Revision Guide

Cambridge
International AS and A Level

NEW
for 2016
exams

Chemistry

Second Edition

David Bevan
Series editor: Mary Jones

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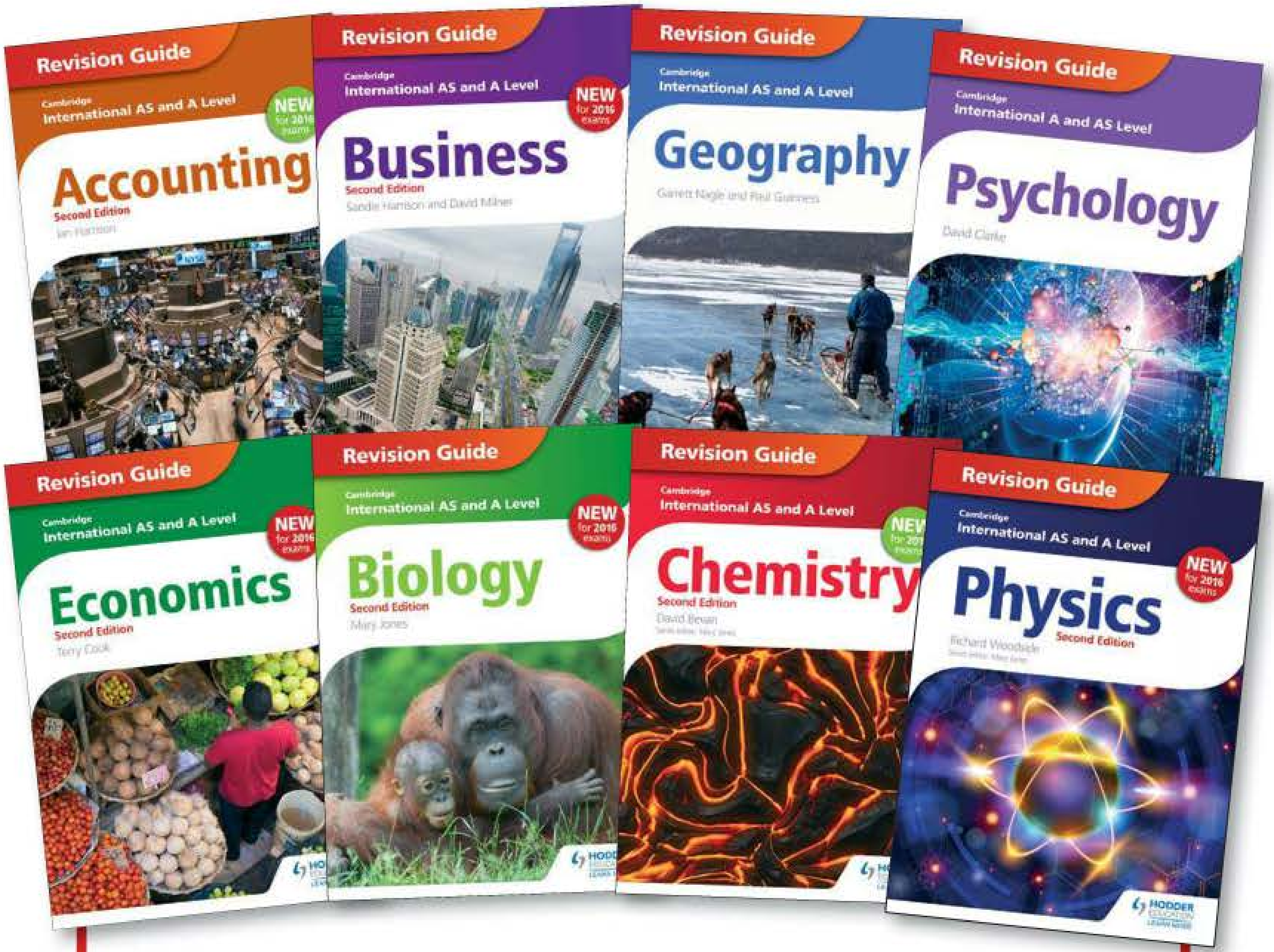
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Get the most from this book

Everyone has to decide his or her own revision strategy, but it is essential to review your work, learn it and test your understanding. This Revision Guide will help you to do that in a planned way, topic by topic. Use this book as the cornerstone of your revision and don't hesitate to write in it — personalise your notes and check your progress by ticking off each section as you revise.

My revision planner

AS topics

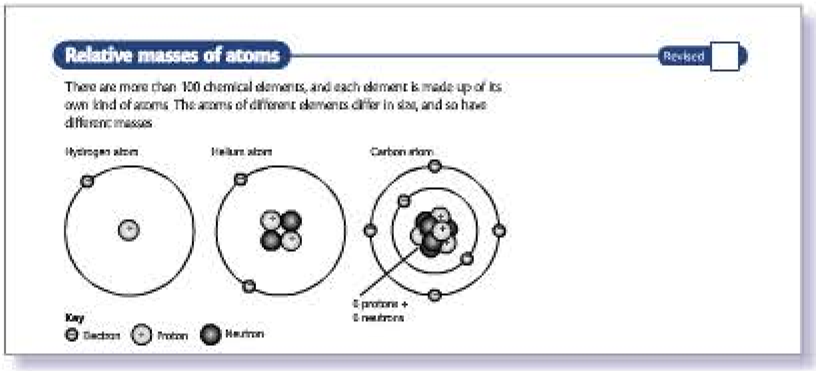
	Revised	Tested	Exam ready
7 1 Atoms, molecules and stoichiometry	☐	☐	☐
14 2 Atomic structure	☐	☐	☐
19 3 Chemical bonding	☐	☐	☐
28 4 States of matter	☐	☐	☐

☑ Tick to track your progress

Use the revision planner on pages 4 and 5 to plan your revision, topic by topic. Tick each box when you have:

- revised and understood a topic
- tested yourself
- practised the exam-style questions

You can also keep track of your revision by ticking off each topic heading in the book. You may find it helpful to add your own notes as you work through each topic.



Relative masses of atoms

Revised ☐

There are more than 100 chemical elements, and each element is made up of its own kind of atoms. The atoms of different elements differ in size, and so have different masses.

Features to help you succeed

Expert tips

Throughout the book there are tips from the experts on how to maximise your chances.

Definitions and key terms

Clear and concise definitions of essential key terms are given on the page where they first appear.

Key words from the syllabus are highlighted in bold for you throughout the book.

Revision activities

These activities will help you to understand each topic in an interactive way.

Now test yourself

These short, knowledge-based questions provide the first step in testing your learning. Answers are at the back of the book.

Questions and answers

Use the exam-style questions and answers to consolidate your revision and practise your exam skills.

My revision planner

AS topics

		Revised	Tested	Exam ready
7	1 Atoms, molecules and stoichiometry	☐	☐	☐
14	2 Atomic structure	☐	☐	☐
19	3 Chemical bonding	☐	☐	☐
28	4 States of matter	☐	☐	☐
37	5 Chemical energetics	☐	☐	☐
44	6 Electrochemistry	☐	☐	☐
52	7 Equilibria	☐	☐	☐
63	8 Reaction kinetics	☐	☐	☐
73	9 The Periodic Table: chemical periodicity	☐	☐	☐
79	10 Group 2	☐	☐	☐
82	11 Group 17	☐	☐	☐
94	13 Nitrogen and sulfur	☐	☐	☐
97	14 An introduction to organic chemistry	☐	☐	☐
107	15 Hydrocarbons	☐	☐	☐
118	16 Halogen derivatives	☐	☐	☐
122	17 Hydroxy compounds	☐	☐	☐
128	18 Carbonyl compounds	☐	☐	☐
132	19 Carboxylic acids and derivatives	☐	☐	☐
155	22 Analytical techniques	☐	☐	☐

A level topics

		Revised	Tested	Exam ready
7	1 Atoms, molecules and stoichiometry	☐	☐	☐
14	2 Atomic structure	☐	☐	☐
19	3 Chemical bonding	☐	☐	☐
28	4 States of matter	☐	☐	☐
37	5 Chemical energetics	☐	☐	☐
44	6 Electrochemistry	☐	☐	☐
52	7 Equilibria	☐	☐	☐
63	8 Reaction kinetics	☐	☐	☐
73	9 The Periodic Table: chemical periodicity	☐	☐	☐
79	10 Group 2	☐	☐	☐
82	11 Group 17	☐	☐	☐
86	12 An introduction to the chemistry of transition elements	☐	☐	☐
94	13 Nitrogen and sulfur	☐	☐	☐
97	14 An introduction to organic chemistry	☐	☐	☐
107	15 Hydrocarbons	☐	☐	☐

		Revised	Tested	Exam ready
118	16 Halogen derivatives	☐	☐	☐
122	17 Hydroxy compounds	☐	☐	☐
128	18 Carbonyl compounds	☐	☐	☐
132	19 Carboxylic acids and derivatives	☐	☐	☐
140	20 Nitrogen compounds	☐	☐	☐
146	21 Polymerisation	☐	☐	☐
155	22 Analytical techniques	☐	☐	☐
166	23 Organic synthesis	☐	☐	☐

AS and A level topics

		Revised	Tested	Exam ready
169	Experimental skills and investigations	☐	☐	☐
177	Questions and answers			
197	Now test yourself answers			

Countdown to my exams

6–8 weeks to go

- Start by looking at the syllabus — make sure you know exactly what material you need to revise and the style of the examination. Use the revision planner on pages 4 and 5 to familiarise yourself with the topics.
- Organise your notes, making sure you have covered everything on the syllabus. The revision planner will help you to group your notes into topics.
- Work out a realistic revision plan that will allow you time for relaxation. Set aside days and times for all the subjects that you need to study, and stick to your timetable.
- Set yourself sensible targets. Break your revision down into focused sessions of around 40 minutes, divided by breaks. This Revision Guide organises the basic facts into short, memorable sections to make revising easier.

Revised ☐

2–5 weeks to go

- Read through the relevant sections of this book and refer to the expert tips and key terms. Tick off the topics as you feel confident about them. Highlight those topics you find difficult and look at them again in detail.
- Test your understanding of each topic by working through the 'Now test yourself' questions in the book. Look up the answers at the back of the book.
- Make a note of any problem areas as you revise, and ask your teacher to go over these in class.
- Look at past papers. They are one of the best ways to revise and practise your exam skills. Write or prepare planned answers to the exam-style questions provided in this book. Check your answers with your teacher.
- Use the revision activities to try different revision methods. For example, you can make notes using mind maps, spider diagrams or flash cards.
- Track your progress using the revision planner and give yourself a reward when you have achieved your target.

Revised ☐

1 week to go

- Try to fit in at least one more timed practice of an entire past paper and seek feedback from your teacher, comparing your work closely with the mark scheme.
- Check the revision planner to make sure you haven't missed out any topics. Brush up on any areas of difficulty by talking them over with a friend or getting help from your teacher.
- Attend any revision classes put on by your teacher. Remember, he or she is an expert at preparing people for examinations.

Revised ☐

The day before the examination

- Flick through this Revision Guide for useful reminders, for example the expert tips and key terms.
- Check the time and place of your examination.
- Make sure you have everything you need — extra pens and pencils, tissues, a watch, bottled water, sweets.
- Allow some time to relax and have an early night to ensure you are fresh and alert for the examination.

Revised ☐

My exams

Paper 1

Date: .... Time: ....

Location:...

Paper 2

Date: .... Time: ....

Location:...

Paper 3

Date: .... Time: ....

Location:...

Paper 4

Date: .... Time: ....

Location:...

Paper 5

Date: .... Time: ....

Location:...

1 Atoms, molecules and stoichiometry

Relative masses of atoms

Revised ☐

There are more than 100 chemical elements, and each element is made up of its own kind of atoms. The atoms of different elements differ in size, and so have different masses.

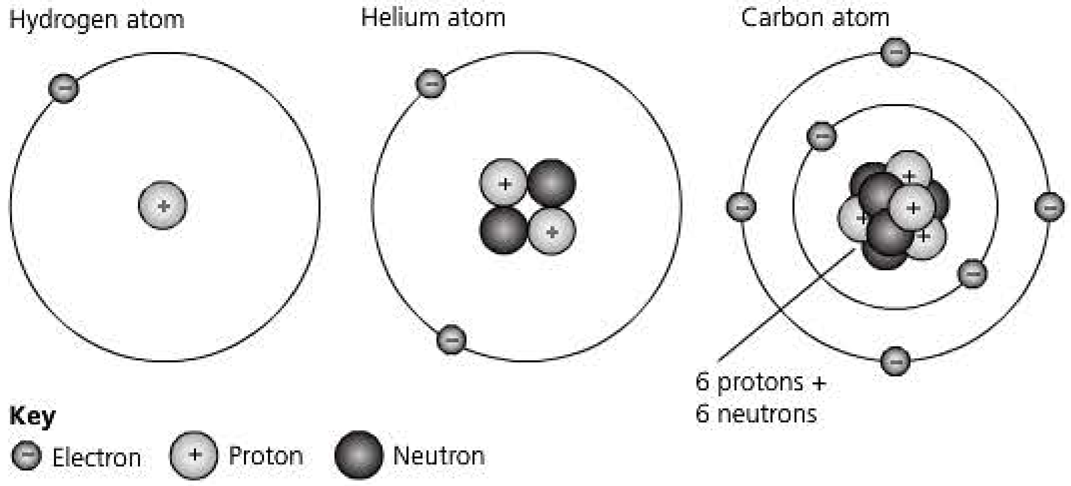


Figure 1.1 Atoms of hydrogen, helium and carbon

You can also see that the atoms are made up of different sorts of and numbers of particles. There is more about this in the section on atomic structure. For now you should be able to identify:

- two types of particle in the **nucleus**, which is in the centre of the atom. The two particles in the nucleus are **protons** and **neutrons**. They have the same mass, but a proton has a single positive charge and a neutron has no charge.
- another type of particle that orbits the nucleus — these particles are called **electrons**. An electron has almost no mass, but carries a single negative charge (Table 1.1).

Table 1.1

Particle	Relative mass	Relative charge
Proton	1	+1
Neutron	1	0
Electron	0	–1

Now test yourself

Tested ☐

1 Make a copy of the table below. Use the Periodic Table to work out which atoms are represented by the particles described in the table below. The final entry needs some careful thought. Can you work out what is going on here?

	Protons	Neutrons	Electrons	Identity of species
a	11	12	11	$^{23}_{11}Na$
b	9	10	9	
c	16	16	16	
d	24	28	24	
e	19	20	18	

Answers on p.197

For AS you need to be able to distinguish between terms that relate to the masses of elements and compounds.

Key terms

Relative atomic mass, A_r, is defined as the mass of one atom of an element relative to one-twelfth of the mass of an atom of carbon-12, ^{12}C, which has a mass of 12.00 atomic mass units.

Relative isotopic mass is like relative atomic mass in that it deals with atoms. The difference is that we are dealing with different atoms of the same element. The isotopes of an element have the same number of protons, but different numbers of neutrons. Hence, isotopes of an element have different masses.

Relative molecular mass, M_r, is defined as the mass of one molecule of an element or compound relative to one-twelfth of the mass of an atom of carbon-12, ^{12}C, which has a mass of 12.00 atomic mass units.

Relative formula mass is used for substances that do not contain molecules, such as sodium chloride, NaC*l*, and is the sum of all the relative atomic masses of the atoms in the formula of the substance.

It is important to remember that because these are all *relative* masses, they have no units.

The mole

Revised ☐

Individual atoms cannot be picked up or weighed, so we need to find a way of comparing atomic masses. One way is to find the mass of the same number of atoms of different types. Even so, the mass of atoms is so small that we need a huge number of atoms of each element to weigh. This number is called the **Avogadro constant**. It is equal to 6.02×10^{23} atoms and is also referred to as **one mole**. The abbreviation for mole is 'mol'.

You may wonder why such a strange number is used. It is the number of atoms of a substance that make up the relative atomic mass, A_r, in grams. The mass is measured relative to one-twelfth of the mass of a carbon atom, ^{12}C.

Mole calculations

You should be able to work out how many moles a given mass of an element or compound represents. To do that you need to know the relative atomic mass, A_r, of the element (or elements) present. You can get this information from the Periodic Table.

A **mole** is Avogadro's number (6.02×10^{23}) of atoms or molecules.

Now test yourself

2 How many moles do the following masses of atoms represent?
  - **a** 6 g of carbon, C
  - **b** 24 g of oxygen, O
  - **c** 14 g of iron, Fe

3 How many grams of substance are in the following amounts?
  - **a** 0.2 mol of neon, Ne
  - **b** 0.5 mol of silicon, Si
  - **c** 1.75 mol of helium, He
  - **d** 0.25 mol of carbon dioxide, CO_2

Answers on p.197

Tested ☐

Mass spectra

Revised ☐

Another way of determining the atomic mass of an element is to use a **mass spectrometer**. You do not need to know how the instrument works, only that it produces positive ions of atoms, or fragments of molecules, and separates them according to their masses. Molecular fragmentation is covered later.

On injecting a sample of an element into a mass spectrometer, atoms of the element become positively charged and then separated according to their masses. Most elements are made up of atoms with the same number of protons but different numbers of neutrons. This means that they have different masses.

The data can be used to calculate the average atomic mass of the sample. Figure 1.2 shows the mass spectrum of a sample of the element magnesium.

The average atomic mass of the sample of magnesium is made up of the contribution each isotope makes:

$$A_r = (24 \times 0.79) + (25 \times 0.10) + (26 \times 0.11)$$
$$= 24.32$$

Remember that samples may not always contain just one isotope, or even the same mix of isotopes.

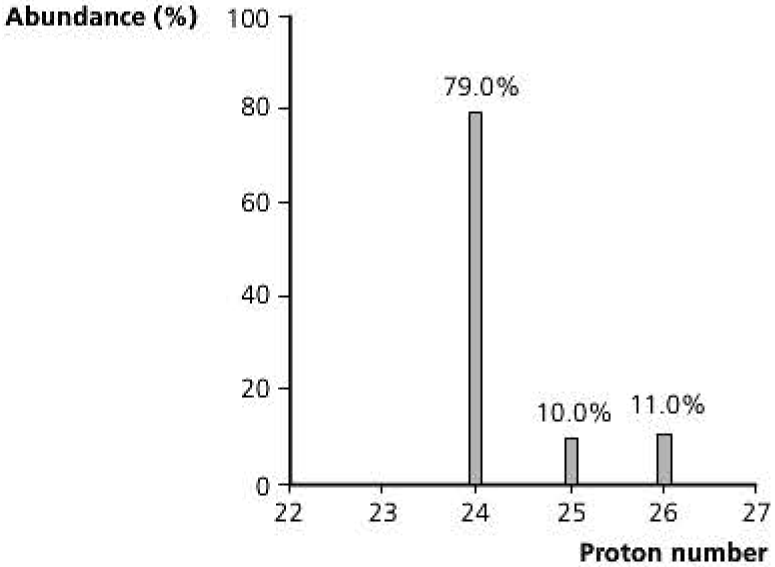


Figure 1.2 Mass spectrum of magnesium

Empirical and molecular formulae

Revised ☐

The **empirical formula** of a compound is its simplest formula. It shows the ratio of the numbers of atoms of the different elements in a compound.

You need to know how to use the composition by mass of a compound to find its empirical formula:

- Divide the mass (or percentage mass) of each element by its A_r.
- Use the data to calculate the simplest whole number ratio of atoms.

Example

A chloride of iron contains 34.5% by mass of iron. Determine the empirical formula of the compound.

Answer

Element	% by mass (m)	A_r	m/A_r	Moles	Ratio
Fe	34.5	56	$\frac{34.5}{56}$	0.616	1
Cl	65.5	35.5	$\frac{65.5}{35.5}$	1.85	3

So the empirical formula of this chloride is $FeCl_3$.

Now test yourself

4 Work out the empirical formulae of the following compounds:
  - **a** compound A — composition by mass: 84.2% rubidium, 15.8% oxygen
  - **b** compound B — composition by mass: 39.1% carbon, 52.2% oxygen, 8.70% hydrogen

Answers on p.197

Tested ☐

By contrast, the **molecular formula** of a compound shows the *actual number* of atoms of every element present in the compound. The molecular formula is always a multiple of the empirical formula.

Example

A compound has the empirical formula CH_2O, and a molar mass of 60. What is its molecular formula?

Answer

You can see that the formula mass of the compound is:

$$(1 \times 12) + (2 \times 1) + (1 \times 16) = 30$$

Because the molar mass is 60, the molecular formula must be twice the empirical formula, $C_2H_4O_2$.

Writing and balancing equations

Revised ☐

Chemical equations are a shorthand way of describing chemical reactions. Using the symbols of elements used in the Periodic Table ensures that they are understood internationally. Whenever you write a chemical equation there are simple rules to follow:

- check the formula of each compound in the equation
- check that the overall equation balances
- try to visualise what is happening in the reaction. This will help you choose the correct **state symbol** — the state symbols are (s) for solid, (l) for liquid, (g) for gas and (aq) for an aqueous solution

Suppose you want to write a chemical equation for the reaction between magnesium and dilute sulfuric acid. You can probably write a word equation for this from your previous studies of chemistry:

magnesium + sulfuric acid → magnesium sulfate + hydrogen

In symbols this becomes:

$$Mg + H_2SO_4 \rightarrow MgSO_4 + H_2$$

Counting up the numbers of each type of atom on each side of the arrow shows that they are equal — the equation is *balanced*.

You can include more detail about the states of the reactants and products and add the state symbols:

$$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$$

You might also remember that dilute sulfuric acid is a mixture of H^+ and SO_4^{2-} ions. So you can write an ionic equation showing just the changes in species (this word refers to a reactant or product that is not a chemical you can get from a bottle, e.g. sulfate ion, SO_4^{2-}), or chemical forms:

$$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$$

A more complicated reaction is that between sodium carbonate and hydrochloric acid. You will have seen the mixture fizz in the laboratory:

sodium carbonate + hydrochloric acid → sodium chloride + carbon dioxide

Using symbols this becomes:

$$Na_2CO_3 + HCl \rightarrow NaCl + CO_2$$

Counting the atoms on each side of the arrow shows that there are 'spare' atoms of sodium, oxygen and hydrogen on the left-hand side and no hydrogen on the right-hand side. You can take care of the sodium by doubling the amount of sodium chloride formed, but what about the hydrogen and oxygen? Water is a compound of hydrogen and oxygen, so let's see what happens if water is added to the right-hand side:

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$$

Doubling the amount of HCl and $NaCl$ now makes the equation balance. Adding the state symbols gives:

$$Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$

Notice that water is a liquid, not aqueous.

The ionic equation for this reaction is:

$$(Na^+)_2CO_3^{2-}(s) + 2H^+(aq) \rightarrow 2Na^+(aq) + CO_2(g) + H_2O(l)$$

Calculations using equations and the mole

Revised ☐

Now that you understand moles and how to write balanced chemical equations, you can use these two ideas to calculate the quantities of substances reacting together and the amounts of products formed in reactions.

There are three main types of calculation you might be expected to perform:

- reacting masses (from formulae and equations)
- volumes of gases reacting or being produced
- volumes and concentrations of solutions of chemicals reacting

In each of these you need to use balanced chemical equations and the mole concept for quantities of chemical compounds.

Calculations involving reacting masses

Suppose copper(II) carbonate is heated. What mass of copper(II) oxide would be formed starting from 5.0 g of the carbonate?

Let's break the calculation down into simple stages.

1. Write the equation for the reaction:

   $CuCO_3 \rightarrow CuO + CO_2$

2. Now work out the relative molecular masses of each of the substances involved:

   $CuCO_3 \rightarrow CuO$

   $63.5 + 12 + (3 \times 16) \rightarrow 63.5 + 16$

   $123.5\,g \rightarrow 79.5\,g$

3. Finally, calculate the mass of CuO formed from 5.0 g of $CuCO_3$:

   $5.0\,g \rightarrow 5 \times \frac{79.5}{123.5}\,g = 3.2\,g$

   mass of CuO = 3.2 g

Expert tip

If you work out this calculation using your calculator, it may show many more decimal places than are given in the answer above. The answer is given as 3.2 g because you use the number of significant figures equal to the smallest number of these in the data. Because the starting mass of copper(II) carbonate and the molar mass of carbon dioxide are quoted to two significant figures, you are not justified in giving an answer to more than two significant figures. This idea is important in scientific calculations. You will also come across its use in practical work involving calculations.

Now test yourself

Tested ☐

Try these calculations using the idea of reacting masses (remember to use the correct number of significant figures).

5. What mass of carbon dioxide is lost when 2.5 g of magnesium carbonate is decomposed by heating?
6. What mass of potassium chloride is formed when 2.8 g of potassium hydroxide is completely neutralised by hydrochloric acid?
7. What is the increase in mass when 6.4 g of calcium is completely burned in oxygen?

Answers on p.197

These questions are relatively straightforward. However, you might be asked to use mass data to determine the formula of a compound. The next example shows you how to do this.

Example

When heated in an inert solvent, tin metal reacts with iodine to form a single orange-red solid compound. In an experiment, a student used 5.00 g of tin in this reaction. After filtering and drying, the mass of crystals of the orange compound was 26.3 g. Using this data, work out the formula of the orange compound.

Answer

First you need to calculate how much iodine was used in the reaction. Do this by subtracting the mass of tin from the final mass of the compound:

$$\text{mass of iodine used} = 26.3\,\text{g} - 5.00\,\text{g} = 21.3\,\text{g}$$

Next, convert the masses of tin and iodine into the numbers of moles of each. Do this by dividing each mass by the relevant atomic mass:

$$\text{moles of tin} = \frac{5.00}{119} = 0.0420\,\text{mol}$$

$$\text{moles of iodine} = \frac{21.3}{127} = 0.168\,\text{mol}$$

As you can see, the ratio of the number of moles used shows that there are four times as many moles of iodine as there are of tin in the compound. So the formula of the orange-red crystals is SnI_4.

Calculations involving volumes of gases

Not all chemical reactions involve solids. For reactions in which gases are involved it is more convenient to measure volumes than masses. You need a way of linking the volume of a gas to the number of particles it contains — in other words a way of converting volume to moles. In the early nineteenth century, Avogadro stated that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules. You now know that one mole of a gas occupies 24 dm^3 at room temperature (25°C) and a pressure of 101 kPa (1 atm); or 22.4 dm^3 at standard temperature (273 K) and the same pressure (stp).

This means that if you measure the volume of gas in dm^3 at room temperature and pressure, it can be converted directly to the number of moles present by dividing by 24.

The easiest way to see how this works is to look at an example. The reaction between hydrogen and chlorine forms hydrogen chloride:

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

It would not be easy to measure the reacting masses of the two gases. You could, however, measure their volumes. When this is done, we find that there is no overall change in volume during the reaction. This is because there are two moles of gas on the left-hand side of the equation and two moles of the new gas on the right-hand side.

Some reactions produce gases as well as liquids, and in others gases react with liquids to form solids, and so on. In these cases, you can use the above method combined with the method used in the first calculation.

For example, 2.0 g of magnesium dissolves in an excess of dilute hydrochloric acid to produce hydrogen:

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

The equation shows that for every mole of magnesium used, 1 mole of hydrogen gas is formed.

Because 2.0 g of magnesium is $\frac{2.0}{24.3}$ mol, this means that $\frac{2.0}{24.3}$ mol of hydrogen gas should be formed.

Each mole of hydrogen occupies 24 dm^3 at room temperature and pressure:

$$\text{volume of hydrogen produced} = \frac{2.0}{24.3} \times 24\,\text{dm}^3 = 1.98\,\text{dm}^3$$

Now test yourself

Try the following calculations involving volumes of gas(es).

8 25 cm^3 of the gas propane, C_3H_8, is burned in an excess of oxygen to form carbon dioxide and water. What volume of oxygen reacts, and what volume of carbon dioxide is formed at room temperature and pressure? (You can assume that the water formed is liquid and has negligible volume.)

9 A sample of lead(IV) oxide was heated in a test tube:

$$2PbO_2(s) \rightarrow 2PbO(s) + O_2(g)$$

and the oxygen gas released was collected. What mass of the oxide would be needed to produce 80 cm^3 of oxygen at room temperature and pressure?

10 Carbon dioxide was bubbled into limewater (a solution of calcium hydroxide) and the solid calcium carbonate precipitated was filtered off, dried and weighed. If 0.50 g of calcium carbonate were formed, what volume of carbon dioxide, at room temperature and pressure, was passed into the solution?

$$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$$

Answers on p.197

Tested ☐

Calculations involving volumes and concentrations of solutions

These types of calculation are particularly important because they often arise in the AS practical paper (see the later section on practical work). The basic principles of the calculations are the same as those covered already, the only complication being that the reactants are in solution. This means that instead of dealing with masses, you are dealing with volumes of solutions of known concentration.

Another way of dealing with this is to work out how many **moles** of substance are dissolved in 1 dm^3 of solution — this is known as the **molar concentration**. Do not confuse this with **concentration**, which is the **mass** of substance dissolved in 1 dm^3.

Think about a 0.1 $mol\,dm^{-3}$ solution of sodium hydroxide. The mass of 1 mole of sodium hydroxide is (23 + 16 + 1) or 40 g. So a 0.1 $mol\,dm^{-3}$ solution contains (40 × 0.1 = 4.0 g) or 0.1 mol per dm^3.

If you know the molar concentration of a solution and the volume that reacts with a known volume of a solution containing another reactant, you can calculate the molar concentration of the second solution using the equation for the reaction.

Example

In a titration between dilute sulfuric acid and 0.1 $mol\,dm^{-3}$ sodium hydroxide, 21.70 cm^3 of the sodium hydroxide was needed to neutralise 25.00 cm^3 of the dilute sulfuric acid. Knowing the equation for the reaction, you can calculate the concentration of the acid in $mol\,dm^{-3}$.

$$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$$

Answer

From the equation you can see that 1 mole of sulfuric acid requires 2 moles of sodium hydroxide for complete reaction. So the number of moles of sodium hydroxide used is $\frac{21.70}{1000} \times 0.1$

This would neutralise $\frac{21.70}{1000} \times 0.1 \times 2$ moles of sulfuric acid.

This number of moles is contained in 25.00 cm^3 of sulfuric acid.

To get the number of moles in 1 dm^3, multiply this number by $\frac{1000}{25.00}$. This gives:

$$\frac{21.70 \times 0.1 \times 1000}{1000 \times 2 \times 25.00} = 0.0434\ mol\,dm^{-3}$$

Now test yourself

Tested ☐

The following calculations involving volumes and concentrations of solutions will give you practice in this important area of the syllabus.

11 **In a titration, 27.60 cm^3 of 0.100 $mol\,dm^{-3}$ hydrochloric acid neutralised 25.00 cm^3 of potassium hydroxide solution. Calculate the molar concentration of the potassium hydroxide solution and its concentration in $g\,dm^{-3}$.**

12 **A 0.2 $mol\,dm^{-3}$ solution of nitric acid was added to an aqueous solution of sodium carbonate. 37.50 cm^3 of the acid was required to react completely with 25.00 cm^3 of the carbonate. Calculate the molar concentration of the carbonate.**

Answers on p.197

Revision activity

1 What is the mass of 0.05 mol of Na_2SO_4?

2 What volume of 0.05 M H_2SO_4 is needed to exactly react with 25 cm^3 of 0.05 M NaOH to form a 0.05 M solution of Na_2SO_4?

3 What volume of 0.05 M HC*l* would exactly neutralise the same volume of 0.05 M NaOH as in part 2?

Answers on p.201

2 Atomic structure

Sub-atomic particles and their properties

Revised ☐

In Chapter 1 you saw that atoms are made up of three different types of particles — protons, neutrons and electrons. You should remember that only the protons and neutrons have significant mass, and that the proton carries a single positive charge while the electron carries a single negative charge. You also need to remember that the protons and neutrons are found in the nucleus of the atom and that the electrons surround the nucleus. These particles behave quite differently if they are passed through an electric field. Protons are attracted to the negative electrode, electrons to the positive electrodes while neutrons are undeviated.

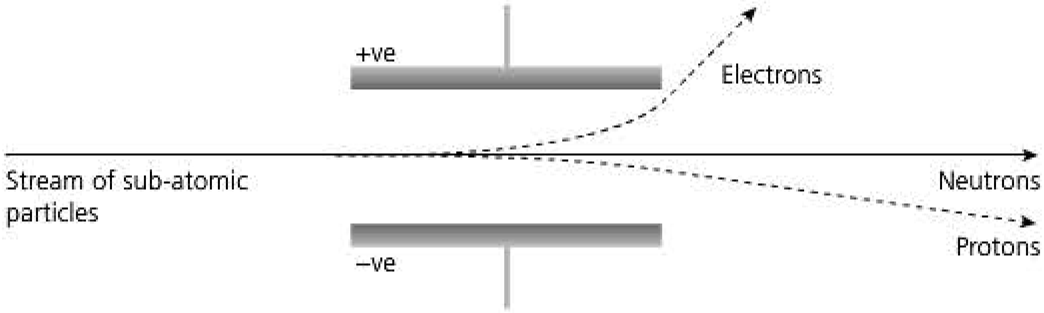


Figure 2.1 The behaviour of protons, neutrons and electrons in an electric field

Look at the numbers of sub-atomic particles in the three particles shown in Table 2.1. What is the major difference between these three species?

Table 2.1

Particle	Number of protons	Number of neutrons	Number of electrons
A	11	12	10
B	11	12	11
C	11	12	12

The difference is in the number of electrons each particle possesses, and so the overall charge on the species. Because particle A has one more proton than electrons, it has a single positive charge. In B the number of protons and electrons are the same, so it is uncharged (neutral). In C there is one more electron than protons, so it has a single negative charge. Notice that because all the species have the same number of protons (proton number), they are all forms of the same element, in this case sodium. The two charged species are called **ions**.

A positive ion is called a **cation**.

A negative ion is called an **anion**.

You might be surprised to see sodium as an anion, Na^-, but it is theoretically possible (and very unlikely).

Table 2.2 shows another way in which the numbers of sub-atomic particles can vary.

Table 2.2

Particle	Number of protons	Number of neutrons	Number of electrons
D	12	12	12
E	12	13	12
F	12	14	12

In this case, it is the number of neutrons that changes, while the element stays the same. These forms of an element are called **isotopes**. In Table 2.2, the three species are all isotopes of magnesium.

The standard way of writing these particles in 'shorthand' form is ${}^{A}_{Z}X^{n+/-}$. In this form the element symbol is X, A is the nucleon or mass number (the number of protons plus neutrons in the nucleus), Z is the proton or atomic number (the number of protons in the nucleus) and $n^{+/-}$ is the charge (if any) on the particle.

Now test yourself

1 Write out structures of the six species A–F described in Tables 2.1 and 2.2 using the form ${}^{A}_{Z}X^{n+/-}$.

Answers on p.197

Tested ☐

Arrangement of electrons in atoms

Revised ☐

As the number of protons in the nucleus increases, the masses of atoms increase. After hydrogen, this increase in mass is also due to the neutrons in the nucleus (Table 2.3).

Table 2.3

Element	Protons	Neutrons	Mass number
H	1	0	1
He	2	2	4
Li	3	4	7
Be	4	5	9
B	5	6	11
C	6	6	12

The addition of electrons to form new atoms is not quite so straightforward because they go into different **orbitals**.

Orbitals are regions in space that can hold a certain number of electrons, and which have different shapes.

The electrons also exist in different **energy levels** (sometimes called shells) depending on how close to, or far away from, the nucleus they are.

The number of protons in a nucleus determines just what the element is. However, it is the *arrangement* of electrons that determines the chemistry of an element and how it forms bonds with other elements. So, for example, metal atoms tend to lose electrons forming positive ions; non-metal atoms tend to accept electrons forming negative ions.

As the number of protons increases, the electron energy levels fill up in the following sequence: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p... (Table 2.4). This sequence can be followed in the Periodic Table.

Table 2.4

Element	Electronic configuration
Hydrogen	$1s^1$
Helium	$1s^2$
Lithium	$1s^2, 2s^1$
Beryllium	$1s^2, 2s^2$
Boron	$1s^2, 2s^2, 2p^1$
Carbon	$1s^2, 2s^2, 2p^2$
Nitrogen	$1s^2, 2s^2, 2p^3$
Oxygen	$1s^2, 2s^2, 2p^4$
Fluorine	$1s^2, 2s^2, 2p^5$
Neon	$1s^2, 2s^2, 2p^6$

As more electrons are added, they go successively into orbitals of increasing energy as shown in Figure 2.2.

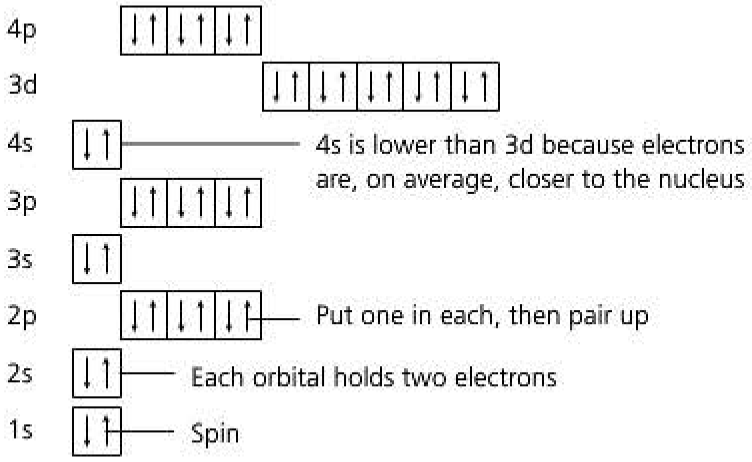


Figure 2.2 Sequence of filling orbitals with electrons

Figure 2.2 illustrates some key points about the arrangement of electrons in atoms.

- The electrons are arranged in **energy levels** (or shells) from level 1, closest to the nucleus. Moving outwards from the nucleus, the shells gradually increase in energy.
- Most energy levels (except the first) contain sub-levels (or sub-shells) denoted by letters s, p and d.
- Different sub-levels contain different numbers of orbitals, with each orbital holding a maximum of two electrons.
- When filling up the energy levels in an atom, electrons go into the lowest energy level first.
- In sub-levels containing more than one orbital, each of the orbitals is populated singly before any are doubly-filled.
- Figure 2.2 has one strange entry — the 4s-orbital has a lower energy than the 3d-orbital.

In an examination, you may be asked to deduce the electron configuration of an atom (or ion) given its proton number (and any charge). The next two examples show how to do this.

Example 1

An atom, X, has a proton number of 16. Deduce the electron configuration of this atom.

Answer

The proton number is 16, so the atom must also contain 16 electrons. Referring back to Figure 2.1, you can count upwards until 16 electrons have been placed. This means that the 1s-orbital, the 2s- and 2p-orbitals and the 3s-orbital are filled, using up 12 of the 16 electrons. The remaining four electrons must go into the 3p-orbital, giving the electron configuration $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^4$.

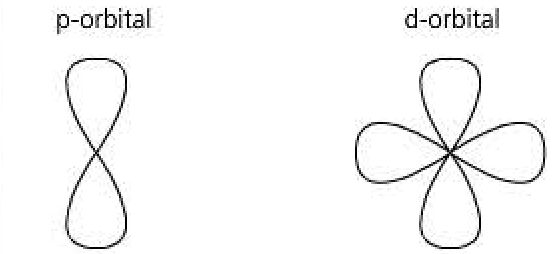
Example 2

Element X forms an ion, X^{2-}. What is the electron configuration of the ion?

Answer

The ion contains an extra two electrons compared with the atom. This means that it contains a total of (16 + 2) or 18 electrons. Looking at Figure 2.2 you can see that these extra two electrons will fit into the remainder of the 3p-orbital giving an electronic configuration of $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$ for the ion X^{2-}.

The different orbitals have different shapes. Cross-sections of these orbitals are shown in Figure 2.3.



s of s-, p- and d-orbitals

ns in the different types of orbital can affect the shapes

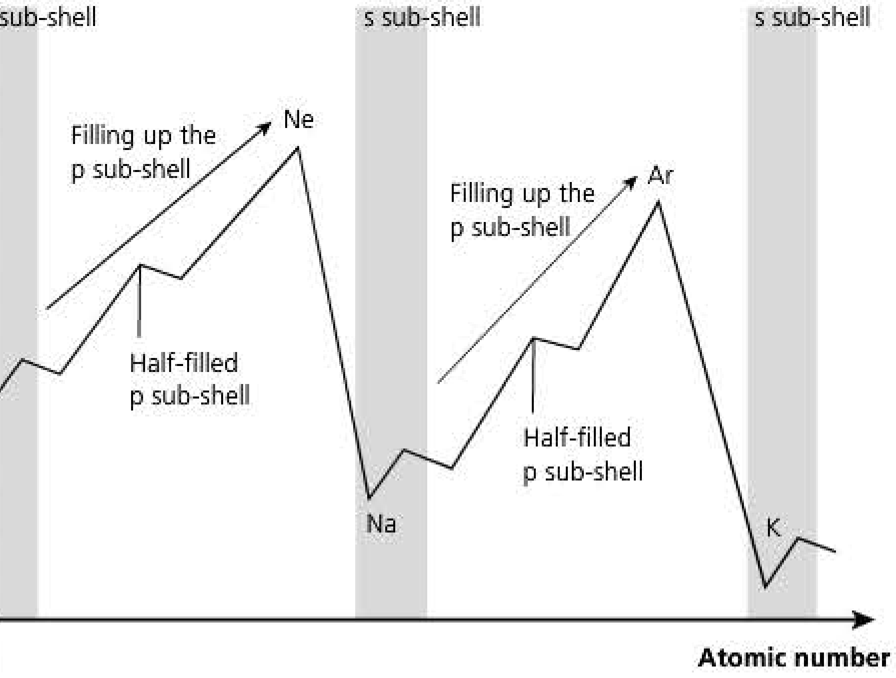
ies

nergy of an atom has a precise definition that you need

ergy is the energy required to convert 1 mole of gaseous
nto 1 mole of gaseous cations, with each atom losing

d:
–

here are changes in the first ionisation energy values as
in the nucleus increases. This leads to a '2-3-3' pattern for
wn in Figure 2.4.



etween first ionisation energy and atomic number

ome textbooks look complicated. For the examination
principles of the change. In an examination you might be

e in first ionisation energy across a period — proton
arge increases across the period; shielding by other
so there is a bigger attraction for the electrons

oups 2 and 3 and/or Groups 15 and 16 — for Groups
n is removed from a p-orbital; which is higher in energy
an s-orbital; so it is easier to remove. For Groups 15 and
electrons in one of the p-orbitals; this causes repulsion;
er to remove one of these electrons

nd of the period — an electron shell has been completed;
ore shielding; so there is less attraction for the outer

the removal of second and subsequent

$\rightarrow M^{2+}(g) + e^-$

$) \rightarrow M^{3+}(g) + e^-$

ergies in an unknown element enables us s in. You know that successive ionisation e removed, and that a big increase occurs new inner orbital closer to the nucleus.

Now test yourself

2 The graph in Figure 2.5 shows successive ionisation energies for an element Q. In which group of the Periodic Table is Q? Explain your answer.

Answers on p.197

Tested ☐

n energies for element Q

n the formation of positive ions. **Electron** ent, and their use is generally confined to Periodic Table. Electron affinity is ionisation energy.

s, in other words energy is released. For chlorine is −349 kJ mol^{-1}.

up 17 elements are shown in Table 2.5.

Electron affinity is defined as the energy change for the addition of one electron to each of one mole of atoms in the gas phase.

$X(g) + e^- \rightarrow X^-(g)$

–1

hat less energy is released as the group is because the electron is being added to a nd there is significant repulsion.

Now test yourself

3 What does the term 'second electron affinity' mean?

4 Give an example of an element for which the second electron affinity is relevant.

Answers on p.197

Tested ☐

e symbol $^{40}_{19}X^+$. How many protons, neutrons and electrons are in the particle?

o the composition of the element with atomic number 19 in the Periodic Table. What is

ge for the process shown here?

nge for the process described below to be smaller, the same or larger than that in part 3?

3 Chemical bonding

Chemical reactions depend on breaking existing bonds and forming of new bonds. To understand this process, you need to be aware of the different types of bonds and forces between atoms and molecules.

Ionic (electrovalent) bonding

Revised ☐

Ions are formed when atoms react and either gain or lose electrons. Metals usually lose electrons to form positively charged **cations** — for example sodium forms Na^+. Hydrogen also loses its electron to form H^+; the ammonium ion, NH_4^+, is another example of a non-metallic cation.

Non-metallic elements gain electrons to form negatively charged **anions** — for example chlorine forms Cl^-. Groups of atoms, such as the nitrate ion, NO_3^-, also carry negative charges.

In forming cations or anions, the elements involved tend to either lose or gain outer electrons to attain the electron configuration of the nearest noble gas, because these are very stable. You can see this when sodium reacts with chlorine to form sodium chloride:

$$\begin{array}{ccccccc} Na & + & Cl & \rightarrow & Na^+ & + & Cl^- \\ 2,8,1 & & 2,8,7 & & 2,8 & & 2,8,8 \end{array}$$

Note that 2, 8 is the electron configuration of neon, and 2, 8, 8 that of argon, the two noble gases nearest in electron configuration to sodium and chlorine respectively.

Now test yourself

Tested ☐

1 **Using your knowledge of the Periodic Table, predict the charges and electronic configuration of the ions formed by the elements in the following table.**

Element	Charge on the ion	Electron configuration
Magnesium		
Lithium		
Oxygen		
Aluminium		
Fluorine		
Sulfur		

Answers on p.197

How do we know that ions exist?

The evidence for the existence of ions comes from electrolysis. An electric current can be passed through a molten salt or an aqueous solution of the salt (Figure 3.1). This relies on the movement of ions in the solution carrying the charge, followed by the loss or gain of electrons at the appropriate electrode to form elements.

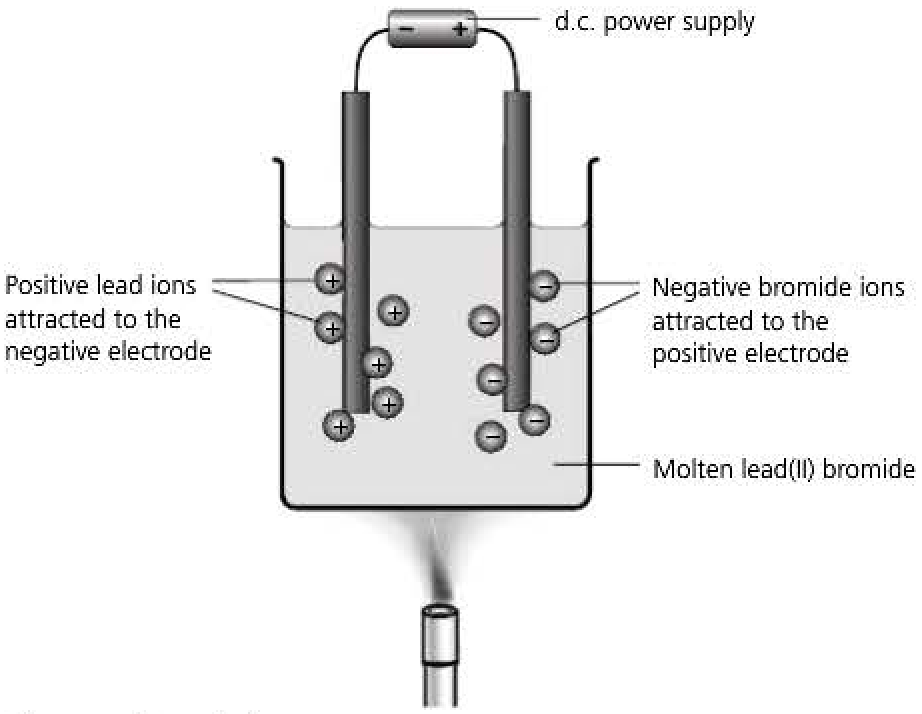


Figure 3.1 Electrolysis

Ionic crystals

In the solid state (see Chapter 4), cations and anions come together to form ionic crystals (Figure 3.2). These consist of a giant three-dimensional lattice of ions. The structure of these crystals depends on the relative sizes of the anions and cations, and on the stoichiometry of the compound concerned.

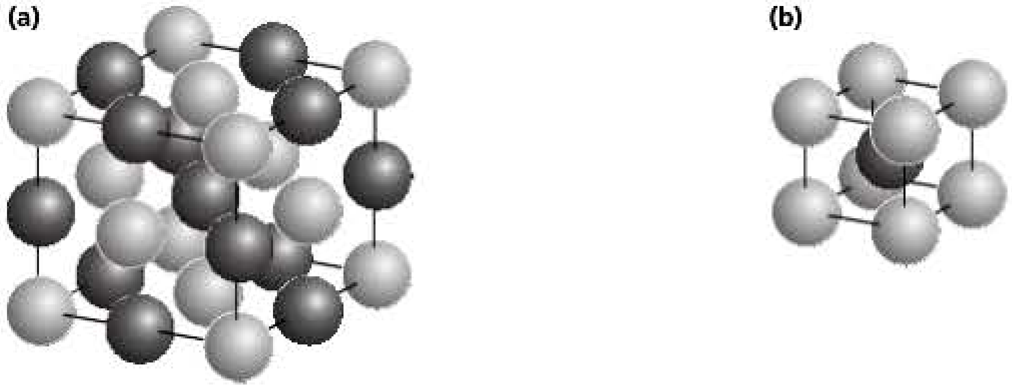


Figure 3.2 (a) Crystal structure of sodium chloride; (b) Crystal structure of caesium chloride

The three-dimensional structure in the crystal is held together by the net attractive forces between the oppositely charged ions. There are also longer-range repulsive forces between ions of the same charge, but because these are longer range they are weaker.

Covalent and coordinate (dative) bonding

Revised ☐

The major difference between ionic (electrovalent) bonding and covalent bonding is that in ionic bonding, electrons are *transferred* from one element to another to create charged ions; in covalent bonding, electrons are *shared* between atoms in pairs.

It is important to remember that electrons do not 'circle around the nucleus' but exist in a volume of space surrounding the nucleus where there is a high probability of finding an electron — these are known as orbitals. A covalent bond is formed by the overlap of orbitals containing electrons and the attraction of these bonding electrons to the nuclei of both atoms involved.

It is not essential to have atoms of different elements to form covalent bonds, so it is possible for an element to form molecules that have covalent bonds between the atoms, e.g. chlorine, Cl_2 (Figure 3.3).

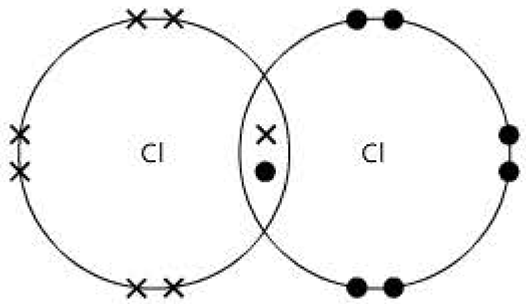


Figure 3.3 Covalent bonding in chlorine

Dot-and-cross diagrams

These are diagrams that represent the behaviour of bonding electrons in the formation of both electrovalent bonds and covalent bonds, with the electrons from one atom represented by 'dots' and those from the other atom by 'crosses'. The electrons are, of course, identical but this system helps to visualise what is happening as the bonds are formed.

In an electrovalent bond, one or more electrons are transferred from one element (usually a metal) to another element (usually a non-metal). The transfer in the formation of magnesium oxide is shown in Figure 3.4.

Now test yourself

2 Use a copy of the Periodic Table to help you draw dot-and-cross diagrams for:
- **a** hydrogen, H_2
- **b** water, H_2O
- **c** carbon dioxide, CO_2
- **d** methane, CH_4
- **e** lithium fluoride, LiF

Answers on p.197

Tested ☐

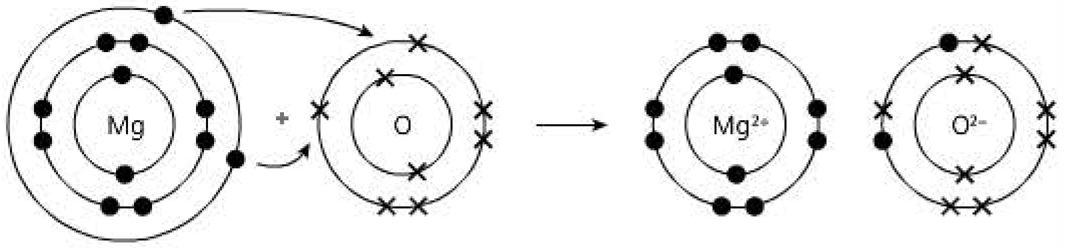


Figure 3.4 Electron transfer in the formation of magnesium oxide

The bonded atoms in a covalent compound usually have a 'share' of an octet of electrons associated with each atom, but this is not always the case. For example in boron trichloride, BCl_3, there are only six electrons associated with the boron atom (Figure 3.5).

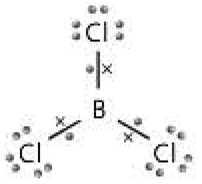


Figure 3.5 Boron trichloride

Coordinate (dative) covalent bonds are formed when both electrons in a pair come from the same atom, for example in NH_4^+ (Figure 3.6(a)). Once formed, the bond cannot be distinguished from the other covalent bonds in the compound. Figure 3.6(b) shows the same behaviour in Al_2Cl_6.

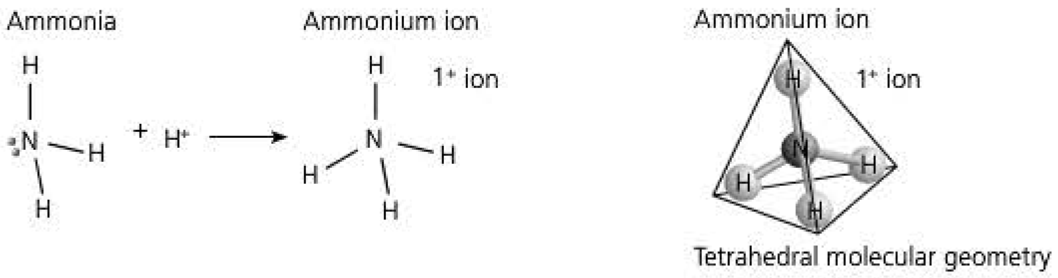
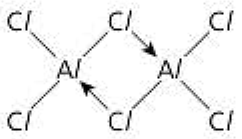


Figure 3.6 (a) Ammonium ion



(b) Aluminium chloride

There are many other examples of this type of covalent bonding — for example, in carbon monoxide, CO, and in the nitrate ion, NO_3^-, and particularly in the formation of transition metal complexes (see Chapter 12).

It is possible to have multiple covalent bonds, depending on the number of pairs of bonding electrons involved. This can occur in simple molecules such as oxygen, O_2 (Figure 3.7(a)) but is particularly important in carbon compounds such as ethene, C_2H_4 (Figure 3.7(b)). (See Chapter 15.)

