻³

(13) **A** $^{23}_{11}Na^+$; **B** $^{23}_{11}Na$; **C** $^{23}_{11}Na^-$; **D** $^{24}_{12}Mg$; **E** $^{25}_{12}Mg$; **F** $^{26}_{12}Mg$

(14) Group III; there is a large jump in energy after the third electron is removed.

(15)

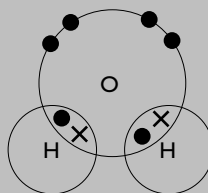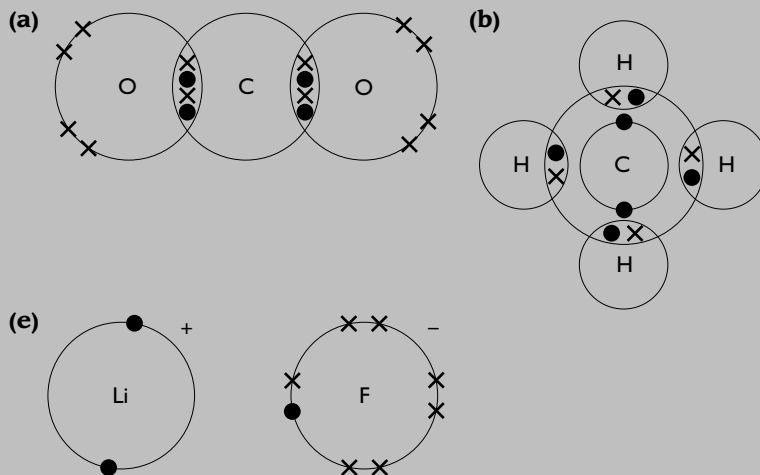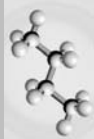| Element	Charge on the ion	Electron configuration
Magnesium	+2	$1s^2 2s^2 2p^6$
Lithium	+1	$1s^2$
Oxygen	−2	$1s^2 2s^2 2p^6$
Aluminium	+3	$1s^2 2s^2 2p^6$
Fluorine	−1	$1s^2 2s^2 2p^6$
Sulfur	−2	$1s^2 2s^2 2p^6 3s^2 3p^6$

(16) (a)

(b)

(a)

(b)

(e)
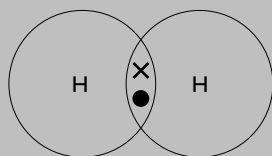
(17)

Material	Intermolecular force
Methanol, CH_3OH	Hydrogen bonding
Magnesium oxide, MgO	Ionic
Iodine chloride, ICl	Dipole–dipole/van der Waals
Argon, Ar	van der Waals
Aluminium, Al	Metallic

(18) It has a low melting point, so bonds between the particles in X are weak. It is an electrical insulator both as a solid and when molten, so it cannot be a metal or have ionic bonds. It dissolves in cyclohexane, which is covalently bonded. Therefore, the data suggest that X has covalent bonds within the molecules and probably van der Waals forces or dipoles between molecules. For example, paraffin wax.

(19) (a) An explosion, e.g. the ignition of hydrogen.

(b) Burning magnesium ribbon in air.

(c) Putting two different metals into an electrolyte, e.g. dilute sulfuric acid and connecting the metals with a wire.

(20) (a) +3 **(b)** 0 **(c)** +6

(21) $KMnO_4$ — Mn is +7; MnO_2 — Mn is +4; K_2MnO_4 — Mn is +6

(22) (a) +0.80 + (+0.76) = 1.56 V **(b)** −0.13 + (+2.38) = 2.25 V
(c) +0.80 + (−0.34) = 0.46 V

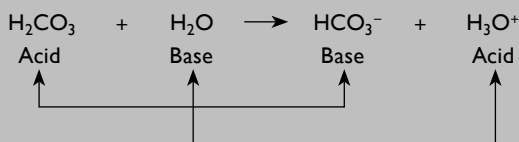**(23) (a)** +2.38 + (+1.36) = 3.74 V **(b)** +0.13 + (+1.07) = 1.20 V
(c) +1.36 + (−0.77) = 0.59 V **(d)** +1.36 + (−1.07) = 0.29 V

(24) (a) (i) Since the reaction is exothermic, the equilibrium will move in the direction which absorbs energy, i.e. to the left.

questions & answers

(ii) Since the reaction has fewer molecules on the right than on the left, increasing the pressure will favour a shift to the right.

(b) (i) The reaction consumes CH_3CO_2H in moving left to right, so this is favoured if the acid concentration is increased.
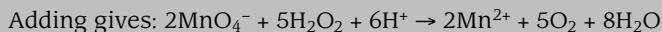
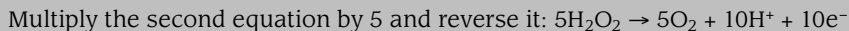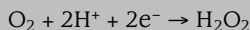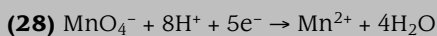**(ii)** Since the reaction produces water in moving from left to right, the removal of water will favour a shift in this direction.