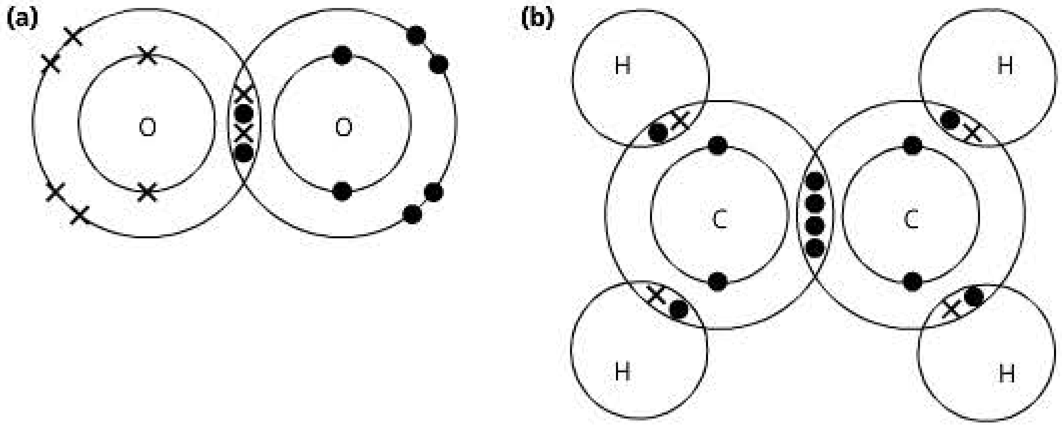


Figure 3.7 Multiple covalent bonding in (a) oxygen; (b) ethene

Simple molecular shapes

Unlike ionic (electrovalent) bonds that have no particular direction, covalent bonds are directional. This means that covalently bonded molecules have distinctive shapes depending on the number of bonds in a molecule — this is because the bonding pairs of electrons repel other pairs. Figure 3.8 shows the basic shapes that molecules containing up to four electron pairs can adopt.

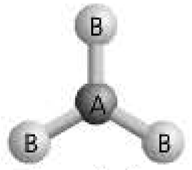
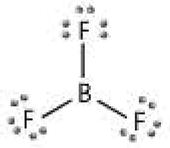
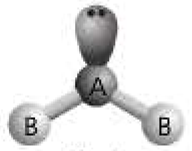
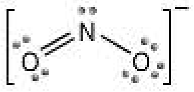
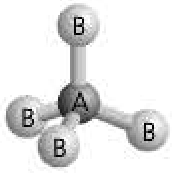
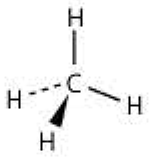
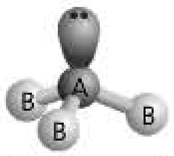
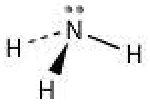
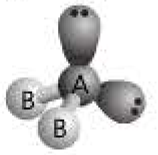
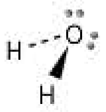
Total number of electron pairs	Electron geometry	Molecular geometry	Example
2 pairs	 Linear	 Linear	
3 pairs	 Trigonal planar	 Trigonal planar	
		 Bent	
4 pairs	 Tetrahedral	 Tetrahedral	
		 Trigonal pyramidal	
		 Bent	

Figure 3.8 Shapes of molecules

In some circumstances more than four pairs of electrons can be involved, as in the case of sulfur hexafluoride, SF_6. The repulsion effect still applies. In this case the molecule is octahedral.

In addition, any non-bonding pairs (lone pairs) of electrons will repel bonded pairs, but occupy rather more space. This means that the bond angles are widened. You can see this effect if you compare three molecules, each with four pairs of electrons — methane, CH_4, ammonia, NH_3, and water, H_2O. The normal tetrahedral angle is 109.5°, but ammonia has one lone pair of electrons that squeezes the H–N–H bond angle to 107°. In water, the two lone pairs of electrons squeeze the H–O–H bond angle even more, reducing it to 104.5°. This is shown in Figure 3.9.

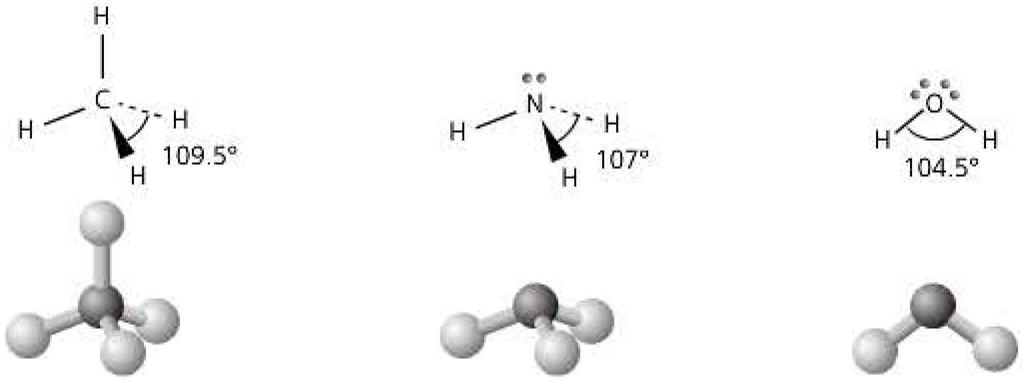


Figure 3.9 Bond angles in methane, ammonia and water

Giant molecular structures

As well as forming simple molecules like those shown in Figure 3.8, it is possible to form giant molecular structures. In the Cambridge syllabus, these are confined to different structural forms of carbon (diamond and graphite) and silicon dioxide, which is similar to diamond. Examples of these are shown in Figures 4.7 and 4.8.

Bond energies, bond lengths and bond polarities

When two atoms join by forming a covalent bond the reaction is exothermic — energy is given out. It follows that to break that covalent bond energy must be supplied.

From this you can see that **bond energies** are an indication of the strength of the forces holding the atoms together in a covalent molecule.

A **bond energy** is defined as the average standard enthalpy change for the breaking of one mole of bonds in a gaseous molecule to form gaseous atoms:

$$Br{-}Br(g) + \text{bond energy} \rightarrow 2Br(g)$$

Bond energies can vary from around 150 kJ mol^{-1} for molecules with weak bonds (such as I–I) to 350–550 kJ mol^{-1} for stronger bonds (such as C–C and O–H), to around 1000 kJ mol^{-1} for very strong bonds such as ($N\equiv N$).

Bond energy, E, increases with the number of electron pairs making up the bond. For example, $E(C{-}C)$ = 350 kJ mol^{-1}, $E(C{=}C)$ = 610 kJ mol^{-1} and $E(C\equiv C)$ = 840 kJ mol^{-1}.

Bond length is defined as the distance between the centres of the atoms at either end of the bond. The length of a bond depends on a number of factors, particularly the number of pairs of electrons making up the bond. For the three carbon–carbon bonds described above, the bond lengths are C–C, 154 pm; C=C, 134 pm and $C\equiv C$, 120 pm (1 pm is 1 picometre or 1×10^{-12} metres).

Because most covalent bonds are formed between different atoms, and different nuclei have different attractions for electrons, it follows that the electrons in many covalent bonds are pulled closer to one atom than the other and this leads to **bond polarity**.

The effect of unequal sharing of electrons is called **bond polarity**.

The degree of attraction depends on the nature of the two atoms involved — in particular, the **electronegativity** difference between the atoms involved.

A measure of this tendency to attract a bonding pair of electrons is called **electronegativity**.

You need to remember that:

- electronegativity increases from left to right across a period in the Periodic Table
- electronegativity decreases down a group
- small atoms with many protons in the nucleus have a high electronegativity
- the bigger the difference in the electronegativities of the two atoms, the more polar the bond will be

Orbital overlap: σ-bonds and π-bonds

Covalent bonds are commonly found in compounds of carbon and it is important to understand how such bonds are formed — but the same principles apply to all covalent bond formation.

In carbon atoms, the 2s- and 2p-orbitals are quite close in energy. This means that it is possible to promote one of the 2s-electrons to the empty 2p-orbital. The energy required for this promotion is more than compensated for by the energy released when four bonds are formed (compared with the two bonds that could have been formed using the two 2p-orbitals that each contained a single electron). This can be seen in Figure 3.10.

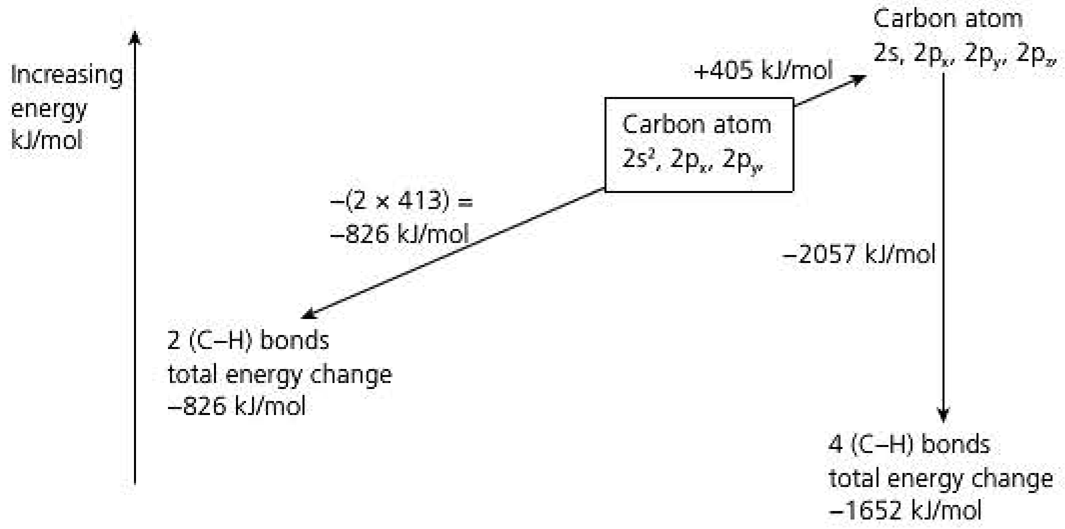


Figure 3.10 Energy benefit in forming four carbon–hydrogen bonds

The four electrons form four identical **sigma** orbitals that each have some s characteristics and some p characteristics. These are known as sp^3 hybrid orbitals. In forming methane, CH_4, they overlap with the s-orbitals of hydrogen atoms.

Bonds formed from the overlap of orbitals with some s character are called **sigma bonds** (σ-bonds).

There are two other ways in which the orbitals of a carbon atom can be sigma hybridised. First the s-orbital can be hybridised with two of the p-orbitals to form three sp^2-orbitals, leaving the remaining 2p-orbital unchanged. The three sp^2-orbitals lie in a plane 120° apart, with the 2p-orbital at right angles to this. This is the type of hybrid orbital formed by the carbon atoms in ethene and benzene.

Look at the structure of ethene. One pair of sp^2-orbitals overlap forming a σ-bond. This brings the 2p-orbitals on the two carbons close enough together for them to overlap forming a **π-bond**. The bonding in ethene is shown in Figure 3.11.

Bonds formed by the overlap of p-orbitals are called **pi-bonds** (π-bonds).

A similar bonding pattern occurs in molecules of benzene, C_6H_6. However, here the carbon atoms are arranged in a hexagonal ring. The 2p-orbitals overlap above and below the ring forming circular molecular orbitals, as shown in Figure 3.12. The electrons are said to be **delocalised** because they no longer belong to individual carbon atoms.

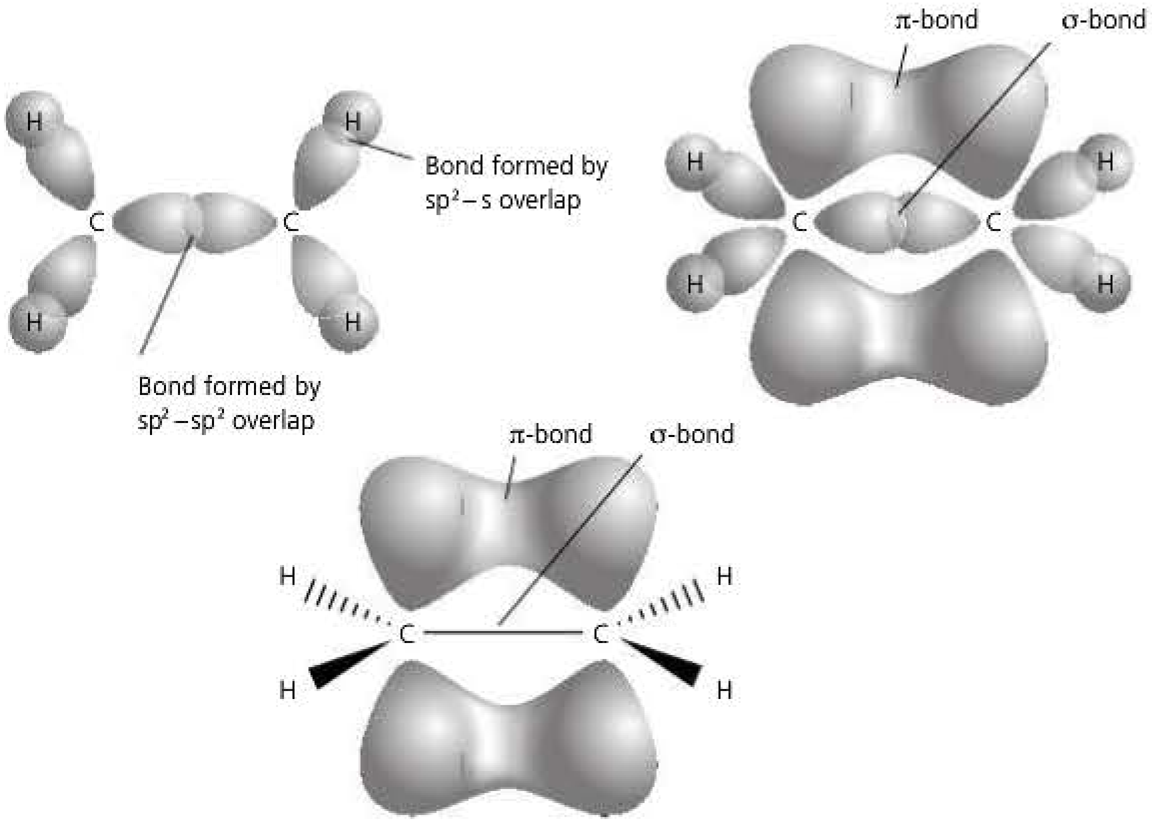


Figure 3.11 Bonding in ethene

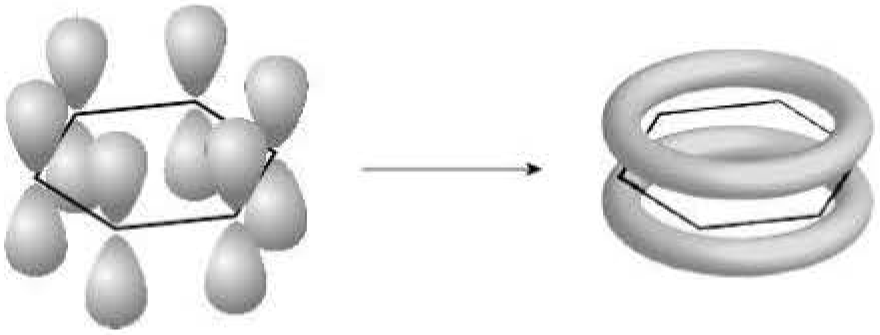


Figure 3.12 Bonding in benzene

Intermolecular forces

Revised ☐

As well as ionic (electrovalent) bonding and covalent bonding there are a number of other forces that exist between molecules. These are:

- van der Waals forces
- permanent dipole–dipole interactions
- hydrogen bonds

Van der Waals forces

These are the weakest of the forces. They act between all particles, whether they are polar or non-polar. They exist because of the movements of electrons in atoms and molecules that in turn cause instantaneous dipoles. These induce dipoles in neighbouring particles. It is because of van der Waals forces that some substances expected to exist as gases actually form liquids. Examples of this include $CHCl_3$, Br_2 and some of the Group 18 elements.

Permanent dipole–dipole interactions

These occur between polar covalent molecules, i.e. those containing different elements. One example is hydrogen chloride, HCl, as shown in Figure 3.13. Chlorine has a higher electronegativity than hydrogen.

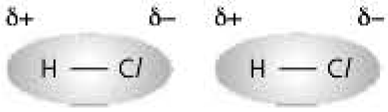


Figure 3.13 Dipole–dipole interactions in hydrogen chloride

Hydrogen bonds

There is a particular sort of comparatively strong dipole–dipole interaction between molecules containing hydrogen bonded to nitrogen, oxygen or fluorine atoms. These bonds result from the lone pairs of electrons on the nitrogen, oxygen or fluorine atoms, so that the hydrogen atoms can be considered to be acting as a 'bridge' between two highly electronegative atoms.

This form of bonding can have significant effects on the physical properties of the compound concerned. The most common, and important to us, is water (Figure 3.14).

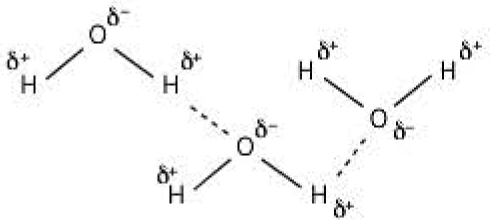


Figure 3.14 Hydrogen bonding in water

Based on its molecular mass, water would be expected to exist as a gas at room temperature. The fact that it exists as a liquid is due to hydrogen bonding. Also water has surface tension, which enables some insects to walk on its surface. The fact that ice is less dense than liquid water and floats on it is also a result of hydrogen bonding. Another of these compounds is ammonia, shown in Figure 3.15, which can be liquefied relatively easily.

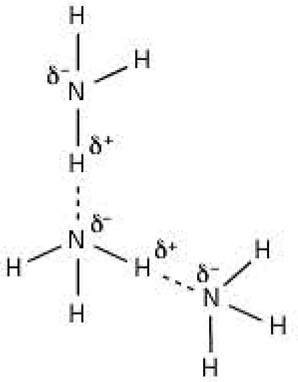


Figure 3.15 Hydrogen bonding in ammonia

Metallic bonding

Revised ☐

Metals have distinctive properties, many of which are based on the fact that metals have a structure involving a regular lattice of atoms, in much the same way as an ionic (electrovalent) crystal. The main difference is that all the atoms in a metallic lattice are the same and the outer electrons are not held by the atoms but are delocalised throughout the lattice (Figure 3.16). It is these mobile electrons that give metals their electrical conductivity.

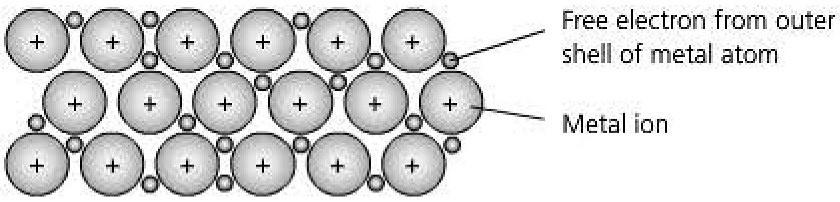


Figure 3.16 Metallic bonding

Now test yourself

Tested ☐

3 For each of the materials in the table, predict the main type(s) of intermolecular forces that exist in the material.

Material	Intermolecular force
Methanol, CH_3OH	
Magnesium oxide, MgO	
Iodine chloride, IC*l*	
Argon, Ar	
Aluminium, A*l*	

Answers on p.197

Bonding and physical properties

Revised ☐

The type of bonding in a substance affects its physical properties. Ionic (electrovalent) compounds, which have giant lattices of oppositely charged ions, tend to have high melting points and boiling points; many dissolve in water and they conduct electricity when molten.

Covalently bonded compounds tend to be gases, liquids or low melting point solids; many dissolve in covalent solvents and they are electrical insulators.

Metals have a giant lattice structure with a 'sea' of mobile delocalised electrons. In general, metals have high melting points, can be bent and shaped, and are good electrical conductors.

Revision activity

1 What is the difference between a covalent bond and an ionic (electrovalent) bond?

2 Put the following intermolecular bonds in order of increasing bond strength starting with the weakest:

hydrogen, permanent dipole–dipole, van der Waals

3 What is the bond angle in BF_3?

4 Why is there a difference in the H–X–H bond angles in CH_4 and NH_3?

5 Draw a dot-and-cross diagram to show the bonding in NH_4^+.

Answers on p.201

4 States of matter

All substances exist in one of the three states of matter — gas, liquid or solid. For AS you need to know the theories concerning particles in a gas, together with the forces between particles in gases, liquids and solids and how these influence the properties of the substances concerned.

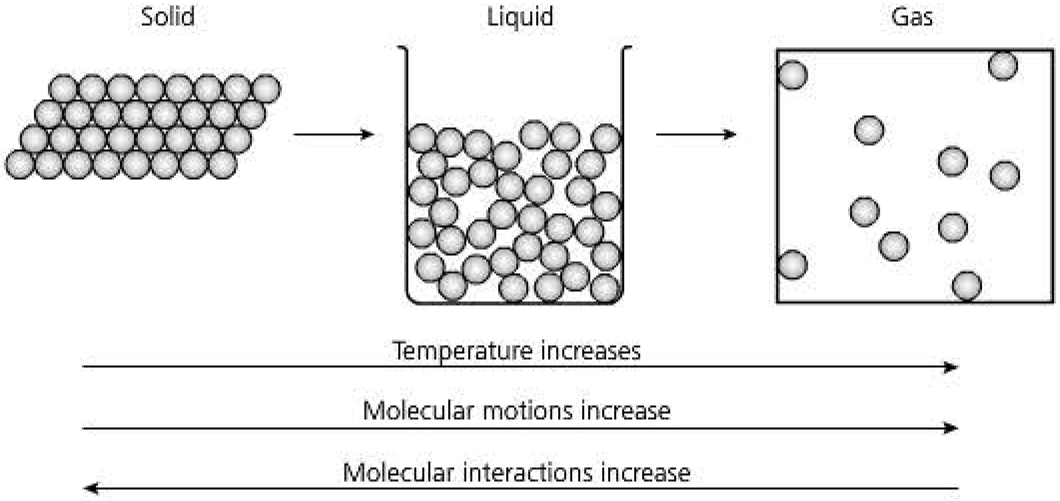


Figure 4.1 States of matter

The gaseous state

Revised ☐

It helps to have some simple ideas about gases:

- Gases have a very low density because the particles are spaced widely apart in the container.
- Gases are easily compressed because of the large spaces between the particles.
- Gases have no fixed shape or volume and, because of the lack of particle attraction, they spread out and fill the container.

The rapid and random movement of the particles in all directions means that gases readily 'spread out' or **diffuse**. The overall movement of the particles is in the direction of lower concentration from a higher concentration. This is why you can smell perfume or food (or less pleasant smells) when the source is some distance away.

Bearing these properties in mind, let's look in more detail at how gas particles interact, both with each other and with the walls of a container.

Ideal gases

You can try to explain the physical properties of gases by imagining the particles in constant random motion, colliding both with each other and with the walls of the container. The idea of an **ideal gas** is based on certain assumptions:

- The volume of the particles themselves is negligible compared with the volume of the container.
- The particles are not attracted to each other, or to the walls of the container.
- All collisions are perfectly elastic, so there is no change in the kinetic energy of the particles.
- The particles are in continuous motion, colliding frequently with each other and with the walls of the container.

These assumptions lead to the following properties of the ideal gas:

- the bombardment of the container walls by the particles causes pressure
- the average kinetic energy of the particles is directly proportional to the absolute temperature on the Kelvin scale (K)

Two laws related to gases under ideal conditions were developed by two scientists called Robert Boyle and Jacques Charles.

Boyle's law states that for a given mass of gas at a constant temperature, the product of the pressure (p) and the volume (V) is a constant:

$$pV = \text{constant}$$

Charles' law can be stated a number of ways — one is at constant pressure, for a given quantity of gas, the ratio of its volume (V) to its absolute temperature (T) is a constant:

$$\frac{V}{T} = \text{a constant}$$

These two laws can be combined to give the **ideal gas equation**:

$$pV = nRT$$

where n is the number of moles and R is a constant called the universal molar gas constant.

It is vital to make sure that you use consistent units for this equation. The most common units are shown in Table 4.1.

Table 4.1

Pressure (p)	Volume (V)	Number of moles (n)	Gas constant (R)	Temperature (T)
Pa (pascals)	m^3	mol	$8.314\,J\,mol^{-1}\,K^{-1}$	K
atm	dm^3	mol	$0.08206\,atm\,dm^3\,mol^{-1}\,K^{-1}$	K

You might be asked to use the ideal gas equation to determine the relative molecular mass, M_r, of a compound. Rearranging the ideal gas equation gives the number of moles:

$$n = \frac{pV}{RT}$$

In a known mass of gas, m, the number of moles present is $\frac{m}{M_r}$. Substituting this for n gives:

$$M_r = \frac{mRT}{pV}$$

Example

In an experiment, 0.217 g of a liquid was vaporised in a syringe placed in an oven at 80°C and 101 000 Pa pressure. The vaporised liquid gave 66.0 cm^3 of gas. Calculate the relative molecular mass of the liquid.

Answer

Using $M_r = \frac{mRT}{pV}$, because p is in Pa, R must be 8.314.

Substituting gives:

$$M_r = \frac{0.217 \times 8.314 \times 353}{101000 \times 6.6 \times 10^{-5}} = 95.2$$

Note that the volume has been converted from cm^3 to dm^3 and the temperature to 353 K.

Non-ideal (real) gases

For real gases, some of the assumptions made about ideal gases no longer apply under all conditions. At very high pressure the particles are closer together; at low temperatures the particles move less rapidly. Under both of these conditions, the volume of the particles themselves becomes significant. Because you know that gases can be liquefied under these conditions, it follows that there must be forces of attraction between the particles.

In an ideal gas, pV is a constant and a plot of pV against p would be expected to give a horizontal line. Figure 4.2 shows the results for some real gases.

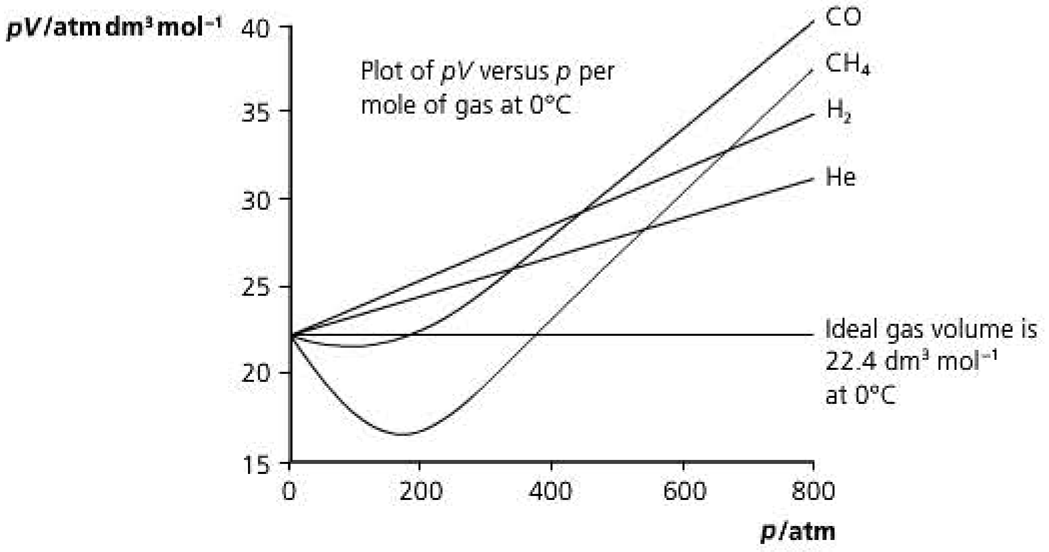


Figure 4.2 Non-ideal gas behaviour

It follows that for a real gas to behave close to ideality, it must be at low pressure and/or high temperature. In addition, it should have a small M_r and have weak forces of attraction between its particles. (Note that, in Figure 4.2, helium is the line closest to ideal.)

The liquid state

Revised ☐

Liquids are very different from gases and the properties of liquids are closer to those of solids than to those of gases. This is not too surprising if you consider the differences in the gaps between the particles in the three different states. This difference means that the intermolecular forces in a liquid are much more like those in solids than the very weak forces in gases. Figure 4.1 shows the difference in particle arrangements in the three states.

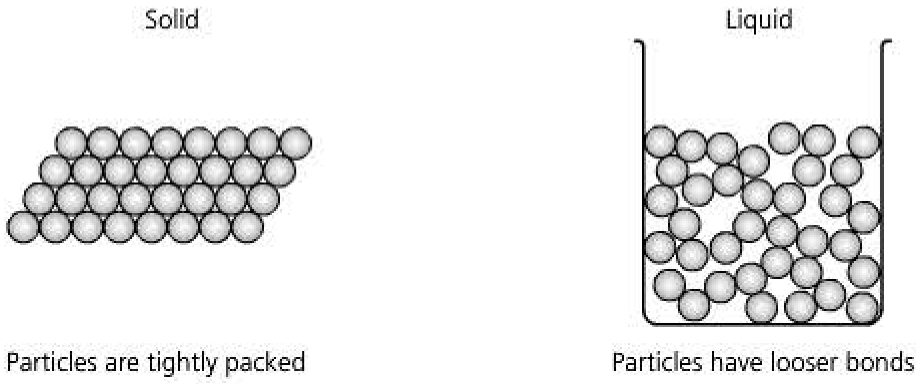
Some familiar properties of liquids are:

- Liquids have a much higher density than gases because the particles are much closer together, resulting in higher attractive forces between them.
- Liquids are not compressed easily because of the lack of space between the particles.
- Liquids have a surface and a fixed volume (at constant temperature) due to the increased particle attraction; the shape is not fixed and is determined by the shape of the container.

The random movement of the particles means that liquids can diffuse, but the diffusion is much slower in liquids compared with in gases. This is because there is less space for the particles to move around and also more collisions occur, slowing down the diffusion process.

Melting

This is the term given to the change of a solid into a liquid. The bonds between the particles in solids have to be broken for the solid to melt — in other words energy must be supplied. The particles separate, but do not move very far apart, so the energy required depends only on the strength of the original bonds in the solid lattice. This is illustrated in Figure 4.3.



Particles are tightly packed

Particles have looser bonds

Figure 4.3 Melting

Vaporisation

The changing of a liquid to a gas is called vaporisation (see Figure 4.4). This requires energy because the bonds between the liquid's particles need to be broken, and these particles are relatively close together in the liquid. The particles must also then be given enough energy for them to separate by considerable distances.

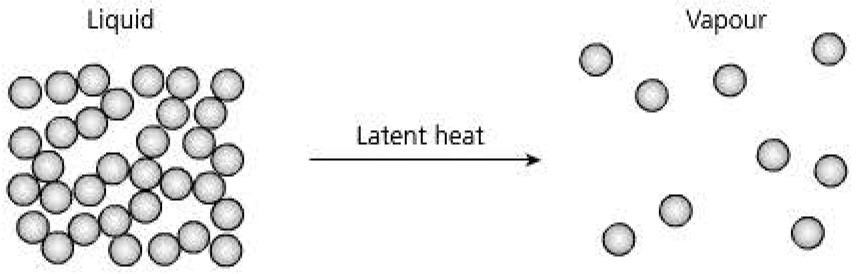


Figure 4.4 Vaporisation

Vaporisation is a process that happens at the surface of a liquid. However, boiling is rapid evaporation anywhere in the body of a liquid at a fixed temperature called the boiling point. It requires a continuous transfer of heat energy. The rate of boiling is limited by the rate of heat transfer into the liquid. Evaporation takes place more slowly than boiling at temperatures between the melting point and boiling point, and only from the surface, and results in the liquid becoming cooler due to loss of only those particles with high kinetic energy.

Heating and cooling 'curves'

There are two changes of state when a solid is heated so that it first melts and then the liquid vaporises. A graph of temperature against time (or energy supplied) for this process has an interesting shape as shown in Figure 4.5.

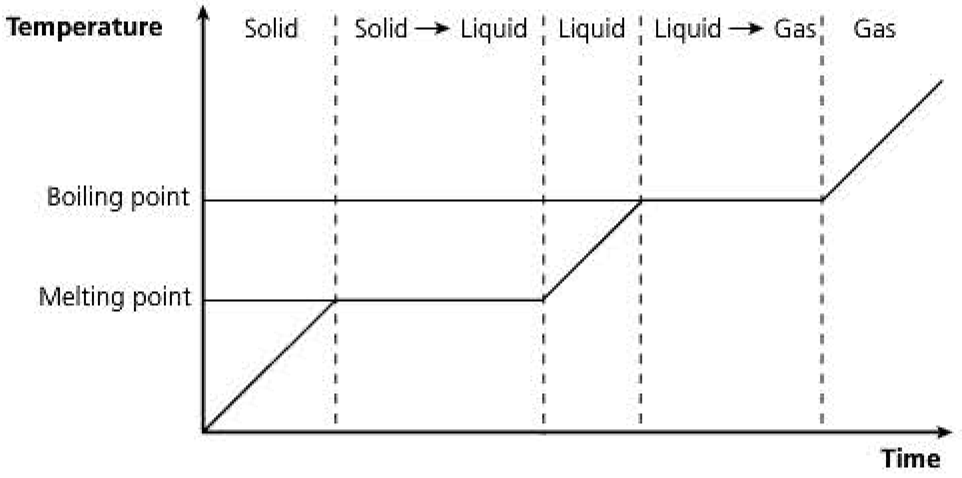


Figure 4.5 Heating curve

The two horizontal portions of the graph show that when the state of a substance changes, the energy absorbed goes into weakening the bonds between particles and so there is no temperature rise until this process is complete. The reverse is true when a hot gas is cooled, with energy being released as bonds form between the particles. This is the reason why steam produces a much worse 'burn' than a small amount of boiling water at the same temperature.

The solid state

Revised ☐

You already looked at some ideas concerned with bonding in Chapter 3, so you are familiar with the types of bonding in solids:

- ionic (electrovalent)
- covalent — simple and giant
- hydrogen
- metallic

To answer questions on this section of the syllabus you need to be able to describe a selection of crystalline solids. To do this it is usually easiest to draw a sketch and then add note annotations. These diagrams do not need to be as complex as those in a textbook, but they must show the important points (see Figure 4.6).

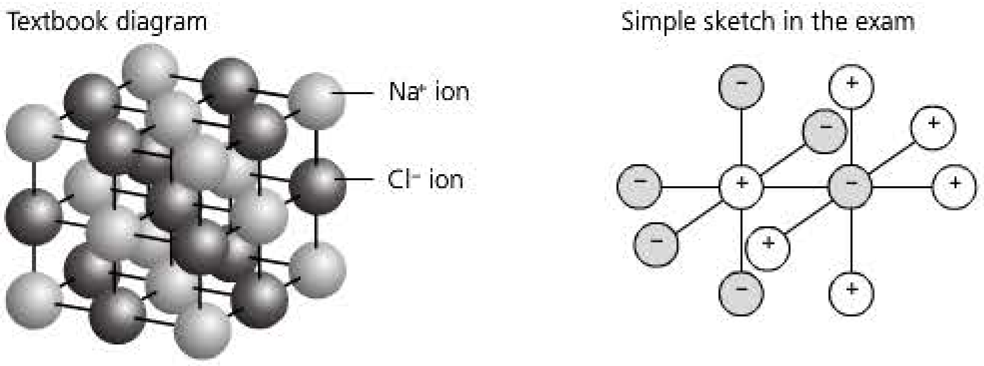


Figure 4.6 Comparison between a textbook diagram and a simple sketch

Expert tip

Exam questions may ask you to use your knowledge of bonding and structure to explain the properties of a given material. In answering such questions it is important to show both the type of structure you are dealing with and the types of bond present.

Your annotations should focus on the physical properties of the solid in terms of melting point, solubility and conductivity. Table 4.2 should help you with this.

Table 4.2

Bonding type	Melting point	Solubility	Electrical conductivity
Electrovalent, e.g. sodium chloride, magnesium oxide	High melting points due to strong electrostatic attractive forces between ions	Soluble in polar solvents because ions interact with water molecules and the lattice breaks down	Insulators when solid, conductors when molten or when in solution because the ions are mobile
Simple covalent, e.g. iodine, fullerenes	Low melting points due to weak attractive forces between the molecules	Insoluble in polar solvents but may dissolve in non-polar solvents	Insulators because there are no ions or 'free' electrons to conduct
Giant covalent, e.g. diamond, graphite, graphene, silicon(IV) oxide	Very high melting points due to strong covalent bonds in the giant lattice	Mostly insoluble in both polar and non-polar solvents	Mostly insulators due to electrons localised in bonds (graphite is an exception because of its delocalised electrons)
Hydrogen bonded, e.g. ice	Low melting points due to relatively weak attractive forces between molecules	Soluble in polar solvents because hydrogen bonds form with the solvent	Insulators having no ions or 'free' electrons to conduct
Metallic, e.g. copper	Relatively high melting points because of strong metallic bonds	Insoluble in water but may react with it	Conduct when solid because of delocalised electrons in the lattice

Allotropes of carbon

Carbon is unusual in that it exists in several different forms, known as **allotropes**. The bonding in each allotrope is different, which gives them different properties. In diamond, all the bonding electrons form a three-dimensional lattice in which each carbon atom is bonded to four adjacent atoms (Figure 4.7).

An **allotrope** is one of a number of structural forms in which an element can exist.

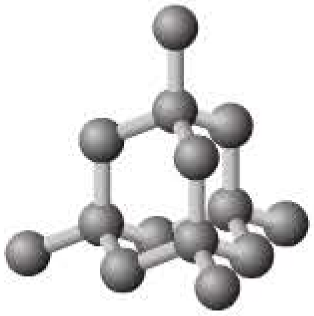


Figure 4.7 Structure of diamond

Another form (allotrope) of carbon called graphite is a good conductor of electricity, despite being a non-metal. In the case of graphite, this can be explained in terms of the structure, which consists of layers of carbon atoms joined in planes, with 'electron-rich' gaps (containing delocalised electrons) between them that carry the current (Figure 4.8).

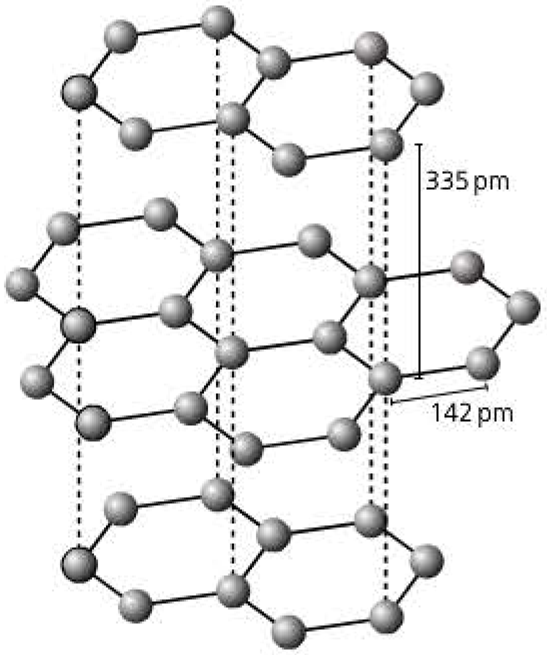


Figure 4.8 Structure of graphite

More recently, two new allotropes of carbon have been studied — fullerenes and graphene. The fullerenes can be thought of as having simple molecular structures, even though the molecules are large.

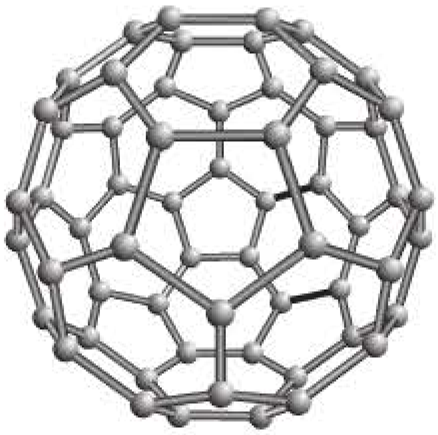


Figure 4.9 Structure of buckminsterfullerene

The discovery of a new form of a pure element is a rather rare occurrence, particularly for a common element like carbon. 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. Because the C_{60} sphere of buckminsterfullerene (a 'buckyball') is hollow, other atoms can be trapped within it.

Graphene has a giant molecular structure, like graphite. 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.

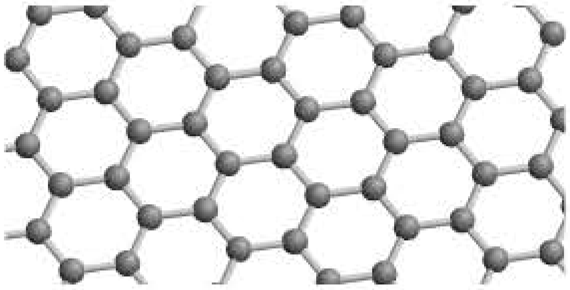


Figure 4.10 Structure of graphene

Transistors made from such samples have been shown to operate at gigahertz (10^9 Hz) frequencies — comparable to the speed of modern computers. The material could theoretically operate at close to terahertz (10^9 Hz) frequencies, hundreds of times faster.

In addition these sheets can be rolled into cylinders known as **nanotubes** (Figure 4.11) and even be combined with half a buckyball to produce nanoscale test tubes.

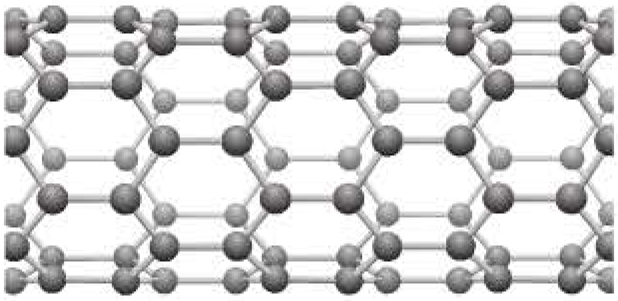


Figure 4.11 A nanotube

Now test yourself

1 What is the difference in structure between diamond and buckminsterfullerene?

Answer on p.197

Tested ☐

Ice and water

Water is an extremely unusual compound. For example, from its relative molecular mass (18.0) you would expect it to be a gas at room temperature (comparable with nitrogen (28.0), oxygen (32.0) and carbon dioxide (44.0)). It is the presence of relatively strong hydrogen bonds between molecules that makes it a liquid. Without these, life would not exist. The boiling points of some hydrogen compounds are compared in Figure 4.12.

Hydrogen bonding is also responsible for surface tension (the 'skin' that allows insects to move on the surface of water) and viscosity (the resistance of a fluid to flow). This is particularly apparent in liquids such as glycerol, $CH_2OHCHOHCH_2OH$.

Many elements form compounds with hydrogen called **hydrides**. The boiling points for the hydrides of Group 14 elements are plotted in the graph shown in Figure 4.12(a). Graphs for the boiling points of hydrides of elements in Groups 15, 16 and 17 are very different as shown in Figure 4.12(b). Although for the second and subsequent elements in each group you get the expected pattern, the first element in each group shows a much higher boiling point than expected. The reason for this is that these compounds have significantly stronger bonds between the particles. These are **hydrogen bonds**, which were discussed in Chapter 3.

Another unusual property of water is that its solid form (ice) is less dense than the liquid form (up to about 4°C). When water freezes, the random orientation of the molecules in the liquid changes gradually as hydrogen bonds form. This produces an open structure with gaps in the lattice, making the solid less dense than the liquid state (Figure 4.13).

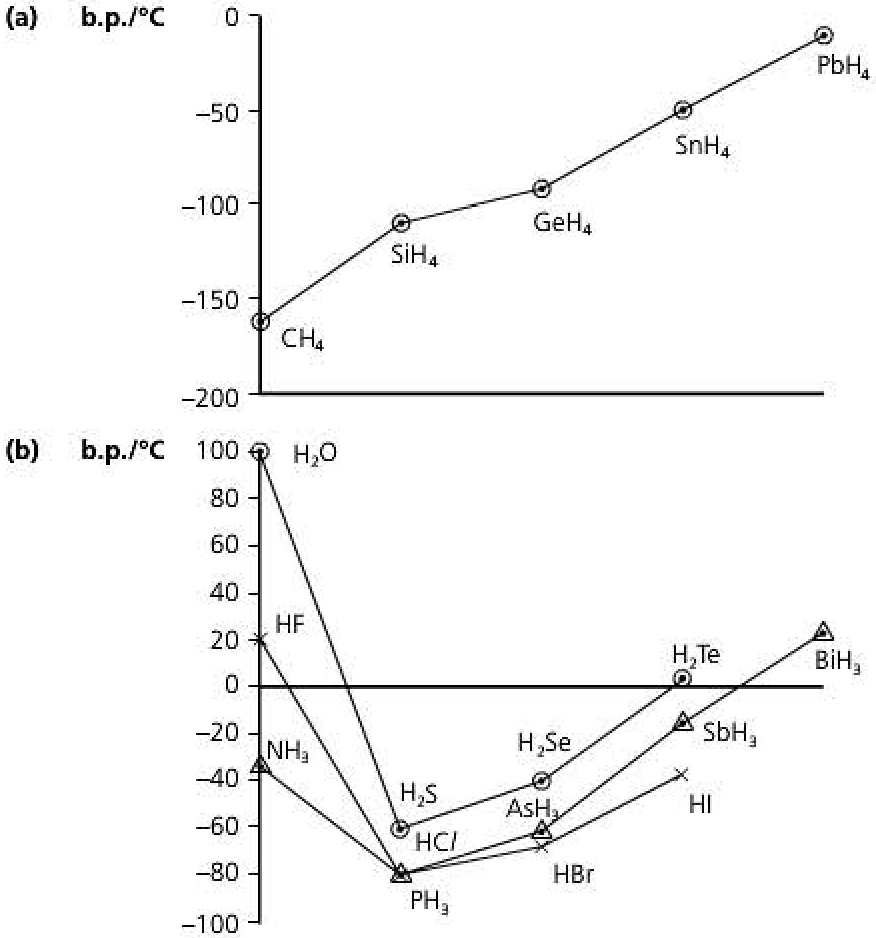


Figure 4.12 A comparison of the boiling points of some hydrogen compounds

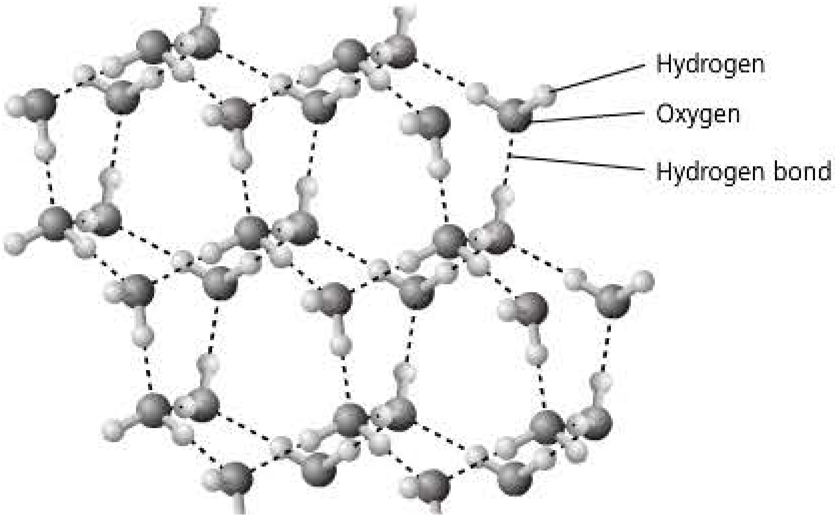


Figure 4.13 Structure of ice

The presence of hydrogen bonds in liquid water also helps it to be a good solvent for ionic (electrovalent) substances. The partially negative oxygen atom is attracted to cations and the partially positive hydrogen atoms are attracted to anions (Figure 4.14).

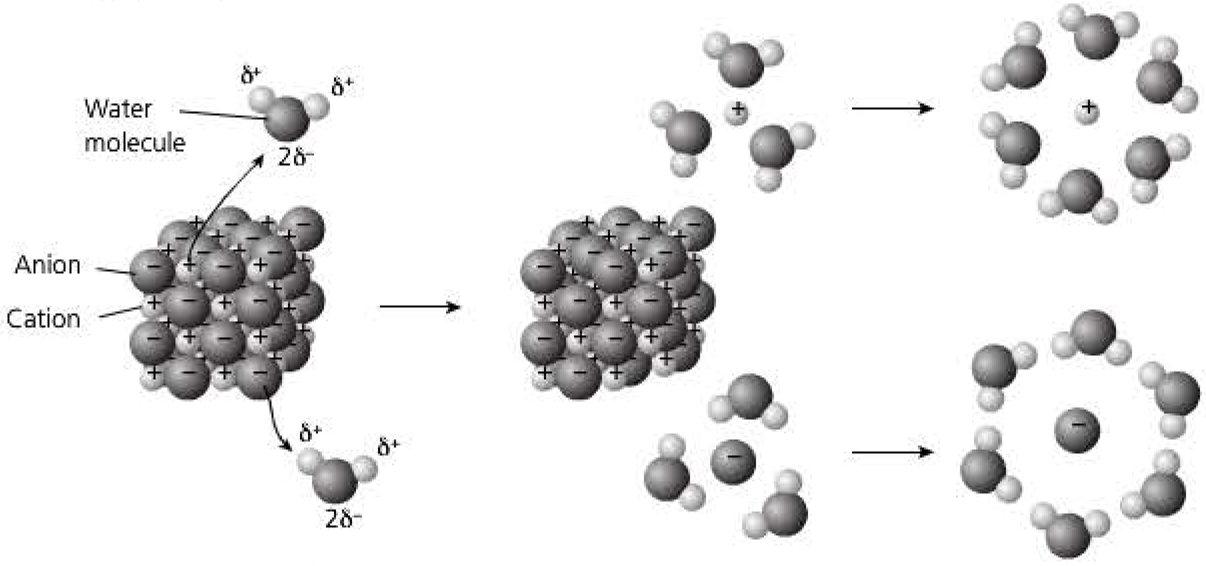


Figure 4.14 Water as a solvent

Metal alloys

Metals are of interest not just in their pure state, but also because some can form alloys — in these some atoms of one metal are substituted for some atoms in the lattice of another metal (substitutional alloys). The alloy has different properties from the original metals, for example:

- colour (as in the case of zinc and copper forming brass)
- hardness (again with brass)

Another example is the use of other metals or a non-metal (like carbon) to produce the variety of specialist steels now available. Aluminium alloys have become increasingly important as the demand for lightweight, strong materials has increased. Figure 4.15 shows the difference between a typical alloy, such as brass, and a steel (interstitial alloy), where the small carbon atoms fit between metal atoms.

Figure 4.15 Structure of (a) a typical alloy and (b) a steel

Metals have to be mined as ores and separated from the waste rock. Today, most of the ores rich in metals have already been mined and we are using ores that contain much lower proportions of metal. Under these circumstances it makes sense to try to recycle metals because new extraction from low-grade ores requires huge amounts of energy.

Now test yourself

2 Study the data given about material X. Suggest, with reasons, the type of structure and bonding present in X.

- X is a soft waxy solid that melts at just under 100°C.
- It is an electrical insulator, both as a solid and when molten.
- It dissolves in cyclohexane to give a solution that does not conduct electricity.

Answers on p.197

Tested ☐

Revision activity

1 The volume of a gas is influenced by pressure and temperature. If you have 100 cm^3 of a gas at 1 atm pressure and 298 K, what will the volume be at:

  a 1 atm and 398 K?

  b 10 atm and 298 K?

  c 10 atm and 398 K?

2 In an ideal gas we assume there are no forces between the gas particles. What physical evidence is there that in real gases there are actually forces between the particles?

3 Name one allotrope of carbon that has a simple molecular structure and two that have a giant molecular structure.

4 Copy and complete the table of properties shown below in general terms.

Substance	Melting point	Solubility	Electrical conductivity
Potassium bromide			
Aluminium			

Answers on pp.201–202

5 Chemical energetics

Almost all chemical reactions are accompanied by energy changes as bonds are broken and formed. Usually the energy changes involve heat, but they can also involve sound, light or even electrical energy.

We are most familiar with reactions that give out heat — a test tube gets warmer or a fuel is burned. These are called **exothermic** reactions. A smaller number of reactions take in energy overall and these are known as **endothermic** reactions. The overall energy changes in these two types of reaction are shown in Figure 5.1.

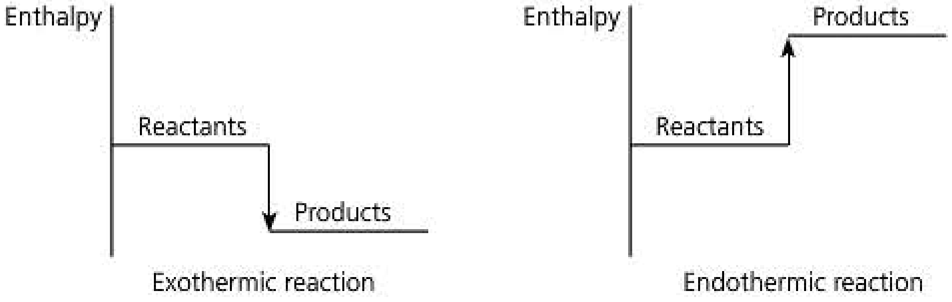


Figure 5.1 Energy change in an exothermic and an endothermic reaction

The vertical (*y*) axes in Figure 5.1 represent the enthalpy (see below) of the compounds.

You can see that in an exothermic reaction the enthalpy change is in the negative direction. This is worth remembering because exothermic reactions always show a negative enthalpy change. It follows that endothermic reactions always show a positive enthalpy change, and this is shown in Figure 5.1. Enthalpy changes are measured in kJ mol^{-1}.

In order to make sense of what happens in a chemical reaction, you need to consider **standard conditions**. Using such conditions means that the results of measurements are reproducible.

Standard conditions are:

- all the reactants and products are in their most stable state
- the pressure is 1 atmosphere
- the temperature is specified (usually 298 K, 25°C)

Now test yourself

1 Think of some examples of chemical reactions that transfer:
  a sound
  b light
  c electrical energy

Answers on p.198

Tested ☐

Enthalpy changes $\Delta H^\ominus$

Revised ☐

In textbooks you will see references made both to *energy changes* and to *enthalpy changes* — it is important to understand the difference in the way these are used in questions and in the syllabus. **Enthalpy changes** always refer to particular sets of conditions.

The examples that follow outline the specific enthalpy changes you need to know about.

The sorts of reactions for which you may need to measure or calculate the enthalpy change are:

- **formation** — the enthalpy change when 1 mole of a substance is formed from its elements under standard conditions, for example:

  $2Li(s) + \frac{1}{2}O_2(g) \rightarrow Li_2O(s) \qquad \Delta H^\ominus = -596\ \text{kJ mol}^{-1}$

A **standard enthalpy change** refers to the energy transferred at 298 K and standard pressure (usually 1 atmosphere or 100 kPa, although some textbooks refer to 1 atmosphere as 101 kPa).

- **combustion** — the enthalpy change when 1 mole of a substance is completely burned in excess oxygen under standard conditions, for example:
  $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \quad \Delta H^\ominus = -882\,kJ\,mol^{-1}$
- **hydration** — the enthalpy change when 1 mole of gaseous ions become hydrated under standard conditions, for example:
  $Al^{3+}(g) + aq \rightarrow Al^{3+}(aq) \quad \Delta H^\ominus = -4613\,kJ\,mol^{-1}$
- **solution** — the enthalpy change when 1 mole of a substance is completely dissolved, under standard conditions, in enough solvent so that no further heat change takes place on adding more solvent, for example:
  $HCl(g) + aq \rightarrow HCl(aq) \quad \Delta H^\ominus = -74.4\,kJ\,mol^{-1}$
- **neutralisation** — the enthalpy change when an acid is neutralised by an alkali to produce 1 mole of water under standard conditions. This can also be thought of as the enthalpy change when 1 mole of hydrogen ions reacts with 1 mole of hydroxide ions:
  $H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \quad \Delta H^\ominus = -57.1\,kJ\,mol^{-1}$
- **atomisation** — the enthalpy change for the formation of 1 mole of gaseous atoms from an element under standard conditions, for example:
  $\tfrac{1}{2}O_2(g) \rightarrow O(g) \quad \Delta H^\ominus = -249\,kJ\,mol^{-1}$

Another enthalpy change you need to understand is **bond energy**, which was described in Chapter 3. This was expressed as the energy needed to *break* a bond, so it was energy supplied. This means that ΔH is positive.