(25) $H_2CO_3 + H_2O \rightarrow HCO_3^- + H_3O^+$

$$H_2CO_3 \quad + \quad H_2O \quad \longrightarrow \quad HCO_3^- \quad + \quad H_3O^+$$

Acid   Base   Base   Acid

(26) J cannot be a gas because when it is in powdered form it reacts with oxygen. J forms a liquid chloride so it must be a non-metallic element. Only **silicon tetrachloride** hydrolyses to give an acidic solution and an insoluble solid.
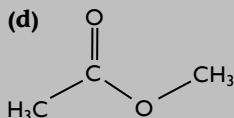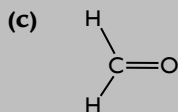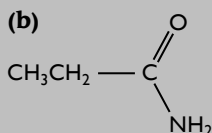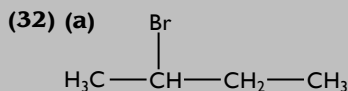
$Si + O_2 \rightarrow SiO_2$

$Si + 2Cl_2 \rightarrow SiCl_4$

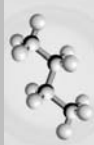$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$
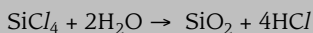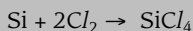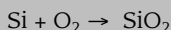
(27) The graph shows a very large increase after the fifth ionisation energy, which suggests that the sixth electron must come from an inner shell. The removal of the first two electrons requires slightly less energy than the next three, which suggests that these are the two 4s electrons. Therefore, the element is vanadium.

(28) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$

Multiply the first equation by 2: $2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$

Multiply the second equation by 5 and reverse it: $5H_2O_2 \rightarrow 5O_2 + 10H^+ + 10e^-$

Adding gives: $2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$

(29) Assume that chromium is in the same oxidation state in each complex. Since the complexes are octahedral they must be of the type $[CrL_6]^{n+}$. Of the three ligands, OH^- gives the smallest d-orbital splitting, then H_2O and finally NH_3. The complex with hydroxide is green, the complex with water is blue and the complex with ammonia is purple.

(30) 2-hydroxypropanoic acid

(31) (a) 1-chlorobutane   **(b)** 2-hydroxypropane or propan-2-ol
(c) Hexanoic acid   **(d)** 3-methylbutylamine

Approved: 0777 023 444

(32) (a)

$$H_3C \text{---} \underset{\underset{Br}{|}}{CH} \text{---} CH_2 \text{---} CH_3$$

(b)

$$CH_3CH_2 \text{---} \underset{\underset{NH_2}{|}}{\overset{\overset{O}{\|}}{C}}$$

(c)

$$\underset{H}{\overset{H}{>}} C{=}O$$

(d)

$$\underset{H_3C}{\overset{\overset{O}{\|}}{\underset{}{C}}} \overset{}{\underset{O}{\diagdown}} CH_3$$

(33) (a) $CH_3CH_2CH_2CHO$ (or $CH_3CH_2COCH_3$)

(b) Examples showing a ketone (or aldehyde) and an enol — for example, $CH_3CH_2COCH_3$ and $CH_3CH{=}CHCH_2OH$

(c) Including butanal, there are 9 isomers excluding *cis-trans*, and 12 isomers including *cis-trans*

(34) (a) 10 **(b)** 3 pairs

(35) If aqueous bromine is used, both Br and OH can add to the double bond forming $CH_2Br\text{--}CH_2OH$.

(36) (a) Ethyl propanoate **(b)** Propyl methanoate
(c) Methyl butanoate **(d)** Propyl ethanoate

(37) K is an aldehyde because it reacts both with 2,4-DNPH and with Fehling's solution. It does not react with alkaline aqueous iodine so it cannot contain the $CH_3C{=}O$ group. Thus **K** must be $CH_3CH_2CH_2CHO$ and **J** could be butan-1-ol, $CH_3CH_2CH_2CH_2OH$, or 2-methylpropan-1-ol, $(CH_3)_2CHCH_2OH$.

(38) With phenylamine, the lone pair of electrons on the nitrogen atom become delocalised with the π-electrons on the benzene ring making it less easy to protonate. In ethylamine, the ethyl group pushes electrons towards the nitrogen enhancing its ability to be protonated.

(39) In condensation polymerisation:
- a small molecule is eliminated
- the monomer(s) need two different functional groups

In addition polymerisation:
- the empirical formula of the polymer is the same as that of the monomer
- an unsaturated carbon–carbon bond must be present

(40) (a) Asp **(b)** Pro **(c)** Lys

(41) Any one of the following triplets:

(a) AGU AGC UCU UCC UCA UCG **(b)** UGU UGC **(b)** UAU UAC