The final enthalpy change you need to be aware of for A level is **lattice energy**. You need to remember that this is the *formation* of a lattice from gaseous ions, so energy is released:

$$Na^+(g) + Cl^-(g) \rightarrow Na^+Cl^-(s) \quad \Delta H^\ominus = -787\,kJ\,mol^{-1}$$

Lattice energy depends on a number of factors because it is effectively a measurement of the strength of the (usually) ionic (electrovalent) bond between particles. This depends on both the size of the particles and the charges they carry. The size also affects the arrangement of particles in the lattice (see Figure 3.2). Table 5.1 shows the lattice energies (LE) of some salts.

Table 5.1

Salt	LE/kJ mol^{-1}	Salt	LE/kJ mol^{-1}	Salt	LE/kJ mol^{-1}	Salt	LE/kJ mol^{-1}
LiF	−1036	LiCl	−853	LiBr	−807	LiI	−757
NaF	−923	NaCl	−787	NaBr	−747	NaI	−704
KF	−821	KCl	−715	KBr	−682	KI	−649

Thinking about ionic radii, it can be seen that as the ionic radius of either ion increases, the lattice energy decreases.

The effect of changing the charge on one of the ions is shown in Table 5.2.

Table 5.2

Salt	LE/kJ mol^{-1}	Salt	LE/kJ mol^{-1}
NaOH	−900	Na_2O	−2481
$Mg(OH)_2$	−3006	MgO	−3791
$Al(OH)_3$	−5627	Al_2O_3	−15916

This shows that lattice energy increases rapidly as the charges on the ions increase.

A number of the enthalpy changes described here can be measured practically, but some have to be determined indirectly using other measurements.

Thermochemical experiments are often presented in the examination practical paper, so it is important to understand how to use the measurements you make. The experiments generally use simple apparatus. You could be asked to determine, for example, the enthalpy of neutralisation of an acid or the enthalpy of displacement of copper by zinc.

Sample practical Measuring ΔH

- A known volume of an acid of known concentration is poured into a polystyrene cup.
- The temperature of the acid is measured every minute for 4 minutes.
- At the fifth minute a known volume of alkali of similar concentration is poured into the cup.
- The temperature is then measured every 30 seconds for the next 3 minutes.

A graph of temperature against time is plotted (like that in Figure 5.2).

- The higher temperature line is extrapolated back to minute 5 to correct for any heat loss from the apparatus.
- The enthalpy change, ΔH, is calculated from $mc\Delta T$, where m is the mass of solution (for dilute solutions this is the same as its volume), c is the specific heat capacity of the solution (usually taken to be that of water) and ΔT is the temperature change based on the extrapolated value.
- The enthalpy change per mole of water formed is then calculated in kilojoules.

This basic method can be used for determining different enthalpy changes.

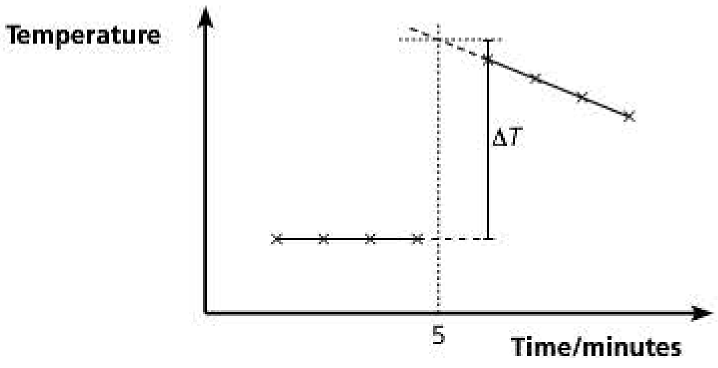


Figure 5.2

Hess' law

In simple terms, Hess' law states that the enthalpy change for a chemical process X → Y is the same whichever route is taken from X to Y, provided that the states of X and Y are the same in all routes. Using **standard enthalpy changes** avoids this problem because the states of X and Y are defined.

This means that when it is difficult to measure an enthalpy change experimentally, other data can be used. For example, the enthalpy of reaction can be calculated using enthalpies of formation:

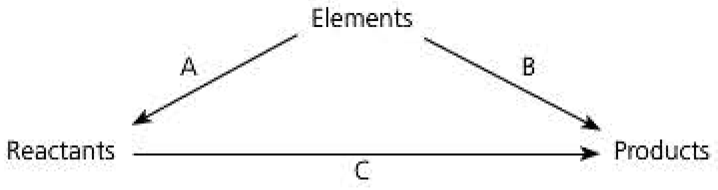


Figure 5.3 A is (sum of the enthalpies of formation of the reactants)
B is (sum of the enthalpies of formation of the products)
C is therefore (B – A)

You can see how this works in practice from this example.

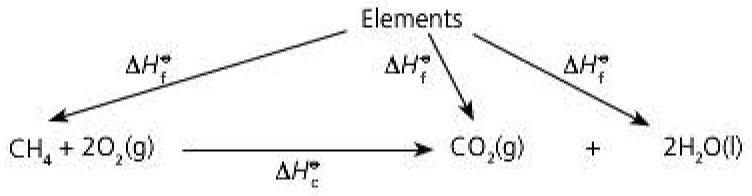


Figure 5.4

Figure 5.4 shows how the enthalpy change for the combustion of methane, CH_4, can be calculated using the enthalpies of formation of methane, carbon dioxide and water.

$$\Delta H^\circ_c(CH_4) = \Delta H^\circ_f(CO_2) + 2\Delta H^\circ_f(H_2O) - \Delta H^\circ_f(CH_4)$$

Inserting the values of $\Delta H_f^\ominus$ for the three compounds gives:

$\Delta H_c^\ominus(CH_4) = -393.5 + 2(-285.8) - (-74.8)$
$= -393.5 - 571.6 + 74.8$
$= -890.3\ kJ\ mol^{-1}$

Reverse calculations to determine the enthalpy of formation of a compound using enthalpy of combustion data can also be done.

Average bond energies

Hess' law can be used to find approximate values for $\Delta H^\ominus$ using average bond energies (sometimes referred to as mean bond enthalpies). These average bond energies are determined from bonds in a variety of molecules. There is a list of those you are likely to need in the *Data Booklet*.

The Hess' law diagram for use with bond energies is shown in Figure 5.5.

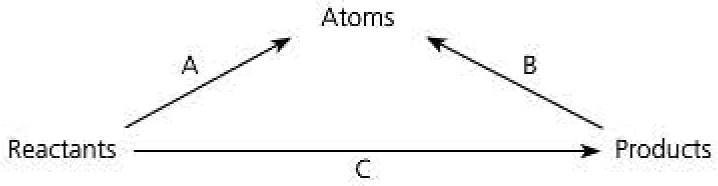


Figure 5.5 A is the sum of the bond energies of the reactants
B is the sum of the bond energies of the products
C is therefore (A – B)

Note that bond energies are always endothermic, i.e. they are *positive*.

When using bond energies it is useful to remember the following:

- Write the reaction using structural formulae so that you can see all the bonds present.
- Ignore bonds or groups of bonds that are unchanged in the reaction.
- Remember to indicate the sign of the bond energy for any bonds formed.

You need to remember something else important about reactions. Even with strongly exothermic reactions, such as the burning of magnesium, the reaction does not happen immediately when magnesium is exposed to air. In order to start the reaction the magnesium has to be heated, i.e. it has to be provided with energy. This is called the **activation energy** (see also p. 63).

Reactions can be summarised in diagrammatic form, as shown in Figure 5.6.

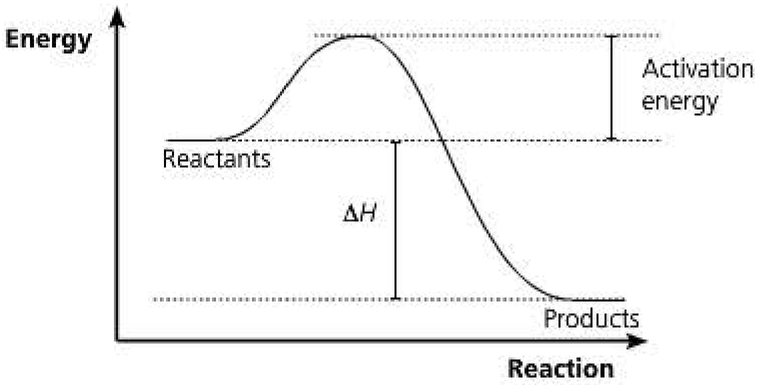


Figure 5.6 Activation energy

Some energy changes are more complicated than others. Take for example the enthalpy of formation of an ionic (electrovalent) solid such as sodium chloride. A number of enthalpy changes are involved in converting the two elements into a solid crystal lattice. These changes can be shown diagrammatically in a **Born–Haber cycle** (Figure 5.7), which uses Hess' law.

Stage 1 is the enthalpy of atomisation of sodium:

$Na(s) \rightarrow Na(g) \qquad \Delta H_1^\ominus = +108\ kJ\ mol^{-1}$

Stage 2 is the enthalpy of atomisation of chlorine:

$\frac{1}{2}Cl_2(g) \rightarrow Cl(g) \qquad \Delta H^{\ominus}_2 = +121\,\text{kJ mol}^{-1}$

Stage 3 is the first ionisation energy of sodium:

$Na(g) \rightarrow Na^+(g) \qquad \Delta H^{\ominus}_3 = +496\,\text{kJ mol}^{-1}$

Stage 4 is the electron affinity of chlorine:

$Cl(g) \rightarrow Cl^-(g) \qquad \Delta H^{\ominus}_4 = -348\,\text{kJ mol}^{-1}$

Stage 5 is the lattice energy of sodium chloride (to be determined):

$Na^+(g) + Cl^-(g) \rightarrow Na^+Cl^-(s) \qquad \Delta H^{\ominus}_5$

Stage 6 is the standard enthalpy of formation of sodium chloride:

$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow Na^+Cl^-(s) \qquad \Delta H^{\ominus}_6 = -411\,\text{kJ mol}^{-1}$

Using Figure 5.7 you can see that:

$+108 + 121 + 496 - 348 + \Delta H^{\ominus}_5 = -411\,\text{kJ mol}^{-1}$

$+377 + \Delta H^{\ominus}_5 = -411\,\text{kJ mol}^{-1}$

$\Delta H^{\ominus}_5 = -788\,\text{kJ mol}^{-1}$

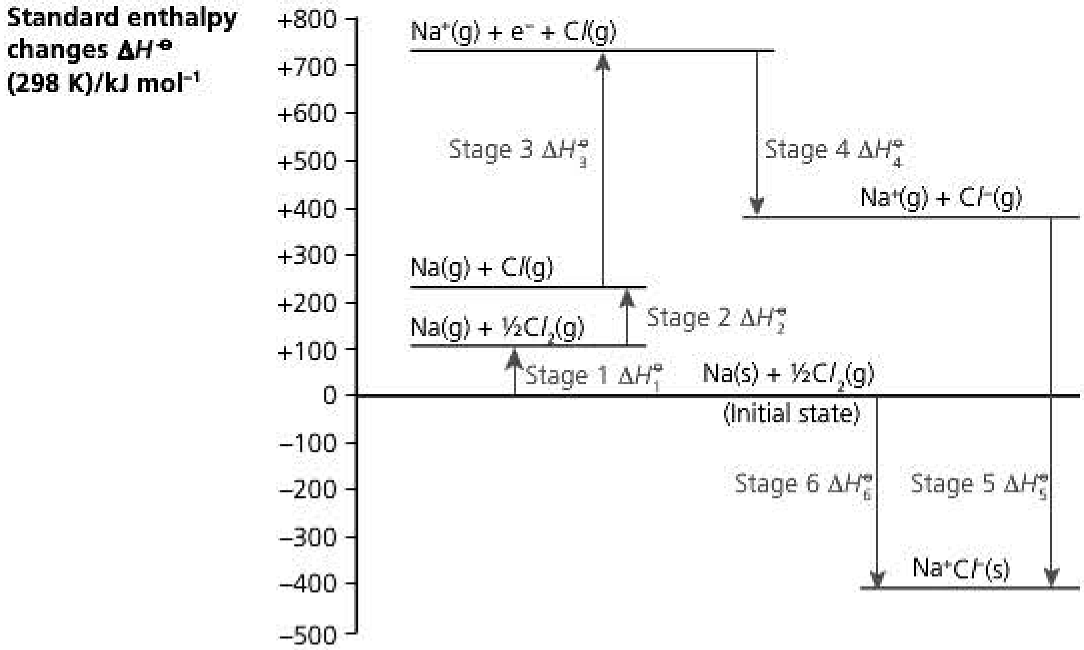


Figure 5.7 Born–Haber cycle for the enthalpy of formation of sodium chloride

You may also be asked to calculate the standard enthalpy of solution of a simple ionic solid. Once again this can be done using a Born–Haber cycle containing the enthalpy changes for the relevant steps.

Entropy change, $\Delta S^{\ominus}$

Revised ☐

Entropy is sometimes explained by saying it is a measure of the 'disorder' of a system. Another way of looking at it is to say that a system becomes more stable when its energy is spread out in a more disordered way. This all sounds very abstract, so let's look at the idea of entropy changes under different conditions.

Entropy is a measure of the number of ways that particles can be arranged in a system and the number of ways in which energy can be shared between the particles in the system.

The physical state of a substance affects its entropy, so changing the state will cause a change in entropy.

The particles in a solid just vibrate about fixed positions. There is very little 'randomness' in their motion, so they have the lowest entropy. By contrast gas particles move freely around any container and as a result show plenty of random arrangements, and have the highest entropy of the three states of matter.

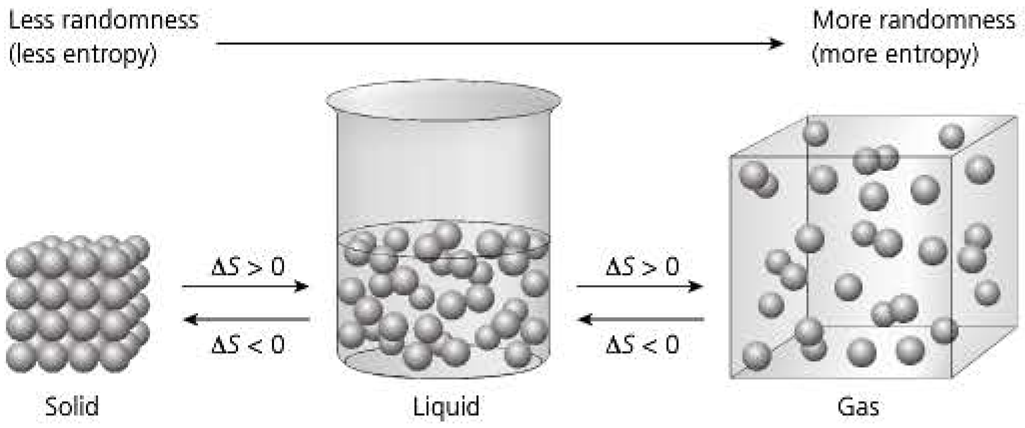


Figure 5.8 How entropy changes with change of state

Dissolving a solid also increases the entropy because the dissolved particles are no longer held in place and can move randomly.

Now let's suppose you have a chemical reaction in which the number of particles changes on heating. An example might be the decomposition of dinitrogen tetraoxide:

$$N_2O_4(g) \rightarrow 2NO_2(g)$$

The more particles there are, the more ways they and their energy can be arranged and hence the entropy increases.

When any reaction takes place, the entropy change is made up of two components — the system and the surroundings. The entropy change in the reactants and the products is the entropy change of the system. The entropy of the surroundings changes because energy is transferred to or from the system. For a chemical reaction to occur the *overall* entropy change, ΔS_{total}, has to be positive:

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

To use this, you need to know how to work out ΔS_{system} and $\Delta S_{surroundings}$. Fortunately this is not too difficult:

$$\Delta S_{system} = S_{products} - S_{reactants}$$

$$\Delta S_{surroundings} = -\frac{\Delta H}{T} = \frac{\text{enthalpy change in J mol}^{-1}}{\text{temperature in K}}$$

Example

Use standard entropies, S°, to calculate the total entropy change for the reaction between ammonia and hydrogen chloride under standard conditions.

$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$: $\Delta H^\circ = -315\,\text{kJ mol}^{-1}$ at 298 K $S^\circ(NH_3(g)) = 192\,\text{J K}^{-1}\,\text{mol}^{-1}$; $S^\circ(HCl(g)) = 187\,\text{J K}^{-1}\,\text{mol}^{-1}$; $S^\circ(NH_4Cl(s)) = 95\,\text{J K}^{-1}\,\text{mol}^{-1}$

Answer

First you need to work out the entropy of the system:

$$\Delta S_{system} = S_{products} - S_{reactants}$$
$$= 95 - (192 + 187)$$
$$= -284\,\text{J K mol}^{-1}$$

Next you need the entropy of the surroundings:

$$\Delta H^\circ = -315\,\text{kJ mol}^{-1} = -3.15 \times 10^5\,\text{J K mol}^{-1}$$

$$\Delta S_{surroundings} = -\frac{\Delta H}{T}$$
$$= -\frac{-3.15 \times 10^5}{298}$$
$$= +1057\,\text{J K}^{-1}\,\text{mol}^{-1}$$

The total entropy change is the sum of these two values:

$$-284 + 1057 = 773\,\text{J K}^{-1}\,\text{mol}^{-1}$$

Now test yourself

2 Explain the change in entropy during:

a melting wax

b condensing steam

Answers on p.198

Tested ☐

Now test yourself

3 State the sign of the entropy change in these reactions:

a $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$

b $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

c $C_6H_{12}(l) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g)$

Answers on p.198

Tested ☐

Gibbs free energy change, $\Delta G^{\ominus}$

Revised ☐

As you have seen, both the change in enthalpy (ΔH) and the change in entropy (ΔS) are important in deciding whether or not a physical or chemical change will take place.

You can link the two factors and the temperature using the **Gibbs free energy** of the system, G.

$$G = H - TS$$

Because you are looking at *changes* in enthalpy and entropy, this is more usefully written as:

$$\Delta G = \Delta H - T\Delta S$$

If the change takes place under standard conditions then the free energy change is equal to the standard free energy change, $\Delta G^{\ominus}$.

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

For any change to be spontaneous it has to happen in the direction that leads to a *decrease* in free energy, in other words ΔG must be negative. Note that any reaction for which ΔG is negative is feasible, but this tells us nothing about the *rate* of the reaction.

The **Gibbs free energy** (G) is the energy associated with a chemical reaction that can be used to do work.

Example

Calculate the change in standard free energy at 420 K and 1000 K for the reaction:

$$MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$$

	$MgCO_3(s)$	$MgO(s)$	$CO_2(g)$
$\Delta H^{\ominus}$/kJ mol^{-1}	−1113	−602	−394
$\Delta S^{\ominus}$/J K^{-1} mol^{-1}	66	27	214

Answer

For the enthalpy change:

$$\Delta H^{\ominus} = (-602) + (-394) - (-1113) = +117\ \text{kJ mol}^{-1}$$

For the entropy change:

$$\Delta S^{\ominus} = 27 + 214 - 66 = 175\ \text{J K}^{-1}\ \text{mol}^{-1} \text{ or } 0.175\ \text{kJ mol}^{-1}$$

For the free energy change:

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

$$\Delta G^{\ominus}_{420} = +117 - (420 \times 0.175) = +43.5\ \text{kJ mol}^{-1}$$

$$\Delta G^{\ominus}_{1000} = +117 - (1000 \times 0.175) = -58\ \text{kJ mol}^{-1}$$

So at 420 K the value of $\Delta G^{\ominus}$ is positive and so the reaction will not occur, whereas at 1000 K the value of $\Delta G^{\ominus}$ is negative and the reaction takes place. We have assumed that $\Delta H^{\ominus}$ and $\Delta SH^{\ominus}$ do not change with temperature.

Revision activity

1 Identify the types of enthalpy changes shown in these equations:
  - **a** $Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$
  - **b** $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$
  - **c** $Fe^{2+}(g) + aq \rightarrow Fe^{2+}(aq)$

2 Sketch a Hess' law cycle to show how you could work out the enthalpy of combustion, $\Delta H^{\ominus}_c$, of ethane, C_2H_6.

3 Use the following data to calculate the enthalpy of combustion, $\Delta H^{\ominus}_c$ of ethane:
$\Delta H^{\ominus}_f(CO_2) = -393.5\ \text{kJ mol}^{-1}$; $\Delta H^{\ominus}_f(H_2O) = -241.8\ \text{kJ mol}^{-1}$; $\Delta H^{\ominus}_f(C_2H_6) = -84.7\ \text{kJ mol}^{-1}$.

4 How would you expect the enthalpy of combustion to change if we used ethene, C_2H_4, instead of ethane, C_2H_6?

Answers on p.202

6 Electrochemistry

This chapter contains a fairly small amount of material needed for AS, and a much larger section of material for A level.

Redox processes

Revised ☐

The word **redox** comes from two familiar words — **red**uction and **ox**idation — and refers to what happens in chemical reactions in which electrons are gained or lost.

When a metal is oxidised, it loses electrons, for example:

$$Mg \rightarrow Mg^{2+} + 2e^-$$

When magnesium is burned in air, the electrons released by magnesium atoms are picked up by oxygen atoms, reducing them to oxide ions:

$$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$$

Oxidation and reduction do not only occur with elements — for example, species such as iron(II) ions can be oxidised to iron(III) ions:

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$$

Reduction of one ion to form another ion can also occur, such as in a manganate(VII) titration:

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$$

You may be given equations and asked for the change in oxidation number (oxidation state) of one of the elements present. In these cases it is often easier to think of oxidation numbers on a line as shown in Figure 6.1.

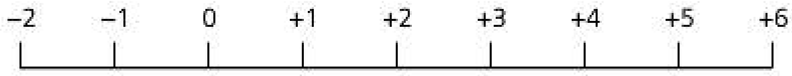


Figure 6.1

Using this idea, if you mark the reduced and oxidised species at the correct points on the line, you can see the change in oxidation number, and the number of electrons lost or gained.

Example

Consider the oxidation of hydrogen sulfide to form sulfur dioxide:

$$2H_2S(g) + 3O_2(g) \rightarrow 2SO_2(g) + 2H_2O(l)$$

What is the change in oxidation number of sulfur?

Answer

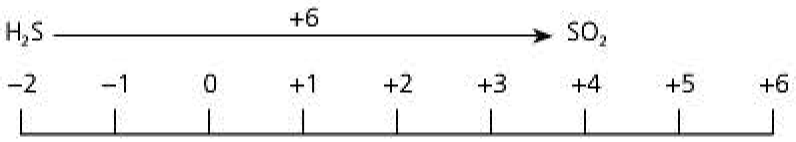


Figure 6.2

As you can see from the diagram, you count the distance between the two oxidation numbers. In this case the change is from −2 to +4; or a change of +6.

To work out oxidation numbers there are some simple rules to follow:

- Atoms of uncombined elements have an oxidation number of zero.
- Simple ions have an oxidation number equal to the charge on the ion.
- In complex ions, the sum of the oxidation numbers in all the elements present equals the overall charge on the ion.

Now test yourself

Tested ☐

1 What is the oxidation number of iron in each of the following substances:

a Fe_2O_3

b Fe

c Na_2FeO_4

2 What are the oxidation numbers of manganese in this reaction?

$2KMnO_4 + MnO_2 + 4KOH \rightarrow 3K_2MnO_4 + 2H_2O$

Answers on p.198

Electrolysis

Revised ☐

The converse of using chemical reactions to generate electricity is to use electricity to bring about chemical reactions. You have already seen examples of this in the chemical industry for GCSE. For A-level you may be asked to predict the identity of substances made during electrolysis knowing the state (molten or aqueous) and concentration of the electrolyte and the position of the element in the redox series (its electrode potential).

Like all chemical reactions, it is possible to calculate quantities of materials used or produced in such a process. In the case of electrolysis you can work out, for example, how many electrons are needed to produce one atom of aluminium:

$$Al^{3+} + 3e^- \rightarrow Al$$

The quantity of electricity needed to make 1 mole of a product depends on the number of electrons needed to make each atom, the charge on an electron and the number of atoms involved. The magnitude of the charge per mole of electrons is called the Faraday constant and is usually quoted as 96 500 C mol^{-1}. This is expressed as:

$$F = Le$$

where L is the Avogadro constant and e the charge on the electron.

In an examination you might be asked to calculate the quantity of charge passed during electrolysis, or the mass and/or volume of a substance made during the process. Let's look at how you might tackle this.

Example

What mass of copper is produced at the cathode when 2.40 A are passed through a solution of copper(II) sulfate for 25 minutes?

Answer

First, calculate the number of coulombs of charge passed. Remember that charge equals current in amps multiplied by time in seconds:

$$2.40 \times 25 \times 60 = 3600\,\text{C}$$

Next, calculate how many moles of electrons this corresponds to:

$$\frac{3600}{96\,500} = 3.73 \times 10^{-2}\,\text{mol}$$

Because copper(II) ions have a charge of +2 this corresponds to:

$$\frac{3.73 \times 10^{-2}}{2}\text{ mol of copper}$$

So the mass of copper produced is $\frac{3.73 \times 10^{-2}}{2} \times 63.5 = 1.18\,\text{g}$

In the electrolysis of a solution of sodium sulfate, Na_2SO_4, or sulfuric acid, H_2SO_4, the product at the cathode is hydrogen gas. Instead of using mass, you can use the volume as a fraction of the molar volume of a gas, $24\,dm^3$.

A value for the Avogadro constant can be determined using electrolysis. This requires the measurement of the mass of an element, such as copper, produced in a fixed period of time at a constant known current, to be measured as accurately as possible. Knowing the charge on the copper(II) ion you can then use $F = Le$ to determine L, the Avogadro constant.

Some exam questions may ask you to predict what substances are liberated at a given electrode. To answer this you need to check if the electrolysis is taking place in the molten salt or in an aqueous solution, and then consider the electrode potentials and concentrations of the ions.

- If it is a molten salt there can only be one element discharged at each electrode.
- If it is an aqueous solution it is possible for hydrogen to be discharged at the cathode and oxygen at the anode:

  $4H^+ + 4e^- \rightarrow 2H_2(g)$ $\quad E^\ominus = 0.00\,V$

  $4OH^- - 4e^- \rightarrow 2H_2O(l) + O_2(g)$ $\quad E^\ominus = -0.40\,V$

To decide which ions are discharged, you need to compare $E^\ominus$ for the half-cell reactions above with those of the other ions in solution.

Consider the electrolysis of a concentrated solution of sodium chloride. Hydrogen is produced at the cathode because hydrogen ions accept electrons more easily than sodium ions. On the other hand, chlorine is produced at the anode because chloride ions are present in a higher concentration than hydroxide ions.

Electrode potentials

Revised ☐

There are two aspects to electrochemistry — the first involves using electricity to make chemical reactions happen (electrolysis). The second involves chemical reactions generating an electric current (electrode potentials).

It is important that you learn two definitions linked to electrode potentials.

A **standard electrode (redox) potential** is defined as the electrode potential measured under standard conditions (temperature 298 K, 1 atmosphere pressure, 1 mole of the redox participants of the half-reaction) against a standard hydrogen electrode.

A **standard hydrogen electrode** is shown in Figure 6.3.

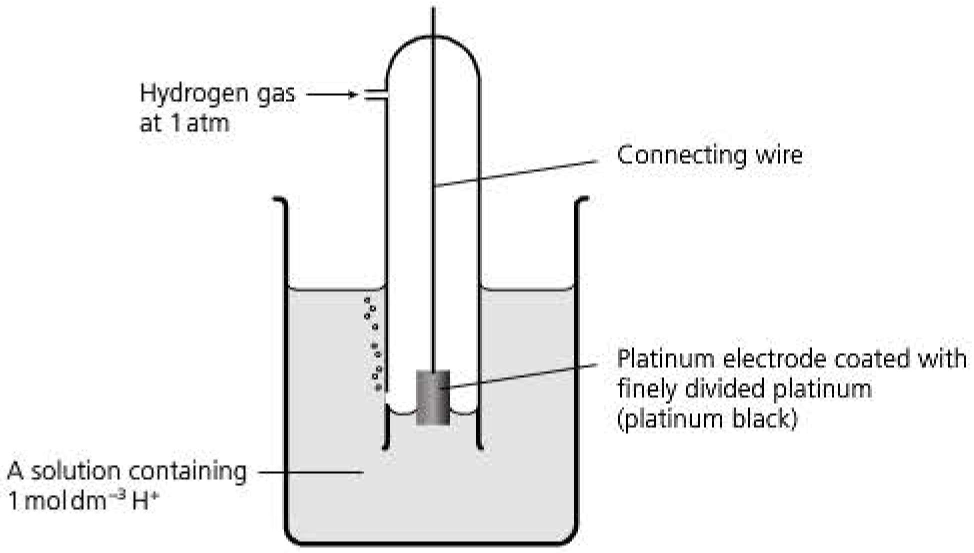


Figure 6.3 A standard hydrogen electrode

Expert tip

It is important to be able to draw a standard hydrogen electrode in an exam.

In Figure 6.4 you can see how the standard electrode potential of another electrode can be measured using the hydrogen electrode.

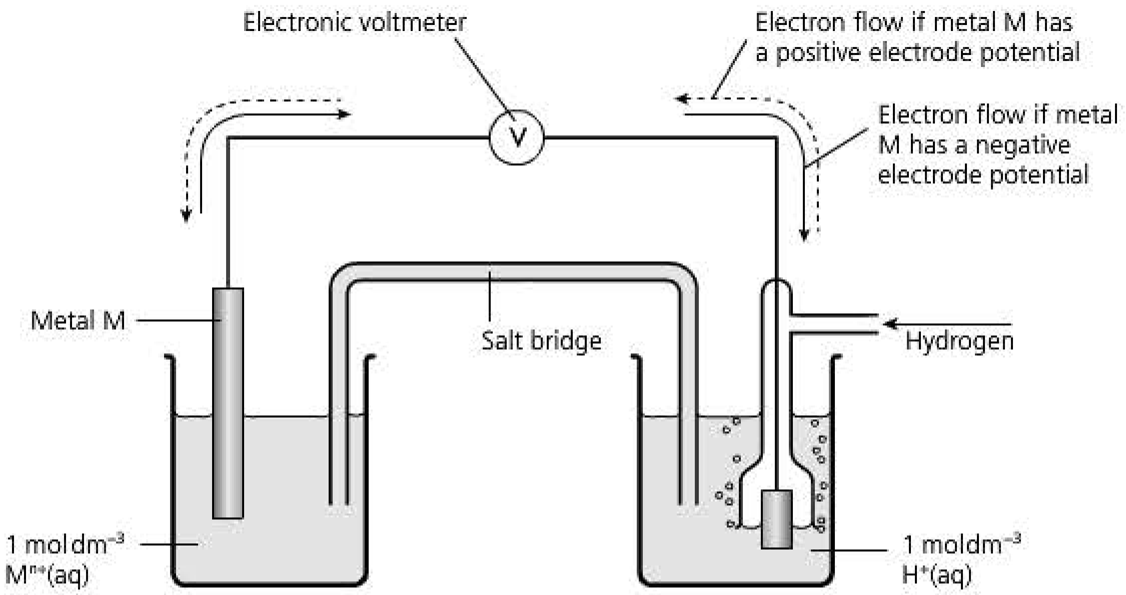


Figure 6.4 Measuring a standard electrode potential

Standard cell potential is the potential produced when two standard electrodes are connected to form a cell.

Two standard electrodes connected to form a cell are shown in Figure 6.5.

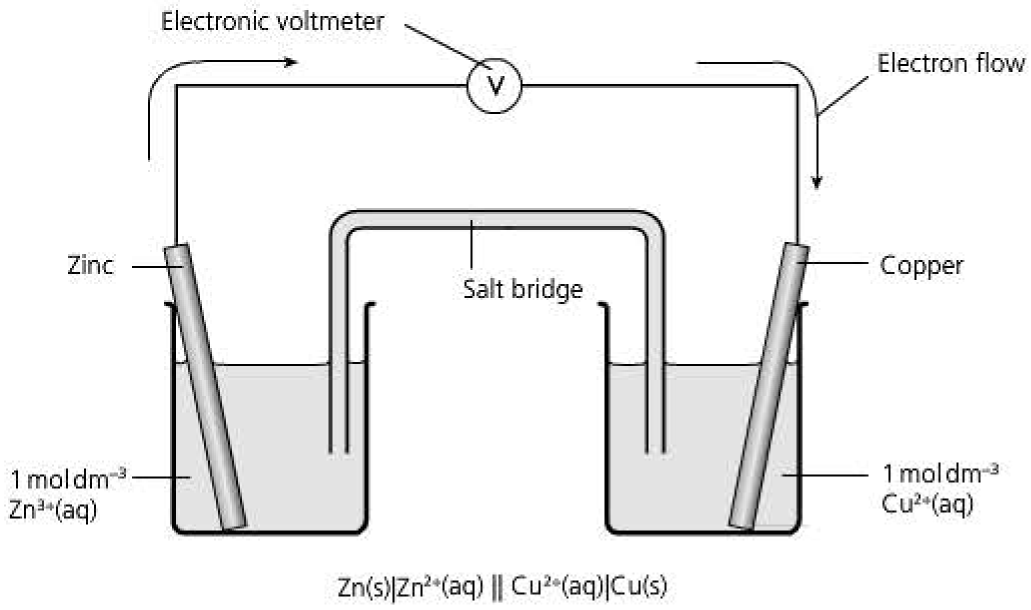


Figure 6.5 Apparatus for determining a standard cell potential

A cell potential has a contribution from the anode, which is a measure of its ability to lose electrons — its **oxidation potential**. The cathode has a contribution based on its ability to gain electrons — its **reduction potential**. The cell potential can then be written as:

$$E_{\text{cell}} = \text{oxidation potential} + \text{reduction potential}$$

As with oxidation numbers, when calculating an overall cell potential it helps to work using a linear scale from negative to positive as shown in Figure 6.6.

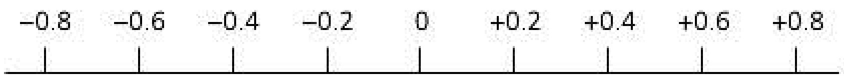


Figure 6.6

In the cell shown in Figure 6.6, the oxidation potential of the zinc anode is +0.76 V, and the reduction potential of the copper cathode is +0.34 V.

$$E_{\text{cell}} = 0.76 + 0.34 = 1.10\text{ V}$$

Care must be taken to change the signs given in electrode potential data tables to reflect what is happening. These data are given in terms of the *reduction* of the ions concerned. When you are drawing a cell, remember to show the reactants with oxidation occurring on the right and reduction on the left. This means that in the cell described in Figure 6.5 you would write:

$Zn(s)|Zn^{2+}(aq) \,||\, Cu^{2+}(aq)|Cu(s)$

because zinc atoms are oxidised and copper ions are reduced.

Non-metal electrodes

Measuring the standard electrode potential of a non-metal element presents different problems. However, you have already seen one way of overcoming this in the hydrogen electrode. The cell shown in Figure 6.7 shows how two non-metallic elements can form a cell.

Now test yourself

3 Use the table of standard electrode potentials in the *Data Booklet* in the syllabus to calculate the cell potentials for the following electrode pairs:

- **a** $Zn(s)|Zn^{2+}(aq) \,||\, Ag^{+}(aq)|Ag(s)$
- **b** $Mg(s)|Mg^{2+}(aq) \,||\, Pb^{2+}(aq)|Pb(s)$
- **c** $Cu(s)|Cu^{2+}(aq) \,||\, Ag^{+}(aq)|Ag(s)$

Answers on p.198

Tested ☐

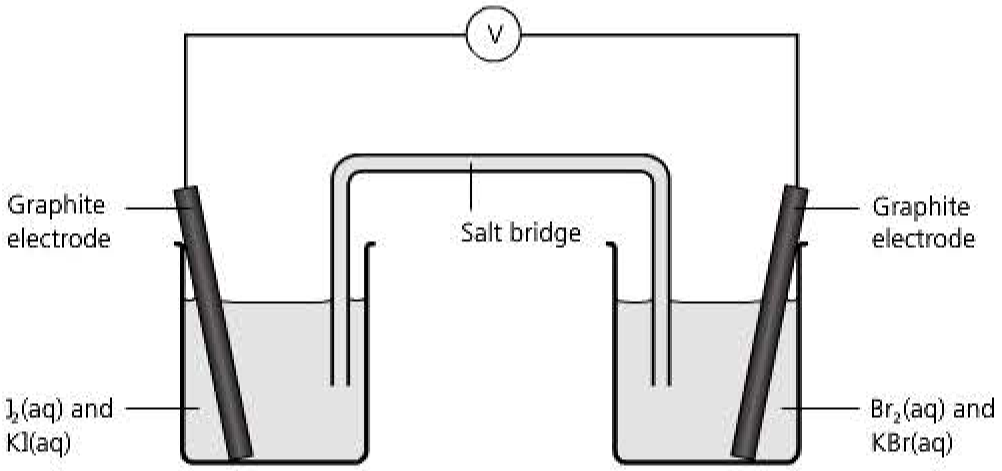


Figure 6.7 A cell formed using two non-metallic elements

The same basic technique can be used for ions of the same element in different oxidation states. The set-up can be seen in Figure 6.8. The electrodes chosen in each case are platinum, although in the laboratory you may have used carbon.

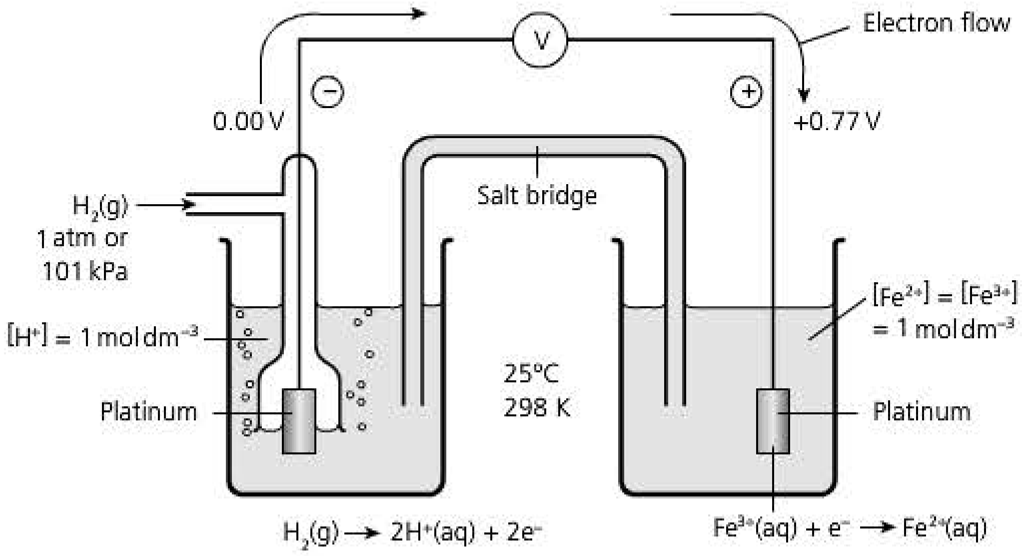


Figure 6.8 A cell formed using ions of the same element

Now test yourself

4 Use the table of standard electrode potentials in the *Data Booklet* in the syllabus to calculate the cell potentials for the following electrode pairs, which include non-metals:

- **a** $Mg(s)|Mg^{2+}(aq) \,||\, \frac{1}{2}Cl_2(g)|Cl^-(aq)$
- **b** $Pb(s)|Pb^{2+}(aq) \,||\, \frac{1}{2}Br_2(l)|Br^-(aq)$
- **c** $Fe^{2+}(aq)|Fe^{3+}(aq) \,||\, \frac{1}{2}Cl_2(g)|Cl^-(aq)$
- **d** $Br^-(aq)|\frac{1}{2}Br_2(l) \,||\, \frac{1}{2}Cl_2(g)|Cl^-(aq)$

Answers on p.198

Tested ☐

Predicting reactions

Revised ☐

As well as using electrode potentials to calculate the voltage that a particular combination of electrodes will produce under standard conditions, they can also be used to predict how likely a given chemical reaction is.

In Table 6.1, the half-reactions with high *negative* $E^\ominus$ values do *not* happen readily (think of the reactions of the Group 1 metals with water). By contrast, those with high *positive* $E^\ominus$ values happen spontaneously (think of manganate(VII) as an oxidising agent).

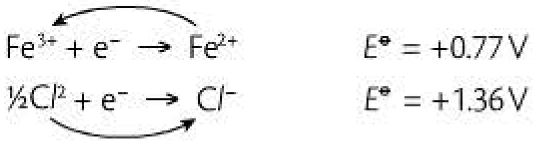
Table 6.1

Metal electrodes	Voltage/V	Non-metal electrodes	Voltage/V
$K^+ + e^- \rightleftharpoons K$	−2.92	$\frac{1}{2}F_2 + e^- \rightleftharpoons F^-$	+2.87
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	−2.38	$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.52
$Al^{3+} + 3e^- \rightleftharpoons Al$	−1.66	$\frac{1}{2}Cl_2 + e^- \rightleftharpoons Cl^-$	+1.36
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0.76	$NO_3^- + 2H^+ + e^- \rightleftharpoons NO_2 + H_2O$	+0.81

Half-equations can be used to construct full equations by making sure that the numbers of electrons balance and that the overall cell potential is positive. There are some key points that help you to get this right:

- Write the half-equation with the more negative $E^\ominus$ value first.
- Remember that the more positive $E^\ominus$ value will involve a reduction.
- Draw anticlockwise arrows to help predict the overall reaction.

For example, consider the reaction between Fe^{2+} ions and chlorine gas. The two half-equations are:



$Fe^{3+} + e^- \rightarrow Fe^{2+}$ $\quad E^\ominus = +0.77\,V$

$\frac{1}{2}Cl^2 + e^- \rightarrow Cl^-$ $\quad E^\ominus = +1.36\,V$

Figure 6.9

Reversing the first equation and adding gives:

$$Fe^{2+} + \tfrac{1}{2}Cl_2 \rightarrow Fe^{3+} + Cl^- \qquad E^\ominus_{cell} = +0.59\,V$$

$E^\ominus_{cell}$ is positive so when chlorine gas oxidises iron(II) ions to iron(III) ions, it is reduced to chloride ions.

The effects of non-standard conditions

For most of the work you will do with electrode potentials, you can assume that conditions are standard, but you do need to know the effects of changing the concentration of an aqueous ion solution.

Think of the half-cell reaction:

$$M^{n+}(aq) + ne^- \rightleftharpoons M$$

Le Chatelier's principle (Chapter 7) predicts that if the concentration of $M^{n+}(aq)$ is increased, then the equilibrium will move to the right. If this were the case, the electrode would become more positive with respect to the solution. Hence, the electrode potential would also become more positive. This also means that the half-cell would become a better oxidising agent. Reducing the concentration of $M^{n+}(aq)$ would have the opposite effect.

The Nernst equation

You can quantify this effect using the Nernst equation:

$$E = E_f + \frac{0.059}{z} \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

to predict how the value of an electrode potential varies with the concentrations of the aqueous ions.

You can see this by considering the oxidising power of dichromate(VI) ions under different conditions.

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$$

$$E = E_f + \frac{0.059}{6} \log \frac{[Cr_2O_7^{2-}][H^+]^{14}}{[Cr^{3+}]^2}$$

Under standard conditions, $[Cr_2O_7^{2-}(aq)] = [Cr^{3+}(aq)] = [H^+(aq] = 1.0\,mol\,dm^{-3}$, so E is very close to $E^\ominus$, i.e 1.33 V.

If you now change the conditions to be in neutral solution, the hydrogen ion concentration is reduced considerably; $[H^+(aq] = 10^{-7}\,mol\,dm^{-3}$. So with the same concentrations of $Cr_2O_7^{2-}(aq)$ and $Cr^{3+}(aq)$:

$$E = 1.33 + \frac{0.059}{6}\log\frac{[1.0][10^{-7}]^{14}}{[1.0]^2}$$
$$= 1.33 + 0.00983 \times (\log 1.0 + 14 \log 10^{-7})$$
$$= 0.37\,V$$

Notice that in neutral solution, the dichromate ion has become a relatively weak oxidising agent.

Batteries and fuel cells

'Battery' is the name commonly given to portable sources of electric current and it is often inaccurate. Many so-called 'batteries' are simple cells, of which the most common is the zinc/alkali or 'dry' cell (Figure 6.10).

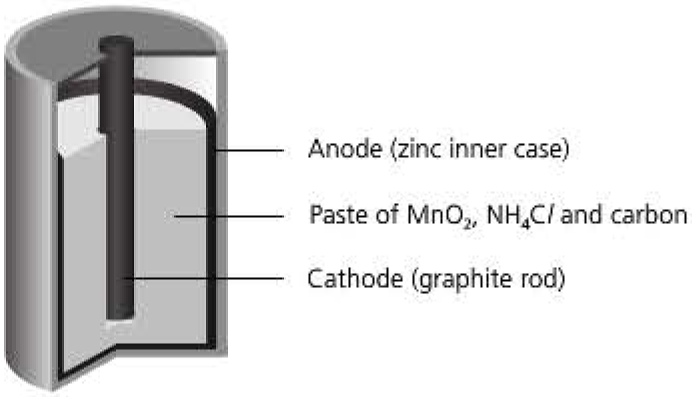


Figure 6.10 A dry cell

The reactions in a dry cell are:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$
$$MnO_2(s) + H_2O(l) + e^- \rightarrow MnO(OH) + OH^-(aq)$$

Such cells are portable and much more practical than 'wet' cells containing aqueous solutions. Others, such as 9 V batteries or 12 V car batteries, are indeed 'batteries' of cells. The problem with all such cells is that they have a finite lifetime because the materials get used up.

Batteries of various sorts have been developed over the years giving different voltages, longer life and the ability to be recharged quickly and easily.

There has also been considerable interest in the development of electrically powered cars. Conventional batteries of the lead/acid type are far too heavy and bulky to provide the power needed, so there has been much research into different ways of supplying this power. One possible development, which allows a continuous supply of electricity, is the **fuel cell.** This consists of a fuel (usually hydrogen gas) and an oxidant (oxygen gas) being pumped through the cell, shown in Figure 6.11.

The technology is relatively new and the challenge is to make sure the cells are efficient and as small and light as possible. One disadvantage of the cell shown in Figure 6.11 is that it is easily poisoned by carbon dioxide, which reacts with the alkali.

Two examples of success in the development of rechargeable batteries are those involving nickel–metal hydride cells and lithium–ion cells. Ni–MH (nickel–metal hydride) batteries were first produced in consumer quantities in the early 1990s. The batteries consist of a nickel oxyhydroxide (NiO(OH)) positive electrode with a hydrogen-absorbing alloy as the negative electrode. The electrolyte is usually a potassium hydroxide paste. The cell generates a typical voltage of 1.2 V and can be recharged between 500 and 2500 times.

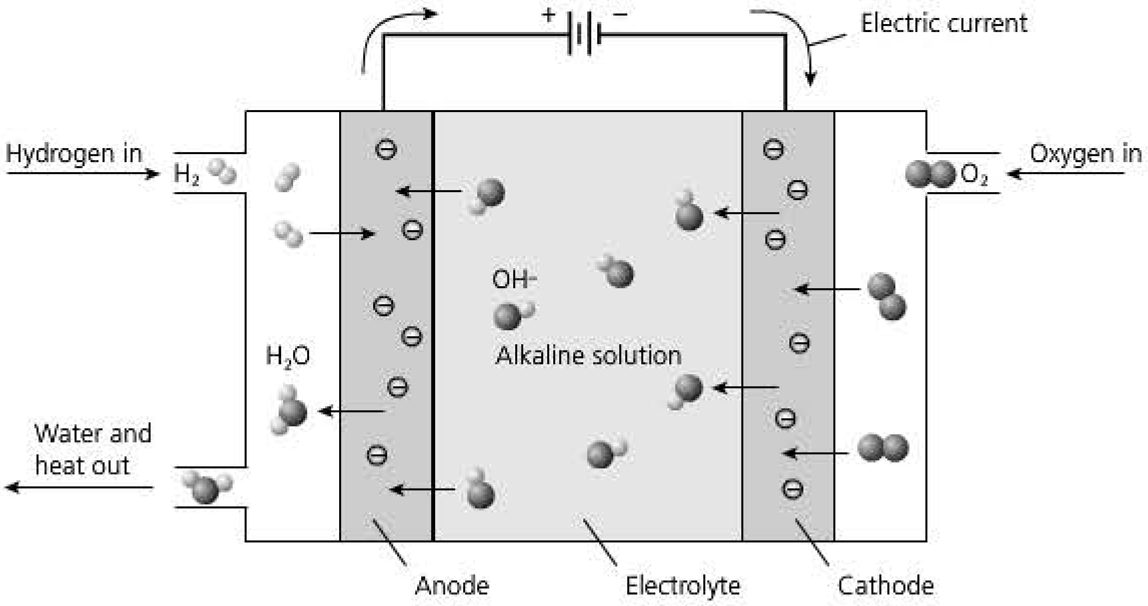


Figure 6.11 A fuel cell

Lithium–ion cells are more complex than nickel–metal hydride cells. The positive electrode consists of a mixed oxide of lithium and cobalt ($LiCoO_2$) and the negative electrode is carbon — the electrolyte consists of a lithium salt dissolved in an organic solvent.

Both of these cells are lighter than conventional alkaline cells, can be recharged a number of times and can be made into a variety of shapes, not just cylinders. The cell produces 3.6 V and can be recharged around 500 times. Although these cells present no environmental hazard they can overheat and cause fire if they are short-circuited.

Revision activity

1. What are the oxidation numbers of chlorine in the following reaction?
   $3ClO^-(aq) \rightarrow 2Cl^-(aq) + ClO_3^-(aq)$
2. Write half-equations to show how chlorine is both reduced and oxidised in the reaction above.
3. Use the table of standard electrode potentials in the *Data Booklet* to calculate these cell potentials:
   - **a** $Mg(s) \mid Mg^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$
   - **b** $Fe^{2+}(aq) \mid Fe^{3+}(aq) \parallel \frac{1}{2}Br_2(l) \mid Br^-(aq)$
4. Use the Nernst equation to predict E_{cell} for a cell containing a standard $Fe^{3+}|Fe^{2+}$ electrode and a $Cu|Cu^{2+}$ electrode in which $[Cu^{2+}(aq)]$ is $0.01\ mol\ dm^{-3}$.

Answers on p.202

7 Equilibria

This first part of this chapter deals with material needed for AS. The second part is only for A level.

Factors affecting chemical equilibria

Revised ☐

You probably think you know what the word 'equilibrium' means, and you may have used it in physics to mean 'forces in balance' or something similar. In chemistry it has a similar meaning, but here it is chemical reactions that are in balance. The $\rightleftharpoons$ sign is used to represent a reaction in equilibrium. What exactly does the word mean in a chemical context?

First, you need to understand that all chemical reactions are reversible, given enough energy. In a reversible reaction at equilibrium, the rates of the forward and backward reactions are the same. In other words, the amount of reactants forming products in a given time is the same as the amount of products breaking down to give reactants in the same time. These are generally called **dynamic equilibria**.

An example of a dynamic equilibrium established in the gas phase is the reaction of nitrogen and hydrogen to form ammonia in the Haber process:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Dynamic equilibria can also happen in the liquid phase:

$$2H^+(aq) + 2CrO_4^{2-}(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

In a dynamic equilibrium:

- there is no net change in the concentration of each substance
- the equilibrium compositions of the substances can be approached from either reactants or products

Le Chatelier's principle

The French chemist Henri le Chatelier studied many dynamic equilibria and suggested a general rule, **Le Chatelier's principle**, to help predict the changes in the position of equilibrium as different factors are changed.

Le Chatelier's principle states that if a closed system at equilibrium is subject to a change, then the system will adjust in such a way so as to minimise the effect of the change.

The factors that can be changed easily are concentration, temperature and pressure. You might also have suggested 'using a catalyst' — this possibility is looked at later.

Expert tip

You should learn the rule, but think carefully when you apply it in examinations.

Consider a general reaction:

$$mA + nB \rightleftharpoons pC + qD \quad \Delta H^\ominus \text{ –ve (exothermic reaction)}$$

If you *increase* the concentration of *either* of the reactants A or B, more of the products C and D will be made.

The general reaction shown above is an exothermic reaction. If you *increase* the temperature, there will be less of the products made. The reverse would be true for an endothermic reaction.

The influence of pressure is relevant *only* for gas phase reactions. Think back to the Haber process for making ammonia:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

There are fewer molecules on the right-hand side of the equation. This means that if you *increase* the pressure, the equilibrium will shift to produce more ammonia, reducing the total number of molecules in the system and therefore reducing the pressure.

In order to see what effect adding a catalyst might have, you have to think about the processes taking place. Look at Figure 7.1, which shows the energy profile of an equilibrium reaction with and without a catalyst present.

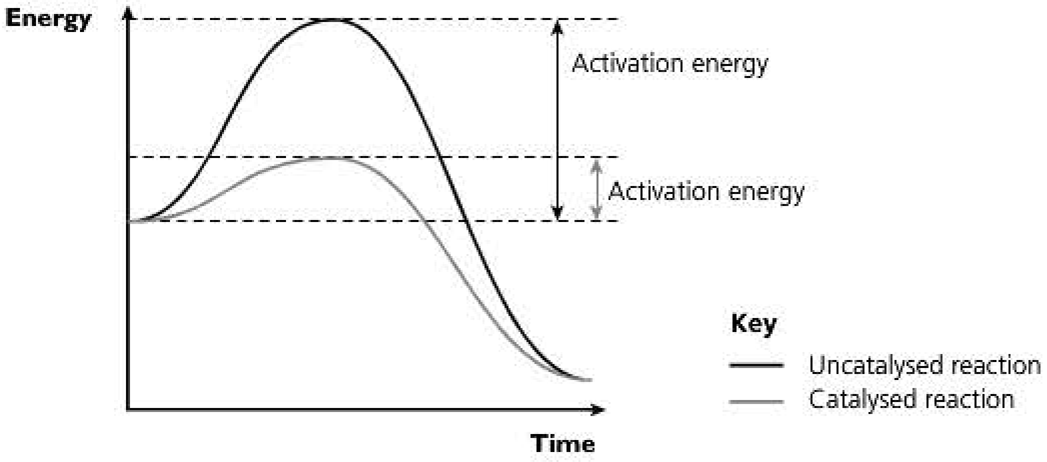


Figure 7.1 Reaction profile with and without a catalyst

Figure 7.1 shows that the catalyst has lowered the activation energy for the forward reaction. Consider the reverse reaction — the activation energy for this has also been lowered by the same amount. In other words, the presence of a catalyst does *not* change the position of equilibrium; it enables equilibrium to be established more quickly.

Equilibrium constants and calculations

For any equilibrium in the liquid state an equilibrium constant, K_c, can be defined in terms of concentration. For our general equation:

$$mA + nB \rightleftharpoons pC + qD$$

$$K_c = \frac{[C]^p[D]^q}{[A]^m[B]^n}$$

The quantities in square brackets represent the concentrations of the different species at equilibrium. It is also important to remember that equilibrium constants depend on temperature.

For gas phase reactions, partial pressures (in atmospheres) of the species involved in the equilibrium are used. To distinguish this from reactions in solution, the symbol K_p is used for the equilibrium constant. So, for the reaction between hydrogen and iodine to form hydrogen iodide:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$$K_p = \frac{p(HI) \times p(HI)}{p(H_2) \times p(I_2)}$$

$$= \frac{p(HI)^2}{p(H_2) \times p(I_2)}$$

where *p* represents the partial pressure of each of the species. Let's look at how these two constants are calculated.

Now test yourself

1 For each of the following reactions, use Le Chatelier's principle to decide what the effect will be on the position of equilibrium as a result of the changes stated:

- **a** $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ $\Delta H^\ominus$ −ve
  - **i** increase the temperature
  - **ii** increase the pressure
- **b** $C_2H_5OH(aq) + CH_3CO_2H(aq) \rightleftharpoons CH_3CO_2C_2H_5(aq) + H_2O(l)$
  - **i** increase the concentration of CH_3CO_2H
  - **ii** remove H_2O from the system

Answers on p.198

Tested ☐

Expert tip

For equilibria involving liquids use K_c for the equilibrium constant, but for gas phase reactions use K_p.

Example 1

Consider the reaction between ethanol and ethanoic acid:

$$C_2H_5OH(aq) + CH_3CO_2H(aq) \rightleftharpoons CH_3CO_2C_2H_5(aq) + H_2O(l)$$

In an experiment, 0.100 mol of ethanol and 0.200 mol of ethanoic acid were mixed together and the mixture was allowed to reach equilibrium. The acid was then titrated with 1.00 mol dm^{-3} sodium hydroxide and 115 cm^3 were needed to neutralise the acid. This volume of sodium hydroxide contains:

$$\frac{1.00 \times 115}{1000} = 0.115 \text{ mol of sodium hydroxide}$$

This means that there were 0.115 mol of ethanoic acid present in the equilibrium mixture.

Table 7.1 shows the other species present.

Table 7.1

	$C_2H_5OH(aq)$	$CH_3CO_2H(aq)$	$CH_3CO_2C_2H_5(aq)$	$H_2O(l)$
Start moles	$\frac{0.100}{V}$ mol	$\frac{0.200}{V}$ mol	$\frac{0.0}{V}$ mol	$\frac{0.0}{V}$ mol
Equilibrium moles	$\frac{?}{V}$ mol	$\frac{0.115}{V}$ mol	$\frac{?}{V}$ mol	$\frac{?}{V}$ mol

You have to divide by the total volume, *V*, because we are using concentrations.

You can deduce that (0.200 – 0.115) moles of ethanoic acid have been used. So the same amount of ethanol will have reacted. At equilibrium, the numbers of moles present are as shown in Table 7.2.

Table 7.2

	$C_2H_5OH(aq)$	$CH_3CO_2H(aq)$	$CH_3CO_2C_2H_5(aq)$	$H_2O(l)$
Equilibrium moles	$\frac{0.015}{V}$ mol	$\frac{0.115}{V}$ mol	$\frac{0.085}{V}$ mol	$\frac{0.085}{V}$ mol

Because there are the same numbers of molecules on each side of the equilibrium, the *V* terms cancel out. Substituting into the expression for K_c gives:

$$K_c = \frac{0.085 \times 0.085}{0.015 \times 0.115} = 4.19$$

You can use a similar process to calculate K_p for reactions taking place in the gas phase. To do this you need to understand what is meant by **partial pressure**.

The **partial pressure** of a gas is its mole fraction multiplied by the total pressure.

Suppose we think of air as consisting of one-fifth oxygen and four-fifths nitrogen at a total pressure of 100 kPa:

$$\text{partial pressure of oxygen, } p(O_2) = \frac{1}{5} \times 100\text{ kPa} = 20\text{ kPa}$$

$$\text{partial pressure of nitrogen, } p(N_2) = \frac{4}{5} \times 100\text{ kPa} = 80\text{ kPa}$$

Together this gives the total pressure of 100 kPa.

Example 2

Consider the dissociation of hydrogen iodide at 700 K:

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

If the value of K_p under these conditions is 0.020, and the reaction started with pure hydrogen iodide at a pressure of 100 kPa, what will be the partial pressure of hydrogen at equilibrium?

Let x be the partial pressure of hydrogen. Table 7.3 shows a summary of the relevant data.

Table 7.3.

Partial pressure	**2HI(g)**	**$H_2(g)$**	**$I_2(g)$**
Start partial pressure	100 kPa	0 kPa	0 kPa
Equilibrium partial pressure	$(100 - 2x)$ kPa	x kPa	x kPa

$$K_p = \frac{p(H_2) \times p(I_2)}{p(HI)^2}$$

Substituting gives:

$$0.020 = \frac{x^2}{(100 - 2x)^2}$$

Taking the square root of each side gives:

$$0.141 = \frac{x}{100 - 2x}$$

Rearranging gives:

$$14.1 - 0.282x = x$$

$$14.1 = 1.282x$$

$$x = 11.0\,\text{kPa (to 3 s.f.)}$$

Now test yourself

2 Write an expression for the equilibrium constant, K_c, for:
$Sn^{2+}(ag) + 2Fe^{3+}(aq) \rightleftharpoons Sn^{4+}(aq) + 2Fe^{2+}(aq)$

3 Write an expression for the equilibrium constant, K_p, for:
$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

Answers on p.198

Tested ☐

The Haber process

In the Haber (or Haber–Bosch) process, ammonia is produced on a massive scale using nitrogen from the air and hydrogen from the reaction of methane, CH_4, with steam:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H^\ominus = -92\,\text{kJ mol}^{-1}$$

To make the process as economic as possible, the conditions needed are:

- a high equilibrium concentration of ammonia
- equilibrium to be reached in a short period of time

To understand the conditions chosen you need to know more about the reaction.

First, at 298 K the equilibrium constant is very large, but only a tiny amount of ammonia is produced at this temperature because the rates of the forward and backward reactions are so low that equilibrium is never reached.

Second, increasing the temperature increases the rates of both reactions but drastically reduces the equilibrium constant because the reaction is exothermic.

Third, increasing the partial pressures of the reactants increases the equilibrium concentration of ammonia — for example, using 7500 kPa of hydrogen and 2500 kPa of nitrogen at 798 K gives a conversion about 10% of ammonia at equilibrium.

The solution is to use an iron catalyst to increase the rate of attaining equilibrium, and then to use a compromise set of conditions — a relatively low temperature (around 750 K) and a moderately high pressure (20 000 kPa). The equilibrium mixture is then passed through a heat exchanger to cool and liquefy the ammonia, which is removed — the unreacted nitrogen and hydrogen are recycled.

The Contact process

Revised ☐

The key stage in the production of sulfuric acid relies on an equilibrium reaction. In this process, sulfur dioxide is reacted with oxygen to form sulfur trioxide:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H^{\circ} = -197\,kJ\,mol^{-1}$$

The forward reaction is exothermic. Therefore, Le Chatelier's principle predicts that cooling the reaction mixture would give an increased yield. However, as you saw in the Haber process, this reduces the rate of attaining equilibrium.

Because there is an overall reduction in the number of molecules moving from left to right, Le Chatelier's principle also predicts that increasing the pressure will drive the equilibrium to the right, increasing the yield of sulfur trioxide.

The conditions used mirror these principles. The gas mixture is passed over three catalyst beds and is cooled after each pass to try to force the equilibrium to the right. Although a higher pressure is predicted to push the equilibrium to the right, most chemical plants producing sulfuric acid operate at just above atmospheric pressure to reduce costs.

Ionic equilibria

Revised ☐

Brønsted–Lowry acids and bases

The Brønsted–Lowry theory is the most commonly used description of acidity. It describes an acid as a substance capable of donating protons (H^+) and a base as a substance capable of accepting them:

$$HCl + NH_3 \rightarrow Cl^- + NH_4^+$$

In this reaction hydrogen chloride is acting as an acid by donating a proton to ammonia, which is acting as a base. In the reverse of this reaction, the chloride ion accepts a proton from the ammonium ion. This means that the ammonium ion would be acting as an acid in donating the proton to the chloride ion, which would be acting as a base. In this reaction, the chloride ion is known as the **conjugate base** of hydrogen chloride and the ammonium ion as the **conjugate acid** of ammonia.

It is also important to know how substances behave with water, the common solvent. Hydrogen chloride reacts with water:

$$HCl + H_2O \rightarrow Cl^- + H_3O^+$$

Here water is acting as a base, accepting a proton from hydrogen chloride; the H_3O^+ ion is its conjugate acid.

Water also reacts with ammonia:

$$H_2O + NH_3 \rightarrow OH^- + NH_4^+$$

Water is acting as an acid, donating a proton to ammonia; the OH^- ion is its conjugate base.

Strong and weak acids and bases

It is important to understand the difference between *dilute* and *weak*, and *concentrated* and *strong* when you are writing about acids and bases:

- A **strong acid** or **strong base** is *completely* ionised in solution. We often refer to the compound as being completely dissociated.
- A **weak acid** or **weak base** is only *partially* ionised in solution. We often refer to the compound as being partly dissociated.
- A **concentrated acid** or **concentrated base** has a *large* number of moles per unit volume of the acid or base.
- A **dilute** solution has a *small* number of moles relative to the solvent.

Now test yourself

4 Look at this equation and label the conjugate acid–base pairs.

$$H_2CO_3 + H_2O \rightarrow HCO_3^- + H_3O^+$$

Answer on p.198

Tested ☐

Examples of strong and weak acids and bases are shown in Table 7.4.

Table 7.4

Acids				Bases			
Strong	**pH**	**Weak**	**pH**	**Strong**	**pH**	**Weak**	**pH**
HC*l*	1	CH_3CO_2H	3	NaOH	14	NH_3	11
HNO_3	1	H_2CO_3	4	KOH	14	CH_3NH_2	12
H_2SO_4	1	H_2O	7	$Ca(OH)_2$	12	H_2O	7

The pH values in Table 7.4 are given to the nearest whole number for 0.1 mol dm^{-3} solutions.

The categories 'strong' and 'weak' are qualitative. To be accurate you need to be able to make quantitative comparisons using dissociation constants or the pH values of solutions of the compounds.

When an acid, HA, dissolves in water, the equilibrium established is:

$$HA(aq) + H_2O(l) \rightleftharpoons H^+(aq) + A^-(aq)$$

The position of the equilibrium depends the strength of the acid. For a strong acid, the equilibrium favours the products, and the reaction goes almost to completion. For a weak acid, the equilibrium favours the reactants with relatively few H$^+$(aq) ions being produced.

A more precise indication of the position of equilibrium can be obtained by working out an equilibrium constant:

$$K = \frac{[H^+(aq)][A^-(aq)]}{[HA(aq)][H_2O(l)]}$$

$[H_2O(l)]$ is in excess and is almost constant, so you use a new equilibrium constant called the **acid dissociation constant**, K_a, which includes this and has units mol dm^{-3}.

$$K_a = \frac{[H^+(aq)][A^-(aq)]}{[HA(aq)]}$$

Values of K_a are small (especially for weak acids and bases) and it is usual to convert them to a logarithm (to base 10) of their value (pK_a), as with [H$^+$(aq)] and pH.

Consider water at 298 K. The concentration of H$^+$(aq) ions is 10^{-7} mol dm^{-3}:

$$pH = -\log [H^+(aq)]$$
$$pH = -\log(10^{-7}) = 7$$

The numbers are not always this simple. Suppose that in a given solution [H$^+$(aq)] = 8.6 × 10^{-9} mol dm^{-3}.

To calculate the pH of this solution you need to understand how to work out the logarithm of this sort of number:

$$pH = -\log [H^+(aq)]$$
$$= -\log(8.6 \times 10^{-9})$$
$$= -\ ((\log 8.6) - 9)$$
$$= -\ (0.9345 - 9)$$
$$= 8.0655 \text{ or } 8.07 \text{ to 3 s.f.}$$

You can also calculate [H$^+$(aq)] given the pH of a solution. A solution with a pH of 2.73 has its hydrogen ion concentration worked out like this:

$$pH = 2.73 = -\log [H^+(aq)]$$
$$\log [H^+(aq)] = -2.73$$
$$[H^+(aq)] = 1.862 \times 10^{-3}$$
$$= 1.86 \times 10^{-3} \text{ mol dm}^{-3} \text{ to 3 s.f.}$$

Another piece of information that is useful is the **ionic product** of water, K_w. This is the product of $[H^+(aq)]$ and $[OH^-(aq)]$ and at 298 K is equal to $10^{-14}\,mol^2\,dm^{-6}$. This enables us to calculate $[OH^-(aq)]$ as well as $[H^+(aq)]$ in any aqueous solution.

Choosing indicators for titrations

When carrying out titration, it is the pH of the solution at the end point that is critical when choosing a suitable indicator. Two main factors need to be considered:

- The colour change should be sharp — no more than one drop of acid or alkali should give a distinct colour change.
- The end point should occur when the solution contains the same number of hydrogen ions as hydroxide ions.

Plotting graphs of the change in pH with the addition of the titrating solution produces different curves for combinations of weak and strong acids with weak and strong bases, as Figure 7.2 shows.

Figure 7.2(a) shows the change in pH during the titration of a 25 cm^3 sample of 0.1 $mol\,dm^{-3}$ strong acid when adding strong base. Notice that there is a long vertical portion at 25 cm^3 showing a large change in pH.

Now test yourself

5 What is the pH of:

- **a** a solution containing $10^{-5}\,mol\,dm^{-3}$ $H^+(aq)$?
- **b** a solution containing $10^{-3.5}\,mol\,dm^{-3}$ $H^+(aq)$?
- **c** a solution containing $10^{-5.5}\,mol\,dm^{-3}$ $OH^-(aq)$?

Answers on p.198

Tested ☐

Expert tip

The vertical portion has to be in the range to give a colour change.

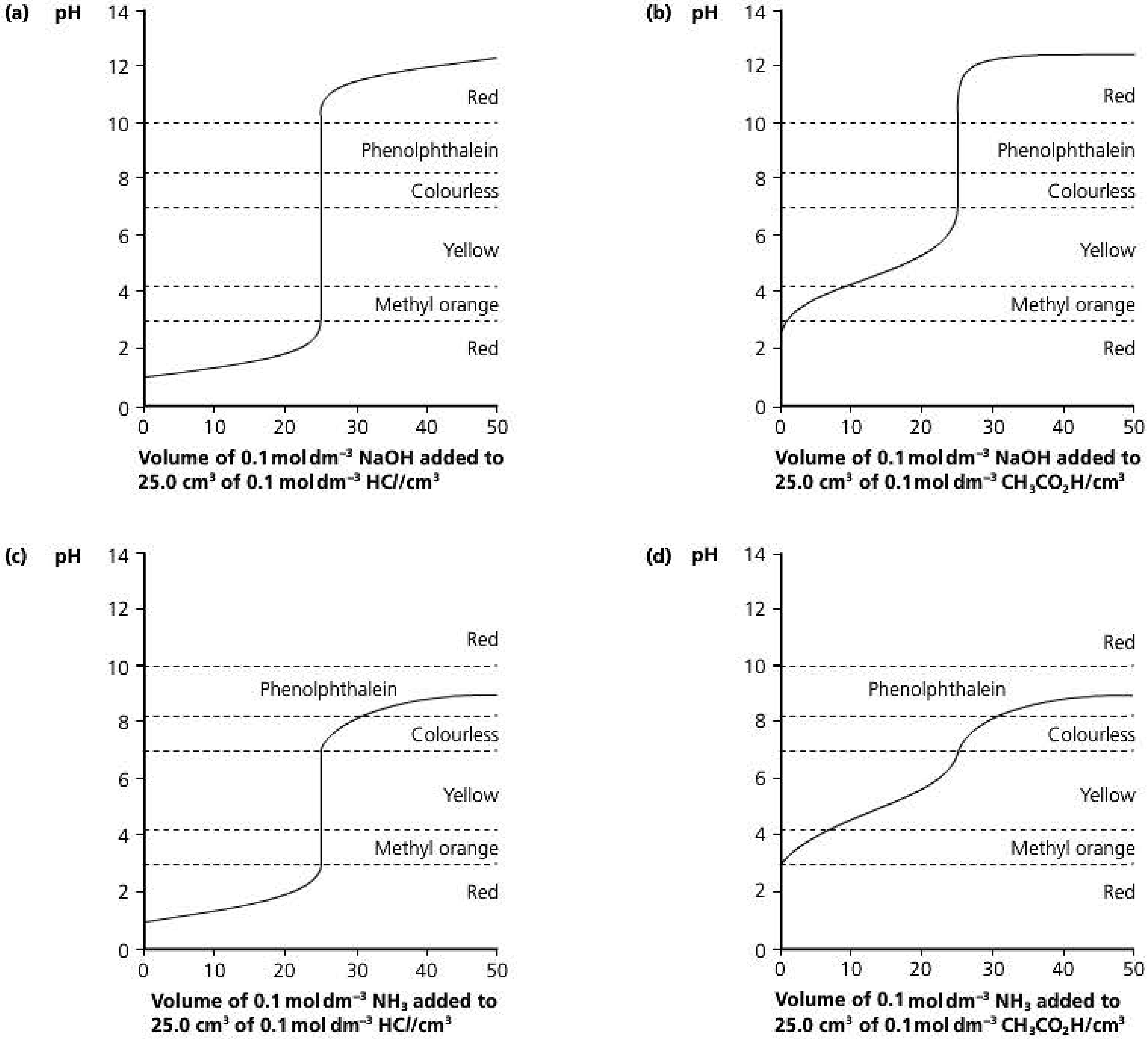


Figure 7.2 Titration curves for (a) a strong acid with a strong base; (b) a weak acid with a strong base; (c) a strong acid with a weak base; (d) a weak acid with a weak base

Figure 7.2(b) shows the change in pH during the titration of a 25 cm^3 sample of 0.1 mol dm^{-3} weak acid when adding strong base. Notice that although the vertical portion occurs at 25 cm^3, it is shorter and it starts at a higher pH than in (a).

Figure 7.2(c) shows the change in pH during the titration of a 25 cm^3 sample of 0.1 mol dm^{-3} strong acid when adding weak base. Notice that although the vertical portion occurs at 25 cm^3, it is shorter and it starts at a lower pH than (a).

Figure 7.2(d) shows the change in pH during the titration of a 25 cm^3 sample of 0.1 mol dm^{-3} weak acid when adding weak base. Notice that now the vertical portion has practically disappeared, but it is closer to pH 7.

The diagrams also show the effective ranges of two common indicators — phenolphthalein and methyl orange. Table 7.5 shows the choice of indicator for the four titrations shown in Figure 7.2. Study the diagrams and try to decide on the reasons for the choices.

Table 7.5

Acid/base combination	Indicator used
Strong acid/strong base	Either would do
Weak acid/strong base	Phenolphthalein
Strong acid/weak base	Methyl orange
Weak acid/weak base	Neither is suitable; a different method is needed

Buffer solutions

Revised ☐

A **buffer solution** is a solution that can resist changes in acidity or alkalinity.

Buffer solutions are able to resist a change in acidity or alkalinity, maintaining an almost constant pH, when a small amount of either substance is added. An important example of such a system occurs in blood, the pH of which is kept close to 7.4 by the presence of hydrogencarbonate ions, HCO_3^-.

Buffers rely on the dissociation of weak acids. Consider the weak acid HA:

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

Because it is a weak acid, $[H^+(aq)]$ is about equal to $[A^-(aq)]$ and is very small. If a small amount of an alkali is added, the OH^- ions react with the H^+ ions, removing them from the solution as water molecules and this disturbs the equilibrium. By Le Chatelier's principle, more HA will dissociate to restore the equilibrium maintaining the pH. On the other hand, if some acid is added, the H^+ ions will react with the A^- ions forming more HA. However $[A^-(aq)]$ is very low and it would soon be used up. This problem is solved by adding more A^- ions in the form of a salt of the acid HA, such as Na^+A^-. Now there are more A^- ions to 'mop up' any added H^+ ions. So a buffer solution consists of a weak acid and a salt of that weak acid.

In the case of the buffer system in blood, the equilibrium is:

$$H^+(aq) + HCO_3^-(aq) \rightleftharpoons CO_2(aq) + H_2O(l)$$

Addition of H^+ ions moves the equilibrium to the right, forming more carbon dioxide and water, while the addition of OH^- ions removes H^+ ions causing the equilibrium to move to the left, releasing more H^+ ions.

To calculate the pH of a buffer you can use the expression:

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

In other words, you need to know the pK_a of the acid, together with the concentration of the acid and its salt in the solution.

Example

Calculate the pH of an ethanoate–ethanoic acid buffer made by mixing 25 cm^3 of 0.100 $mol\,dm^{-3}$ sodium ethanoate solution with 25 cm^3 of 0.100 $mol\,dm^{-3}$ ethanoic acid solution. K_a for ethanoic acid is $1.8 \times 10^{-5}\,mol\,dm^{-3}$.

Answer

Mixing the two solutions means that the total volume is 50 cm^3, so the concentration of each is halved. Substituting these values in the equation gives:

$$pH = -\log(1.8 \times 10^{-5}) + \log\frac{0.050}{0.050}$$
$$= -\log(1.8 \times 10^{-5}) + \log 1$$
$$= -\log(1.8 \times 10^{-5}) \qquad \text{(since } \log 1 = 0)$$
$$= 4.7$$

Solubility product

Another application of equilibrium involves the solubility of sparingly soluble salts. All the applications looked at so far have involved homogeneous equilibria (all the substances in the same phase). With sparingly soluble substances there are heterogeneous equilibria to consider, with one component in the solid phase and the remainder in the aqueous phase.

For example, in a saturated solution of silver chloride this equilibrium exists:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

The equilibrium constant for this system can be written as

$$K_c = \frac{[Ag^+(aq)][Cl^-(aq)]}{[AgCl(s)]}$$

However, it is not possible to change the concentration of a solid, so a new equilibrium constant is defined that allows for this. This is called the solubility product, K_{sp}, and is the product of the concentrations of the ions present in solution:

$$K_{sp} = [Ag^+(aq)][Cl^-(aq)]$$

In this case, the units of K_{sp} are $mol^2\,dm^{-6}$.

Example

Suppose you want to know if a precipitate will form when you mix equal quantities of solutions of silver nitrate and potassium chloride. Let's assume that the concentration of potassium chloride is $1.0 \times 10^{-3}\,mol\,dm^{-3}$ and that of silver nitrate is $1.0 \times 10^{-5}\,mol\,dm^{-3}$. K_{sp} for silver chloride at 298 K is $1.8 \times 10^{-10}\,mol^2\,dm^{-6}$.

Answer

On mixing equal quantities of the two solutions, each concentration is halved. Substituting the numbers into the expression for K_{sp} gives:

$$K_{sp} = [Ag^+(aq)][Cl^-(aq)]$$
$$[Ag^+(aq)]\,[Cl^-(aq)] = (5.0 \times 10^{-6}) \times (5.0 \times 10^{-4})$$
$$= 2.5 \times 10^{-9}\,mol^2\,dm^{-6}$$

This is higher than $1.8 \times 10^{-10}\,mol^2\,dm^{-6}$ so a precipitate will form.

This same method can be used to calculate the concentration of one ion if you know that of the other ion along with the relevant K_{sp}. It is also important to remember to write out the equilibrium equation and expression because not all salts have a 1 : 1 ratio of ions.

If a substance is added that has an ion in common with the sparingly soluble salt, the concentration of that ion affects the equilibrium. This is known as the **common ion effect**.

So, if sodium chloride solution is added to a saturated solution of silver chloride:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

more solid is precipitated. This is because the added chloride ions push the equilibrium backwards, according to Le Chatelier's principle.

Now test yourself

6 Magnesium fluoride is sparingly soluble in water.

$$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2F^-(aq)$$

- a Write an expression for the solubility product, K_{sp}, for magnesium fluoride.
- b What are the units for K_{sp} in this case?

Answers on p.198

Tested ☐

Partition coefficients

Revised ☐

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 particles and the solvent molecules are similar to those between the solvent molecules themselves.

Molecules can attract each other in a variety of ways:

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

As a general rule:

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

Iodine is a molecular solid and is unlikely to be as soluble in water (polar solvent) as it is in hexane (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, you find that the ratio of the concentrations is constant, no matter how much iodine is used. This constant is known as the **partition coefficient**, $\boldsymbol{K_{pc}}$:

$$K_{pc} = \frac{[I_2(\text{hexane})]}{[I_2(\text{water})]}$$

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

Example

0.95 g of iodine ($M_r = 254$) was shaken with a mixture of 50 cm^3 of water and 50 cm^3 of tetrachloromethane. The organic layer was run off, and the aqueous layer titrated with 0.5 mol dm^{-3} standard sodium thiosulfate solution. 25.0 cm^3 of the aqueous layer required 4.30 cm^3 of thiosulfate for complete reaction. Calculate the partition coefficient of iodine between water and tetrachloromethane.

$$2S_2O_3^{2-}(aq) + I_2(aq) \rightleftharpoons S_4O_6^{2-}(aq) + 2I^-(aq)$$

Answer

Concentration of I_2 in the aqueous layer $= \frac{0.5 \times 4.30 \times 10^{-5}}{25 \times 10^{-5}}$

$= 8.6 \times 10^{-4}$ mol dm^{-3}

Mass of I_2 in the aqueous layer $= 8.6 \times 10^{-4} \times 254 \times 50 \times 10^{-3}$

$= 0.0109$ g

So the mass of iodine in the CCl_4 layer was 0.95 − 0.0109 = 0.931 g

The partition coefficient of I_2 between water and CCl_4 is $\frac{0.0109}{0.0931}$ or 1.17×10^{-2}

Revision activity

Parts 1 and 2 of this question are for AS and the remainder for A level.

1 Consider the reaction:

$2X(aq) + Y(aq) \rightleftharpoons X_2Y(aq)$; ΔH is +ve

a Write an expression for K_c for this reaction.

b What will be the effect on K_c of increasing the temperature of the reaction mixture?

c What will be the effect on K_c of increasing the concentration of Y(aq)?

d What will be the effect on K_c of adding a catalyst to the reaction mixture?

2 Consider the reaction of $N_2(g)$ with $H_2(g)$ to form ammonia, $NH_3(g)$. At 800 K, K_p for the reaction is 1.45×10^{-5}. In an equilibrium mixture of the three gases, the partial pressure of H_2 is 0.928 atm and that of N_2 is 0.432 atm. What is the partial pressure of NH_3?

3 **a** Sort these compounds into acids and bases:

H_3PO_4, PH_3, HCO_2H, NH_3, H_2S

b Indicate whether each of the acids and bases are strong or weak.

4 Assuming that the dissociation of carbonic acid, H_2CO_3, to form HCO_3^- is the major contributor to the pH of the solution, and that K_a for this reaction is 2.5×10^{-4}, calculate the pH of a solution containing $0.01\,mol\,dm^{-3}$ of H_2CO_3.

5 Calculate the pH of an ethanoate–ethanoic acid buffer solution made by mixing $50\,cm^3$ of $0.200\,mol\,dm^{-3}$ sodium ethanoate solution with $25\,cm^3$ of $0.200\,mol\,dm^{-3}$ ethanoic acid solution. K_a for ethanoic acid is $1.8 \times 10^{-5}\,mol\,dm^{-3}$.

Answers on p.202

8 Reaction kinetics

This first part of this chapter deals with material needed for AS and the remainder for A level.

Simple rate equations

Revised ☐

You know from practical work that the rates of chemical reactions are affected by three main conditions:

- temperature
- concentration
- presence of a catalyst

For AS you need to be able to explain the effects of changes in these conditions using the collision theory. It is important that you learn the correct terms to use when describing how reactions are influenced.

A reaction cannot take place unless the reacting particles collide with sufficient energy. Not all collisions result in changes and the minimum energy required is called the **activation energy, E_a**. Increasing the temperature increases the proportion of successful collisions. Increasing the concentration increases the chance of collisions taking place. In the presence of a catalyst, a reaction has a different mechanism — one of lower activation energy giving more successful collisions. For AS you need to be able to link these observations to the distribution of molecular energies and also to explain the effects.

Boltzmann distribution of energies

The energy of molecules is directly proportional to their absolute temperature. The graph in Figure 8.1 shows a typical distribution of energies at constant temperature. This is known as the Boltzmann distribution.

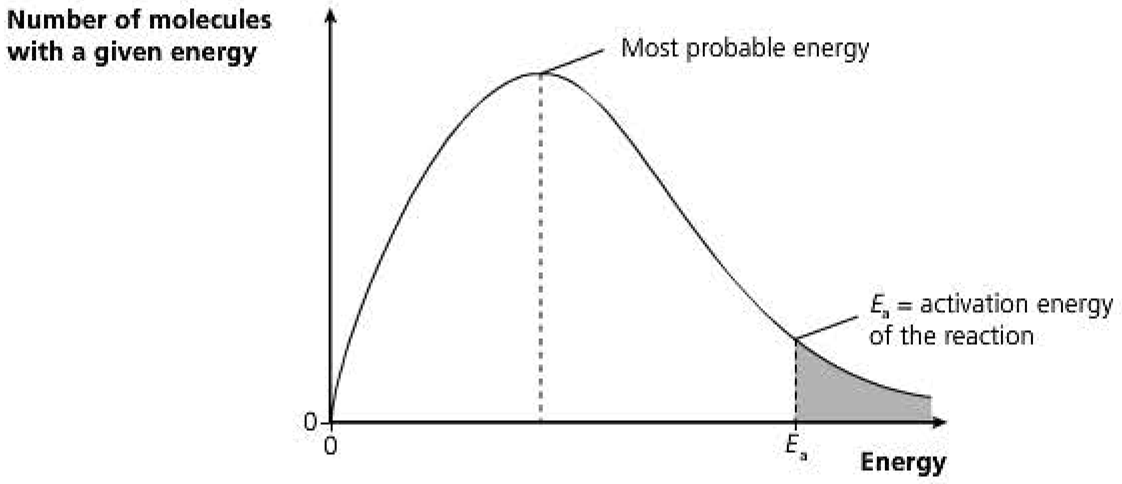


Figure 8.1 Boltzmann distribution

There are a number of points to remember about this graph:

- The distribution always goes through the origin.
- The curve approaches the *x*-axis but does not touch it.
- The peak represents the most probable energy.
- The area under the curve represents the total number of particles.
- E_a represents the activation energy (the minimum energy needed for reaction). The shaded portion represents the number of particles with energy higher than or equal to the activation energy ($E \geq E_a$).

The effect of temperature

An increase in temperature changes the shape of the Boltzmann distribution curve as shown in Figure 8.2.

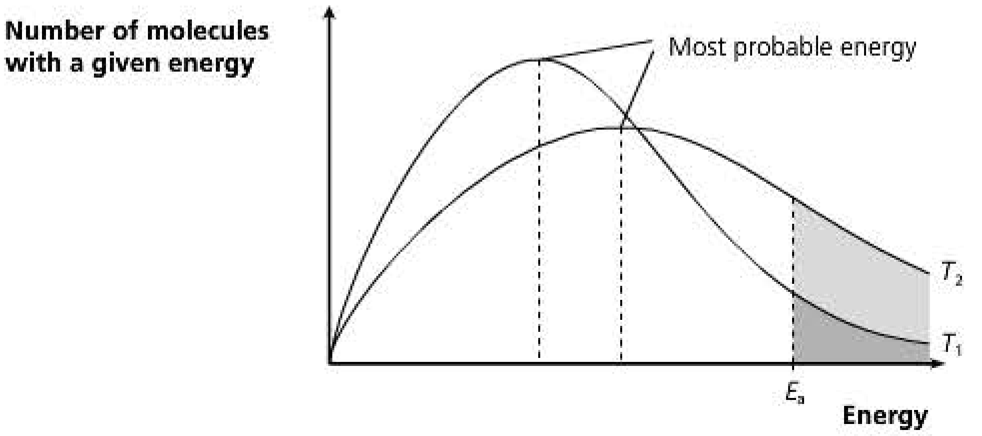


Figure 8.2 Boltzmann distribution at different temperatures

Notice that only the temperature has changed, so the areas under the two curves are the same. The graph shows that at a higher temperature, T_2:

- there are fewer particles with lower energy (the curve is flatter)
- the most probable energy is higher
- more particles have $E \geq E_a$

At higher temperature a bigger proportion of particles have sufficient energy to react, and hence the rate of reaction increases. The reverse is true at lower temperatures.

The effect of concentration

The Boltzmann distribution is not relevant here. The explanation given at the beginning of the chapter in terms of increasing the chance of collisions is adequate. It is worth remembering that increasing the pressure of a gas phase reaction has the same effect as increasing concentration in the liquid phase.

The effect of a catalyst

You should remember that catalysts speed up chemical reactions without being permanently changed themselves. In the presence of a catalyst, a reaction has a different mechanism with a different activation energy, E_{cat}. This is shown in Figure 8.3.

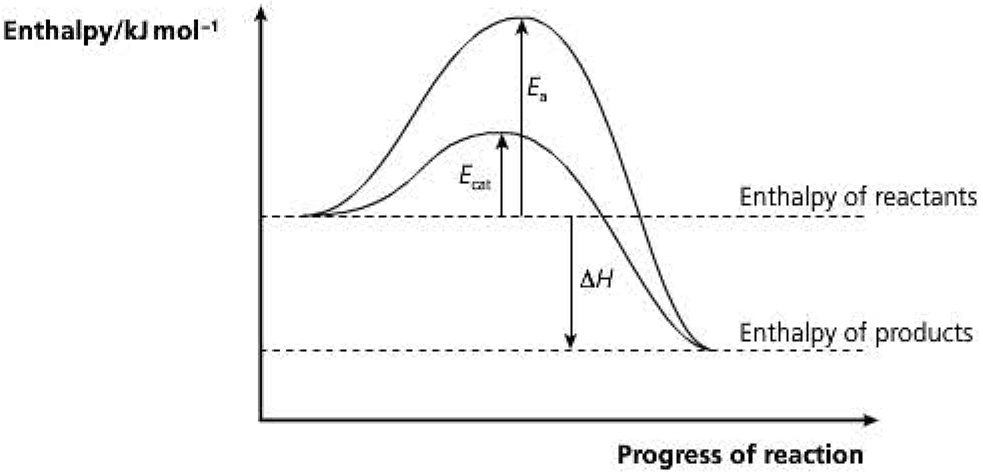


Figure 8.3 Activation energy in the presence and absence of a catalyst

It is important to remember that catalysts do not change the Boltzmann distribution for the temperature concerned. In a reaction that is speeded up the position of E_a simply moves to the left, increasing the proportion of particles with $E \geq E_a$ as shown in Figure 8.4.

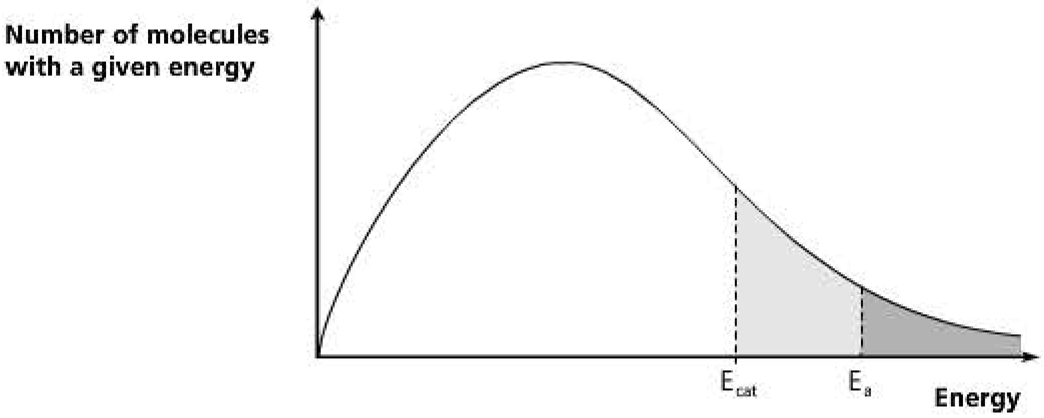


Figure 8.4 Position of E_a in the presence and absence of a catalyst

Enzymes are a particular type of catalyst found in biological systems. They are protein molecules and are specific in terms of the reaction they catalyse (see p. 69).

For A level you need to be able to manipulate data about rates of reactions in a more mathematical way. Some of this will come from practical work or from data based on practical work.

Now test yourself

1 **a** Look at Figure 8.2. Explain what the two shaded portions to the right of the graph tell you.
  b Now look at Figure 8.4. Again, explain what the two shaded portions to the right of the graph tell you.

Answers on p.198

Tested ☐

Order of reaction

To describe rate relationships in a reaction mathematically, a rate equation is used — these have the form:

$$\text{rate} = k[A]^m[B]^n$$

Here, k is the **rate constant** for the reaction between substances A and B, and m and n are the powers to which the concentrations of these substances are raised in the experimentally determined rate equation. Each is called the **order** with respect to each substance. For the reactions in A level work, m and n can be 0, 1 or 2.

It is important to remember that not all reactions take place in a single step. For multi-step reactions one step will *always* be slower than all the others. This is called the **rate-determining step**, because it is on this that the overall reaction rate depends.

The **rate-determining step** is the slowest step in a multi-step reaction and the overall reaction rate depends on this.

It is easier to understand what this means by looking at some examples. Consider the reaction:

$$A + B \rightarrow \text{products}$$

If you measure the way in which the rate of this reaction changes depending on the concentrations of A and B, you might find that doubling the concentration of A doubles the rate. You might also find that doubling the concentration of B doubles the rate.

This tells us that the order with respect to A is 1, and that the order with respect to B is also 1 — so the overall order of the reaction is 2. The rate equation could be written:

$$\text{rate} = k[A]^1[B]^1$$

However, you do not need to show m and n when they are 1:

$$\text{rate} = k[A][B]$$

In another reaction:

$$X + Y \rightarrow \text{products}$$

the rate might not depend on Y reacting with X, but on X breaking down and then Y reacting with those products. When this is the case, the rate equation has the form:

$$\text{rate} = k[X]^1[Y]^0$$

Remembering that anything to the power 0 equals 1, this rate equation can be written:

$$\text{rate} = k[\text{X}]$$

Now test yourself

2 Why does the slowest step in a reaction decide the overall rate?

Answer on p.198

Tested ☐

Deducing order by the initial rates method

Most reaction kinetic studies are based on experimental work. Consider a reaction for which the rate can be measured at the start. Data from such an experiment are given in Table 8.1.

Table 8.1

Run	Initial [A]/mol	Initial [B]/mol	Initial rate/mol s^{-1}
1	1.00	1.00	1.25×10^{-2}
2	1.00	2.00	2.5×10^{-2}
3	2.00	2.00	2.5×10^{-2}

Look at runs 1 and 2. If you double the concentration of B and keep the concentration of A constant, then the rate doubles. Look at runs 2 and 3 — doubling the concentration of A and keeping the concentration of B constant has no effect on the rate. This tells us that the reaction is first order with respect to B and zero order with respect to A. In other words, A does not feature in the rate equation. You can now calculate the rate constant:

$$\text{rate} = k[\text{B}]$$

$$2.5 \times 10^{-2}\,\text{mol}\,\text{s}^{-1} = k \times 2.0\,\text{mol}$$

$$k = 1.25 \times 10^{-2}\,\text{s}^{-1}$$

Deducing order from graphs

Another way of deducing the order of a reaction with respect to a given reagent is to look at a graph of concentration against time. Zero-order (Figure 8.5(a)) and first-order reactions (Figure 8.5(b)) have characteristic shapes.

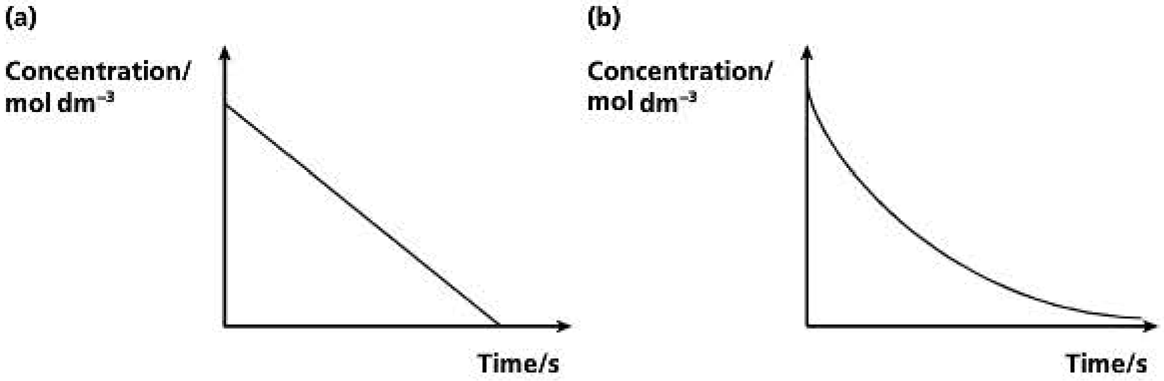


Figure 8.5 Concentration–time graph for (a) a zero-order reaction; and (b) a first-order reaction

It is also possible to compare graphs of rate against concentration (Figure 8.6).

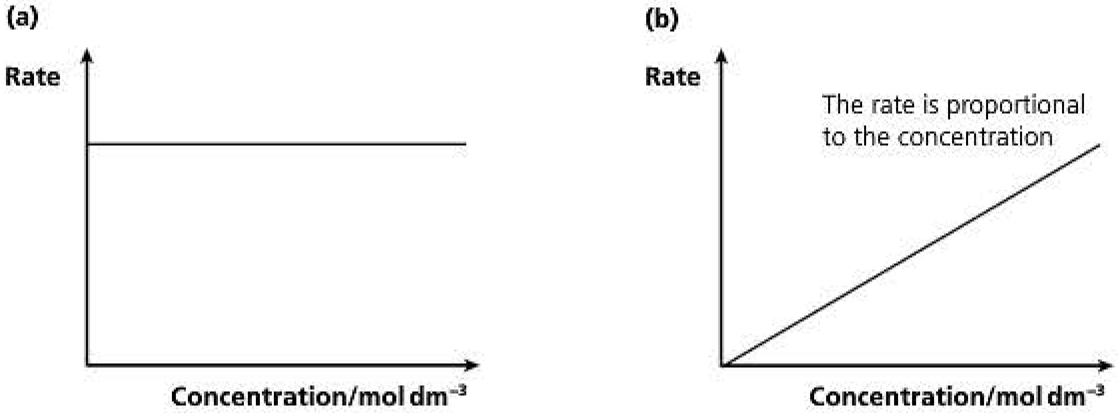


Figure 8.6 Rate–concentration graph of (a) a zero-order reaction and (b) a first-order reaction

These graphs show that in a zero-order reaction, the rate is independent of concentration and gives a horizontal line (Figure 8.6(a)). For a first-order reaction, the reaction shows a constant time for the concentration of a reactant to halve (Figure 8.5(b)). This is known as the **half-life** of the reaction and is similar to the half-life concept in radioactive decay.

A half-life can be used to calculate the rate constant of a reaction. Look at this reaction:

$$CH_3N_2CH_3(g) \rightarrow CH_3CH_3(g) + N_2(g)$$

When the compound is heated it decomposes into the two gases shown. No other reactants are needed so:

$$\text{rate} = k[CH_3N_2CH_3(g)]$$

The half-life of this reaction at 500 K is about 1750 s. This means that if the starting concentration is $0.10\,\text{mol dm}^{-3}$, after 1750 s the concentration will have halved to $0.05\,\text{mol dm}^{-3}$. After another 1750 s, the concentration will have halved to $0.025\,\text{mol dm}^{-3}$, and so on.

A half-life can be used to calculate the rate constant, *k*. For a first-order reaction:

$$k = \frac{0.693}{t_{½}}$$

$$= \frac{0.693}{1750}$$

$$= 3.96 \times 10^{-4}\,\text{s}^{-1}$$

Multi-step reactions and predicting order

Reactions can happen in a single step or more than one step (multi-steps). For the examination, you need to be able to predict the order of a reaction from a given mechanism (and vice versa).

Consider this reaction of a primary halogenoalkane:

$$C_4H_9Br + OH^- \rightarrow C_4H_9OH + Br^-$$

This could occur in one step as shown above or in two steps:

slow step: $C_4H_9Br \rightarrow C_4H_9^+ + Br^-$

fast step: $C_4H_9^+ + OH^- \rightarrow C_4H_9OH$

If the first mechanism is correct you would predict that the reaction is first order with respect to both C_4H_9Br and OH^-. If the second mechanism is correct you would predict that the reaction is first order with respect to only C_4H_9Br, because this is the rate-determining step. The slowest step is *always* the one (bottleneck) that determines the rate (the rate-determining step). In this example, practical evidence suggests that the first mechanism is correct.

Now test yourself

Tested ☐

3 The reaction between $(CH_3)_3Br$ and OH^- ions can happen by two possible mechanisms:

$(CH_3)_3Br + OH^- \rightarrow (CH_3)_3OH + Br^-$

or

$(CH_3)_3Br \rightarrow (CH_3)_3^+ + Br^-$ slow

$(CH_3)_3^+ + OH^- \rightarrow (CH_3)_3OH$ fast

If the rate equation for the reaction is:

$\text{rate} = k[(CH_3)_3Br]$

which mechanism is correct and why?

Answer on p.198

Experimental techniques for studying rates

Revised ☐

It is important to consider the methods that are available to follow the progress of a reaction and to determine the rate.

Sampling followed by titration

Small amounts of the reaction mixture are withdrawn by pipette at regular intervals. Further reaction in this sample is prevented, often by adding a large volume of a common inert solvent. The concentration of one of the reactants or products is then determined by titration of the samples. Common examples are the formation of an acid and an iodination reaction.

Using a colorimeter

This method only works if one of the reactants or products is coloured. It has advantages over titration in that no sampling is needed and it gives an almost instantaneous result. An example is the formation of a transition metal complex.

Measurement of gas evolved

One of the products has to be a gas for this method to work. The volume of the gas is measured in a syringe or by the displacement of water from an upturned burette. An example is the reaction between an acid and a carbonate.

Catalysis

Revised ☐

You will already have come across the use of catalysts in your GCSE work. You need to know how catalysts are able to speed up reactions. Catalysts can be homogeneous (in the same physical state as the reactants) or heterogeneous (in a different physical state to the reactants).

The Haber process

You saw in Chapter 7 how this equilibrium process was made economic by the use of an iron catalyst. The catalyst is heterogeneous — in a different phase from the gases. Transition metals are particularly good at acting as catalysts because their atoms have unfilled d-orbitals. The gases are adsorbed on to the surface of the metal forming weak bonds (Figure 8.7). This can have one of two consequences:

- The formation of bonds with the metal surface may weaken the bonds within the gas molecules.
- The orientation of the adsorbed molecules may be favourable for the reaction.

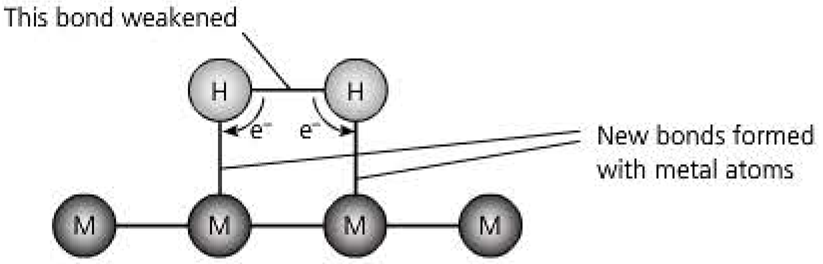


Figure 8.7 Adsorption of a gas onto the surface of a metal catalyst

Catalytic converters in vehicle exhausts

Catalytic converters have become important in recent years — they are designed to remove pollutant gases from vehicle exhausts. The problem is complex because some pollutants, such as carbon monoxide, have to be oxidised while others, such as nitrogen oxides, have to be reduced.

The converter consists of a ceramic honeycomb with a very thin coat of platinum, rhodium and palladium (all expensive metals). The platinum and rhodium help to reduce the NO_x to nitrogen, while platinum and palladium help to oxidise the CO and unburnt hydrocarbons. The car has to run on unleaded petrol because lead would 'poison' the catalyst, making it ineffective. This is a heterogeneous system.

Nitrogen oxides in the atmosphere

This is an example of homogeneous catalysis — the reactants and the catalyst are in the same phase, in this case gases. Studies on acid rain have shown that in the atmosphere the presence of oxides of nitrogen, particularly nitrogen(IV) oxide (NO_2), increases the rate of oxidation of sulfur dioxide to sulfur trioxide. Nitrogen(IV) oxide is unchanged by the reaction and is thought to form a weak intermediate with sulfur dioxide.

The role of Fe^{2+} in the $I^-/S_2O_8^{2-}$ reaction

The oxidation of iodide ions by peroxodisulfate ions is another example of homogeneous catalysis. In this case, all the species are in the aqueous phase. It is believed that this oxidation occurs in two steps in the presence of Fe^{3+} ions:

Overall: $S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$

Catalysed reaction: $S_2O_8^{2-}(aq) + 2Fe^{2+}(aq) \rightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)$

$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

Although there are two steps in the reaction, the overall activation energy is lower than in the single-step reaction, as can be seen in Figure 8.8.

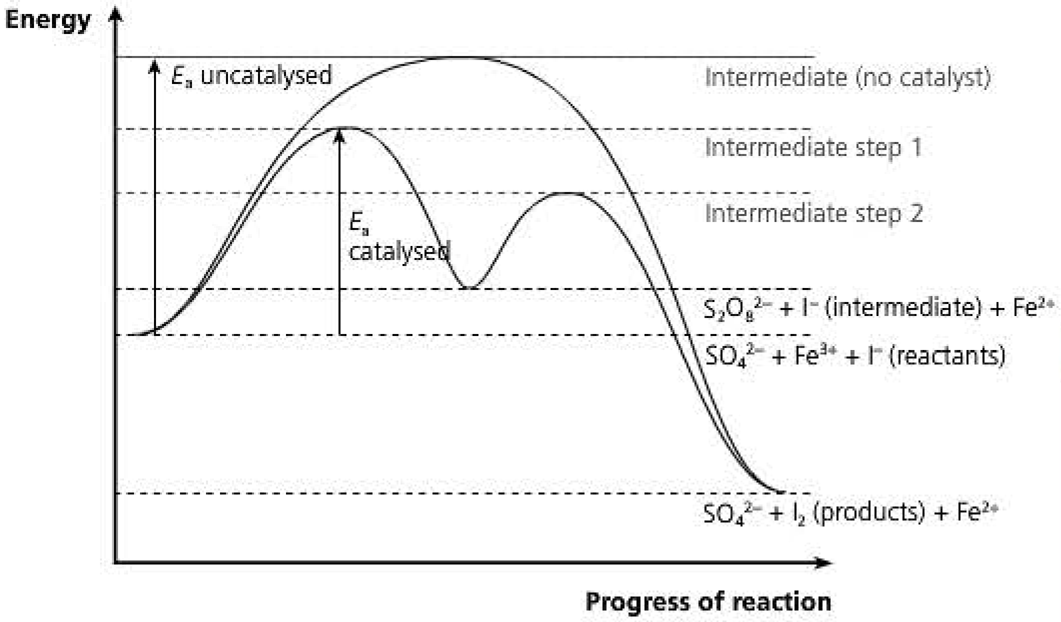


Figure 8.8 The effect of a catalyst on a reaction profile

Now test yourself

4 **a** What is the difference between a heterogeneous catalyst and a homogeneous catalyst?

b Suggest what this means in practical terms.

Answers on p.198

Tested ☐

Proteins as enzymes

Revised ☐

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 fits a given substrate molecule when it reacts. This is called the **active site** of the enzyme.

Enzymes are particular types of protein that behave as catalysts enabling chemical reactions to take place efficiently at body temperature.

You may be asked to draw a diagram to help explain this, so think about the important parts of the process (Figure 8.9).

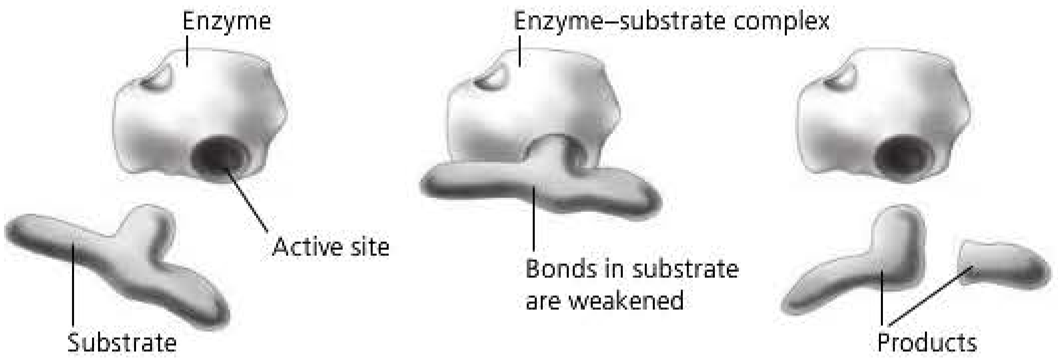


Figure 8.9 Interaction between an enzyme molecule and a substrate molecule

Enzymes, like other catalysts, work by providing an alternative reaction pathway that has a lower activation energy, E_{cat}, as shown in Figure 8.10.

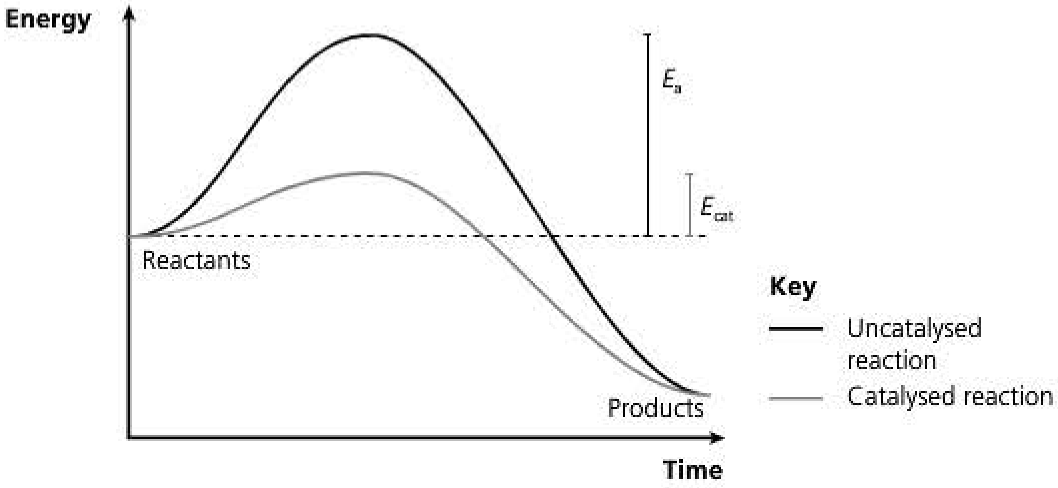


Figure 8.10 A reaction with and without an enzyme catalyst

The catalysed reaction has a lower activation energy than the uncatalysed reaction. It is usual to describe the reaction using:

enzyme + substrate ⇌ enzyme–substrate complex → enzyme + products

The first step is reversible because unless the available energy is higher 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 depends 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 the 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 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 8.11).

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.

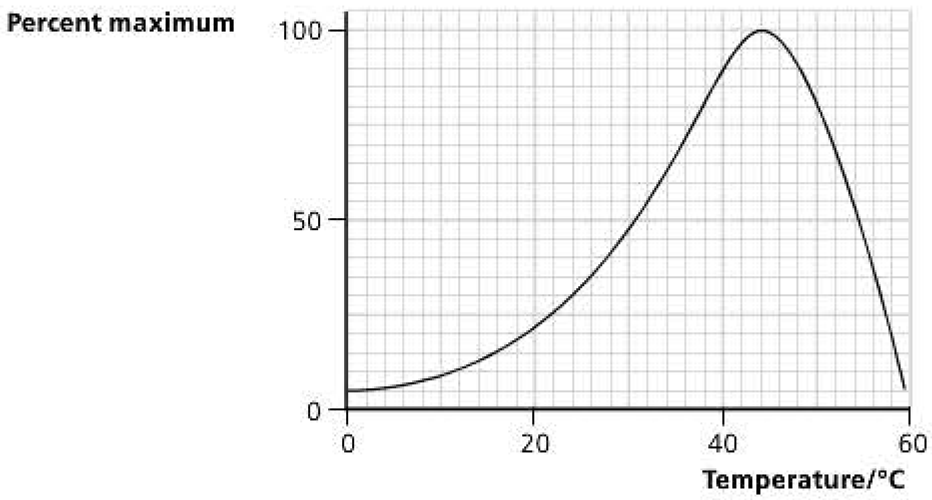


Figure 8.11 The effect of temperature on enzyme activity

The effect of changing pH

Enzyme activity depends 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 8.12).

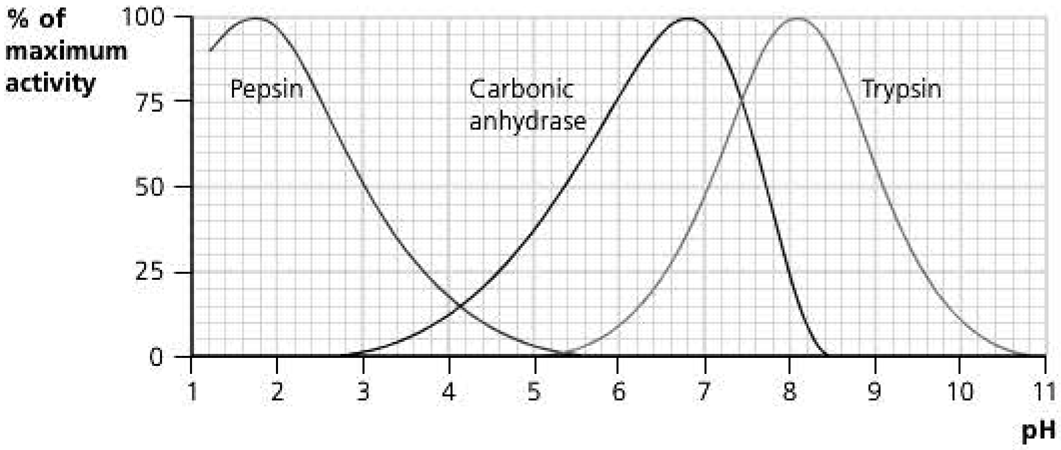


Figure 8.12 The effect of pH on the activity of three different enzymes

As you can see in Figure 8.12, pepsin, which acts on proteins in the acid conditions in 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.

Now test yourself

5 Enzymes work best at temperatures lower than 60°C. What type of bonds would be disrupted at temperatures higher than this?

Answer on p.198

Tested ☐

Revision activity

The first two parts of this question are for AS and the remainder for A level.

1 Sketch the energy profile for an endothermic reaction:

$A + B \rightarrow C + D$; $\Delta H^{\ominus}$ is +ve

On your profile, label the activation energy for the reaction E_a and $\Delta H^{\ominus}$.

2 Sketch the Boltzmann distribution curves for a reaction at two different temperatures where $T_2 > T_1$.

Use your curves to explain why the reaction is faster at T_2 than at T_1.

3 The table shows some rate data from an experiment.

Run	Initial [A]/mol	Initial [B]/mol	Initial rate/mol s^{-1}
1	1.00	1.00	1.25×10^{-2}
2	1.00	2.00	1.25×10^{-2}
3	2.00	2.00	2.5×10^{-2}

Use the data to deduce the rate equation for the reaction, explaining your answer.

4 Car engines produce a number of pollutant gases. Most of these are converted to less harmful gases using catalytic converters.

a What metals are commonly used in catalytic converters?

b What are the following pollutants converted into: NO_x, CO, unburnt hydrocarbons?

5 **a** Give an example of a homogeneous catalyst.

b Write equations to show this substance behaving as a homogeneous catalyst.

Answers on pp.202–3

9 Chemical periodicity

All the material in this chapter is needed for AS.

Physical properties of elements

Revised ☐

You need to know and be able to explain the variation of four key physical properties across the third period (sodium to argon). These are:

- atomic and ionic radius
- melting point
- electrical conductivity
- ionisation energy

Atomic and ionic radius

The Periodic Table is an arrangement of the chemical elements according to their proton numbers. The word 'periodic' suggests a regular recurrence of a feature. Look at the graph of atomic volume (which is linked directly to atomic radius) shown in Figure 9.1.

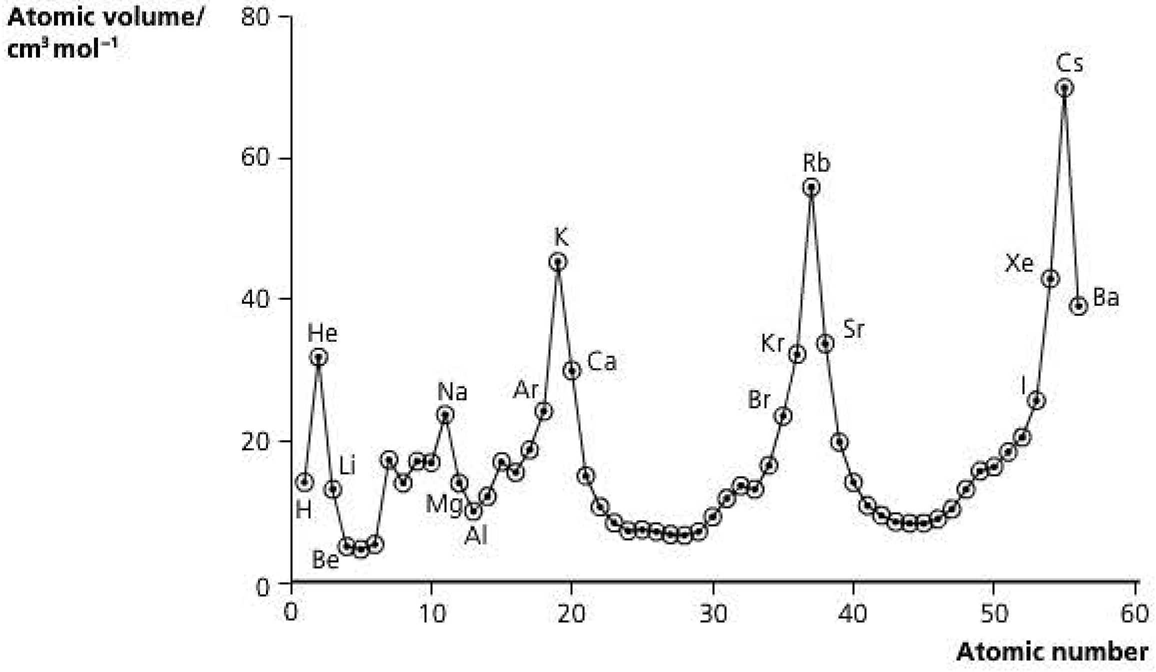


Figure 9.1 Relationship between atomic volume and atomic number

A pattern is apparent — the Group I metals occur at peaks on the graph. The other thing that is noticeable is that atoms of the Group I metals get larger moving down the group.

Moving across Period 3 from left to right, the ionic radii change (Figure 9.2). To begin with, elements lose electrons to form positive ions. The increasing positive charge pulls the remaining electrons closer to the nucleus to give a smaller ionic radius. Beyond silicon, Si^{4+}, the atoms form negative ions with a decreasing charge. The electrons gained fill the outer electron shell. This means that the ionic radius is much larger for phosphorus, P^{3-}, and then decreases steadily to chlorine, Cl^{-}.

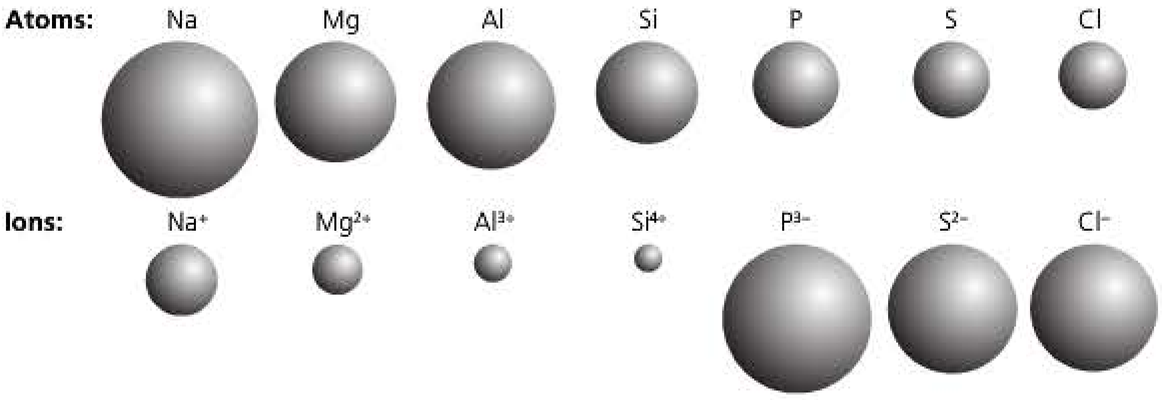


Figure 9.2 Atomic and ionic radii of Period 3 elements

Melting point

Period 3 contains different types of elements, from metals on the left-hand side through non-metallic solids to gases on the right-hand side. The melting points and boiling points of these elements are shown in Figure 9.3.

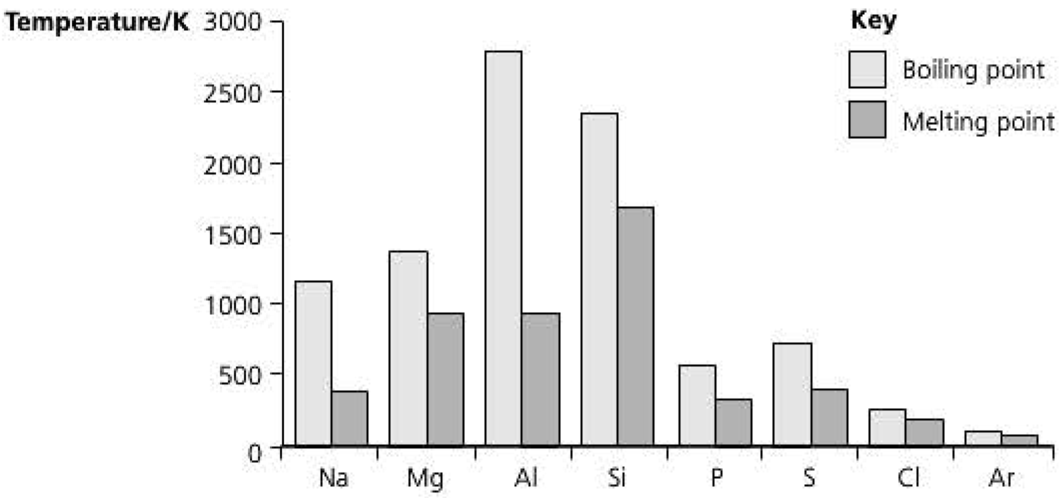


Figure 9.3 Melting points and boiling points of Period 3 elements

The elements sodium, magnesium and aluminium are metals and their atoms are bonded using a 'sea' of delocalised electrons. The melting (and boiling) points increase because the number of electrons each atom contributes to the 'sea' increases.

Silicon is a semi-conductor with a giant covalent structure (similar to that of diamond), so it has a high melting point. Phosphorus is a non-metal with four atoms in its molecules. To melt it, only van der Waals forces have to be overcome, so phosphorus has a low melting point. Sulfur, another non-metal, is made up of S_8 molecules. Because the molecules are big, there are stronger van der Waals forces between them than in phosphorus. So sulfur has a higher melting point than phosphorus. A chlorine molecule, Cl_2, has only two atoms so the melting point is lower than that of sulfur. Finally, argon consists of single atoms with very weak van der Waals forces so argon has the lowest melting (and boiling) point in Period 3.

Electrical conductivity

Sodium, magnesium and aluminium are good electrical conductors because of the 'sea' of delocalised electrons they have. Silicon is a semi-conductor, but not as good a conductor as graphite. All the other elements are electrical insulators.

Ionisation energy

Ionisation energy was discussed in Chapter 2. Figure 9.4 shows the change in first ionisation energy across Period 3.

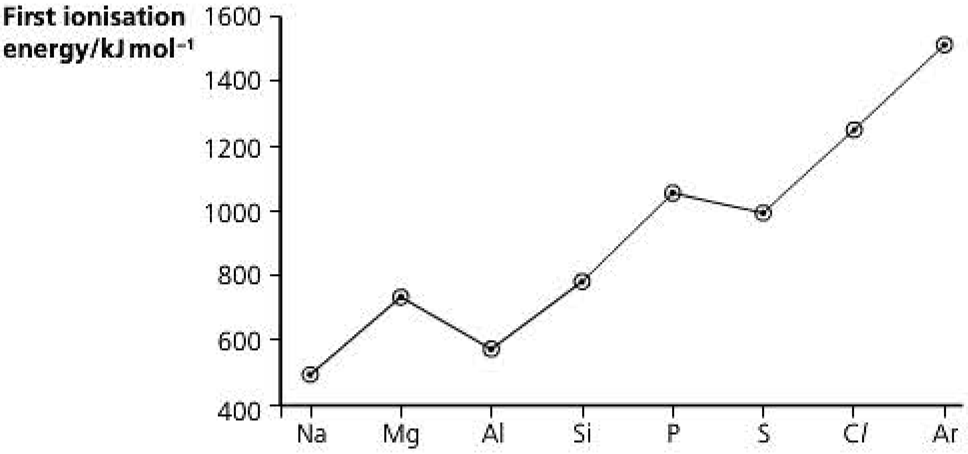


Figure 9.4 Change in first ionisation energy across Period 3

There are four things that affect the size of the first ionisation energy:

- the charge on the nucleus
- the distance of the electron from the nucleus
- the number of electrons between the outer electrons and the nucleus
- whether the electron to be removed is alone or paired

Across Period 3, the charge on the nucleus increases by one unit for each element. In all cases, electrons are being removed from the third shell and these are screened by the $1s^2$, $2s^2$ and $2p^6$ electrons. The graph is not a straight line because of the orbitals the electrons are removed from.

The first ionisation energy of aluminium is lower than that of magnesium. This fall is because in aluminium the electron being removed is in a p-orbital and is, on average, further away from the nucleus than an electron in an s-orbital. There is another drop between phosphorus and sulfur — this is caused by removing a paired electron in a p-orbital. The repulsion between these two electrons makes it easier to remove one of them than a single electron in a p-orbital.

Now test yourself

1 Why do the following affect the ionisation energy of an element?

  a the charge on the nucleus

  b the distance from the nucleus of the electron being removed

Answers on p.198

Tested ☐

Chemical properties of elements

Revised ☐

You have to be able to recall the reactions of these elements with oxygen, chlorine and water, and to know about the reactions of any oxides and chlorides formed.

Reactions with oxygen

You have probably seen most of the Period 3 elements reacting with air, or perhaps with oxygen. They are summarised in Table 9.1.

Table 9.1

Element	Reaction	Product(s)	Equation
Sodium	Burns with an orange-yellow flame to give white products	Sodium oxide and peroxide	$4Na + O_2 \rightarrow 2Na_2O$ $2Na + O_2 \rightarrow Na_2O_2$
Magnesium	Burns with a bright white flame to give a white product	Magnesium oxide	$2Mg + O_2 \rightarrow 2MgO$
Aluminium	Powder burns to give a white product	Aluminium oxide	$4Al + 3O_2 \rightarrow 2Al_2O_3$
Silicon	Burns if heated strongly	Silicon dioxide	$Si + O_2 \rightarrow SiO_2$
Phosphorus	Burns with a yellow flame producing clouds of white smoke	Phosphorus(III) oxide; phosphorus(V) oxide in excess O_2	$P_4 + 3O_2 \rightarrow P_4O_6$ $P_4 + 5O_2 \rightarrow P_4O_{10}$
Sulfur	Burns with a blue flame producing a colourless gas	Sulfur dioxide (sulfur trioxide is produced in the presence of a catalyst and excess O_2)	$S + O_2 \rightarrow SO_2$
Chlorine	Does not react directly with oxygen		
Argon	No reaction		

Reactions with chlorine

You may not have seen as many of the elements reacting with chlorine. The reactions are summarised in Table 9.2.

Table 9.2

Element	Reaction	Product	Equation
Sodium	Burns with a bright orange flame giving a white product	Sodium chloride	$2Na + Cl_2 \rightarrow 2NaCl$
Magnesium	Burns with a bright white flame giving a white product	Magnesium chloride	$Mg + Cl_2 \rightarrow MgCl_2$
Aluminium	Burns with a yellow flame giving a pale yellow product	Aluminium chloride	$2Al + 3Cl_2 \rightarrow 2AlCl_3$
Silicon	Reacts when chlorine gas is passed over it to form a colourless liquid	Silicon tetrachloride	$Si + 2Cl_2 \rightarrow SiCl_4$
Phosphorus	Burns with a yellow flame to form a mixture of chlorides	Phosphorus(III) chloride and phosphorus(V) chloride	$P_4 + 6Cl_2 \rightarrow 4PCl_3$ $P_4 + 10Cl_2 \rightarrow 4PCl_5$
Sulfur	Reacts when chlorine gas is passed over it to form an orange liquid	Disulfur dichloride	$2S + Cl_2 \rightarrow S_2Cl_2$
Chlorine	No reaction		
Argon	No reaction		

Reactions with water

Sodium reacts violently with water, releasing hydrogen gas and dissolving to form sodium hydroxide solution:

$$2Na + 2H_2O \rightarrow 2NaOH + H_2$$

Magnesium reacts slowly with cold water, forming magnesium hydroxide and hydrogen:

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$$

It reacts vigorously if steam is passed over the heated metal, forming magnesium oxide and hydrogen:

$$Mg + H_2O \rightarrow MgO + H_2$$

Oxidation numbers in oxides and chlorides

Figure 9.5 shows a plot of the oxidation numbers of the Period 3 elements in their oxides and chlorides.

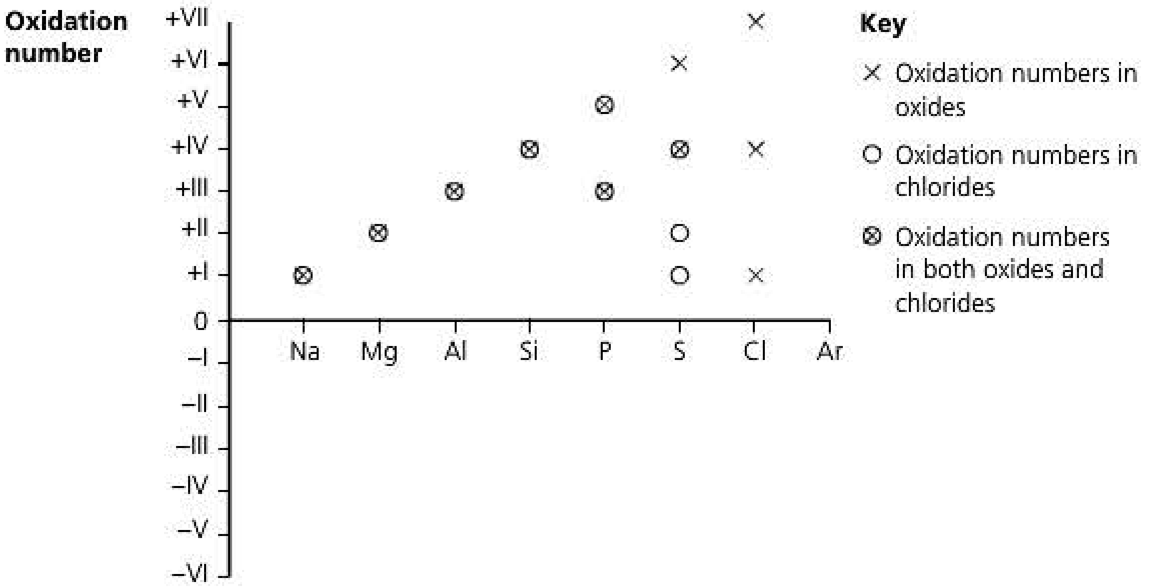


Figure 9.5 Oxidation numbers of the oxides and chlorides of Period 3 elements

The first four elements have positive oxidation numbers that correspond to the loss of all their outer electrons (silicon can also gain four electrons in forming its hydride, SiH_4 — its oxidation number is still +4). Elements in Groups 15, 16 and

17 can also show positive oxidation numbers in their oxides and chlorides. You may think that it is unusual for non-metals to have positive oxidation numbers, but carbon has a positive oxidation number in carbon dioxide.

Now test yourself

2 Study Figure 9.5 and then explain the pattern of oxidation number for the chlorides.

Answer on p.198

Tested ☐

Reactions of oxides with water and their acid–base behaviour

The general trend is that alkalis are formed on the left-hand side of the period, aluminium and silicon oxides are almost insoluble, and acids are formed on the right-hand side (Table 9.3).

Table 9.3

Oxide	Reaction	pH of solution	Equation
Sodium	Dissolves exothermically	14	$Na_2O + H_2O \rightarrow 2NaOH$
Magnesium	Slight reaction	9	$MgO + 2H_2O \rightarrow Mg(OH)_2$
Aluminium	No reaction		
Silicon	No reaction		
Phosphorus	Phosphorus(III) oxide reacts with cold water Phosphorus(V) oxide reacts violently	1–2 1–2	$P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$ $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$
Sulfur	Sulfur dioxide dissolves readily Sulfur trioxide reacts violently	1 0	$SO_2 + H_2O \rightarrow H_2SO_3$ $SO_3 + H_2O \rightarrow H_2SO_4$
Chlorine	Does not react with water		
Argon	No oxide is formed		

Aluminium oxide is **amphoteric**. This means that it reacts with both acids and alkalis. Aluminium oxide contains oxide ions, so it reacts as a base with acids, in a similar way to magnesium oxide:

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$$

It also has significantly acidic tendency, reacting with alkalis, such as sodium hydroxide, to form an aluminate:

$$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$$

Reactions of the chlorides with water

The reactions of the chlorides of Period 3 elements with water (Table 9.4) give clues about the bonding present. This is linked to the electronegativity of the element. As you saw in Chapter 3, the bigger the difference in electronegativity, the more polar is the bond. Sodium and chlorine have a difference of 2.1 whereas sulfur and chlorine have a difference of only 0.5.

Table 9.4

Chloride	Bonding	Electronegativity	Reaction	Equation
Sodium	Ionic (electrovalent)	0.9	Dissolves to give Na^+ and Cl^- ions	
Magnesium	Ionic (electrovalent)	1.2	Dissolves to give Mg^{2+} and Cl^- ions	
Aluminium	Mainly covalent	1.5	Hydrolyses	$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl$
Silicon	Covalent	1.8	Hydrolyses	$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$
Phosphorus	Covalent	2.1	Hydrolyses	$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$
Sulfur	Covalent	2.5	Hydrolyses	$2S_2Cl_2 + 2H_2O \rightarrow SO_2 + 4HCl + 3S$
Chlorine	No reaction	3.0		
Argon	No reaction			

Now test yourself

Tested ☐

3 An element J in Period 3 reacts vigorously with oxygen when in powder form. It forms a liquid chloride that hydrolyses in water to give an acidic solution and an insoluble solid.

Identify J and write balanced equations for the three reactions described.

Answers on p.198

Revision activity

1 Sketch a graph to show how the first ionisation energy changes across Period 3 from sodium to argon.

2 For the elements in Period 3:

- **a** Write the formulae of two oxides that do not react with water.
- **b** Identify the element that can exist in oxidation states +3 and +5.
- **c** Identify the element whose oxide forms a very strong giant covalent lattice.
- **d** Identify the element that reacts with nitrogen when it is burned in air.

3 Write equations to show that aluminium oxide is amphoteric.

Answers on p.203

10 Group 2

Group chemistry

Revised ☐

You need to know about the chemistry of two groups in the Periodic Table —Groups 2 and 17 — as well as the transition metals, which are covered in Chapter 12, and the elements nitrogen and sulfur, which are covered in Chapter 13. Group 2 is covered in this chapter and Group 17 in Chapter 11.

Most of the Group 2 learning outcomes (except the trends in thermal stability of the nitrates and carbonates and the variability in solubility of the hydroxides and sulfates) are needed for AS.

Physical properties of the elements

Revised ☐

Some of the most useful physical properties of the Group 2 metals are shown in Table 10.1.

Table 10.1

Element	Atomic radius/nm	1st ionisation energy/kJ mol^{-1}	Electronegativity	Melting point/°C
Beryllium	0.111	900	1.57	1278
Magnesium	0.160	738	1.31	649
Calcium	0.197	590	1.00	839
Strontium	0.215	550	0.95	769
Barium	0.217	503	0.89	729

The first three physical properties show steady trends — increasing upwards in atomic radius and downwards in first **ionisation energy** and electronegativity. The decrease in melting point would fit this pattern if it were not for the anomalous low value for magnesium.

You can explain the change in atomic radius in terms of the additional shell of electrons added for each period and the reduced effective nuclear charge as more electron shells are added.

As Group 2 is descended, the increase in charge of the nucleus is offset by the number of inner electrons. However, the distance of the outer electrons from the nucleus increases and the first ionisation energy decreases down the group.

The **electronegativity** of the atoms decreases down the group. As the size of the atoms increases, any bonding pair of electrons is further from the nucleus, which means it is less strongly held and the electronegativity decreases. The effect of this is to increase the ionic (electrovalent) character of any compounds as the group is descended.

Expert tip

You need to remember that **ionisation energy** is governed by:

- the charge on the nucleus
- the amount of screening by the inner electrons
- the distance between the outer electrons and the nucleus

Expert tip

You need to remember that **electronegativity** is the ability of an atom to attract a pair of bonding electrons.

Now test yourself

Tested ☐

1 As Group 2 is descended the nuclear charge increases, but the electronegativity decreases. Explain this behaviour.

Answer on p.198

Reactions of the elements with oxygen, water and dilute acids

The only reactions you need to remember for the Group 2 elements are their reactions with oxygen, water, and dilute acids. These are summarised in Table 10.2.

Table 10.2

Element	Reaction with oxygen	Reaction with water	Reaction with dilute acids
Beryllium	Reluctant to burn, white flame	No reaction	Reacts rapidly
Magnesium	Burns easily with a bright white flame	Reacts vigorously with steam but only slowly with water	Reacts vigorously
Calcium	Difficult to ignite, flame tinged red	Reacts moderately forming the hydroxide	Reacts vigorously
Strontium	Difficult to ignite, flame tinged red	Reacts rapidly forming the hydroxide	Reacts violently
Barium	Difficult to ignite, flame tinged green	Reacts vigorously forming the hydroxide	Reacts violently

The general equation for the reaction with oxygen is:

$$2X(s) + O_2(g) \rightarrow 2XO(g)$$

where X is any metal in the group.

Both strontium and barium can also form a peroxide as well as the oxide:

$$Y(s) + O_2(g) \rightarrow YO_2(g)$$

where Y is strontium or barium.

The general equation for the reaction with water is:

$$X(s) + 2H_2O(l) \rightarrow X(OH)_2(s) + H_2(g)$$

The exception to this is magnesium, which forms the oxide when reacted with steam.

The general equation for the reaction with dilute acids is:

$$X(s) + 2H_3O^+(aq) \rightarrow X^{2+}(aq) + H_2(g) + 2H_2O(l)$$

Behaviour of the oxides, hydroxides and carbonates with water and dilute acids

Beryllium oxide is amphoteric, but all the other oxides are sparingly soluble in water, producing solutions of increasing base strength:

$$XO(s) + H_2O(l) \rightarrow X(OH)_2(aq)$$

The hydroxides increase in solubility down the group due to the decrease in lattice dissociation enthalpy, which outweighs the change in the enthalpy of hydration of the metal ion.

The carbonates decrease in solubility down the group due to the decrease in the enthalpy of hydration of the metal ion.

The compounds react with dilute acids depending on the solubility of the salts they produce. They all react easily with dilute nitric acid because the nitrates are soluble, although there is a decrease in solubility for strontium and barium. Only the magnesium compounds react appreciably with sulfuric acid because the other sulfates are sparingly soluble. In general, the reactions with hydrochloric acid are similar to those with nitric acid.

Thermal decomposition of nitrates and carbonates

The changes in thermal stability stem from the ability of a cation to polarise the anion. This is more pronounced at the top of the group, where the cations are smaller and have a high charge density. This applies to both the nitrate and carbonate where polarisation results in the formation of the oxide:

$$2X(NO_3)_2(s) \rightarrow 2XO(s) + 4NO_2(g) + O_2(g)$$

$$XCO_3(s) \rightarrow XO(s) + CO_2(g)$$

You can examine this trend by comparing the decomposition temperatures of the carbonates (Table 10.3).

Table 10.3

Element	Decomposition temperature of the carbonate/K
Beryllium	Unstable at 298
Magnesium	700
Calcium	1200
Strontium	1580
Barium	1660

Now test yourself

2 Why are the nitrates of Group 2 elements less stable at the top of the group than at the bottom?

Answer on p.198

Tested ☐

Solubility of Group 2 sulfates and hydroxides

The **solubility** of the sulfates of Group 2 elements decreases down the group.

This is due to a combination of the relative sizes of the enthalpy change of hydration of the cations and the lattice energy of the sulfate concerned.

As the cations get bigger, the energy released when the ions bond to water molecules (the enthalpy change of hydration) falls. Larger ions are not as strongly attracted to the water molecules. As you go down a group, the energy needed to break up the lattice decreases as the positive ions get bigger. The bigger the ions, the more distance there is between them and the weaker are the forces holding them together. Because both energy changes decrease, it is a question of which is the more significant. For large ions, such as SO_4^{2-}, it is the enthalpy change of hydration factor that dominates.

Conversely the hydroxides of Group 2 elements become *more* soluble descending the group, but there isn't a simple explanation for this.

Expert tip

The **solubility** of the sulfates of Group 2 decreases down the group.

Important uses of Group 2 compounds

Revised ☐

Calcium carbonate and calcium hydroxide

Limestone is a naturally occurring form of calcium carbonate. It has been used for thousands of years in the construction of buildings and roads. It is also used in the manufacture of cement. Marble is another form of calcium carbonate and is also used in building.

'Lime' (calcium hydroxide) is used to reduce the acidity of soils in agriculture. It neutralises the soil to provide better growing conditions for crops. The application of lime must be controlled carefully to achieve the appropriate soil pH and not make it too alkaline.

Revision activity

1 How do the chemical properties of the Group 2 elements compare with those of Group 1?

2 Suggest a reason for this.

Answers on p.203

11 Group 17

All of this chapter is needed for AS.

Characteristic physical properties

Revised ☐

Group 17 — the halogens — consists of reactive non-metals, all of which exist as diatomic molecules, X_2. Their properties are summarised in Table 11.1.

Table 11.1

Element	Appearance	Boiling point/K	$E^\ominus$: $X_2 + 2e^- \rightleftharpoons 2X^-$/V	Electronegativity
Fluorine	Pale yellow gas	85	+2.87	4.0
Chlorine	Yellow-green gas	238	+1.36	3.0
Bromine	Dark red liquid	332	+1.07	2.8
Iodine	Shiny dark grey solid	457	+0.54	2.5

The Group 17 elements are volatile non-metals. They exist as diatomic molecules that attract each other using van der Waals forces. The larger the halogen molecules, the bigger the van der Waals forces, and hence the higher the boiling point.

There is a decrease in **reactivity** on moving down the group. This is due, in part, to the increase in atomic radius because the incoming electron has to go into a shell further away from an increasingly shielded nucleus. Nonetheless, the elements are still too reactive to occur uncombined, unlike some metals and other non-metals such as carbon. The electronegativity and the $E^\ominus$ values show that these elements are oxidising agents with reactivity that decreases down the group.

Expert tip

There is a **decrease** in reactivity on moving down the group.

Now test yourself

Tested ☐

1 What does the physical state of the Group 17 elements tell you about the forces between the molecules?

Answer on p.199

Important chemical reactions

Revised ☐

Hydrogen halides

One of the most important set of compounds of the Group 17 elements is the hydrogen halides, HX. These are prepared in different ways depending on the oxidising power of the halogen concerned. Hydrogen chloride can be prepared by heating sodium chloride with concentrated sulfuric acid:

$$\mathrm{NaC}l(\mathrm{s}) + \mathrm{H_2SO_4(l)} \rightarrow \mathrm{NaHSO_4(s)} + \mathrm{HC}l(\mathrm{g})$$

However, neither hydrogen bromide nor hydrogen iodide can be prepared by this method because they would be oxidised further by the sulfuric acid.

The only acid that can be used to prepare all three hydrogen halides is phosphoric(V) acid:

$$\mathrm{NaX(s)} + \mathrm{H_3PO_4(s)} \rightarrow \mathrm{NaH_2PO_4(s)} + \mathrm{HX(g)}$$

Hydrogen fluoride is much harder to produce in a pure state because fluorine is such a strong oxidising agent. It will even oxidise water, giving a mixture of hydrogen fluoride and oxygen:

$$2F_2(g) + 2H_2O(l) \rightarrow 4HF(g) + O_2(g)$$

You have to be able to compare the bond energies of the hydrogen halides (Table 11.2) and use these data to explain their relative thermal stabilities.

Table 11.2

	Bond energy/kJ mol^{-1}			
Element	**Fluoride**	**Chloride**	**Bromide**	**Iodide**
H	568	432	366	298
C	467	346	290	228

The bond energies of fluorine with hydrogen and carbon are significantly higher than those of the other Group 17 elements. This means that the formation of covalent fluorides is usually strongly exothermic because this means breaking F–F bonds and making E–F bonds (where E is the element concerned).

H–X bond energies decrease steadily down the group, making it easier to break the H–X bond. So, for example, plunging a red-hot wire into a halogen halide has the following effects:

- The HI decomposes.
- The HBr shows some evidence of decomposition.
- HC*l* is unaffected.

Now test yourself

2 What do you think the effect would be of plunging a red-hot wire into HF? Explain your answer.

Answer on p.199

Tested ☐

Reactions of the halide ions, other than fluoride ions

Testing for halide ions

The characteristic test for halide ions in solution is to add silver nitrate solution followed by aqueous ammonia (Table 11.3). You have probably carried out this test a number of times in practical sessions.

Table 11.3

Halide ion	Reaction with $Ag^+(aq)$	Subsequent reaction with $NH_3(aq)$
Chloride	White precipitate is formed	Dissolves to form colourless solution
Bromide	Cream precipitate is formed	Only dissolves in concentrated ammonia
Iodide	Yellow precipitate is formed	Insoluble in ammonia

$$Ag^+(aq) + X^-(aq) \rightarrow AgX(s)$$

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$$

The equilibrium in the first equation lies to the right so it can be regarded as a forward reaction. However, the equilibrium in the second equation also lies to the right and, therefore, removes silver ions from the remaining solution causing the silver halide to dissolve. This is true for chloride and bromide ions. Silver iodide is so insoluble that even concentrated ammonia solution is unable to reverse the process.

Reactions with other halogens

The halide ions in aqueous solution react with halogens higher up the group, being oxidised to their respective halogen. Aqueous chlorine reacts with both bromide ions and iodide ions, liberating bromine and iodine respectively:

$$2Br^-(aq) + Cl_2(aq) \rightarrow Br_2(aq) + 2Cl^-(aq)$$

Aqueous bromine liberates iodine from iodide ions.

Reactions with concentrated sulfuric acid

The reactions of the halide ions with concentrated sulfuric acid can also be used as a test (Table 11.4).

Table 11.4

Ion present	Observations
Chloride	Steamy acidic fumes (of HCl)
Bromide	Steamy acidic fumes (of HBr) mixed with brown bromine vapour
Iodide	Some steamy fumes (of HI) and lots of purple iodine vapour

Although a hydrogen halide is formed in each case, hydrogen bromide and hydrogen iodide are oxidised by the sulfuric acid:

$$NaCl(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HCl(g)$$

$$2HBr(g) + H_2SO_4(l) \rightarrow SO_2(g) + 2H_2O(l) + Br_2(l)$$

$$8HI(g) + H_2SO_4(l) \rightarrow H_2S(g) + 4H_2O(l) + 4I_2(s)$$

Note that one molecule of sulfuric acid oxidises two molecules of hydrogen bromide, but eight molecules of hydrogen iodide. This shows how much easier it is to oxidise iodide ions, I^-, than it is to oxidise bromide ions, Br^-.

Reactions of chlorine with sodium hydroxide

Chlorine reacts differently with sodium hydroxide depending on the temperature and the concentration of the alkali.

With cold, dilute sodium hydroxide solution the reaction is:

$$Cl_2(aq) + 2OH^-(aq) \rightarrow Cl^-(aq) + ClO^-(aq) + H_2O(l)$$

In this reaction, the element chlorine (oxidation number 0) has been converted into chloride ions (oxidation number −1) and chlorate(I) ions (oxidation number +1).

With hot, concentrated sodium hydroxide solution this reaction takes place:

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

In this case, the element chlorine has been converted into chloride ions (oxidation number −1) and chlorate(V) ions (oxidation number +5).

These are both examples of **disproportionation** reactions in which an element is both oxidised and reduced.

The reason for the difference in the two reactions is the instability of the chlorate(I) ion, in which the chlorine disproportionates at higher temperatures:

$$3ClO^-(aq) \rightarrow 2Cl^-(aq) + ClO_3^-(aq)$$

A **disproportionation** reaction is one in which an element in a compound is both oxidised and reduced.

Now test yourself

3 Can you think of (or research) an example of disproportionation not using chlorine?

Answer on p.199

Tested ☐

Important use of halogens and halogen compounds

Chlorine, and to a lesser extent the other halogens, have a number of important economic and industrial uses.

Chlorine in water purification

Chlorine is used to kill bacteria and sterilise water for domestic supplies in many parts of the world — it is also used in some swimming pools. The ability of chlorine to destroy bacteria is a result of its powerful oxidising power, which disrupts the chemistry of bacterial cells. However, traces in our drinking water are insufficient to do us any harm and the benefits of water chlorination far outweigh the risks. The chlorine may be supplied as the gas, or added as solid sodium chlorate(I).

Manufacture of bleach

Sodium hydroxide and chlorine can be combined chemically to make the bleach, sodium chlorate(I), $NaClO$. This is used in some domestic cleaning agents. It chemically cleans materials such as washbasins and toilets, and 'kills' microorganisms.

Manufacture of PVC

PVC, or poly(chloroethene), is a tough, useful plastic and a good electrical insulator. It is much tougher than poly(ethene) and very hard wearing with good heat stability. It is used for covering electrical wiring and plugs. It is also replacing metals for use as gas pipes and water pipes, and replacing wood in window frames. It is made by reacting chlorine with ethene, heating the product and then polymerising the chloroethene formed (see Chapter 15).

Halogenated hydrocarbons

Many hydrocarbons react with halogens and a number of the products are commercially important. You have already seen how chlorine is important in making the polymer, PVC. It is also important in making solvents such as trichloroethane, used in dry-cleaning, and tetrachloromethane. It is used to produce antiseptics and disinfectants and has been used to make CFCs (chlorofluorocarbons), which, in the past, were used as refrigerants and aerosol propellants. This use has now been reduced dramatically because CFCs break down in the upper atmosphere, and the chlorine atoms catalyse the destruction of ozone, which is important for absorbing ultraviolet radiation.

Revision activity

1. What does 'disproportionation' mean?
2. Write an equation showing a disproportionation reaction.
3. A compound is known to contain a halide ion. Describe chemical tests that you could use to find out whether it is a chloride, a bromide or an iodide.

Answers on p.203

12 An introduction to the chemistry of transition elements

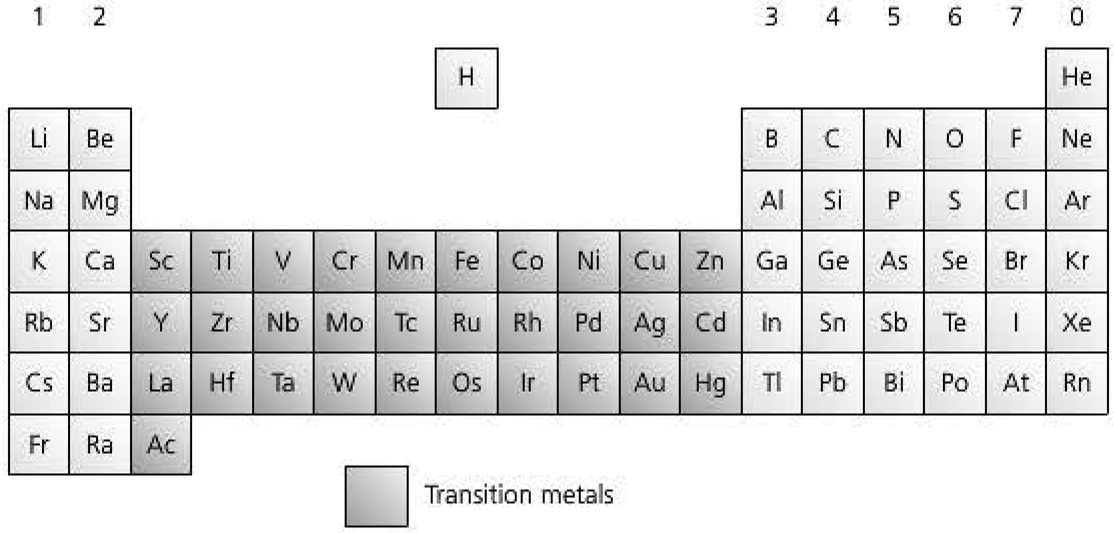
All this chapter is needed for A level. The only part relevant to AS is the use of iron as a catalyst in the Haber process and vanadium pentoxide as a catalyst in the Contact process, which are dealt with in Chapter 7.

Physical properties

Revised ☐

Electronic structures of atoms and ions

Although you can probably identify the block of elements that make up the transition elements in the Periodic Table (Figure 12.1), you need to know *why* these elements are different from other metals, and what makes them special.



1	2											3	4	5	6	7	0
							H										He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

▨ Transition metals

Figure 12.1 The Periodic Table

The **transition elements** are shaded and represent the filling of the d-electron orbitals in each of the 3d-, 4d- and 5d-orbitals.

You only really need to know details about the 3d elements — scandium, Sc, to zinc, Zn.

You can see this best by looking at the electron configurations of the elements and ions of this group of elements (Figure 12.2).

Table 12.1 shows some of the common properties of the elements scandium to zinc. If you look first at the electron configurations of the elements, you can see that all except copper and zinc have incompletely filled d-orbitals.

Considering the common oxidation states, you can see that Sc^{3+} ions have no d-electrons, and that Zn^{2+} ions have full d-orbitals. Based on this evidence there is a case for saying that scandium is a transition element, but that no case can be made for zinc.

On examining the common stable ions of the transition elements you can see that, with the exception of scandium, all the elements lose their two 4s-electrons to form a 2+ ion. For elements that have two to five 3d electrons, the loss of these, together with the 4s electrons, gives the highest oxidation state (the ion with the highest positive charge). Note that there are no d^4 or d^9 arrangements for chromium or copper. This is because half-full and completely full d-orbitals are favoured energetically.

Now test yourself

1 Study the data in Table 12.1.
  - **a** Give **two** pieces of data that show scandium differing from a typical transition metal.
  - **b** Give **two** pieces of data that show zinc differing from a typical transition metal.

Answers on p.199

Tested ☐

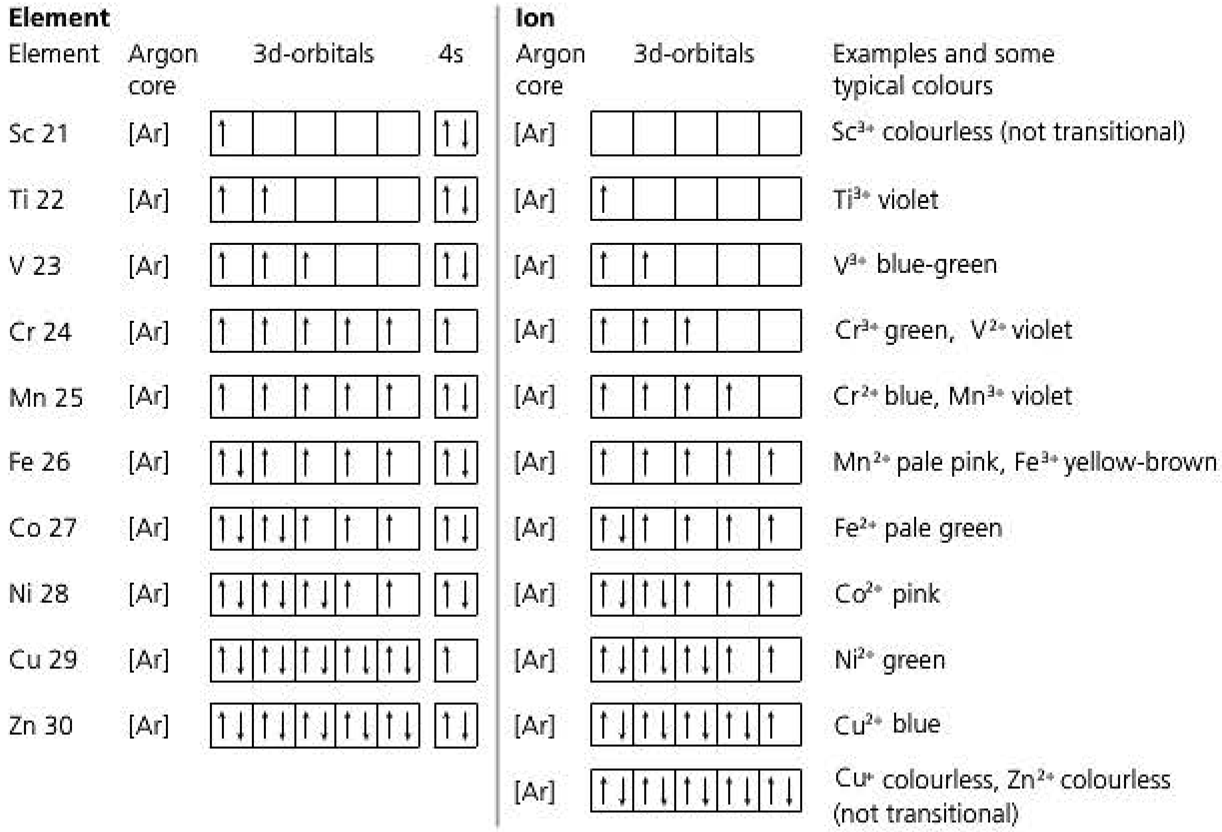


Figure 12.2 Electron configuration of the elements and some ions of transition metals

Table 12.1

Property	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Melting point/°C	1541	1668	1910	1857	1246	1538	1495	1455	1083	420
Density/g cm^{-3}	2.99	4.54	6.11	7.19	7.33	7.87	8.90	8.90	8.92	7.13
Atomic radius/pm	161	145	132	125	124	124	125	125	128	133
M^{2+} ionic radius/pm	n/a	90	88	84	80	76	74	72	69	74
M^{3+} ionic radius/pm	81	76	74	69	66	64	63	62	n/a	n/a
Common oxidation states	+3	+2,3,4	+2,3, 4,5	+2,3,6	+2,3,4,6,7	+2,3,6	+2,3	+2,3	+1,2	+2
Outer electron configuration	$3d^14s^2$	$3d^24s^2$	$3d^34s^2$	$3d^54s^1$	$3d^54s^2$	$3d^64s^2$	$3d^74s^2$	$3d^84s^2$	$3d^{10}4s^1$	$3d^{10}4s^2$
First ionisation energy/kJ mol^{-1}	632	661	648	653	716	762	757	736	745	908

You might be asked to state the electron configuration of a given transition element and suggest its stable ions. You can do this from the Periodic Table:

- Use the proton (atomic) number to work out the total number of electrons.
- Then put the electrons into orbitals, bearing in mind the exceptions mentioned above.

Look at the rows in Table 12.1 that give data about atomic radii, ionic radii and first ionisation energies. You can see that across the transition elements there is a relatively small change in each of these properties.

Other physical properties

You are also expected to be able to contrast the properties of the transition elements with those of the s-block metal, calcium (Table 12.2).

You can see from the melting points and densities that the transition elements are much more similar to each other than they are to calcium. This is also borne out by the atomic and M^{2+} ionic radii and, to a lesser extent, by the first ionisation energies.

Table 12.2

Property	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Melting point/°C	839	1541	1668	1910	1857	1246	1538	1495	1455	1083
Density/g cm^{-3}	1.55	2.99	4.54	6.11	7.19	7.33	7.87	8.90	8.90	8.92
Atomic radius/pm	197	161	145	132	125	124	124	125	125	128
M^{2+} ionic radius/pm	106	n/a	90	88	84	80	76	74	72	69
1st ionisation energy/ kJ mol^{-1}	590	632	661	648	653	716	762	757	736	745

The syllabus also refers to conductivity, but comparisons are harder to make here because all metals are much better electrical conductors than semi-conductors or non-metals.

Chemical properties

Revised ☐

Oxidation states

As you can see from Table 12.1, most of the transition elements form more than one ion or oxidation state. You can see the details more clearly in Figure 12.3. The reason that these other oxidation states exist is that there is not a large energy barrier to the removal of subsequent electrons.

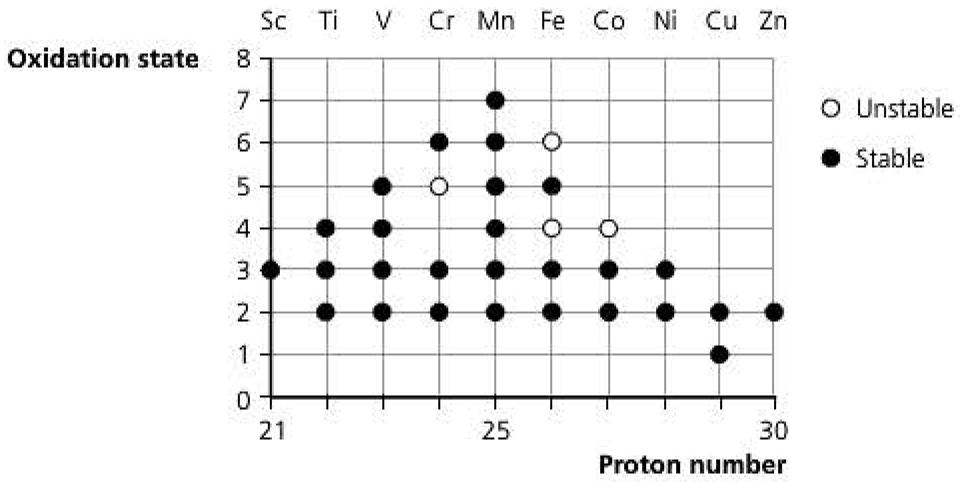


Figure 12.3 Oxidation states in transition metals

You can see an example of this if you compare the first four ionisation energies of calcium with those of chromium and manganese (Table 12.3).

Table 12.3

Element	Proton number	1st IE/kJ mol^{-1}	2nd IE/kJ mol^{-1}	3rd IE/kJ mol^{-1}	4th IE/kJ mol^{-1}
Calcium	20	590	1150	4940	6480
Chromium	24	653	1590	2990	4770
Manganese	25	716	1510	3250	5190

It is clear from the data in Table 12.3 that to remove the third electron from calcium requires about as much energy as removing the fourth from chromium or manganese. However, it is not as simple as just comparing ionisation energies. Having ionised the metal, it then has to react to form a compound. There are two key enthalpies to consider — the lattice enthalpy (if a solid is being formed) and the enthalpies of hydration of the ions (if an aqueous solution is being formed).

The more highly charged an ion, the more electrons have to be removed and the more ionisation energy has to be provided. Offsetting this, however, the more highly charged the ion, the more energy is released either as lattice enthalpy or as the hydration enthalpy of the metal ion.

Now test yourself

Tested ☐

2 The graph in Figure 12.4 was obtained for one of the first row transition metals. Explain the important points on the graph and identify the metal.

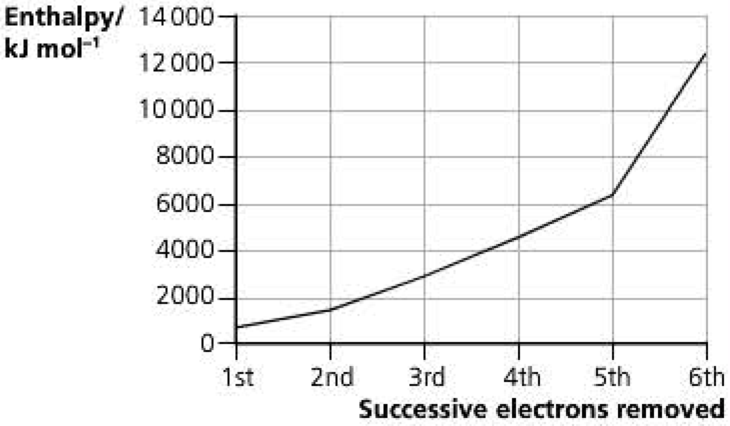


Figure 12.4

Answers on p.199

Redox systems

There are three important redox systems that you need to know about and also for the practical syllabus: Fe^{3+}/Fe^{2+}, MnO_4^-/Mn^{2+} and $Cr_2O_7^{2-}/Cr^{3+}$. You have already looked at some simple redox processes in Chapter 6.

The reaction between acidified manganate(VII) ions and iron(II) ions

This reaction is used to estimate iron(II) ions quantitatively. It is self-indicating — on the addition of a standard solution of potassium manganate(VII) to an iron(II) solution, decolorisation of manganate(VII) occurs as the almost colourless manganese(II) ion (a very pale pink) is formed. The end point is when the first permanent pale pink is seen with one drop excess of the manganate(VII). The dilute sulfuric acid prevents the formation of a manganese(IV) oxide precipitate and ensures the reduction of manganate(VII) ions to manganese(II) ions.

The two half-equations are:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l) \qquad E^\ominus = +1.52\,V$$

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \qquad E^\ominus = +0.77\,V$$

Because each iron(II) ion supplies one electron, each manganate(VII) ion can oxidise five iron(II) ions. Thus, the overall equation is:

$$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$$

The reaction between acidified dichromate(VI) ions and iron(II) ions

As with potassium manganate(VII), a standard solution of potassium dichromate(VI) can be used to estimate iron(II) ions in solution quantitatively. In this case, however, a redox indicator must be used to detect the end point.

The indicator changes colour when oxidised to another form, but only after the iron is oxidised, i.e. it is not as easily oxidised as Fe^{2+} — the $E^\ominus$ of the indicator is more positive than that of Fe^{2+} but lower than that for the dichromate(VI) ions. Hence, it is oxidised by the dichromate to show the end point.

The two half-equations are:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l) \qquad E^\ominus = +1.33\,V$$

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \qquad E^\ominus = +0.77\,V$$

Because each iron(II) ion supplies one electron, each dichromate(VI) ion can oxidise six iron(II) ions. The overall equation is:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Fe^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(l)$$

Other redox reactions

The transition metals take part in a range of redox reactions, some of which could form part of the titrimetric work you may be asked to carry out in the practical paper. You might also be asked to predict whether or not a given reaction will take place based on $E^\ominus$ data. If you are not sure how to do this, read Chapter 6 again.

The important things to remember are:

- Metals react by electron loss (oxidation state increases) to form positive cations (e.g. sodium ion, Na^+) — so, as the electron-loss potential increases, the reactivity of the metal increases.
- Non-metallic elements react by electron gain (oxidation state decrease) to form single covalent bonds (e.g. HCl) or the negative anion (e.g. chloride ion Cl^- in $NaCl$) — so, as the electron-accepting power decreases, so does the reactivity of the element.
- For a reaction to be feasible, the E_{cell} value must be *positive* — so if you calculate it to be negative, the reverse reaction will be the feasible one.

Now test yourself

3 Work out the overall equation for the reaction of manganate(VII) ions with hydrogen peroxide in acid solution.

Answer on p.199

Tested ☐

The geometry of the d-orbitals

In Chapter 3 you looked at the shape and symmetry of s- and p-orbitals, which can hold two and six electrons respectively. In considering the transition elements you need to understand the shape and symmetry of the d-orbitals, which can hold up to ten electrons.

The d-orbitals can be divided into two groups, as shown in Figure 12.5.

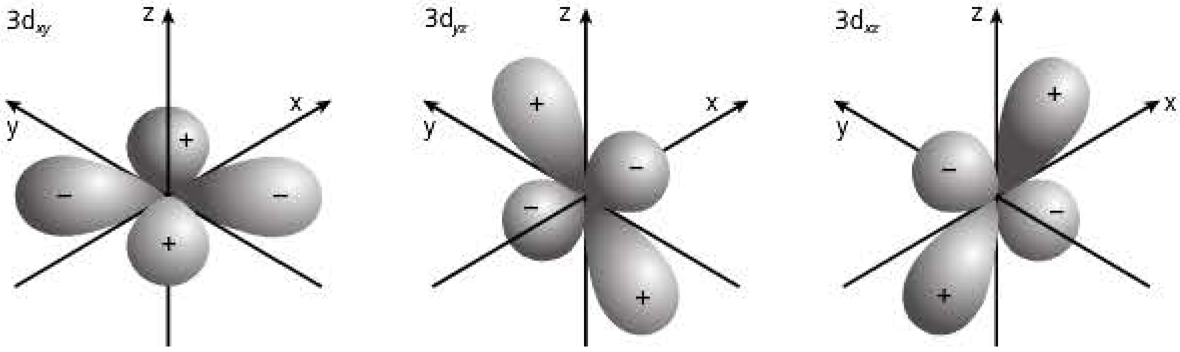


Figure 12.5(a)

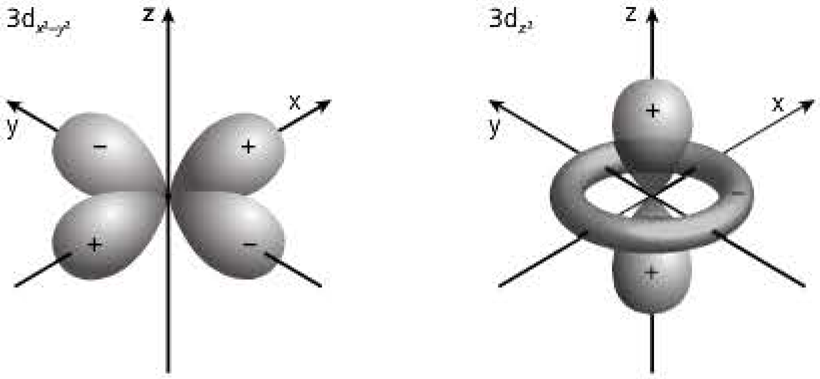


Figure 12.5(b)

Each of the first group is similar to a pair of p-orbitals at right angles to one another, and as you can see the lobes lie between the *xy*, *yz* and *zx* axes.

The second group is different in that the lobes lie on the *xy* and z axes. You do *not* need to know *why* they are these shapes, only the shapes and symmetry of the five orbitals.

The shape and symmetry of these orbitals are important when transition metal cations react to form **complexes**.

The metal cations do this by interacting with **ligands**.

Imagine electron-rich ligands approaching a transition metal ion with electrons in its d-orbitals. There will be some repulsion, raising the energy of some d-orbitals more than that of others.

A **complex** is a transition metal ion bound to a number of ligands (see below), usually four or six, which reacts as a large ion.

A **ligand** is an atom, ion or molecule that can act as an electron-pair donor, and usually forms a dative covalent or 'coordinate' bond with the central metal ion. Ligands can be monodentate, bidentate or polydentate depending on the number of dative bonds they form with the transition metal ion.

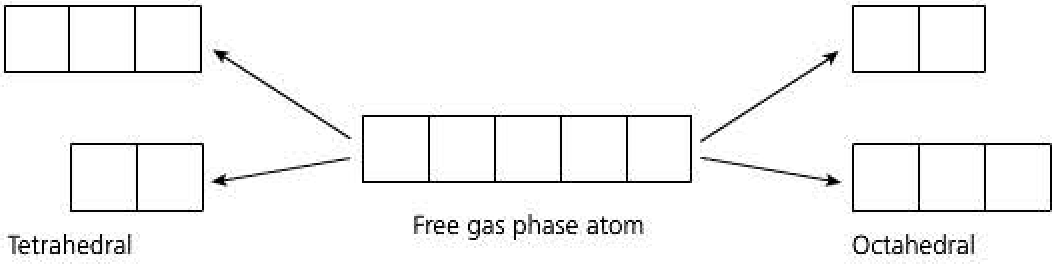


Figure 12.6 Splitting of d-orbitals in transition metal complexes

Figure 12.6 shows that for the formation of a tetrahedral complex, three orbitals have higher energy ($3d_{xy}$, $3d_{yz}$ and $3d_{zx}$), whereas for an octahedral complex the reverse is true ($3d_{x^2-y^2}$ and $3d_{z^2}$). This is because in octahedral complexes the ligands approach the central metal ion along the axes, and there is repulsion between the electrons on the ligands and those in the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals. In tetrahedral complexes the four ligands approach the central metal ion between the axes and now there is repulsion between the electrons on the ligands and those in the $3d_{xy}$, $3d_{yz}$ and $3d_{zx}$ orbitals.

Formation of complexes

As well as forming simple compounds, such as oxides and salts, one of the characteristic properties of transition metals is their ability to form complex ions, many of which have distinctive colours. The reason for the colour is the absorption of light from different parts of the electromagnetic spectrum. This absorption occurs because of the movement of an electron from a lower energy d-orbital to one of higher energy (see Figure 12.6). In the case of aqueous copper(II) ions the transition is shown in Figure 12.7.

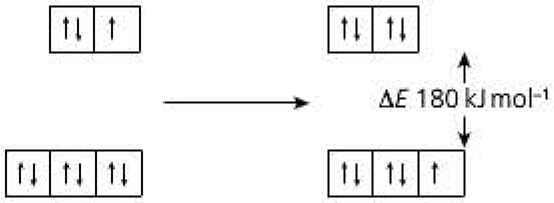


Figure 12.7 Promotion of an electron in copper(II)

Expert tip

The **colour** you observe for a complex ion is what remains from white light after the energy required to promote an electron from one group of d-orbitals to the other group has been removed.

The promotion of this electron requires 180 kJ mol^{-1}, and the frequency corresponding to this lies in the red-orange region of the spectrum. As a result, these colours are absorbed leaving yellow, green, blue and purple to be transmitted, resulting in the familiar pale blue colour of aqueous Cu(II) ions.

The **colour** of a complex depends on the energy gap in the d-orbitals, which is a result of two factors:

- the nature of the metal and its oxidation state
- the nature of the ligand

You are familiar with the colours of the two common oxidation states of iron, Fe^{2+} and Fe^{3+} in aqueous solution — Fe^{2+} is pale green and Fe^{3+} is yellow-brown.

When copper ions are dissolved in water, they form the complex ion $[Cu(H_2O)_6]^{2+}$, which is pale blue. On adding aqueous ammonia to this solution until the ammonia is present in an excess, the solution turns a deep blue:

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

The deepening blue is a sign of a bigger energy gap between the two sets of orbitals (Figure 12.7).

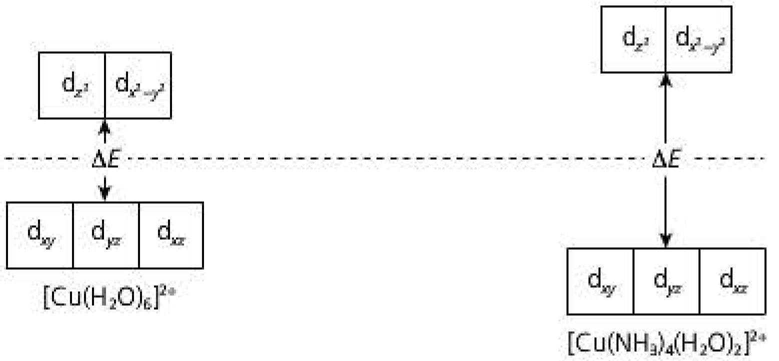


Figure 12.8 Energy gap in copper(II) complexes

Other ligands can have a bigger or smaller energy gap and some indication of the order is given in Figure 12.9.

Smallest splitting Cl^-

↓ OH^-

H_2O

NH_3

Largest splitting CN^-

Figure 12.9

Coordination number

You need to be able to say a little more about the structure of transition metal complexes. First of all the coordination number is the number of coordinate bonds formed by the metal ion. In many cases this will be the same as the number of ligands, but some ligands can form more than one coordinate bond, so be careful. The most common coordination numbers are 4 and 6 (Figure 12.10).

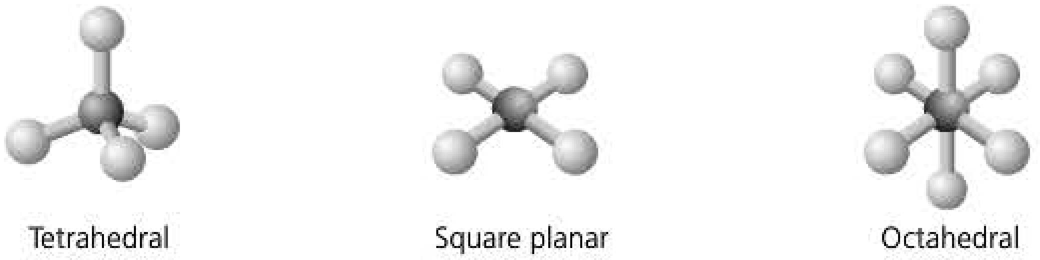
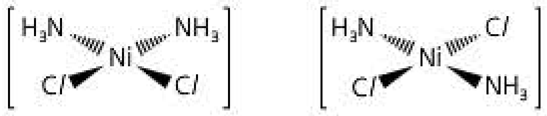

Tetrahedral Square planar Octahedral

Figure 12.10 Transition metal complexes with coordination numbers 4 and 6

You also need to be able to predict the formula and charge of a complex ion given the metal ion, its charge, its ligand(s) and its coordination number.

The ability of transition metals to form complexes with four or six coordinate bonds gives rise to the possibility of different structure. This means that both *cis–trans* isomerism (Figure 12.11a and b) and optical isomerism (Figure 12.12) can occur (see also Chapter 13). This can occur with both mono- and bidentate ligands.



Cis *Trans*

Figure 12.11a *Cis–trans* isomerism in square planar transition metal complexes

Cis-tetraammine cobalt dichloride *Trans*-tetraammine cobalt dichloride

Figure 12.11b *Cis–trans* isomerism in octahedral transition metal complexes

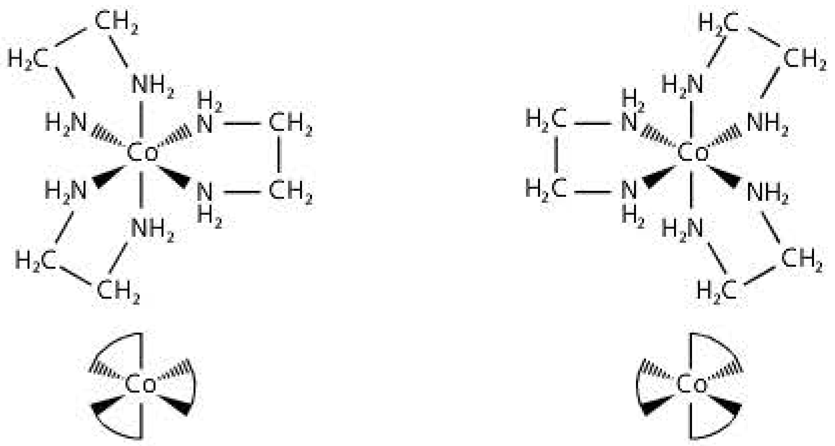


Figure 12.12 Optical isomerism in octahedral transition metal complexes

Now test yourself

4 Three octahedral complexes of chromium are coloured blue, green and purple. Each complex contains one type of ligand — ammonia, water or hydroxide ions.

Identify the formula of each complex and match it to the correct colour, explaining your reasoning.

Answers on p.199

Tested ☐

A **coordination number** is the number of coordinate bonds formed by a metal ion.

Now test yourself

5 Predict the formula, including the overall charge, of the 4-coordinate complex of cobalt(II) with chloride ions.

Answer on p.199

Tested ☐

Stereoisomerism refers to the ability of transition metal complexes to form isomers that have different three-dimensional arrangements of ligands. Both *cis–trans* and optical isomerism is possible.

The structure of different isomers can affect their properties, particularly in biochemical reactions. One example is '*cis*-platin' (see Figure 12.13) which is an important anticancer drug, whereas '*trans*-platin' is ineffective.

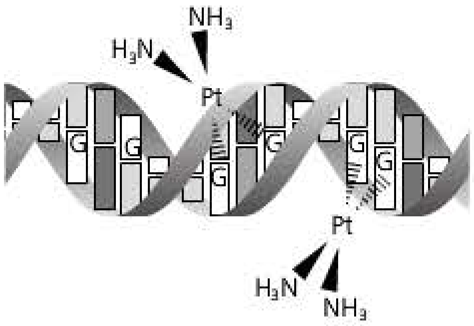


Figure 12.13 *Cis*-platin binding to DNA

Cis-platin works by binding to two guanine bases in the same strand of DNA and preventing replication of the DNA.

Complex stability and ligand exchange

The different colour changes seen on adding different reagents to aqueous solutions that contain transition metal ions occur because some complexes are more stable than others. Remember that most aqueous reactions involve equilibria and that using a high concentration of a reagent will change the position of equilibrium. However, this only becomes significant if the **stability constant** for the complex has a reasonable magnitude. The stability constant is the term used for the equilibrium constant for any change.

The **stability constant** of a complex, K_{stab}, is the equilibrium constant for the formation of the complex from its constituent ions or molecules, for a given solvent. The larger the value of K_{stab} the more stable is the complex.

You have already seen how, in the case of aqueous copper(II) ions and ammonia, the pale blue of the hexaaquacopper(II) ion is replaced by the much darker blue tetraamminediaquacopper(II) ion.

Another example is the addition of aqueous hydroxide ions to a solution of Cu^{2+} ions in concentrated hydrochloric acid. The initial complex is $[CuCl_4]^{2-}$ which is yellow-green. On adding hydroxide ions the solution gradually turns pale blue as $[Cu(H_2O)_6]^{2+}$ ions are formed. As more hydroxide ions are added, a pale blue precipitate is formed as the hydroxide ions displace water molecules in the complex.

$$[CuCl_4]^{2-} + 6H_2O \rightleftharpoons [Cu(H_2O)_6]^{2+} + 4Cl^-$$

$$[Cu(H_2O)_6]^{2+} + 2OH^- \rightleftharpoons [Cu(H_2O)_4(OH^-)_2]$$

If you consider the reaction:

$$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$$

the value of K_{stab} is $1.20 \times 10^{13}\,mol^{-4}\,dm^3$, which suggests that the equilibrium will lie to the right-hand side making the ammine complex the more stable.

Revision activity

1 Calcium and chromium are both metals in Period 4 of the Periodic Table. Explain why chromium is a transition metal but calcium is not.

2 Give three properties shown by chromium not shown by calcium.

3 What forms of isomerism are shown by transition metal complexes?

4 Draw diagrams to show examples of each type.

Answers on p.203

13 Nitrogen and sulfur

This chapter is needed for only AS.

Nitrogen

Revised ☐

The lack of reactivity

You know that nitrogen is an unreactive gas because it is mixed with reactive oxygen in Earth's atmosphere and reacts very little. The reason for this lack of reactivity is the very strong N≡N bond in the molecule. The two nitrogen atoms share three electron pairs, which form a triple covalent bond, and each atom retains a lone pair of electrons. This is shown in Figure 13.1. The bond energy for nitrogen is 944 kJ mol^{-1} compared with the bond energy in fluorine, F_2, which is 158 kJ mol^{-1}.

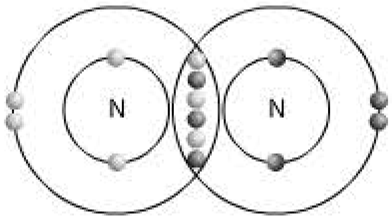


Figure 13.1 Structure of nitrogen

Although nitrogen is unreactive, it does react under the right conditions. For example, burning magnesium reacts with the nitrogen in air to form magnesium nitride:

$$3Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$$

At high temperatures nitrogen reacts with oxygen to form oxides of nitrogen, for example:

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

In car engines (and in thunderstorms) nitrogen combines with oxygen to produce a mixture of oxides of nitrogen often referred to as NO_x.

Nitrogen also reacts with hydrogen to form ammonia:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

This is the basic reaction in the Haber process for the manufacture of ammonia. This is covered in Chapter 7 and in more detail later in this section.

Finally, the roots of some plants of the pea and bean family have nodules that contain bacteria able to 'fix' nitrogen chemically. The bacteria convert the nitrogen into ammonium ions, which plants can use to make proteins.

Now test yourself

1 Use the *Data Booklet* to compare the bond energies of nitrogen and oxygen. Does this explain the relative inertness of nitrogen? Why is this not a complete answer?

Answers on p.199

Tested ☐

Ammonia

Ammonia, NH_3, is an alkaline gas. You might expect it to have a trigonal planar shape, but it is pyramidal with a lone pair of electrons occupying the apex, as shown in Figure 13.2.

Figure 13.2 Structure of ammonia

Remember that a lone pair takes up more space than a pair of bonding electrons. In the case of ammonia this reduces the H–N–H bond angles to about 107°. The relatively high electronegativity (3.0) of nitrogen means that ammonia can form hydrogen bonds, and as a result it is very soluble in water.

Ammonia is also a base, accepting a proton to form the ammonium ion, NH_4^+:

$$NH_3(g) + H^+(aq) \rightleftharpoons NH_4^+(aq)$$

This ion is tetrahedral, the proton forming a coordinate (dative) bond with the nitrogen atom using the lone pair (Figure 13.3).

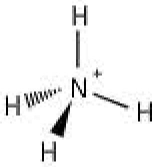


Figure 13.3 Structure of the ammonium ion

In the laboratory, ammonia is easily displaced from ammonium compounds by warming with a strong base such as sodium hydroxide:

$$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(g) + H_2O(l)$$

Now test yourself

2 Find out the H–X–H bond angles for methane, CH_4, ammonia, NH_3, and water, H_2O. Can you explain the differences between them?

Answers on p.199

Tested ☐

The uses of ammonia and its compounds

You have already looked at some aspects of the Haber process in Chapters 7 and 8. You may wonder why you have to study this manufacturing process. Ammonia is one of the most important bulk chemicals manufactured, mainly because of its use in the production of fertilisers. In 2008, more than 150 million tonnes of ammonia were produced worldwide.

As well as its use in fertiliser manufacture (mainly as the sulfate or nitrate), ammonia can be oxidised using a platinum catalyst to form nitrogen monoxide:

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l) \quad \Delta H^\ominus = -909\,kJ\,mol^{-1}$$

This exothermic reaction is the starting point for the manufacture of nitric acid. The hot gas is cooled, reacted with more oxygen to form nitrogen dioxide, and then dissolved in water to form nitric acid:

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

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

$$3N_2O_4(g) + 2H_2O(l) \rightarrow 4HNO_3(aq)$$

Nitrogen compounds and pollution

Revised ☐

Nitrates

Nitrogen compounds, particularly nitrates such as NH_4NO_3, are used to make fertilisers. These have had significant benefits in increasing crop yields around the world. However, if excessive amounts of fertilisers are used they can get washed into streams and rivers and this can have two effects:

- The nitrates can get into drinking water supplies, from which they are difficult to remove. They can affect the ability of babies under 6 months to carry oxygen in the bloodstream.
- They can increase the growth of aquatic vegetation, which then decays reducing oxygen levels in streams and rivers, and affecting other forms of aquatic life.

Now test yourself

3 Why are nitrate fertilisers such a problem in the environment, no matter what nitrate is used?

Answer on p.199

Tested ☐

Nitrogen oxides

The combustion of motor fuels generates temperatures high enough to form oxides of nitrogen, NO_x, in exhaust gases. These gases in air at street level are known to contribute to respiratory problems. They also have a pollution effect in the upper atmosphere where they catalyse the oxidation of sulfur dioxide. The main source of sulfur dioxide in the atmosphere is the combustion of fuels (mainly coal and oil) that contain sulfur or its compounds. Some of the sulfur dioxide is removed from the waste gases emitted by major users of these fuels, such as power stations.

The exact mechanism is uncertain, but the following is a possibility:

$$2NO_2(g) + H_2O(g) \rightarrow HNO_2(l) + HNO_3(l)$$
$$SO_2(aq) + HNO_3(l) \rightarrow NOHSO_4(l)$$
$$NOHSO_4(l) + HNO_2(l) \rightarrow H_2SO_4(l) + NO_2(g) + NO(g)$$
$$SO_2(aq) + 2HNO_2(l) \rightarrow H_2SO_4(l) + 2NO(g)$$

The emission of nitrogen oxides from vehicles has reduced greatly since the introduction of catalytic converters. These also reduce the emission of carbon monoxide and unburnt hydrocarbons (see also Chapter 8).

$$2NO_x(g) \rightarrow xO_2(g) + N_2(g)$$
$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$
$$C_nH_{2n+2}(g) + \frac{3n+1}{2}O_2(g) \rightarrow nCO_2(g) + (n+1)H_2O(g)$$

Sulfur

Revised ☐

Sulfur dioxide

Acid rain

You have already seen that the combustion of sulfur-containing fuels releases sulfur dioxide into the atmosphere, and that in the presence of oxides of nitrogen this can be converted into sulfuric acid. This decreases the pH of rain. Acid rain can harm plants and animals both directly and indirectly by making lakes acidic. It also releases toxic metals such as aluminium from soils, and below pH 4.5 no fish are likely to survive. This has further effects up the food chain. Acid rain also increases the erosion of limestone-based buildings and statues. The production and some effects of acid rain are shown in Figure 13.4.

Now test yourself

4 Write equations to show:
  - **a** the release of aluminium ions from $Al_2O_3(s)$ in soils by acid rain
  - **b** the erosion of limestone by acid rain

Answers on p.199

Tested ☐

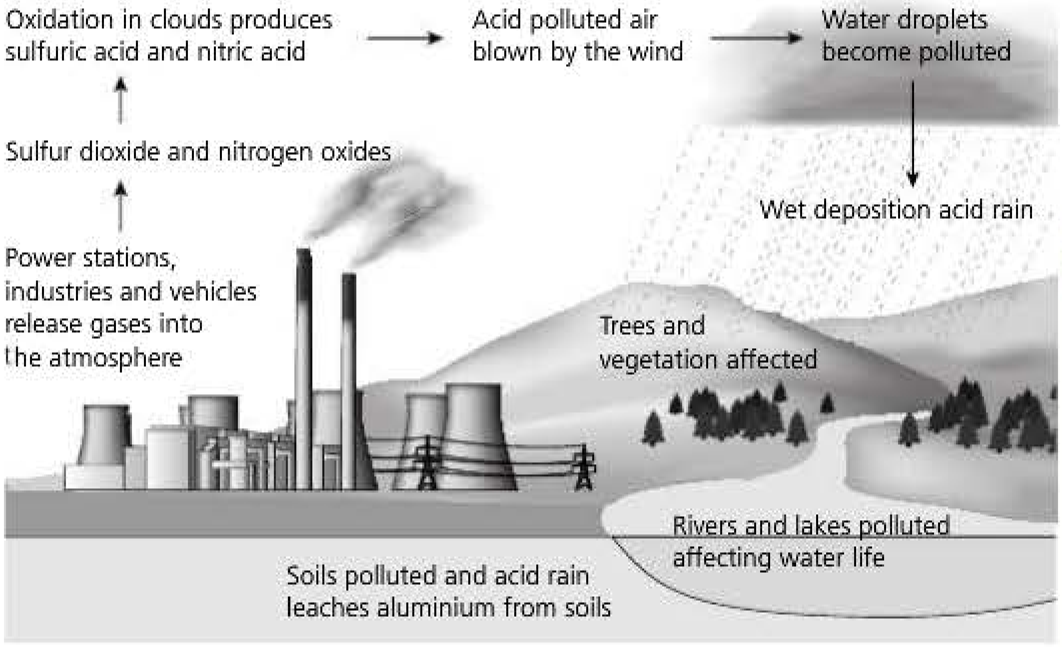


Figure 13.4 Acid rain

Revision activity

1 Explain why nitrogen shows a low reactivity.
2 Explain the difference in shapes of the ammonia molecule and the ammonium ion.
3 What is the link between oxides of nitrogen, sulfur dioxide and acid rain?

Answers on p.203

14 An introduction to organic chemistry

Most of this chapter is needed for AS. The aspects that are needed for A level only are clearly indicated.

Formulae

Revised ☐

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

Molecular formula

A **molecular formula** summarises the numbers and types of atoms present in a molecule. The functional group is shown separately from the hydrocarbon chain —

The **molecular formula** of a compound summarises the numbers and types of atom present in a molecule.

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.

The **structural formula** of a compound gives the minimum detail to provide an unambiguous structure.

Displayed formula

A **displayed formula** shows the correct positioning of the atoms and the bonds between them. For example ethanoic acid, with the structural formula CH_3CO_2H, has the displayed formula shown in Figure 14.1.

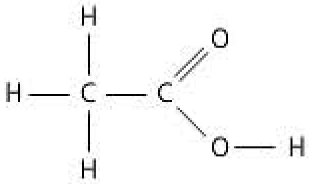


Figure 14.1

The **displayed formula** of a compound shows the correct positioning of the atoms and the bonds between them.

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

Skeletal formula

A **skeletal formula** 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 in Figure 14.2.

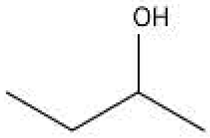


Figure 14.2

The **skeletal formula** of a compound shows the carbon 'backbone' of a molecule, together with any functional groups.

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 in Figure 14.3:

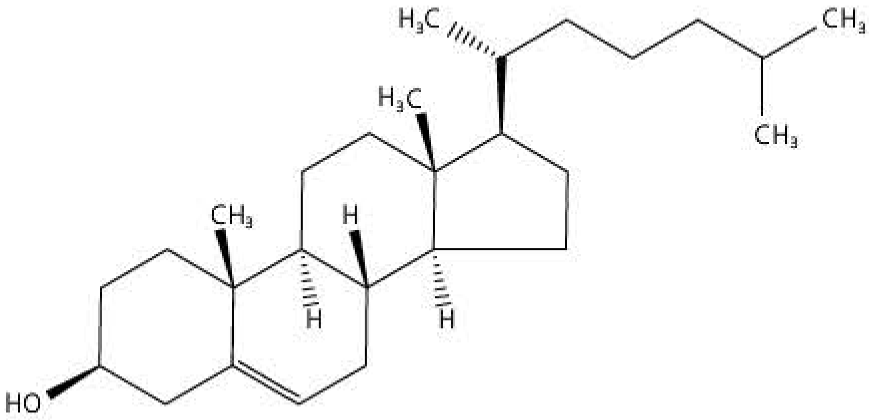


Figure 14.3

Three-dimensional structures

There are times when you need to be able to show the three-dimensional structures of relatively simple molecules — for example in Figure 14.4, 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.

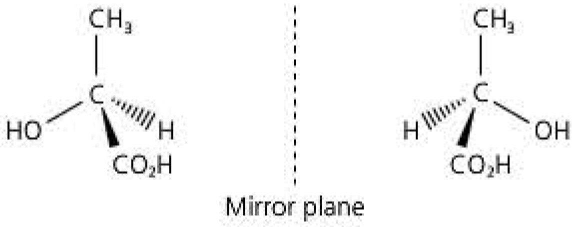


Figure 14.4

Now test yourself

1 What is the name of the compound shown in Figure 14.4?

Answer on p.199

Tested ☐

Names and functional groups

Revised ☐

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 a molecule

There are some simple rules that will help you.

The hydrocarbon chain

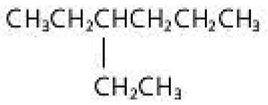
The key thing to remember is that the prefix indicates the number of carbon atoms in the main chain (Table 14.1).

Table 14.1

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 atom 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.

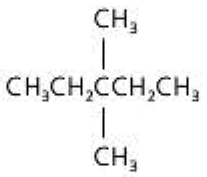


$CH_3CH_2\underset{\substack{|\\ CH_2CH_3}}{C}HCH_2CH_2CH_3$

or $CH_3CH_2CH(CH_2CH_3)CH_2CH_2CH_3$

Figure 14.5(a)

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



$CH_3CH_2\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}CH_2CH_3$

or $CH_3CH_2C(CH_3)_2CH_2CH_3$

Figure 14.5(b)

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 than alkanes 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).

A **functional group** is the reactive part of an organic molecule

Arenes

Arenes are a family of hydrocarbons that contain a benzene ring made up of six carbons (Figure 14.6).

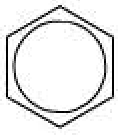


Figure 14.6

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.

Expert tip

Arenes are important for A level. For 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

Revised ☐

Some functional groups are shown in Table 14.2.

Naming compounds is not too difficult. Some examples are shown in Table 14.3.

Table 14.2

Name of compound	Formula of group
Halogenoalkane/halogenoarene	–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	$-CONH_2$

Table 14.3

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

For A level you need to be able to name simple aromatic compounds with one benzene ring and one or more simple substituents – such as those shown in Figure 14.7.

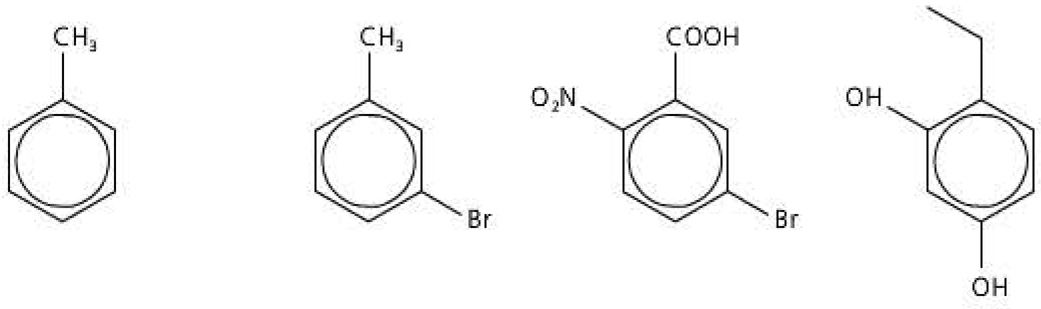


Figure 14.7

Now test yourself

2 Name these compounds:
  - **a** $CH_3CH_2CH_2CH_2Cl$
  - **b** $CH_3CHOHCH_3$
  - **c** $CH_3CH_2CH_2CH_2CH_2CO_2H$
  - **d** $CH_3CH(CH_3)CH_2CH_2NH_2$

3 Draw structural formulae for these compounds:
  - **a** 2-bromobutane
  - **b** propanamide
  - **c** methanal
  - **d** methyl ethanoate

Answers on p.199

Tested ☐

Organic reactions

Revised ☐

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 allow.

Fission of bonds

Organic molecules 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 (Figure 14.8) one electron goes to each fragment:

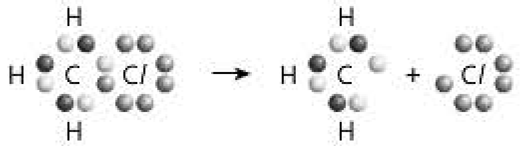


Figure 14.8

In **homolytic fission** the bond splits so that one electron goes to each fragment.

- In **heterolytic fission** (Figure 14.9) both electrons go to one fragment and none to the other:

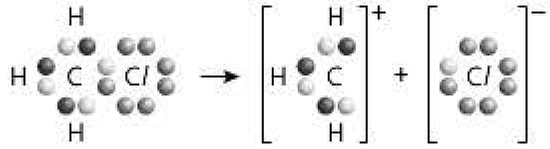


Figure 14.9

In **heterolytic fission** both electrons go to one fragment and none to the other.

Free radical reactions

Free radicals are highly reactive species having at least one 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 Earth's 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**.

Step 1: initiation

The reaction you will study is the reaction of methane with chlorine in the presence of ultraviolet light.

Free radicals are formed by the breaking of bonds by homolytic fission:

$$Cl{-}Cl \rightarrow Cl\bullet + Cl\bullet$$

Initiation is the first stage in a free radical reaction in which the free radicals are formed.

Step 2: propagation

The free radicals formed begin a chain reaction in which each free radical is used to form another:

$$H{-}CH_3 + Cl\bullet \rightarrow CH_3\bullet + HCl$$

$$CH_3\bullet + Cl{-}Cl \rightarrow CH_3Cl + Cl\bullet$$

Propagation is the second stage in a free radical reaction. In this, for each free radical used, a new one is formed.

Step 3: termination

These are reactions in which free radicals combine and hence end that part of the chain reaction:

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

$$CH_3\bullet + Cl\bullet \rightarrow CH_3Cl$$

$$CH_3\bullet + CH_3\bullet \rightarrow CH_3CH_3$$

Termination is the final stage in a free radical reaction. In this, free radicals combine together removing them from the reaction.

Nucleophilic and electrophilic reactions

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

Expert tip

Here is a way to remember this — 'nucleo like nucleus, which is 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 having lone pairs of electrons, such as water and ammonia, or even ethanol. A typical nucleophilic substitution reaction is:

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

A **nucleophile** is a negatively charged ion or a molecule with lone pairs of electrons which can attack positive centres in organic molecules.

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:

$$CH_3CH{=}CH_2 + HBr \rightarrow CH_3CHBrCH_3$$

An **electrophile** is a positively charged ion, which can attack negative centres in organic molecules.

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 section on the structure of ethene on p. 103).

An **addition** reaction increases the saturation in a molecule, for example such as adding HBr to the double bond in ethene.

Substitution

Substitution refers to the replacement of one group in an organic molecule by another, as in nucleophilic substitution on p. 118. Both nucleophiles and electrophiles can take part in substitution reactions.

A **substitution** reaction replaces one group in an organic molecule by another.

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 p. 110.

An **elimination** reaction involves the removal of atoms from two adjacent carbon atoms to leave a double bond.

Hydrolysis

Hydrolysis is a reaction, usually in aqueous solution, between organic molecules and water, or acid or alkali, that leads to the formation of at least two products. Two examples are:

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

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

A **hydrolysis** reaction involves the reaction of an organic molecule with (usually) water to form at least two products.

Condensation

A **condensation** reaction is the reverse of hydrolysis. Water is eliminated when two organic molecules react together. An example of this is the reaction of an alcohol with a carboxylic acid to form an ester:

$$CH_3CO_2H + CH_3OH \rightarrow CH_3CO_2CH_3 + H_2O$$

It is also the reaction by which an important group of polymers is made (see p. 146).

A **condensation** reaction occurs when two organic molecules react and eliminate a small molecule such as water.

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 it is permissible to show the oxidising agent as [O]:

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

Oxidation generally refers to the conversion of a C–OH group to form a C=O group, but can also refer to the combustion of hydrocarbons.

Reduction

This is the opposite of oxidation and, in general, applies to compounds containing a C=O group. **Reduction** can 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]:

$$CH_3CO_2H + 4[H] \rightarrow CH_3CH_2OH + H_2O$$

Reduction is the opposite of oxidation and, in general, applies to compounds containing a C=O group reacting to form a single C–O bond.

Shapes of molecules

Revised ☐

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

Ethane

An ethane molecule is formed (Figure 14.10) 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.

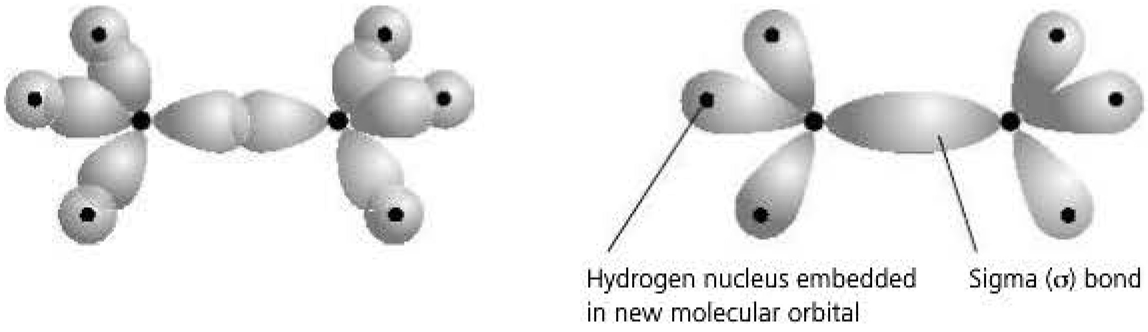


Figure 14.10

A single C–C σ-bond, formed by the overlapping of one sp^3-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.

Ethene

In ethene, the carbon atoms form 2sp^2-hybrid orbitals using three of the electrons, leaving one electron in a 2p-orbital (Figure 14.11).

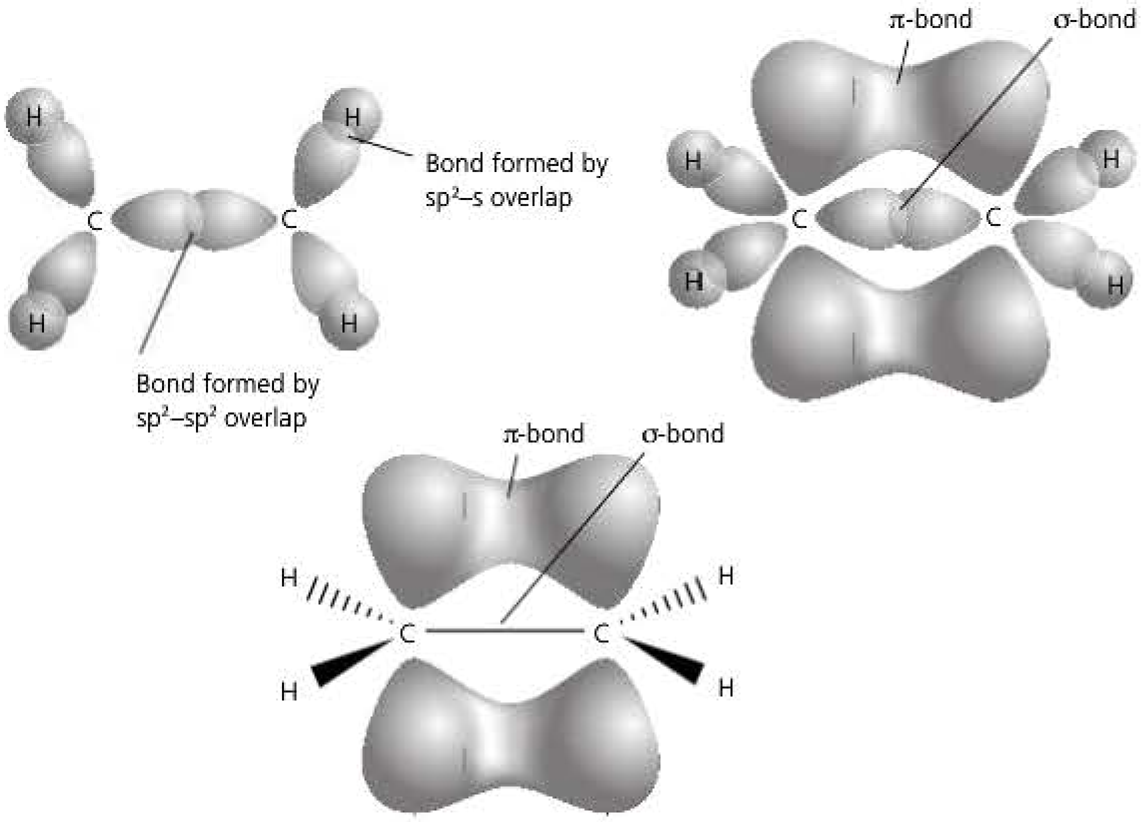


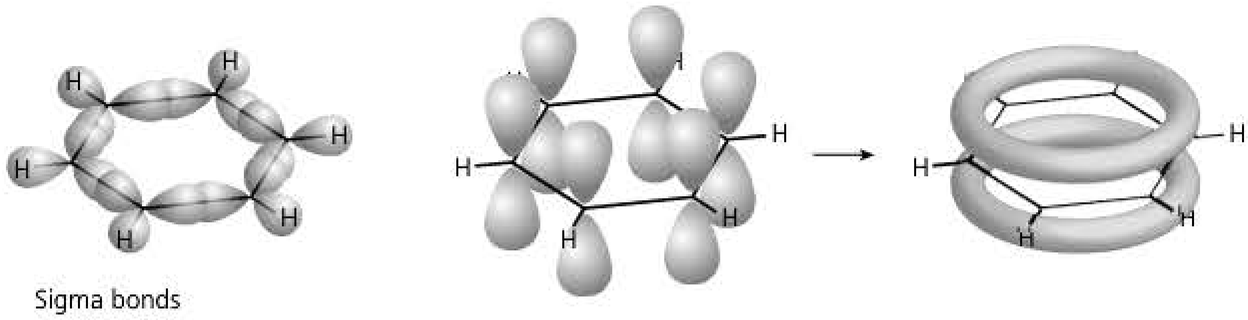
Figure 14.11

An ethene molecule is formed by the overlap of two sp^2-orbitals on each carbon atom with two hydrogen 1s-orbitals. The third sp^2-orbital on each carbon atom overlaps 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:

Benzene

A molecule of benzene has six carbons arranged in a hexagonal ring. These carbon atoms have hybridised orbitals in the same manner as ethane

(Figure 14.12). 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 hybridised orbitals

6 p_z-orbitals

Delocalised π system

Figure 14.12

Isomerism

Revised ☐

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:

Chain isomerism arises due to branching of the carbon chain.

$CH_3CH_2CH_2CH_3$ $\qquad$ $CH_3\underset{\underset{\textstyle CH_3}{|}}{C}HCH_3$

Butane

2-methylpropane

Figure 14.13

The compounds have different names based on the system described on p. 99. The branched chain is three carbon atoms 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:

Position isomerism arises due to variation in the position of substituent groups on the carbon chain.

$CH_3CH_2CH_2OH$ $\qquad$ $CH_3\underset{\underset{\textstyle OH}{|}}{C}HCH_3$

Propan-1-ol

Propan-2-ol

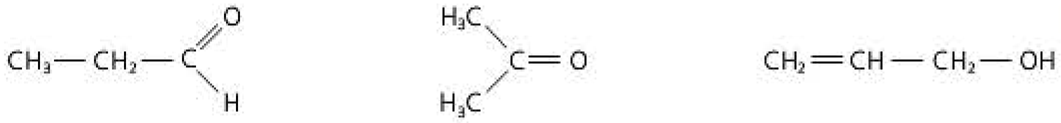
Figure 14.14

Changing the position of a group can affect how readily 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

Revised ☐

In **functional group isomerism** the nature of the functional group in the molecules is different. This is significant because it changes the chemical reactions that the molecules undergo. The formula C_3H_6O can represent three molecules in Figure 14.15, each with a different functional group:



Propanal Propanone 2-propen-1-ol

Figure 14.15

Functional group isomerism arises because rearrangement of the atoms in the molecule means that the nature of the functional groups are different in the isomers.

Geometric (*cis–trans*) isomerism

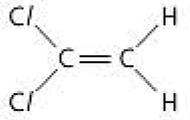
Geometric isomerism occurs when there is restricted rotation around a bond, such as in alkenes. It also needs two groups, one on each end of the double bond, such as in 1,2-dichloroethene.

Cis-1,2-dichloroethene *Trans*-1,2-dichloroethene

Figure 14.16

The two forms in Figure 14.16 are different because the double bond prevents the rotation needed to make the two forms identical. Note that there is another isomer (Figure 14.17), but this one is a position isomer rather than a *cis–trans* isomer.

Free radicals are usually highly reactive species consisting of an atom or fragment of a molecule with an unpaired electron.



1,1-dichloroethene

Figure 14.17

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 polarised light clockwise, and the other isomer rotates it an equal amount anticlockwise. This occurs when there is a carbon atom with four different groups attached to it — this is called a **chiral** carbon. An example is shown on p. 98 and another example, butan-2-ol, is shown in Figure 14.18.

A **chiral** carbon atom is one with four different groups attached to it.

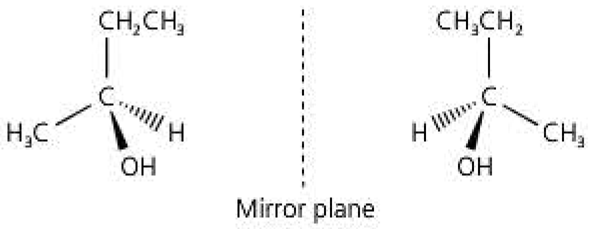


Figure 14.18

Notice that the two molecules in Figure 14.18 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 in Figure 14.19 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 14.19 shows what you need to do.

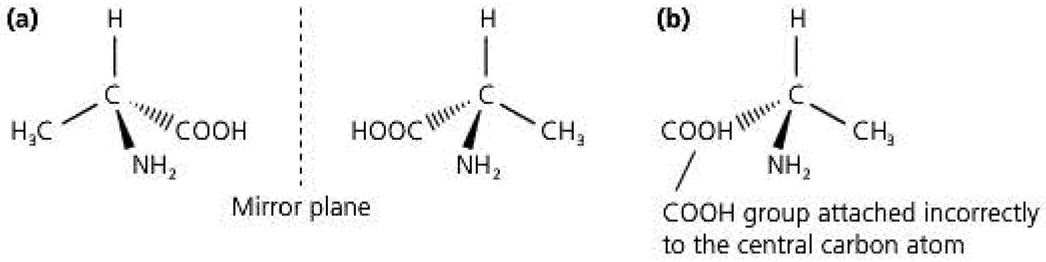


Figure 14.19 (a) Optical isomers of 2-aminopropanoic acid; (b) Incorrectly drawn isomer

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 in Figure 14.20:

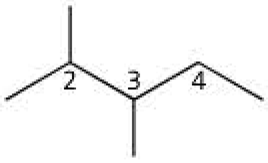


Figure 14.20

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 14.21.

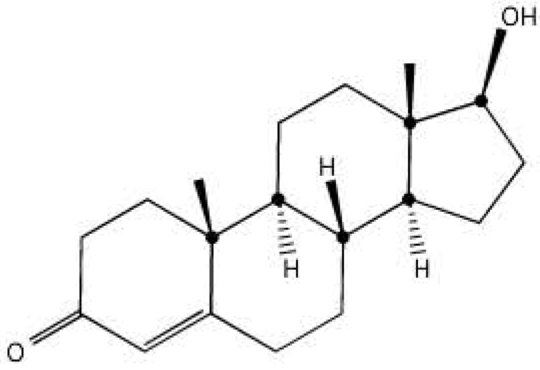


Figure 14.21 Synthetic testosterone

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

Now test yourself

4 Compound P has the molecular 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 14.2?

5 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.

Answers on p.199

Tested ☐

Revision activity

1 Draw the structures for the following compounds:
  - **a** 3-ethylpentane
  - **b** 4-methylheptane
  - **c** 3-heptene

2 Draw all the chain isomers of butene. Which of these exist as *cis–trans* isomers?

3 What is the difference between an electrophilic reagent and a nucleophilic reagent?

4 Why can't an alkane undergo addition reactions?

Answers on p.203

15 Hydrocarbons

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

Alkanes

Revised ☐

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.

Alkanes are hydrocarbons that contain only carbon–carbon single bonds. They have the general formula C_nH_{2n+2}.

Ethane is used as an example of an alkane, noting that it has the molecular formula C_2H_6.

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

Plenty of oxygen: $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$
Less oxygen: $2C_2H_6 + 5O_2 \rightarrow 4CO + 6H_2O$
Restricted oxygen: $2C_2H_6 + 3O_2 \rightarrow 4C + 6H_2O$

Progressively restricting the amount of oxygen reduces the amount by which the carbon in ethane is oxidised until it cannot be oxidised at all. Midway it 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.

Cracking is a process in which a large-molecule hydrocarbon of limited use is broken into small-molecule hydrocarbons that are in greater demand.

Not all sources of crude 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'.

Some of the most important processes in an oil refinery are shown in Figure 15.1.

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 hydrocarbons and one or more alkenes — for example:

$$C_{15}H_{32} \rightarrow 2C_2H_4 + C_3H_6 + C_8H_{18}$$
$$C_{12}H_{26} \rightarrow C_3H_6 + C_9H_{20}$$
$$C_8H_{18} \rightarrow C_6H_{14} + C_2H_4$$

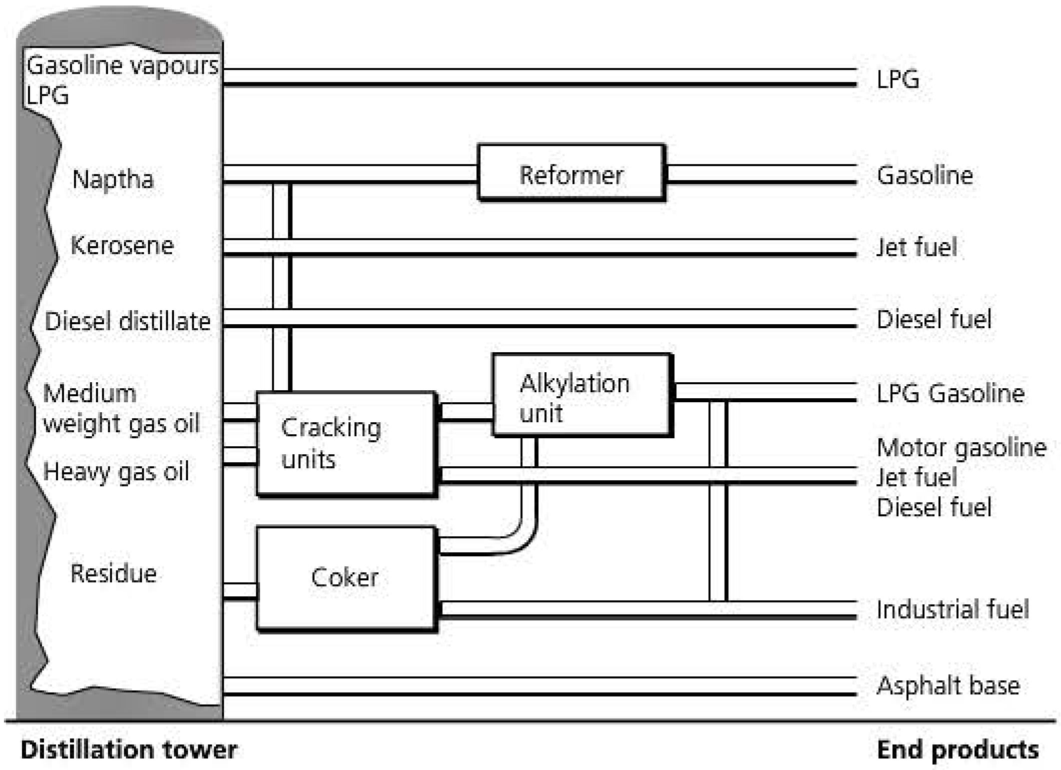


Figure 15.1 Processes in an oil refinery

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 p. 101.

Now test yourself

1 What sort of substitution reaction is shown above?

Answer on p.199

Tested ☐

Alkenes

Revised ☐

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}.

Alkenes are hydrocarbons that contain a carbon–carbon double bond. They have the general formula 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 double bonds 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 or propan-1-ol respectively:

$$CH_3{-}CH{=}CH_2 + H_2O \rightarrow CH_3CHOHCH_3 \text{ or } CH_3CH_2CH_2OH$$

Markovnikov's rule means that in the above reaction, propan-2-ol is favoured.

Markovnikov's rule 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.

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 Markovnikov'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 a pure halogen. Often, as in testing for alkenes using bromine water, a competing reaction can take place:

$$CH_2{=}CH_2 + Br_2 + H_2O \rightarrow CH_2BrCH_2OH + HBr$$

The new compound is 1-bromo-2-hydroxyethane (or 2-bromoethanol).

Now test yourself

2 a Write an equation to show the addition of HBr to but-1-ene.
  b Give the systematic name for the product of this reaction.

Answers on p.199

Tested ☐

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-dihydroxyethane.

$$CH_2{=}CH_2 + [O] + H_2O \rightarrow CH_2OHCH_2OH$$

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–carbon double bond of the alkene is ruptured. You may not think that this is a very useful reaction, but by identifying 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 formula shown in Figure 15.2:

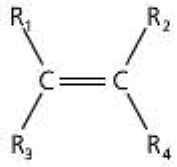


Figure 15.2

When the acidified manganate(VII) ions oxidise the alkene, two C=O double bonds are formed:

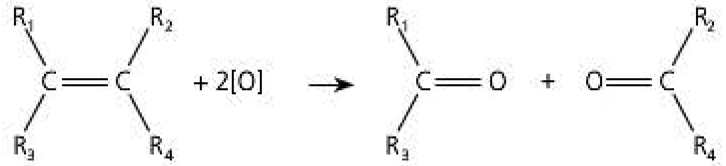


Figure 15.3

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** (Figure 15.4) and this can be oxidised further by acidified manganate(VII) to form a **carboxylic acid**.

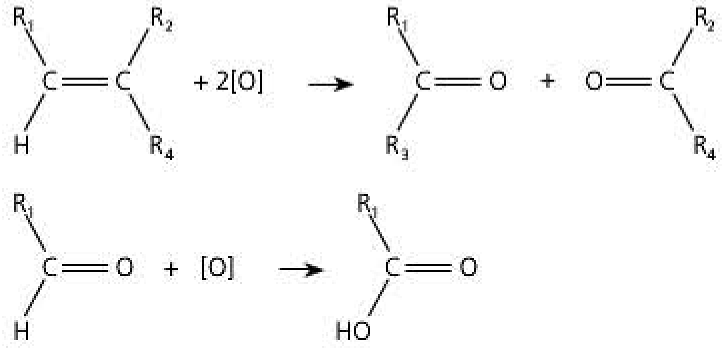


Figure 15.4

There is one further complication that occurs when there are no R groups at one end of the double bond (Figure 15.5). The carboxylic acid formed under those circumstances (methanoic acid) is itself oxidised by the acidified manganate(VII) ions to form carbon dioxide and water.

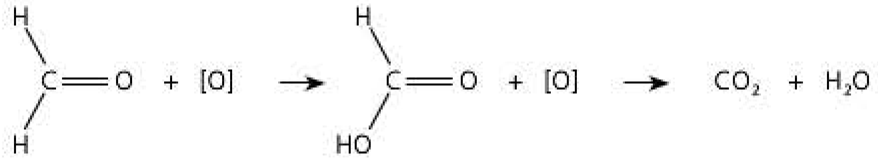


Figure 15.5

Electrophilic addition

You saw in the Chapter 14 that halogens behave as electrophiles, and you know that alkenes have a relatively high concentration of electrons round the double bond. You need to understand the mechanism of electrophilic addition, including the specific example of bromine reacting with ethene. The reaction takes place in two stages.

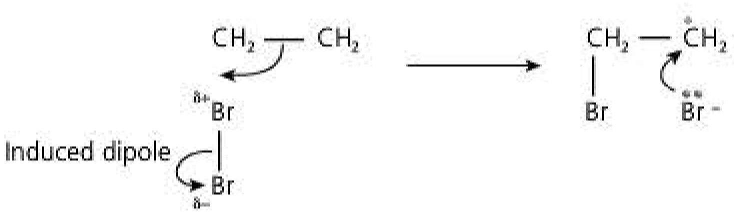


Figure 15.6

First, bromine molecules approach the ethene molecules, and the π-electrons in ethene induce a dipole on the bromine molecules. A bond is formed between the carbon and the bromine forming a positively charged species called a **carbocation**.

Second (Figure 15.7), the carbocation is rapidly attacked by Br⁻ ions to form the dibromide product.

Expert tip

Here are some 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 then 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 then that part of the molecule will give a carboxylic acid.
- If there are two hydrogen atoms at one end of the bond then that part of the molecule will give carbon dioxide and water.

Combine the information to work back to the structure of the original alkene.

Now test yourself

3 Name the products of reacting propene with:
  a cold, dilute, acidified manganate(VII) ion
  b hot, concentrated, acidified manganate(VII) ions

Answers on p.199

Tested ☐

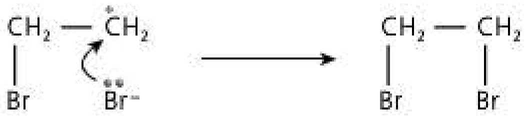


Figure 15.7

You need to be aware of the inductive effects of alkyl groups in stabilising such carbocations. Alkyl groups tend to push electrons towards the carbon they are attached to, and this helps to stabilise a carbocation.

Now test yourself

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

Answer on p.199

Tested ☐

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 to hydrocarbon alkenes only but also to substituted alkenes such as chloroethene ($CH_2{=}CHCl$), which is used to make PVC.

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:

$$nCH_2{=}CH_2 \rightarrow (-CH_2-CH_2-)_n$$

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 resulting 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 made are branched 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 tougher polymer is used to make plastic containers, washing-up bowls and some plastic pipes.

Poly(chloroethene)

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

$$nCH_2{=}CHCl \rightarrow (-CH_2-CHCl-)_n$$

This polymer is still commonly 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 chlorine atoms bonded to one side of the chain (Figure 15.8).

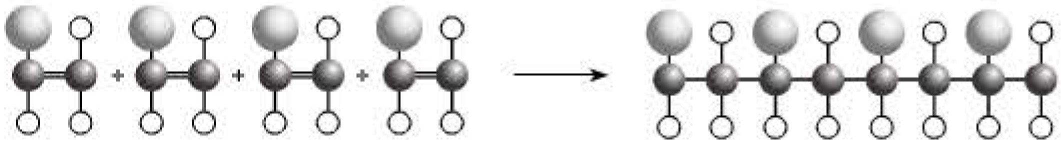


Figure 15.8

The equation used to show this is given in Figure 15.9.

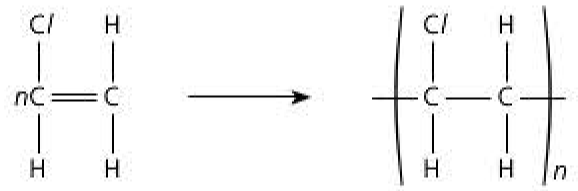


Figure 15.9

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.

As well as knowing the polymers formed from alkenes (and substituted alkenes) you will need to be able to identify the monomer from which a given addition polymer has been formed, and also the repeat unit for the polymer.

Now test yourself

5 The synthetic fibre Orlon® is produced by polymerising the monomer CH_2=CHCN. Draw a section of this polymer showing two repeat units.

Answer on p.199

Tested ☐

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 materials 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.

The environmental consequences of using hydrocarbons as fuels

Although hydrocarbons are important fuels in industry, domestically and in transport, the products of these uses have an effect on the environment, particularly the atmosphere.. In the internal combustion engine carbon monoxide and unburnt hydrocarbons formed by incomplete combustion, and oxides of nitrogen formed by the high temperatures present, are all atmospheric pollutants.

- Carbon monoxide is a toxic gas, combining irreversibly with haemoglobin. It is oxidised to carbon dioxide, which is a 'greenhouse' gas.
- Unburnt hydrocarbons are greenhouse gases and they contribute to the formation of photochemical smog.
- Oxides of nitrogen (mainly NO and NO_2) in the lower atmosphere can cause breathing problems, help cause smog and are involved in the formation of acid rain. They also play a role in the formation of ozone in the lower atmosphere.

One method for monitoring air pollution is using infrared spectroscopy. This identifies the bonds in the pollutants as they vibrate at particular frequencies producing sharp peaks. It can also be calibrated to give a measure of the quantities of different pollutants in the atmosphere at a given time (see Chapter 22).

Arenes

Revised ☐

You need to know about two **arenes** — benzene and methylbenzene (Figure 15.10).

Figure 15.10

Arenes are organic compounds that contain a benzene ring.

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 atom or a bromine atom. A typical catalyst is the aluminium halide of the halogen being substituted, or iron (which reacts with the halogen to form 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 being added to the ring (Figure 15.11).

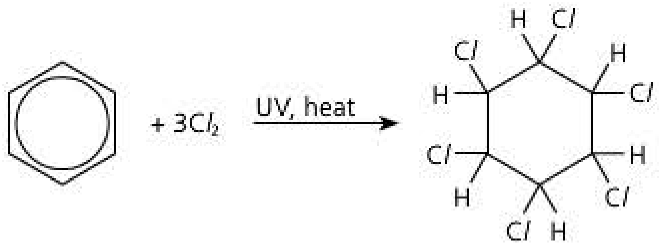


Figure 15.11

As you might expect, the reaction is faster with chlorine than with bromine.

Now test yourself

6 Suggest why benzene undergoes a substitution reaction rather than an addition reaction with chlorine.

Answer on p.199

Tested ☐

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). The reaction with either chlorine or bromine under these conditions results in the formation of a mixture of 2-halo- and 4-halomethylbenzene (Figure 15.12).

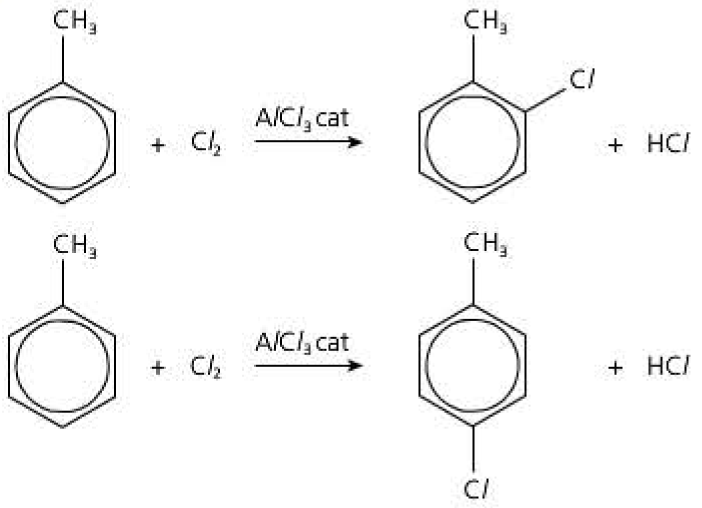


Figure 15.12

When boiling methylbenzene is reacted with chlorine or bromine in the presence of ultraviolet light, the methyl hydrogen atoms are substituted (Figure 15.13). Provided sufficient halogen is present, all three hydrogen atoms are eventually substituted.

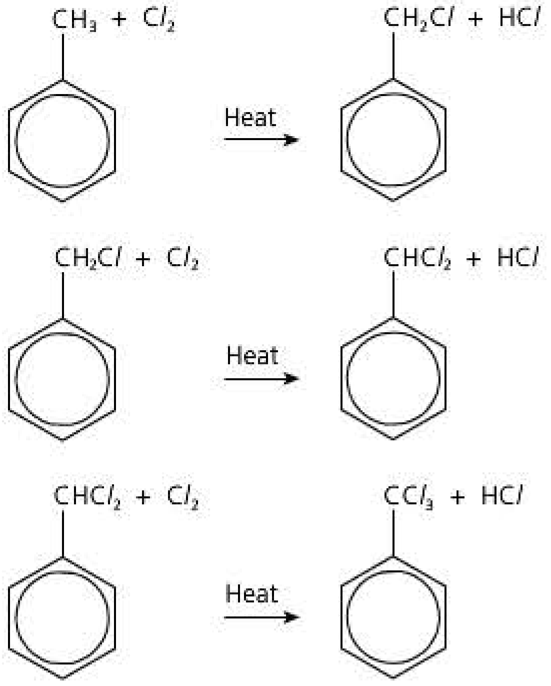
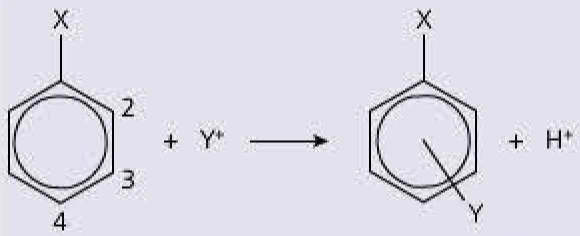


Figure 15.13

You also need to be able to predict the positions of substituents in arenes that have already undergone substitution. Table 15.1 is reproduced from the *Data Booklet*.

Table 15.1 The orientating effect of groups in aromatic substitution reactions



X- groups that direct the incoming Y group to the 2- or 4- positions	X- groups that direct the incoming Y group to the 3- position
$-NH_2$, $-NHR$ or $-NR_2$	$-NO_2$
$-OH$ or $-OR$	$-NH_3$
$-NHCOR$	$-CN$
$-CH_3$, $-$alkyl	$-CHO$, $-COR$
$-Cl$	$-CO_2H$, $-CO_2R$

The position of the incoming group, Y, is determined by the nature of the group, X, already bonded to the ring, and not by the nature of the incoming group Y.

Now test yourself

7 If chlorobenzene is reacted with concentrated nitric acid where, in relation to the chlorine atom, will the nitro group go in the ring?

Answer on p.199

Tested ☐

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 (Figure 15.14) with a second nitro group being substituted into the ring. The second nitro group goes into the 3-position:

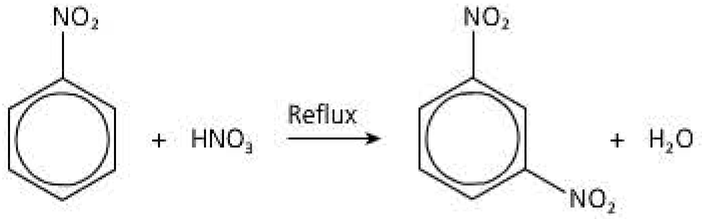


Figure 15.14

Compare this with the methyl group in methylbenzene (p. 114). 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 acid and concentrated sulfuric acid 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 delocalised electrons in benzene and two of these form a bond with the positive charge (Figure 15.15a) now spread over the rest of the atoms in the ring.

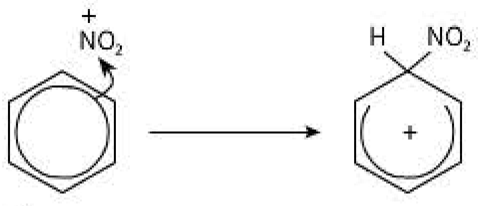


Figure 15.15a

The HSO_4^- ion produced in the nitrating mixture now removes (Figure 15.15b) a hydrogen atom, reforming the sulfuric acid catalyst.

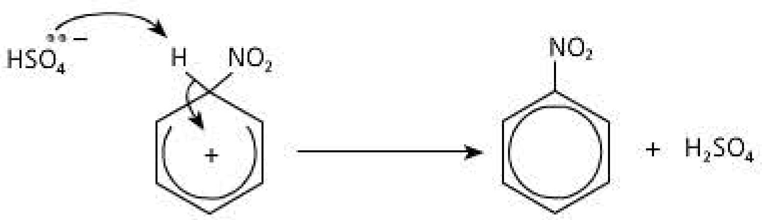


Figure 15.15b

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 acid and nitric acid is used.

As with the halogens, a mixture of the 2- and 4-nitro substituted arenes (Figure 15.16) is formed.

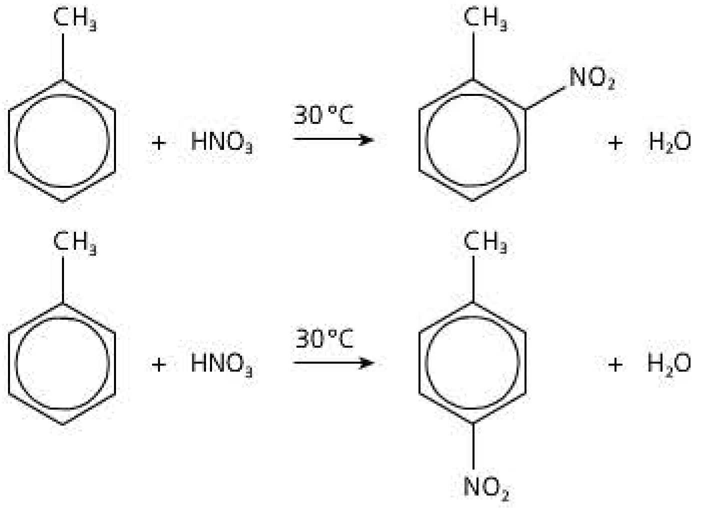


Figure 15.16

Alkylation and acylation

Using alkyl halides you can substitute an alkyl group into a benzene ring, and using an acyl halide you can substitute an acyl, RCO– group. These are known as Friedel–Crafts reactions.

Benzene can be **alkylated** by reaction with a halogenoalkane (Figure 15.17), such as chloroethane, in the presence of an aluminium chloride catalyst to form ethylbenzene.

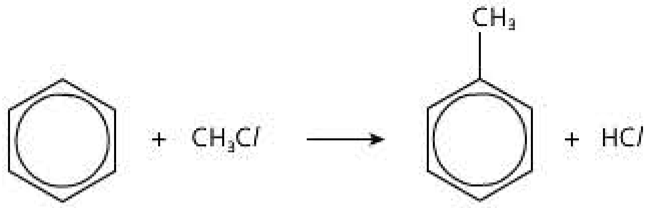


Figure 15.17

Alkylation is the substitution of an alkyl group, RC–, on a benzene ring.

Benzene can be **acylated** by reaction with an acyl halide (Figure 15.18) such as ethanoyl chloride in the presence of an aluminium chloride catalyst to form phenylethanone.

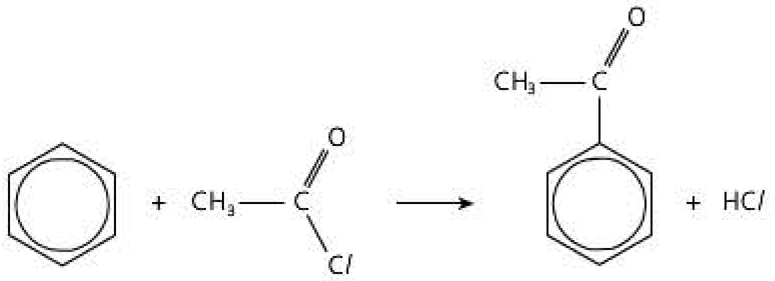


Figure 15.18

Acylation is the addition of an acyl group, RCO–, to a benzene ring.

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 (Figure 15.19). Heating methylbenzene (or any alkylbenzene) with alkaline potassium manganate(VII) solution, followed by acidification with dilute sulfuric acid, gives benzoic acid.

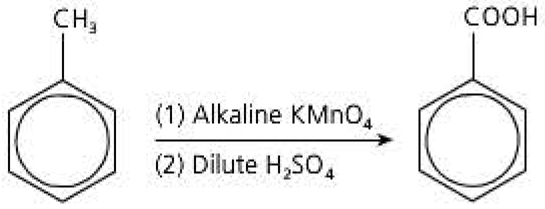


Figure 15.19

Hydrogenation

It is possible to completely hydrogenate a benzene ring to form cyclohexane (Figure 15.20). This is usually done using a nickel catalyst. The aromatic nature of the ring means that this requires more vigorous conditions than the hydrogenation of ethene.

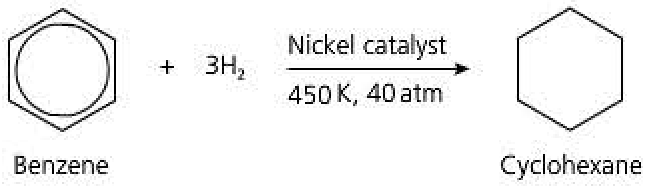


Figure 15.20

Revision activity

Parts 1 and 2 are for AS and the remainder for A level.

1. Why are large alkane molecules often subjected to 'cracking'?
2. What other type of hydrocarbon is formed in the cracking process?
3. What is the source of alkenes used in the manufacture of margarine?
4. Draw the structure of the product formed when water is added to propene.
5. Give two reasons why addition polymers should be recycled.
6. Give a typical reaction of benzene that indicates it does not contain carbon–carbon double bonds.
7. Outline the two different reactions that methylbenzene can undergo with bromine.

Answers on p.204

16 Halogen compounds

This chapter is for AS.

Halogenoalkanes behave differently depending on which other groups are attached to the carbon that the halogen is attached to (you will also see this 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 because of the difference in electronegativities of 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

Revised ☐

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 a hydroxyl group and ethanol is formed:

$$CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$$

You need to know the mechanism for this reaction, which can be represented in two ways. Figure 16.1 shows the first of these.

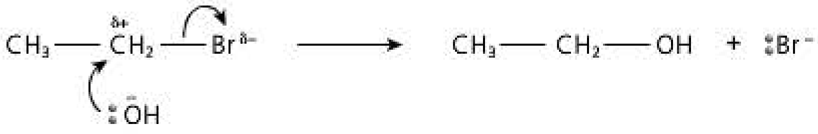


Figure 16.1

Expert tip

Think of S_N2 as 'Substitution Nucleophilic, 2 reactants'.

The reaction is described as S_N2, because there are two reactants in the rate-determining or slow step.

The other way of representing this reaction is to show it as a two-stage process (Figure 16.2):

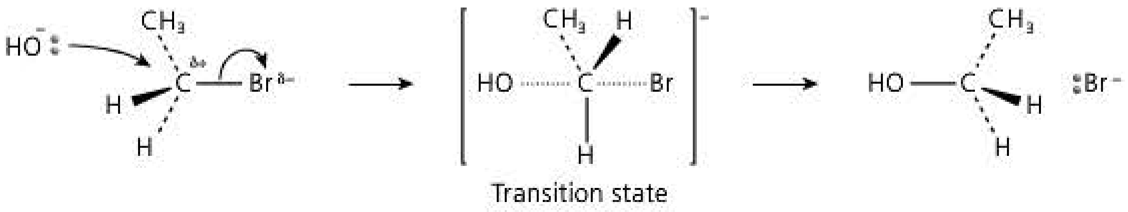


Figure 16.2

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 step (slow step). This is an S_N1 mechanism, even though there are two stages (Figure 16.3).

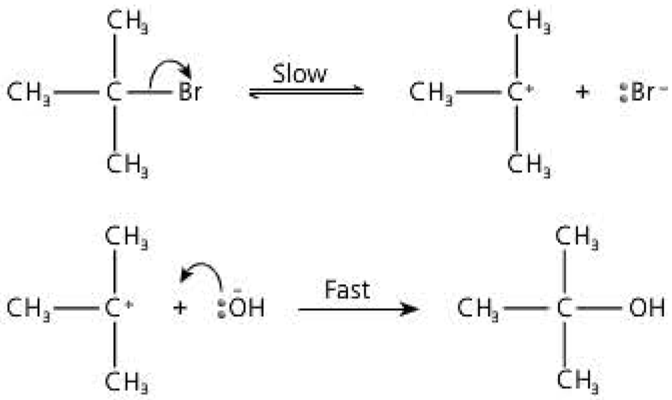


Figure 16.3

Expert 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 under 'Elimination of hydrogen bromide' below.

Now test yourself

1 Write equations to show the two reactions by which $(CH_3)_2CHBr$ reacts with OH^-.

Answers on p.199

Tested ☐

Formation of nitriles

When a halogenoalkane is heated under reflux with cyanide ions dissolved in ethanol, the cyanide ion is substituted for the halogen atom 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.

Now test yourself

2 Why is the reaction of CN^- ions with halogenoalkanes important?

Answer on p.199

Tested ☐

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 amines and then 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:

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

It is important to remember that different halogenoalkanes favour one type of reaction over the other (Table 16.1).

Table 16.1

Halogenoalkane	Reaction favoured
Primary	Mainly **substitution**
Secondary	Both
Tertiary	Mainly **elimination**

Expert tip

For a given halogenoalkane, 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 exemplar halogenoalkane and for most purposes that is fine. However, you must not forget that different halogens have different effects on the halogenoalkanes they form, not least because of the relative strengths of the C–Hal bond (Table 16.2).

Table 16.2

Bond	Bond energy/kJ mol^{-1}
C–F	467
C–C*l*	338
C–Br	276
C–I	238

For a halogenoalkane to react, the C–Hal bond has to be broken. From Table 16.2 you can see that this is much more difficult for fluoroalkanes than for the other members of the group.

Halogenoalkanes have important uses and in looking at these you need to bear the above factor in mind.

Now test yourself

3 Explain why fluoroalkanes are more difficult to react with OH$^-$ ions than are bromoalkanes.

Answer on p.199

Tested ☐

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 big decrease in their use.

CFCs are largely responsible for destroying the ozone layer. In the high atmosphere, ultraviolet light causes carbon–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. For example, one molecule of CCl_3F has a global warming potential about 5000 times greater than one 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(tetrafluoroethene)) are commercially important. The plastics themselves are not halogenoalkanes, 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.

Figure 16.4 shows chlorobenzene — a halogenoarene.

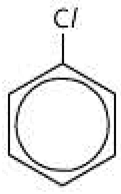


Figure 16.4

It is much less reactive towards nucleophilic substitution than the halogenoalkanes. The C–C*l* bond in the molecule is stronger than expected. This is because one of the lone pairs of electrons on the chlorine atom (Figure 16.5) delocalises with the ring electrons on benzene.

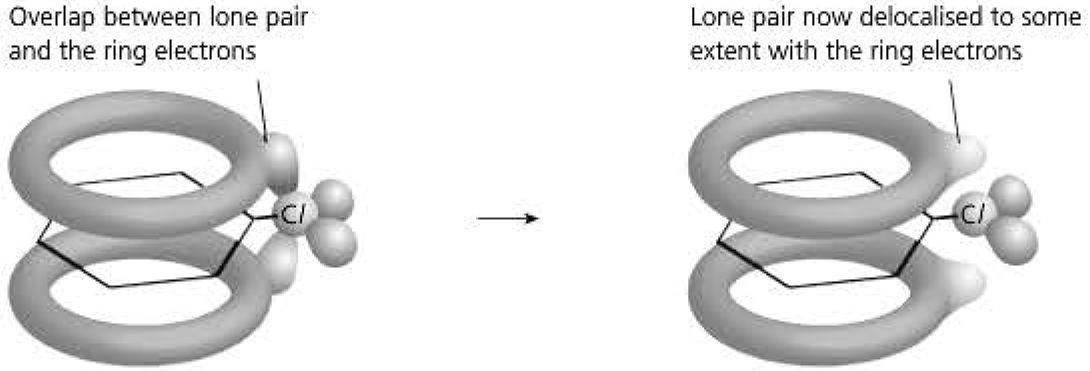


Figure 16.5

Revision activity

1 Why is a carbon–halogen bond polar?
2 Why does iodoethane react faster than chloroethane with warm, aqueous sodium hydroxide?
3 Put the following compounds in order of ease of hydrolysis with warm, aqueous sodium hydroxide starting with the most reactive:
CH_3CH_2Br, $(CH_3)_2CHBr$, C_6H_5Br, CH_3CH_2Cl

Answers on p.204

17 Hydroxy compounds

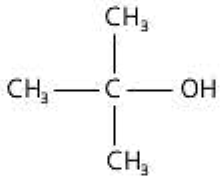
The first part of this section dealing with alcohols is for AS. The second part, dealing with the formation of esters by acylation and the material on phenol, is for A level.

Different types of alcohols

Revised ☐

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 (Figure 17.1) is a tertiary alcohol



$$\begin{array}{c} CH_3 \\ | \\ CH_3-C-OH \\ | \\ CH_3 \end{array}$$

Figure 17.1

Now test yourself

1 Draw skeletal structures for these alcohols:
  a butan-2-ol
  b 2-methylpropan-1-ol
  c 2-methylpropan-2-ol
  d cyclohexanol

2 For your structures in question 1, label each alcohol as primary, secondary or tertiary.

Answers on p.200

Tested ☐

Reactions of alcohols

Revised ☐

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 make alcohols, and alcohols can be converted into halogenoalkanes — but using different reagents.

One way of carrying out the substitution is to use the appropriate hydrogen halide. This method works for the bromoalkanes 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 hydrogen iodide formed. The equations for the formation of bromoethane and iodoethane are:

$$CH_3CH_2OH + HBr \rightarrow CH_3CH_2Br + H_2O$$

$$CH_3CH_2OH + HI \rightarrow CH_3CH_2I + H_2O$$

The method shown in Figure 17.2 only works with tertiary alcohols, forming the tertiary chloroalkane.

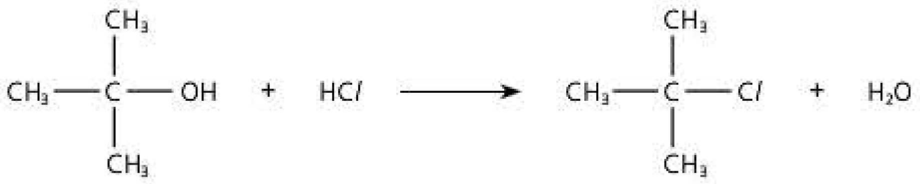


Figure 17.2

For other chloroalkanes you 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 and reacts producing bubbles of hydrogen gas. It leaves a colourless solution that produces a white solid, if evaporated to dryness. 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.

This reaction 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

Whether or not an alcohol can be oxidised depends on its structure. On addition to an oxidising agent such as acidified dichromate(VI) solution, 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 (Figure 17.3(a)).
- If this is not removed from the reaction vessel it is further oxidised to a carboxylic acid (Figure 17.3(b)). The mixture turns from orange to blue-green.

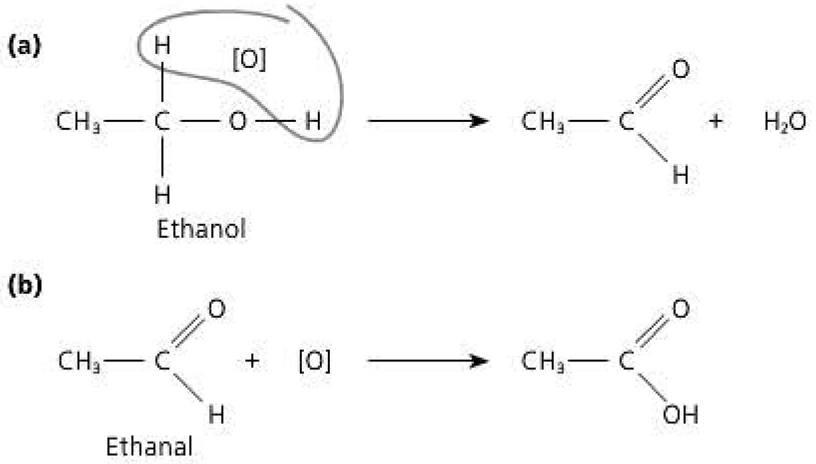


Figure 17.3 (a) and (b) Oxidation of a primary alcohol

- On refluxing a secondary alcohol with acidified dichromate(VI), a ketone is formed (Figure 17.4), which is not oxidised further. Again the mixture turns from orange to blue-green.

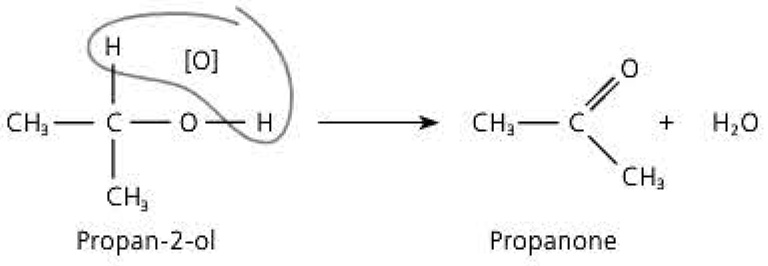
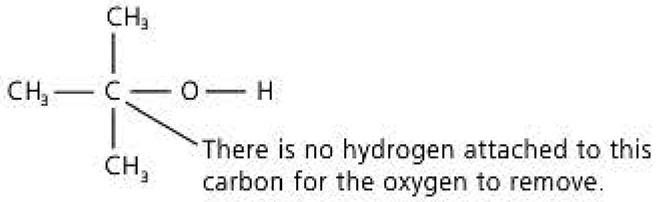


Figure 17.4

- With a tertiary alcohol (Figure 17.5), there are no hydrogen atoms on the carbon atoms that can be oxidised, so there is no reaction.



There is no hydrogen attached to this carbon for the oxygen to remove.

Figure 17.5

Provided that we can distinguish between an aldehyde and a ketone, 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 18).

Now test yourself

3 Draw skeletal structures for the products, if any, of reacting these alcohols with acidified dichromate(VI):

a butan-2-ol

b 2-methylpropan-1-ol

c 2-methylpropan-2-ol

Answers on p.200

Tested ☐

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 (Figure 17.6).

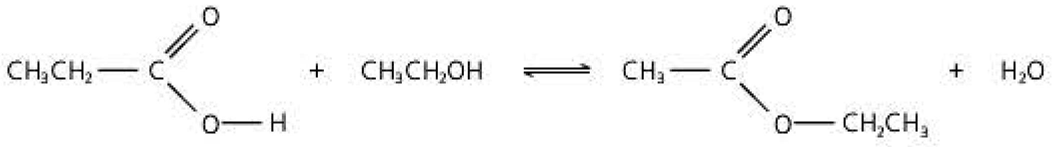


Figure 17.6

This is an equilibrium reaction and 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 19).

With ethanoyl chloride and ethanol, this reaction occurs:

$$CH_3COCl + CH_3CH_2OH \rightarrow CH_3CO_2CH_2CH_3 + HCl$$

With ethanoic anhydride and ethanol, this reaction takes place:

$$(CH_3CO)_2O + CH_3CH_2OH \rightarrow CH_3CO_2CH_2CH_3 + CH_3CO_2H$$

When 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).

Now test yourself

Tested ☐

4 Name the four esters whose structures are shown in Figure 17.7.

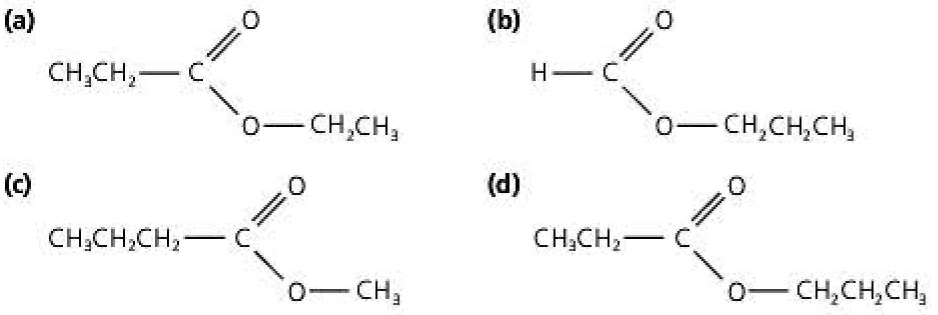


Figure 17.7

Answers on p.200

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.

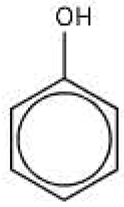


Figure 17.8

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:

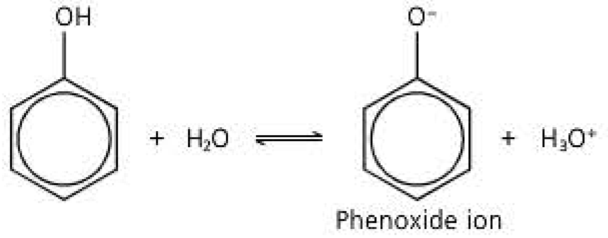


Figure 17.9

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 (Figure 17.10).

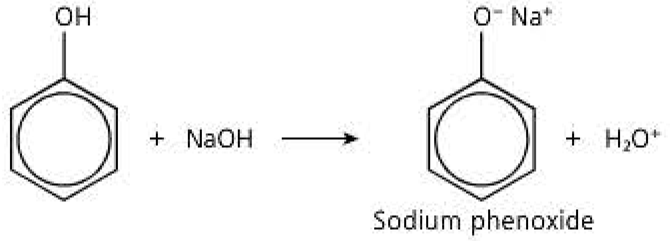


Figure 17.10

But phenol is neither acidic enough to turn blue litmus paper red, nor to release carbon dioxide from sodium carbonate.

Reaction with sodium

When sodium is heated in a test tube until it is molten and a small piece of sodium is added, some effervescence takes place with hydrogen being evolved (Figure 17.11). Sodium phenoxide is formed.

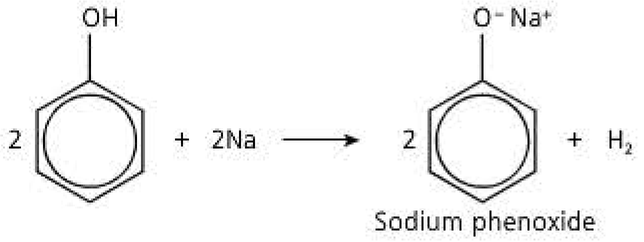


Figure 17.11

Reaction with diazonium salts

This is covered in Chapter 20, but phenols react with diazonium salts (Figure 17.12) in a 'coupling' reaction forming a dye.

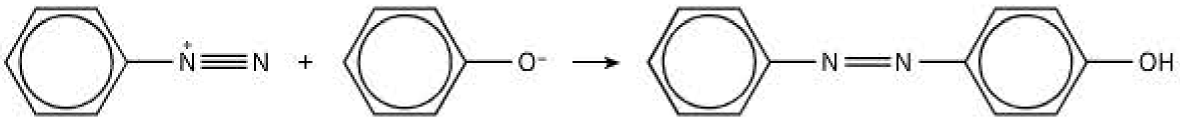


Figure 17.12

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 acid and sulfuric acid. The reason for this is that 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 (Figure 17.13), 4-nitrophenol is formed.

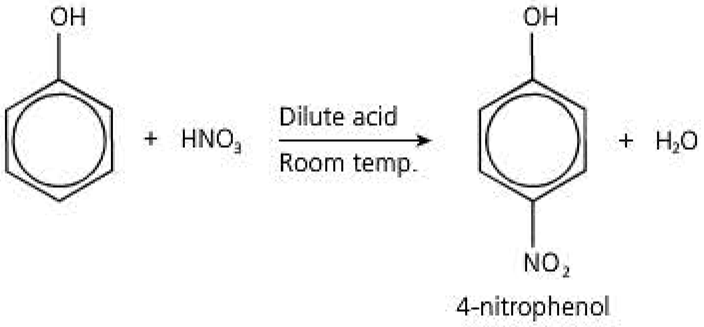


Figure 17.13

With concentrated nitric acid (Figure 17.14), 2,4,6-trinitrophenol is formed.

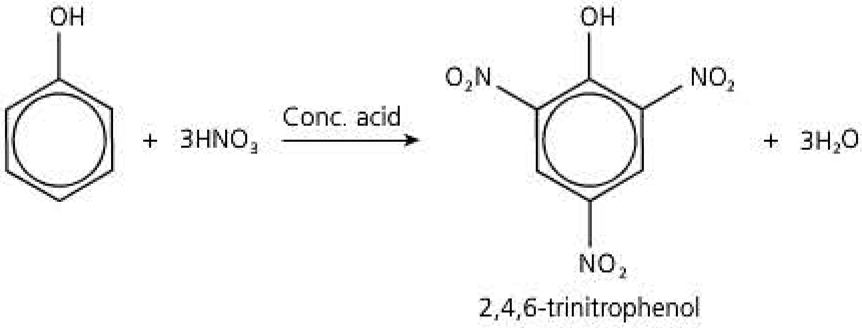


Figure 17.14

Bromination

When bromine water is added to phenol, there is a similar effect to nitration (Figure 17.15). The activated ring gives an almost instantaneous white precipitate of 2,4,6-tribromophenol.

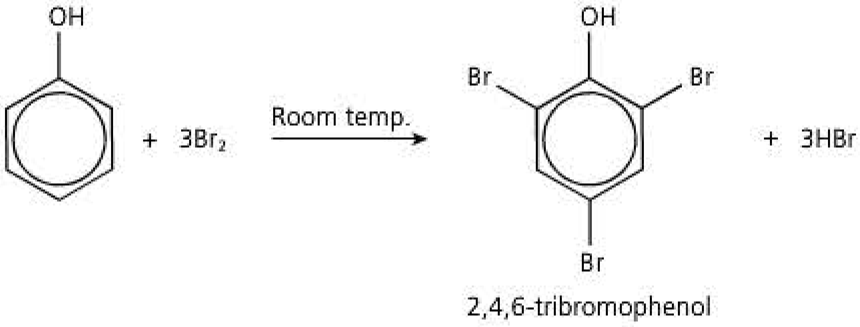


Figure 17.15

Relative acidities of water, phenol and ethanol

Revised ☐

In considering ethanol and phenol it is useful to be able to compare their acidities with that of water and to explain the differences using their structures. Alcohols such as ethanol are such weak acids that their acidic properties can almost be ignored — only in the presence of sodium do they form the ethoxide ion to any degree. Phenol on the other hand is sufficiently acidic to have noticeable acidic properties, as you have seen. The reason for this is that when phenol loses a proton, the remaining negative charge on the oxygen atom is able to delocalise into the benzene ring (Figure 17.16). This is possible because the lone pairs of electrons on the oxygen can overlap with the ring, spreading the charge.

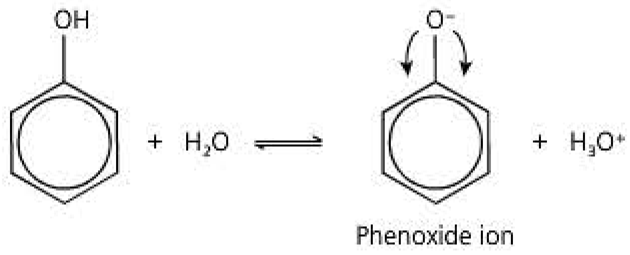


Figure 17.16 Phenol's acidity

However, it must be remembered that oxygen is still a more electronegative atom than carbon and will retain an overall small negative charge. In the case of ethanol no delocalisation of the negative charge is possible and so it is a much weaker acid with a pK_a similar to that of water.

Now test yourself

5 Explain why phenol is a stronger acid than ethanol.

Answer on p.200

Tested ☐

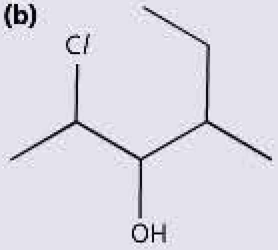
Revision activity

The first two parts are for AS and the remainder for A level.

1 Classify the following as primary, secondary or tertiary alcohols.

(a)

(b)



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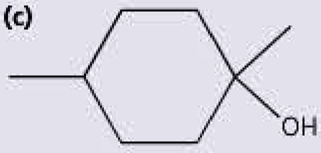
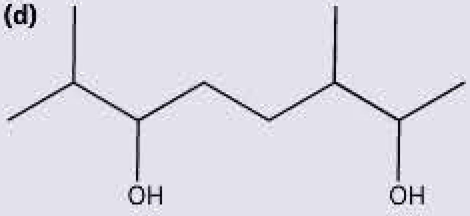


(d)



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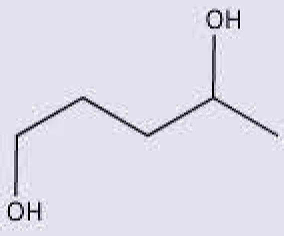
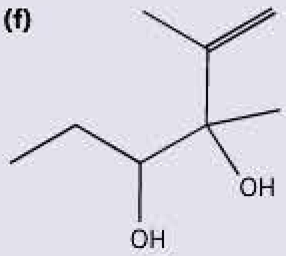


(f)



2 How does reaction with acidified potassium dichromate(VI) enable you to decide whether an unknown alcohol has a primary, secondary or tertiary structure?

3 Why is phenol a stronger acid than ethanol?

4 How does the reaction of phenol with nitric acid differ from that of benzene?

Answers on p.204

18 Carbonyl compounds

This chapter is only for AS.

Formation

Revised ☐

The oxidation of alcohols by acidified dichromate(VI) was covered in Chapter 17.

- With a primary alcohol (Figure 18.1) an aldehyde is formed first.

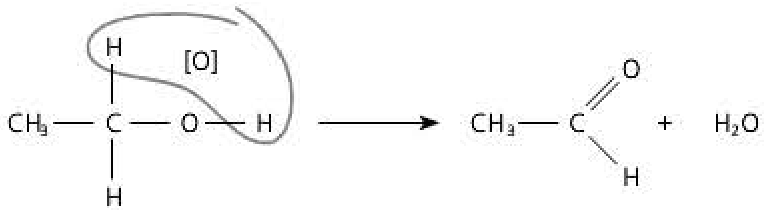


Figure 18.1

- If this is not removed from the reaction vessel, it is oxidised further (Figure 18.2) to give a carboxylic acid.

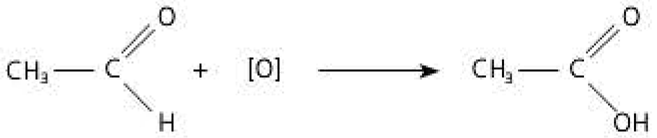


Figure 18.2

- With a secondary alcohol, a ketone is formed (Figure 18.3). This is not oxidised further.

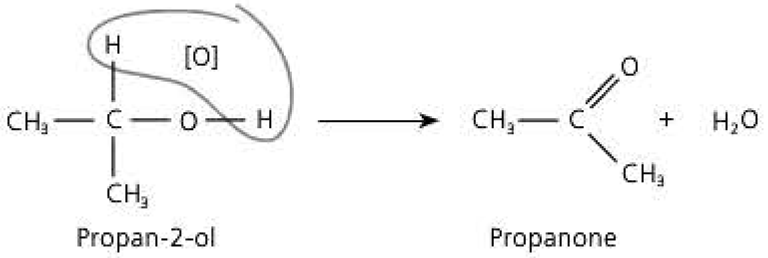


Figure 18.3

Reactions

Revised ☐

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 shown in Figure 18.4, forming a primary alcohol.

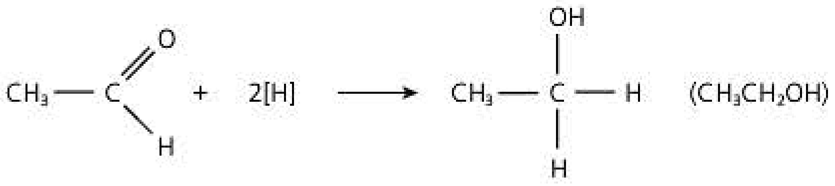


Figure 18.4

With ketones such as propanone (Figure 18.5) the reaction is similar. A secondary alcohol is formed.

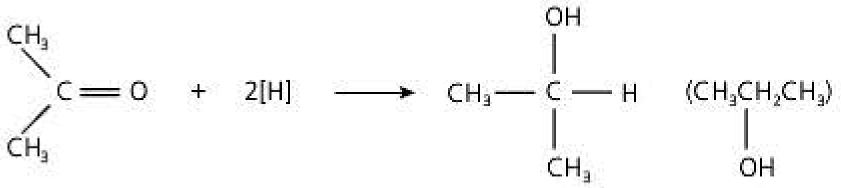


Figure 18.5

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 (Figure 18.6).

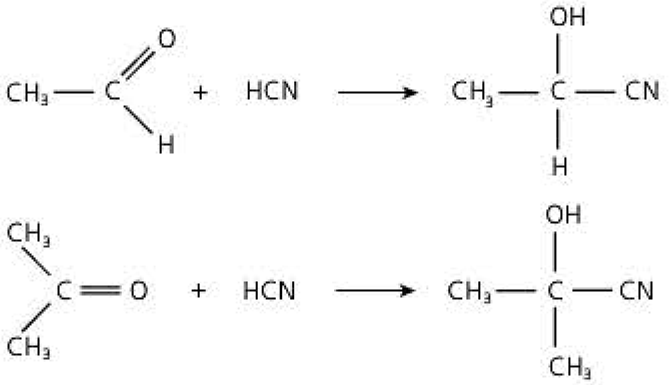


Figure 18.6

For AS you need to know the mechanism for the reaction, using hydrogen cyanide as the nucleophile. You may think that this is a strange reactant to choose, but as you saw earlier it adds a carbon atom to the chain, which is often an important step in a reaction.

The reactions are started (Figure 18.7) by the nucleophilic attack on the carbonyl compound by hydrogen cyanide. The C=O bond is polarised with a partial positive charge on the carbon atom and a partial negative charge on the oxygen atom.

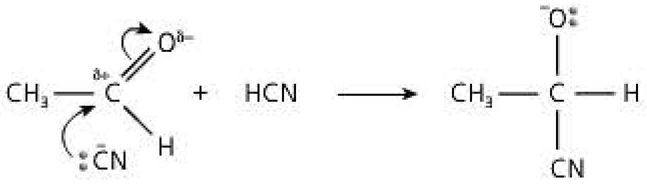


Figure 18.7

Hydrogen cyanide itself is not used in the reaction because it is a highly toxic gas. Instead, sodium cyanide 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 from the mechanism.

Completing the addition of hydrogen cyanide to an aldehyde

The negative ion formed then picks up a hydrogen ion (Figure 18.8). It could come from a hydrogen cyanide molecule or from the water or the H_3O^+ ions present in the slightly acidic solution.

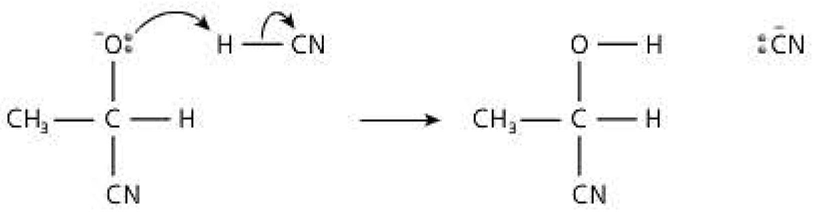


Figure 18.8

Completing the 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 as above in Figure 18.7.

The negative ion formed then picks up a hydrogen ion (Figure 18.9) to give the hydroxynitrile (cyanohydrin as it is sometimes called in older textbooks).

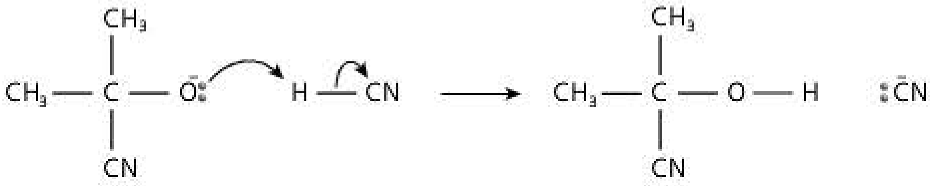


Figure 18.9

Now test yourself

1 What is the reagent used for adding hydrogen cyanide to a carbonyl compound?

Answer on p.200

Tested ☐

Chirality

You may have noticed that the product formed with the aldehyde has four different groups attached to the central carbon. If you have covered the section on isomerism in Chapter 14 you will know that this is 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. However, the product of this particular reaction is *not* optically active because ethanal is a planar molecule and the mechanism means that attack by the cyanide ion can occur from either above or below the molecule. This produces a 50:50 mixture of isomers, so the net result is a lack of optical activity.

Now test yourself

2 Give the structure of the product formed when hydrogen cyanide is added to butanal.

Answer on p.200

Tested ☐

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

This rather complicated-sounding reagent is used in 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.

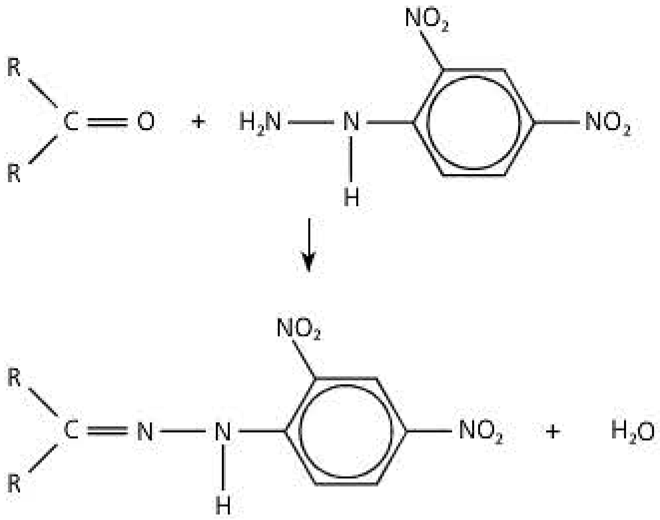


Figure 18.10

The equation for the reaction is shown in Figure 18.10, but it is unlikely that you will be asked to produce this in an examination.

The reaction is rather more useful than just testing for a carbonyl compound. If the precipitate is filtered off, washed and recrystallised, 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 17, you saw that primary, secondary and tertiary alcohols can be distinguished by looking at their oxidation products. These same reactions enable us to distinguish between aldehydes and ketones.

Table 18.1 summarises the behaviour of the two types of carbonyl compound with different reagents.

Table 18.1

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

The tri-iodomethane (iodoform) reaction

You saw in Chapter 17 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 shown in Figure 18.11.

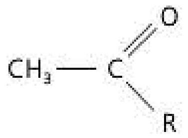


Figure 18.11

Ethanal is the *only* aldehyde to give a positive reaction (Figure 18.11). Any methyl ketone (Figure 18.12) will give a positive result.

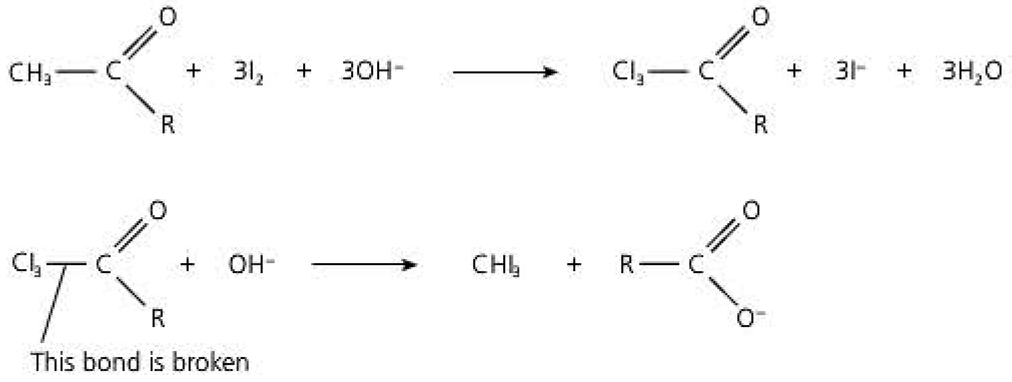


Figure 18.12

Now test yourself

3 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.

Answers on p.200

Tested ☐

Revision activity

1 Why can a primary alcohol be oxidised to an aldehyde and then a carboxylic acid, but a secondary alcohol can only be oxidised to a ketone?

2 Carbonyl compounds react with HCN to form hydroxynitriles (cyanohydrins).

- **a** What sort of reagent is HCN?
- **b** What type of reaction is this?

3 Why can the iodoform reaction not be used to *exclusively* identify a methyl ketone?

Answers on p.204

19 Carboxylic acids and derivatives

This chapter is a mix of material for AS and for A level.

Carboxylic acids

Revised ☐

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 17 that a primary alcohol can be oxidised using acidified dichromate(VI) ions to give an aldehyde and that, if this is not distilled off, it is oxidised further to a carboxylic acid (Figure 19.1).

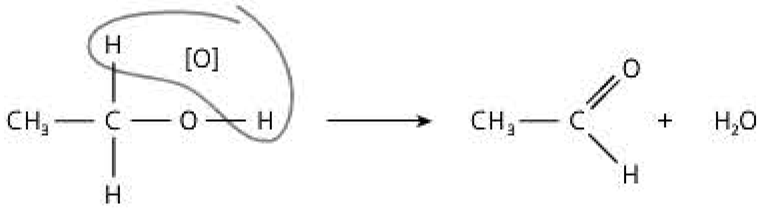


Figure 19.1

From an aldehyde

You could start with an aldehyde and oxidise it with acidified dichromate(VI) ions to form the carboxylic acid (Figure 19.2).

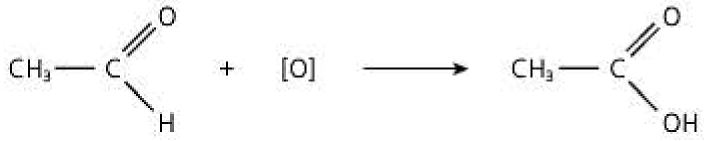


Figure 19.2

This is rarely used because to make an aldehyde you have to start with a primary alcohol.

From a nitrile

You saw in Chapter 16 how nitriles can be produced from halogenoalkanes. They can then be hydrolysed to form either carboxylic acids or their salts, depending on whether an acid or a 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:

$$CH_3CN + 2H_2O + H^+ \rightarrow CH_3CO_2H + NH_4^+$$

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:

$$CH_3CN + NaOH + H_2O \rightarrow CH_3CO_2^-Na^+ + NH_3$$

To obtain the carboxylic acid, a strong acid such as hydrochloric acid is added and the carboxylic acid is distilled off.

Now test yourself

1 Give three starting materials you could use to produce ethanoic acid.

Answer on p.200

Tested ☐

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 about 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 a 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 a salt:
  $CH_3CO_2H + NaOH \rightarrow CH_3CO_2^-Na^+ + H_2O$
- Aqueous solutions of carboxylic acids react with carbonates and hydrogen carbonates making 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. However, if you chose to use marble chips as the carbonate the reaction would be noticeably slower.
- Ethanoic acid reacts with ammonia in just the same way as other acids, forming an ammonium salt:
  $CH_3CO_2H + NH_3 \rightarrow CH_3CO_2^-NH_4^+$

Formation of alkyl esters

Making alkyl esters from alcohols was covered in Chapter 17, and you learned that a range of reagents can be used to react with the –OH group. Here, you are considering a single reaction — the formation of an ester from a carboxylic acid and an alcohol.

An alkyl ester is formed when a carboxylic acid is heated with an alcohol in the presence of an acid catalyst (Figure 19.3), usually concentrated sulfuric acid. The reaction is slow and reversible:

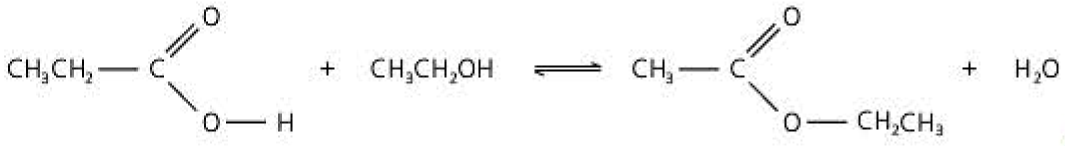


Figure 19.3

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 reaction mixture 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.

Now test yourself

2 Find out why esters are important. Give two important uses of these compounds.

Answers on p.200

Tested ☐

Formation of alcohols

Carboxylic acids can be reduced to alcohols using lithium tetrahydridoaluminate(III) (lithium aluminium hydride), $LiAlH_4$. This powerful reducing agent is extremely useful in organic chemistry, the reaction taking place (Figure 19.4) in ethoxyethane solution.

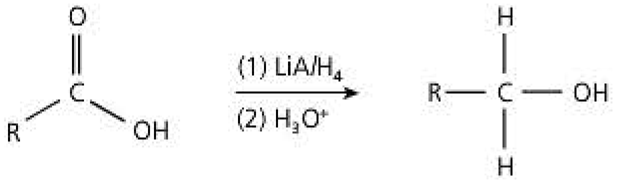


Figure 19.4

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 17 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.

Further oxidation of some carboxylic acids

It is possible to oxidise two carboxylic acids further, although these are rather specialised examples.

Methanoic acid, HCO_2H, does not contain an alkyl group and can be oxidised to carbon dioxide and water using either Fehling's solution or Tollens' reagent:

$HCO_2H + [O] \rightarrow H_2O + CO_2$

Ethanedioic acid, HO_2CCO_2H, is a dicarboxylic acid, again with no alkyl groups. On warming with acidified potassium manganate(VII), it is oxidised to carbon dioxide and water:

$HO_2CCO_2H + [O] \rightarrow H_2O + 2CO_2$

Relative acidity of acids

For A level it is not enough just to know that carboxylic acids are relatively weak because the equilibrium for dissociation lies well to the left. You also need to know what makes some acids stronger or weaker than others and be able to explain the relative acidities of carboxylic acids, phenols and alcohols (see Chapter 17 for the latter two groups of compounds).

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

Before comparing carboxylic acids, it is useful to look at the ionisation of ethanoic acid in more detail (Figure 19.5).

Expert tip

It would be a good idea to re-read the section on pK_a and pH on p. 57.

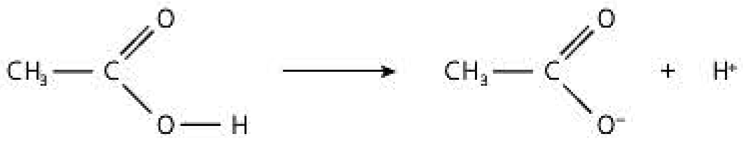
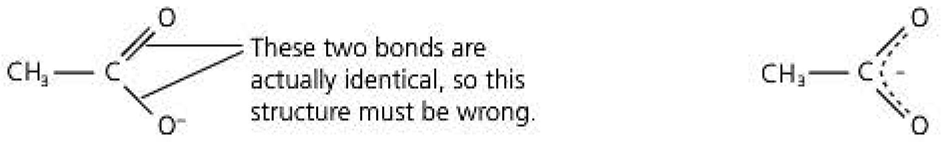


Figure 19.5 Ethanoic acid in solution

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 group and a C–O– group cannot be correct. The representation in Figure 19.6 is more accurate.



These two bonds are actually identical, so this structure must be wrong.

Figure 19.6 The structure of the ethanoate ion

The dashed line represents the 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 19.1.

Table 19.1

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 lower pK_a (stronger acid) than ethanoic acid. You know that alkyl groups 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. Note that the extra CH_2 in propanoic acid makes little difference to the pK_a.

Now let's see what happens if a highly **electronegative** atom, which pulls electrons away from the O–C–O group, is introduced. Chlorine is a good example of such an electronegative atom.

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons.

The pK_a values for ethanoic acid and its chlorinated derivatives are shown in Table 19.2.

Table 19.2

Formula	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 ions to be removed.

Now test yourself

3 Use the pK_a values for ethanoic acid and trichloroethanoic acid in Table 19.2 to compare the hydrogen ion concentrations in equimolar solutions of each acid.

Answer on p.200

Tested ☐

Acyl chlorides

Revised ☐

You saw earlier how to make acyl chlorides from carboxylic acids. Their reactions are covered here.

Hydrolysis

Acyl halides react quite violently with water, releasing steamy fumes of HCl and forming the appropriate carboxylic acid (Figure 19.7).

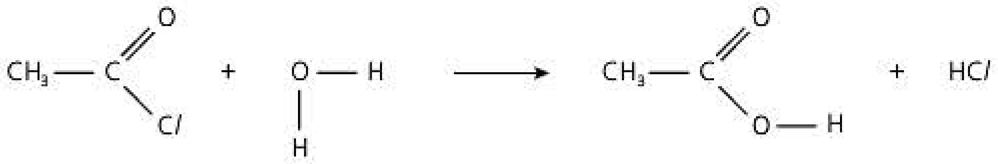


Figure 19.7 The reaction of ethanoyl chloride with water

The equation can also be written as:

$$CH_3COCl + H_2O \rightarrow CH_3CO_2H + HCl$$

However, when studying the reactions of acyl chlorides with alcohols and phenols, it is useful to think about the form shown in Figure 19.7.

The ease with which acyl chlorides react with water is in contrast with the reactivity of alkyl chlorides and aryl chlorides. In Chapter 16 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 groups 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 (Figure 19.8). Perhaps a more significant reason is the interaction between one of the lone pairs of electrons on chlorine and the delocalised ring electrons.

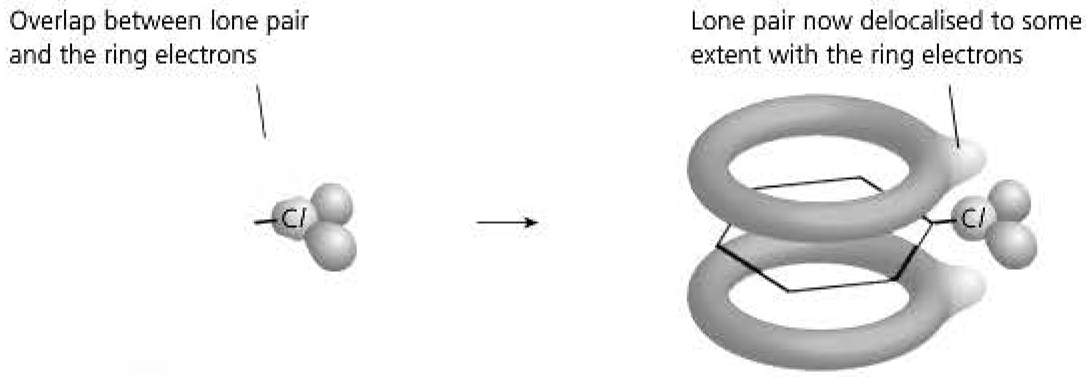


Figure 19.8

Reaction with alcohols and phenols

With alcohols

The reaction between an acyl chloride and an alcohol (Figure 19.9) is similar to the reaction between an acyl chloride and water, with the release of hydrogen chloride.

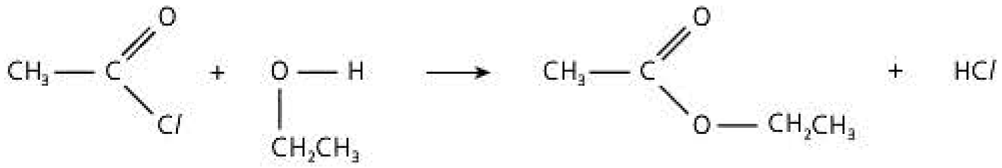


Figure 19.9

Compare this reaction with the equation shown in Figure 19.1.

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 because of the benzene ring (Figure 19.10). Apart from this the reaction is very similar.

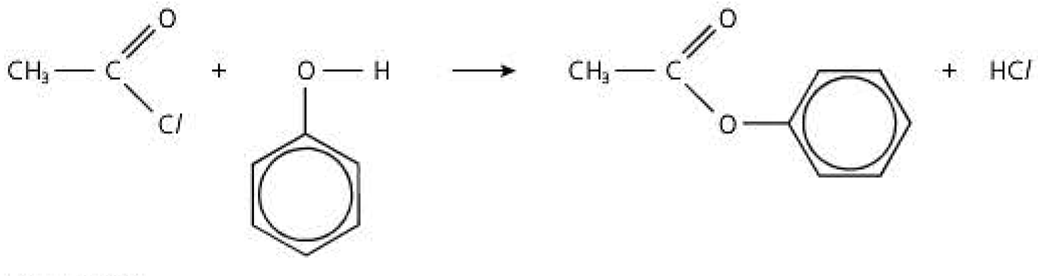


Figure 19.10

The product is called phenyl ethanoate (remember alcohol/phenol part first, then the carboxylic acid part). The reaction is called **acylation**.

Reaction with ammonia and primary amines

Ethanoyl chloride reacts violently with a cold concentrated solution of ammonia. The white solid product formed (Figure 19.11) is a mixture of ethanamide (an amide) and ammonium chloride.

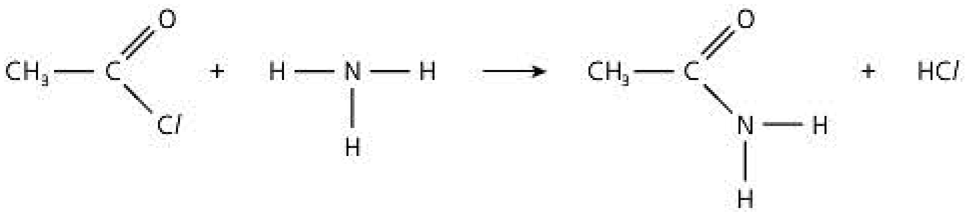


Figure 19.11

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

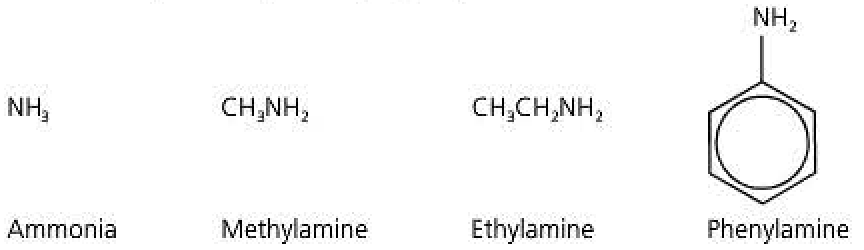


Figure 19.12

Primary amines react with acyl chlorides by substitution (Figure 19.13), replacing the chlorine atom and joining via the nitrogen atom.

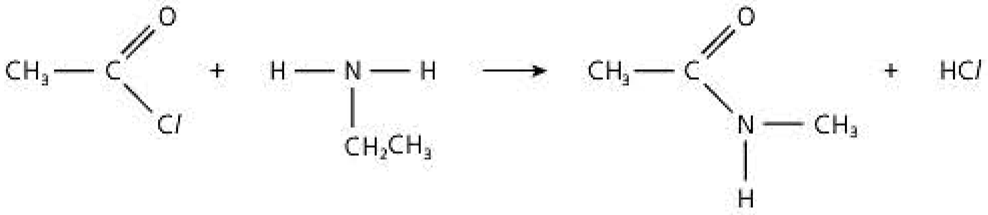


Figure 19.13 The product is an N-substituted amide

Now test yourself

4 What functional groups are produced when acyl chlorides react with:
  a alcohols?
  b phenols?
  c primary amines?

5 Draw the structure of ethanamide.

Answers on p.200

Tested ☐

Esters

Revised ☐

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:

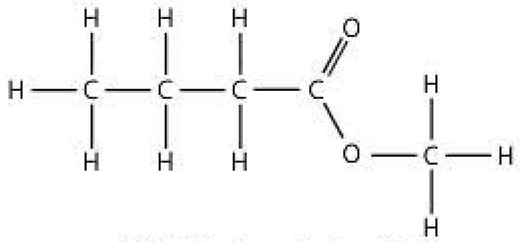
$$CH_3CO_2CH_2CH_3 + NaOH \rightarrow CH_3CO_2^-Na^+ + CH_3CH_2OH$$

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.

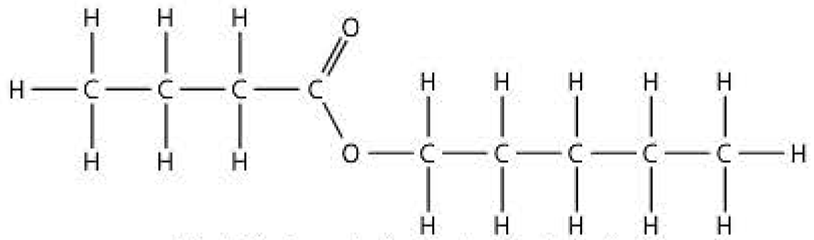
Commercial uses

Perfumes and flavours

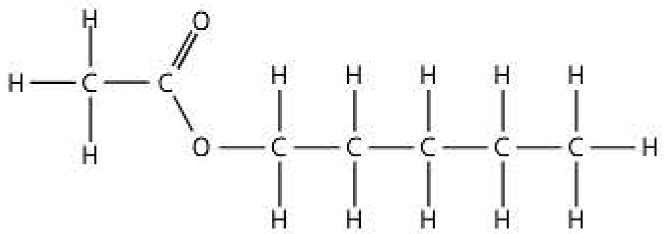
Esters can be formed from many combinations of alcohols with carboxylic acids. They are distributed widely in nature and are responsible for many of the smells and flavours associated with fruits and flowers. This has led to the development of artificial esters for the food industry — for example, ice cream — and for products that need a nice smell — such as detergents and air fresheners. Figure 19.14 shows some of the esters that are used.



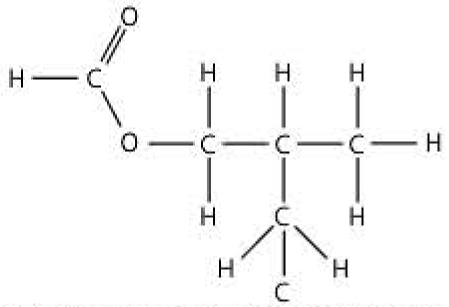
Methyl butanoate (apple)



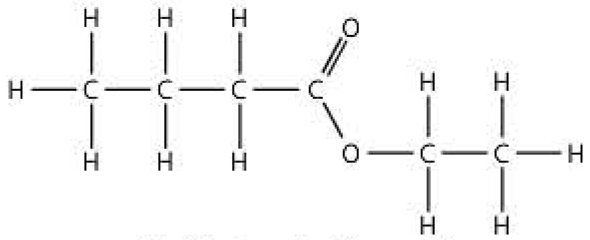
Pentyl butanoate (apricot, strawberry)



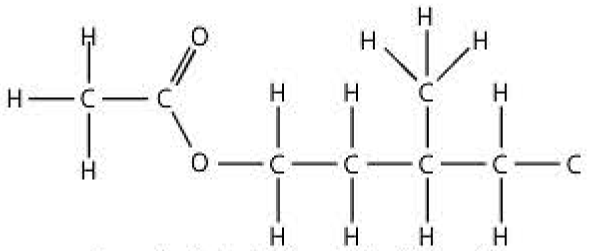
Pentyl ethanoate (pear)



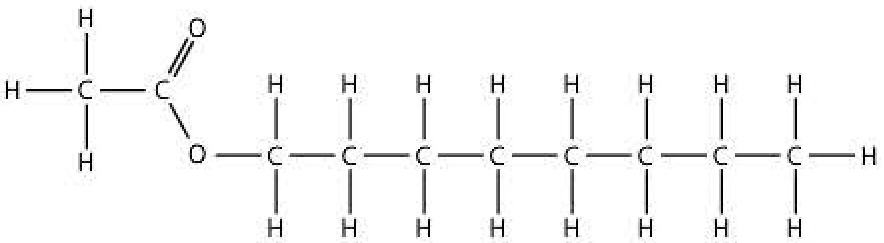
Methylpropyl methanoate (raspberry)



Ethyl butanoate (pineapple)



3-methylbutyl ethanoate (banana)



Octyl ethanoate (orange)

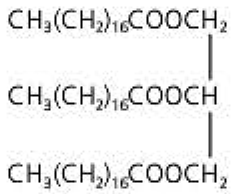
Figure 19.14 Esters used in industry

Natural esters are still used in perfumes.

Margarine production

Most oils and fats are esters of long-chain carboxylic acids with the alcohol glycerol ($CH_2OHCHOHCH_2OH$). Many oils 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 19.15).

It is this that makes the oils liquid and the fats low-melting-point solids. These esters are often called glycerides because the common name for the tri-alcohol is glycerol.



$$\begin{array}{r} CH_3(CH_2)_{16}COOCH_2 \\ | \\ CH_3(CH_2)_{16}COOCH \\ | \\ CH_3(CH_2)_{16}COOCH_2 \end{array}$$

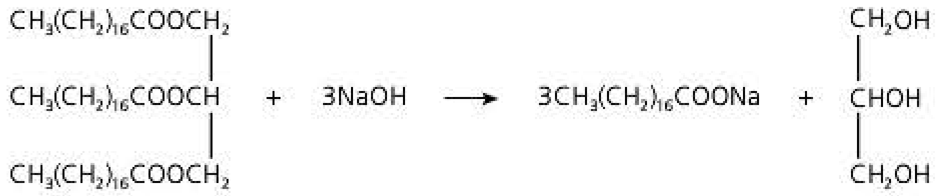
Figure 19.15 A molecule of a fat

To make margarine, the vegetable oils must 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 fats 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 (Figure 19.16). 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).



$$\begin{array}{r} CH_3(CH_2)_{16}COOCH_2 \\ | \\ CH_3(CH_2)_{16}COOCH \\ | \\ CH_3(CH_2)_{16}COOCH_2 \end{array} + 3NaOH \longrightarrow 3CH_3(CH_2)_{16}COONa + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Figure 19.16 Making soap

Solvents

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

Now test yourself

6 Explain why esters can be hydrolysed in both acid solutions and alkaline solutions.

Answer on p.200

Tested ☐

Polyesters

Polymers are covered in more detail in Chapter 21.

Revision activity

The first three parts are for AS and the remainder for A level.

1 What three functional groups can be readily converted into carboxylic acids?
2 What three types of compound can be formed from carboxylic acids?
3 Give three important uses of esters.
4 Why is CCl_3CO_2H a much stronger acid than CH_3CO_2H?
5 Why are acyl chlorides particularly useful when reacting with the –OH group of an alcohol?
6 How can an acyl chloride be made from a carboxylic acid?

Answers on p.204

20 Nitrogen compounds

This chapter is needed only for A level.

Primary amines

Revised ☐

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), $LiAlH_4$. The reaction takes place in ethoxyethane solution and the amine is produced on adding a small amount of a dilute acid. (This does *not* work with $NaBH_4$):

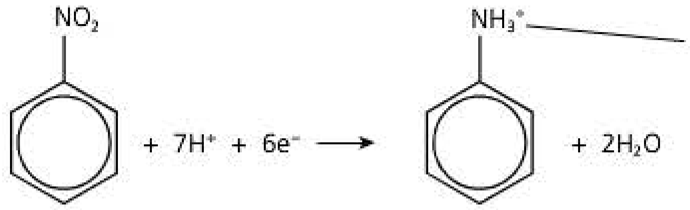
$CH_3CN + 4[H] \rightarrow CH_3CH_2NH_2$

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 with a mixture of tin and concentrated hydrochloric acid on a boiling water bath. Because of the acidic conditions, rather than producing phenylamine directly, the nitrobenzene is reduced to phenylammonium ions (Figure 20.1(a)). The lone pair on the nitrogen in the phenylamine picks up a hydrogen ion from the acid:



Notice the positively charged ion formed.

Figure 20.1(a)

The second stage (Figure 20.1(b)) is to add sodium hydroxide solution to remove the hydrogen ion:

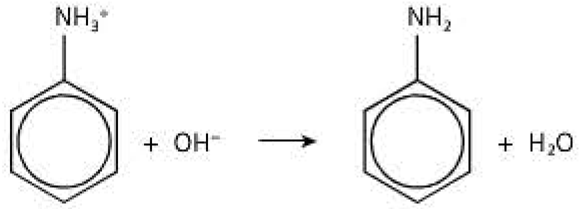


Figure 20.1(b)

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.

Now test yourself

1 Give two reagents that could be used to bring about the following reaction.

$(CH_3)_2CHCN \rightarrow (CH_3)_2CHCH_2NH_2$

2 Give the conditions for using each of the reagents you have chosen.

Answers on p.200

Tested ☐

Reactions of phenylamine

With aqueous bromine

With bromine water (Figure 20.2) phenylamine gives a fairly instant white precipitate of 2,4,6-tribromophenylamine at room temperature.

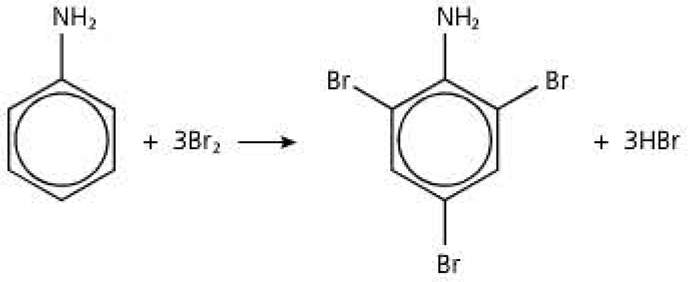


Figure 20.2

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 slowly added. The slow addition ensures that the reaction mixture remains around 5°C. A solution containing **benzenediazonium ions** (Figure 20.3) is obtained.

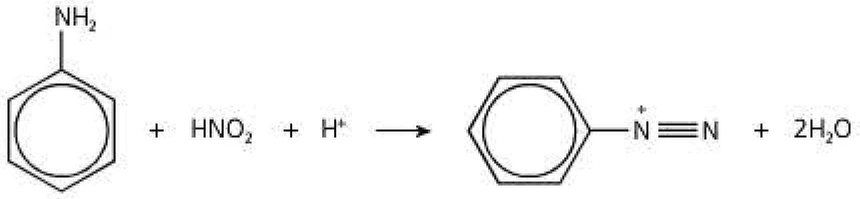


Figure 20.3

Expert tip

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 (Figure 20.4) by adding a cold solution of phenol in sodium hydroxide to the mixture.

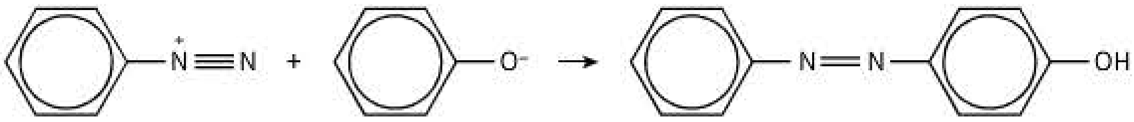


Figure 20.4

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 compound in Figure 20.5 is formed.

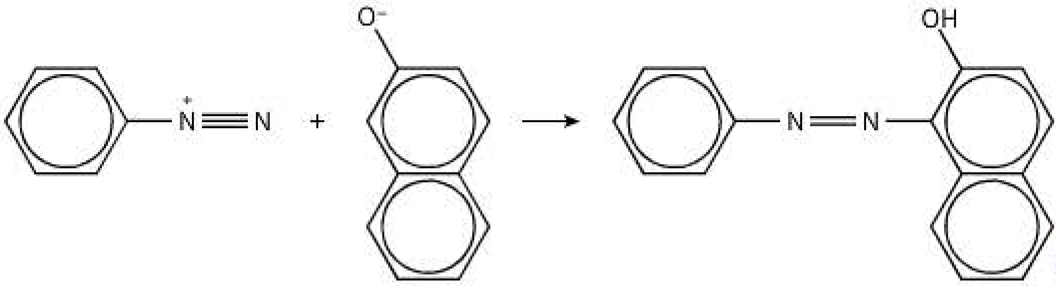


Figure 20.5

At temperatures above 10°C, a reaction takes place that produces a complex organic mixture containing mainly phenol. Nitrogen gas is evolved:

$$C_6H_5NH_2 + HNO_2 \rightarrow C_6H_5OH + N_2 + H_2O$$

Now test yourself

3 Explain why phenylamine is a much weaker base than ethylamine.

Answer on p.200

Tested ☐

Amides

Revised ☐

Formation from acyl halides and ammonia

You saw in Chapter 19 how acyl halides react with primary amines and ammonia. 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 neutral compounds, but 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 visually.

Reduction

Amides can be reduced to amines using lithium tetrahydridoaluminate(III) (lithium aluminium hydride), $LiAlH_4$. This reaction (Figure 20.6) takes place in ethoxyethane solution.

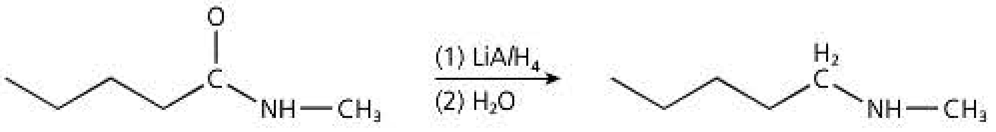


Figure 20.6

Amino acids and proteins

Revised ☐

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

A **zwitterion** is formed from an amino acid when a proton is lost from the carboxyl group and accepted by the nitrogen of the amine group.

So 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.

Zwitterions exhibit acid–base behaviour because they can accept and donate protons. In acids a proton is accepted by 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 alkalis 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.

Now test yourself

4 Use Table 10 from the *Data Booklet* to explain why the amino acids Asp and Lys show different charges to Gly at pH 7.0.

5 Draw the structure, showing charge(s), of Glu at low pH.

Answers on p.200

Tested ☐

Formation of peptide bonds

If you 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.

A **peptide bond** is the same as an amide bond, but is used in biological systems.

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

Consider two simple amino acids, glycine (2-aminoethanoic acid) and alanine (2-aminopropanoic acid). Figure 20.7 shows that these can be joined in two ways.

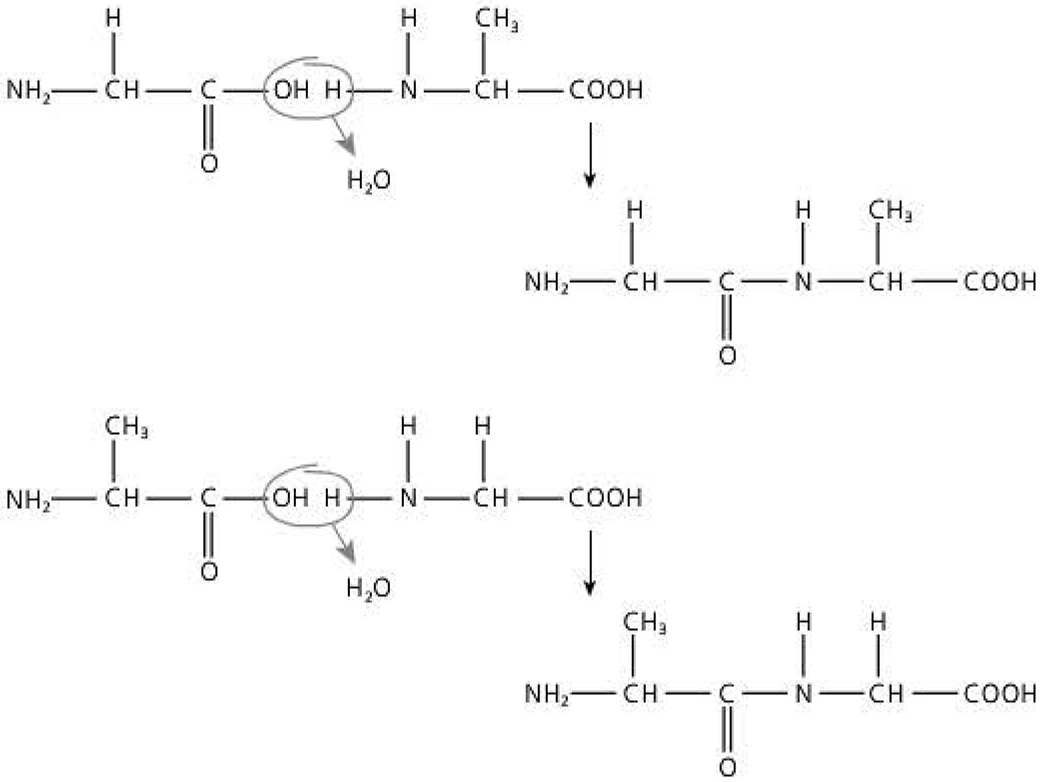


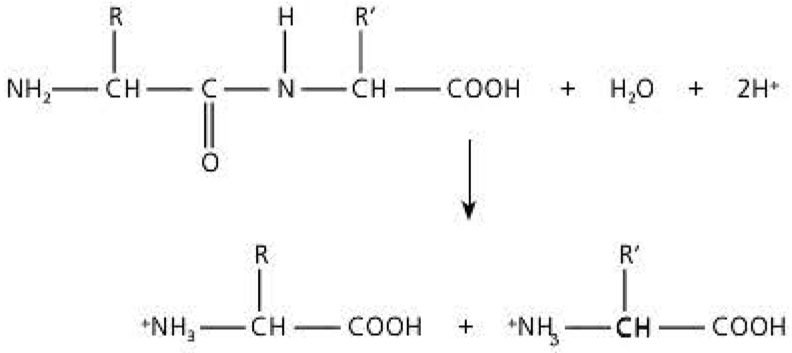
Figure 20.7 Joining amino acids in different ways

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 subjected to microwave heating for up to 30 minutes. The amide (peptide) bonds are broken (Figure 20.8) leaving the amino acids in their protonated form, for example:



$$NH_2-CH(R)-C(=O)-N(H)-CH(R')-COOH + H_2O + 2H^+ \rightarrow {}^+NH_3-CH(R)-COOH + {}^+NH_3-CH(R')-COOH$$

Figure 20.8 Hydrolysing peptide bonds

Electrophoresis and DNA fingerprinting

Revised ☐

You saw earlier that amino acids form zwitterions in aqueous solution, and that the exact nature of a zwitterion depends on the pH of the solution:

zwitterion $H_3N^+-CH_2-CO_2^-$

low pH: $H_3N^+-CH_2-CO_2^- + H_3O^+ \rightarrow H_3N^+-CH_2-CO_2H + H_2O$

high pH: $H_3N^+-CH_2-CO_2^- + OH^- \rightarrow H_2N-CH_2-CO_2^- + H_2O$

This effect can be seen when an electric potential is applied to a mixture of the amino acids glycine, lysine and glutamic acid at pH 7 using the set-up shown in Figure 20.9.

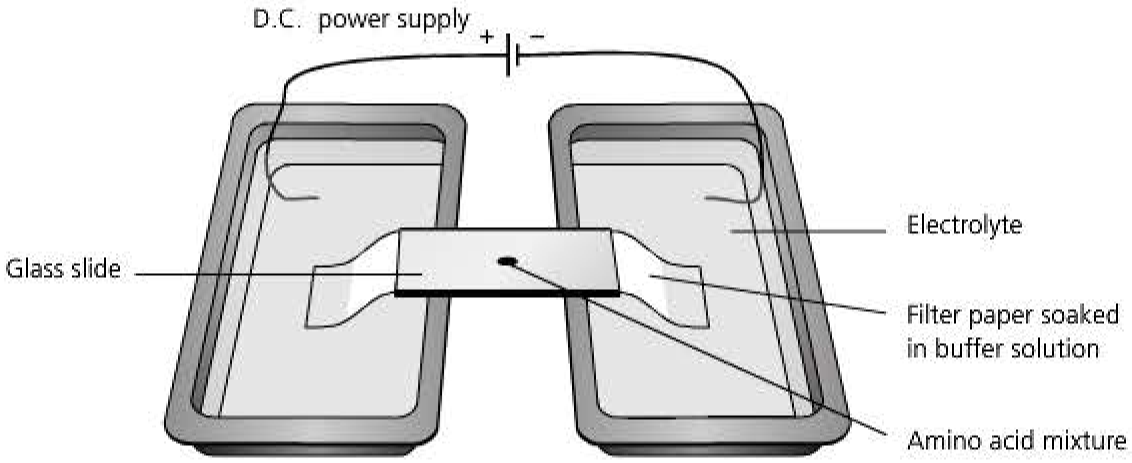


Figure 20.9 Apparatus for electrophoresis

If the power supply is switched on and the apparatus left for a period of time, the amino acid mixture is separated as shown in Figure 20.10.

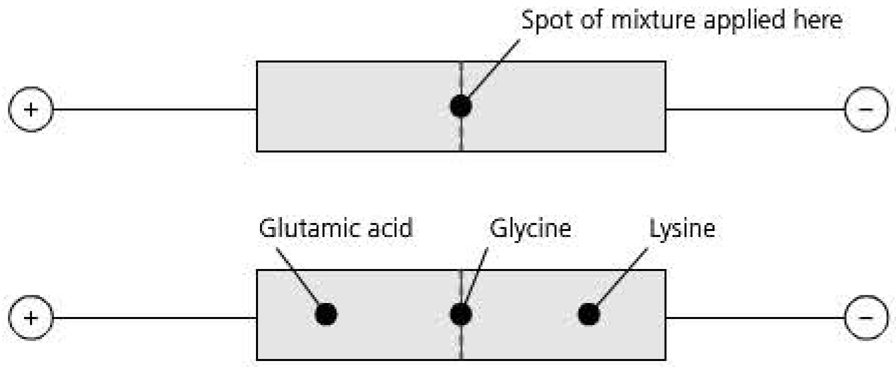


Figure 20.10 Results of the electrophoresis of a mixture of three amino acids

You can explain how different amino acids are affected by looking at the structures of glycine, lysine and glutamic acid at pH 7:

glycine $H_3N^+CH_2CO_2^-$
lysine $H_3N^+CH(CH_2CH_2CH_2CH_2NH_3^+)CO_2^-$
glutamic acid $H_3N^+CH(CH_2CH_2CO_2^-)CO_2^-$

Note that at pH 7:

- lysine carries an extra positive charge, and hence moves towards the negative electrode
- glutamic acid carries an extra negative charge and moves towards the positive electrode
- glycine carries one of each type of charge so it is attracted equally to both electrodes and does not move

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 with 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 its movement and direction.

Revision activity

1. What is the starting material for making ethylamine in a single-step reaction?
2. What is the name given to the process in which phenol is reacted with benzenediazonium chloride in cold, aqueous sodium hydroxide to form a coloured product?
3. What type of compound is formed when amides react with $LiAlH_4$?
4. Explain why amino acids have higher than expected melting points.
5. The amino acid alanine, $CH_3CH(NH_2)COOH$, reacts with glycine, $H_2NCH_2CO_2H$. Show how this produces two dipeptides with different structures.

Answers on p.204

21 Polymerisation

This chapter deals with condensation polymerisation and is needed for A level. Remember that addition polymerisation is covered in Chapter 15.

Condensation polymerisation

Revised ☐

Characteristics of condensation polymerisation

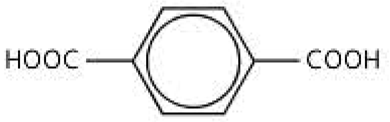
The points to remember about condensation polymerisation are:

- 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.

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 you covered polyalkenes. The polymerisation here is different because two different molecules are needed, rather than just one.

The most important commercial polyester is called Terylene® and is produced by reacting a dicarboxylic acid with a dialcohol as shown in Figure 21.1.



Benzene-1,4-dicarboxylic acid

HO — CH_2CH_2 — OH

Ethane-1,2-diol

Figure 21.1

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 (Figure 21.2) alternately adding a dialcohol and a dicarboxylic acid.

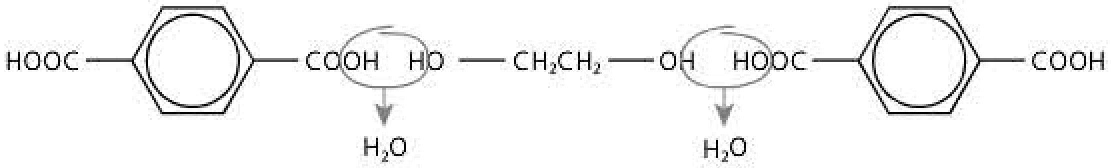


Figure 21.2

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 (Figure 21.3) between them.

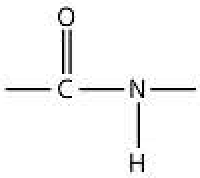


Figure 21.3

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 making ropes. In its solid form it has become a replacement for metals in low–medium stress applications, such as gears. For nylon, the monomers are hexanedioic acid and 1,6-diaminohexane:

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

Each of these molecules has six carbon atoms, so this form of nylon (Figure 21.4) is called nylon-6,6. Water is lost in the formation of each amide bond.

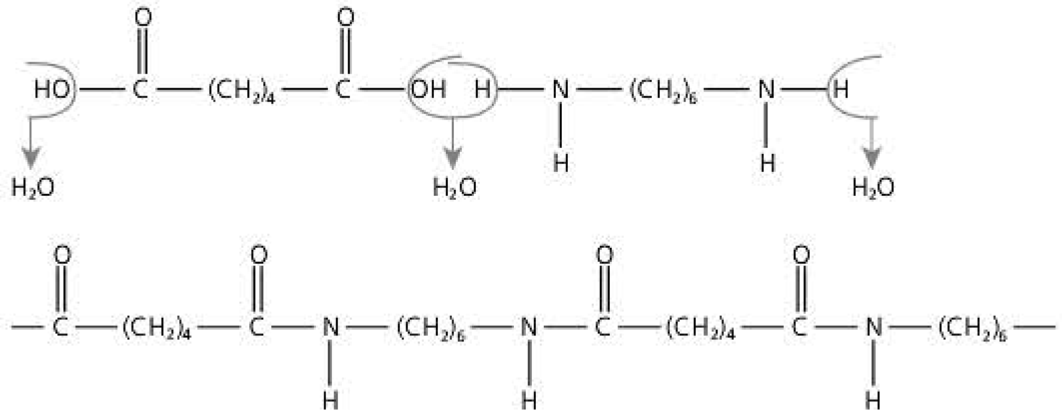


Figure 21.4 Making nylon-6,6

Nylon-6

Another form of nylon can be produced from a single monomer called caprolactam (Figure 21.5).

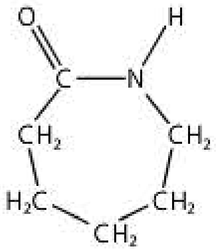


Figure 21.5 Caprolactam

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 atom and the nitrogen atom and an amino acid is formed. The amino acid is then able to polymerise by a condensation reaction (Figure 21.6) with the elimination of water to form nylon-6.

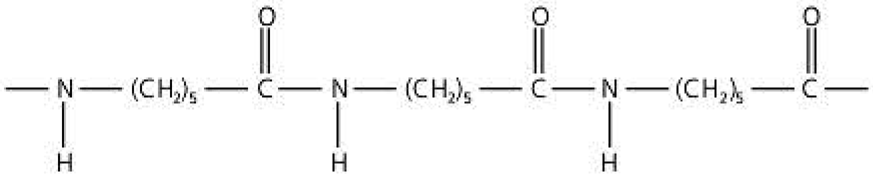


Figure 21.6

Kevlar®

Kevlar® is a relatively new polymer with exceptional strength-to-weight properties. It is used in making 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® (Figure 21.7) are the aryl equivalents of those used for making nylon.

Figure 21.7

Figure 21.8 shows that a similar condensation reaction takes place.

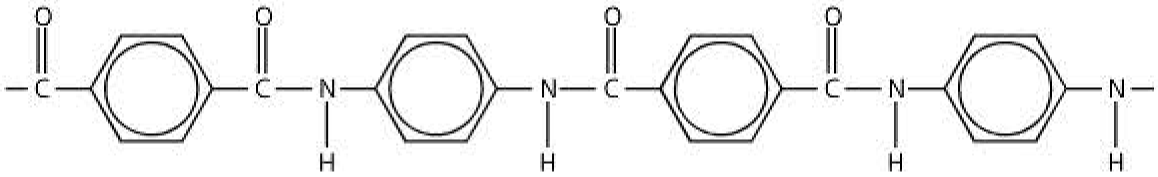


Figure 21.8

One disadvantage of polyamides is that they are hydrolysed by strong acids (although Kevlar® is more resistant).

Now test yourself

1 Describe two main differences between *condensation* polymerisation as described here and *addition* polymerisation as described in Chapter 15.

2 Draw diagrams to show the displayed structures of the links in:

  a a polyamide

  b a polyester

Answers on p.200

Tested ☐

Predicting the type of polymerisation

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.

Example 1

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

a 1,2-dihydroxyethane and 1,4-benzenedicarboxylic acid

b aminoethanoic acid (glycine)

Answer

a 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. So this is condensation polymerisation.

b 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 because the monomer has functional groups at each end, polymerisation can take place. When an amide is formed a condensation reaction takes place and water is eliminated, so this is also 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 — see Figure 21.5

Answer

a In order to tackle these questions you must think about the way the monomers combine. In this case (Figure 21.9) 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, Figure 2.10 shows it is the part indicated between the vertical lines.

→

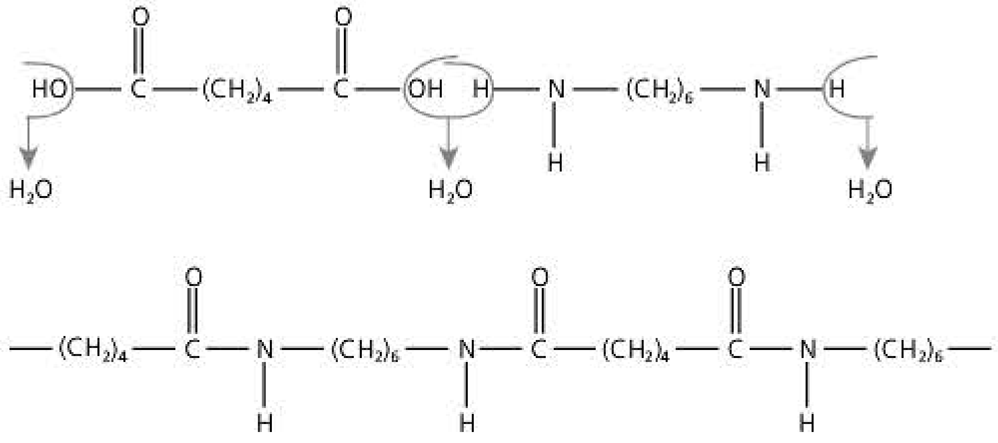


Figure 21.9

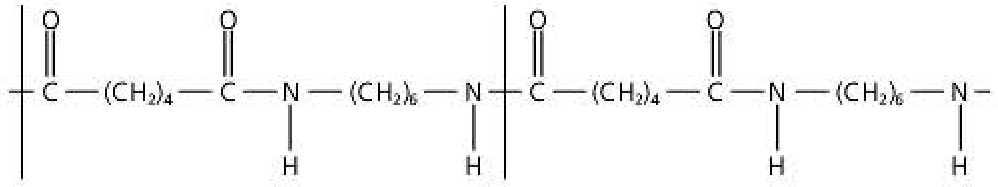


Figure 21.10

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 atom and the nitrogen atom. Figure 21.11 shows the molecule formed.

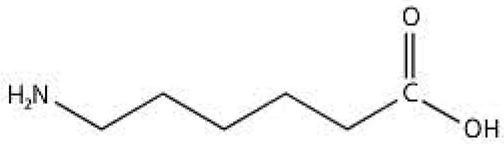


Figure 21.11

These molecules then polymerise. Starting from only one monomer, the repeat unit (Figure 21.12) has to include most of it. The repeat unit is indicated between the vertical lines.

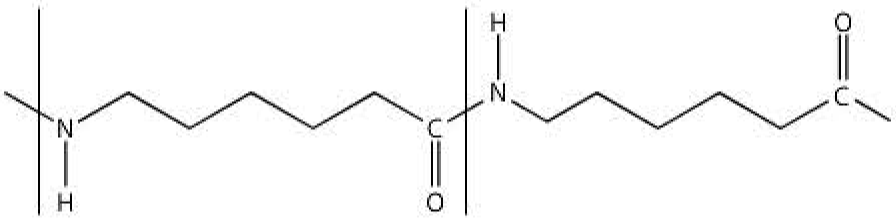


Figure 21.12

Properties of polymers

In this section you need to draw on your knowledge of intermolecular bonding and organic structures to explain how the structure of a polymer can affect its properties. This can include:

- the method of formation of the polymer
- the presence of side chains and the intermolecular bonds that can form between them

Let's first consider three commercial polymers – polyethene, PTFE (Teflon®) and Kevlar®.

Polythene is an addition polymer with forms classified according to the degree of branching and density. The two common forms are:

- LDPE — low-density polyethene (Figure 21.13(a)) has a high degree of branching that prevents the chains from packing together closely and this reduces the density of the bulk polymer. It has relatively weak intermolecular forces of attraction because the instantaneous dipole–induced dipole attraction is weak resulting in a low tensile strength.

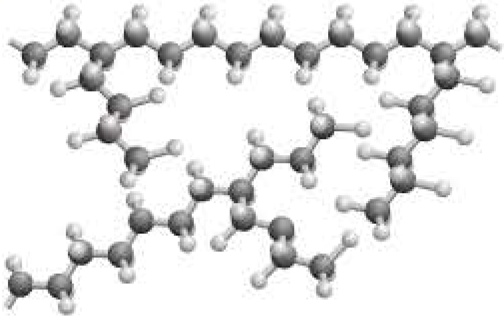


Figure 21.13(a)

- HDPE — high-density polyethene (Figure 21.13(b)) has fewer side branches giving it a higher density because the chains can pack together more closely. This results in stronger van der Waals forces and a higher tensile strength.

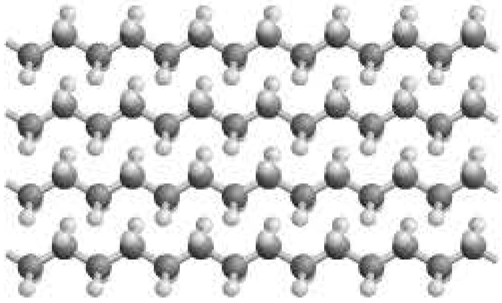


Figure 21.13(b)

All this influences the uses of the two forms — LDPE being used to make, for example, plastic bags and HDPE being used for more rigid uses such as bottles, bins and outdoor furniture.

PTFE or **Teflon**® was developed in the late 1940s having been produced by accident in 1938. The polymer is like polyethene, but all the hydrogen atoms have been replaced by fluorine atoms. The fluorine atoms have three lone pairs of electrons and this means that rotation about the carbon–carbon single bonds is inhibited whereas in polyethene there is free rotation about these bonds. This produces rod-like molecules that are packed together closely giving strong intermolecular forces and increasing the crystallinity of the polymer. The strong C–F bonds make the polymer chemically inert, but the effect of the fluorine atom lone pair electrons effectively means that for small molecules, with a limited 'point of contact', the van der Waals forces are weak: this causes the 'non-stick' property of PTFE.

Kevlar® is a polyamide made from two aromatic monomers (Figure 21.14).

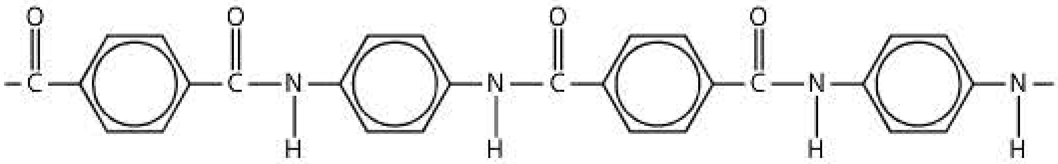


Figure 21.14

Kevlar is extremely strong because of the hydrogen bonds that form between the carbonyl groups and the –NH groups. Further strength is gained as a result of stacking the aromatic rings, which produces interactions between adjacent strands. The polymer can be spun to produce fibres that can be woven to make body armour capable of stopping a knife or a bullet, but it has a wider range of uses from sports equipment to musical instruments and the motor industry.

Now test yourself

3 Describe how the intermolecular forces in polyethene and Kevlar® affect the properties of these polymers.

Answer on p.200

Tested ☐

DNA and proteins

Revised ☐

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

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 a chain by linking sugar (deoxyribose) and phosphate groups to form the backbone of the molecule with bases attached as side chains. You can see this in block diagram form (the only form you will be asked to work with) in Figure 21.15.

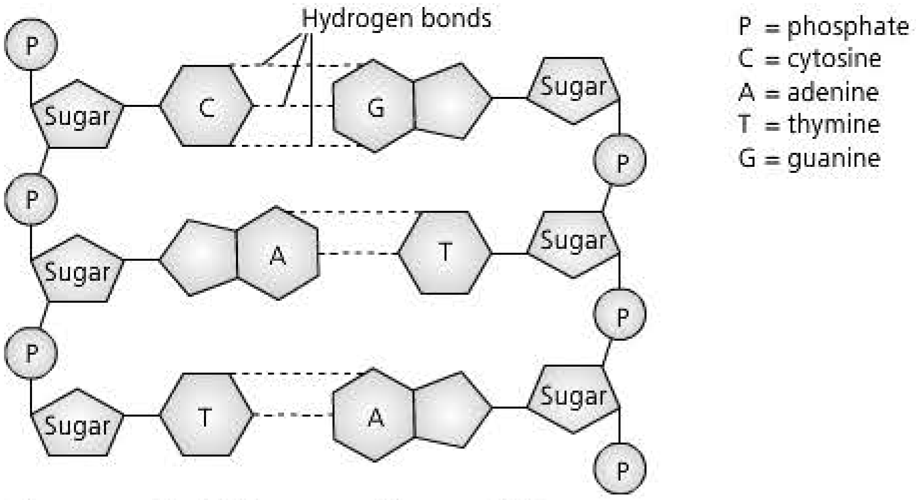


Figure 21.15 Block diagram to illustrate DNA structure

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.

Expert tip

A way to remember the base pairs is **All** **T**hings **C**ome **G**ood.

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

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 that 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 21.16.

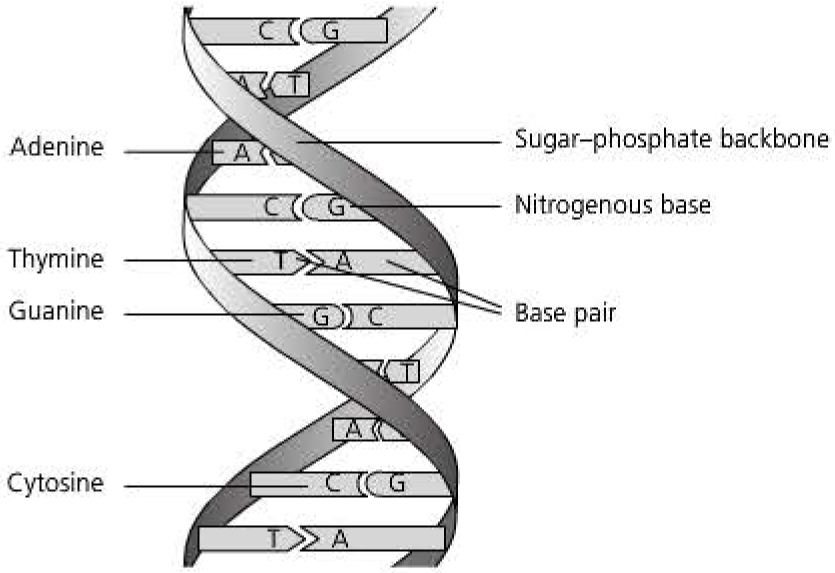


Figure 21.16 The structure of DNA

Now test yourself

4 Suggest a reason why the base pairs in DNA are always A–T and C–G.

Answer on p.201

Tested ☐

You should know that proteins are polymers formed by the condensation of amino acids (Figure 21.17). You also need to remember that there are 20 different biologically active amino acids.

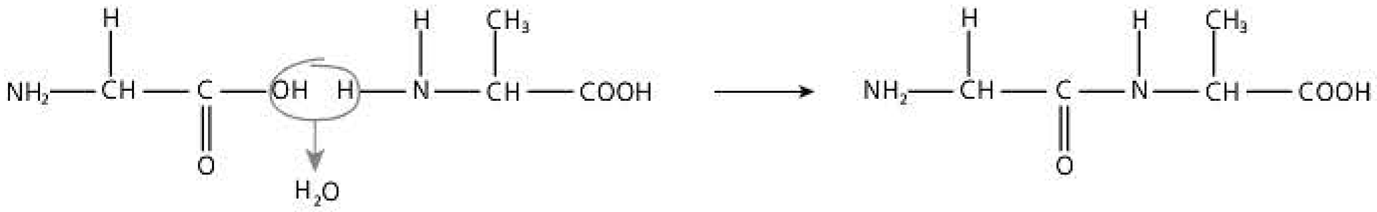


Figure 21.17 Condensation of amino acids

Figure 21.16 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 many, many combinations. How many do you think there are? Think about ABCD, ABDC, ADBC, ACBD... etc.

A sequence of amino acids is called the **primary structure** of a protein. Polypeptides have a 'backbone' that runs the length of the chain. If you look at Figure 21.18 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–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 21.18(a)) and the β-pleated sheet (Figure 21.18(b)).

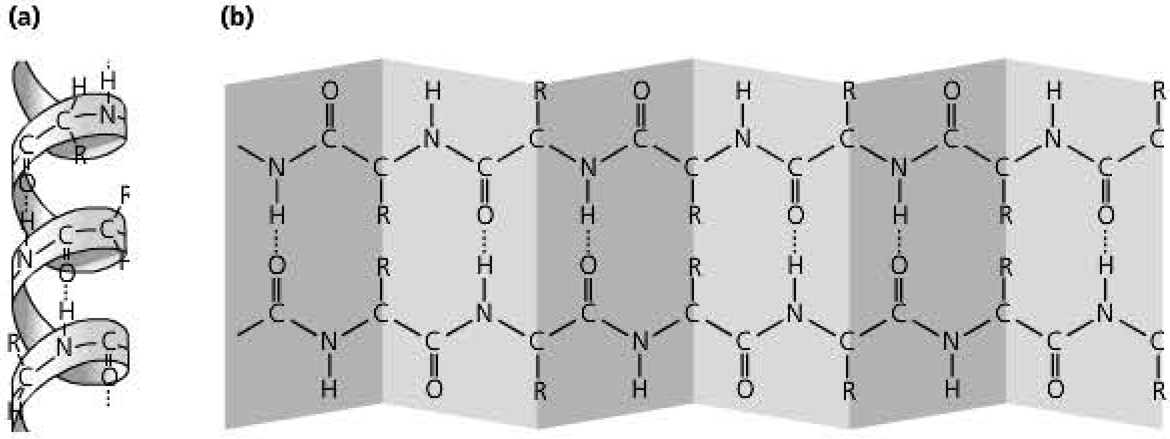


Figure 21.18 Secondary structure of a protein (a) α-helix; (b) β-pleated sheet

The sequence of amino acids in a primary chain 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 21.1.

Table 21.1

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

Now test yourself

5 Study Table 21.1 and suggest which type of bonding is the 'odd one out' and describe why.

Answers on p.201

Tested ☐

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.
- A 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 20).

Polymers by design

Revised ☐

Polymer chemistry has developed enormously because of the need to find substitutes for increasingly expensive (and rare) metals. This has also led to a polymer 'problem-solving' approach to chemistry. Two examples specified in the syllabus are non-solvent based adhesives and conducting polymers.

Non-solvent based adhesives

These include epoxy resins and 'superglues'. Epoxy resins consist of two components that react with each other forming a hard, inert material. One consists of an epoxy resin and the other is the epoxy curing agent, sometimes called the 'hardener'. When mixed together these react to form a strong polymer that contains lots of cross-links, which make it very strong. This type of adhesive is particularly useful because it forms strong bonds to the surfaces it is joining as well as within the resin.

'Superglues' are a more recent development and consist of a single component based on compounds called cyanoacrylates, which are the monomers for the polymerisation reaction. In the presence of moisture, typically from the air, these molecules polymerise rapidly forming long, strong chains. They bond to many surfaces including human skin.

Conducting polymers

The ability to create a polymer that conducts an electric current was a goal from the beginning of the large-scale industrial use of polymers. The possibility of forming such compounds was suggested in the mid-nineteenth century but it wasn't until the 1960s that the first polymer to show appreciable conductivity was developed.

One example of a conducting polymer is polyacetylene. This is formed by polymerising ethyne (acetylene), C_2H_2, molecules. Using catalysts it is possible to make the polymer 'all-*trans*' and conductivity occurs using the extended π bonding.

Degradable polymers

One of the major problems associated with polyalkenes is that they are chemically inert and as a result are very slow to degrade in the environment. As a result, litter made from these polymers is not easily broken down in landfill sites unlike the natural materials that these polymers have replaced. As a result there has been considerable research to try to find alternative polymers that have similar physical properties, but which can be degraded by the action of water.

Based on the hydrolysis reactions that occur in living organisms, research was focused on polymers that contain amide or ester bonds. One of the more promising biodegradable polymers is 'polylactic acid' (PLA). This polyester is formed (Figure 21.19) by the polymerisation of lactic acid (2-hydroxypropanoic acid).

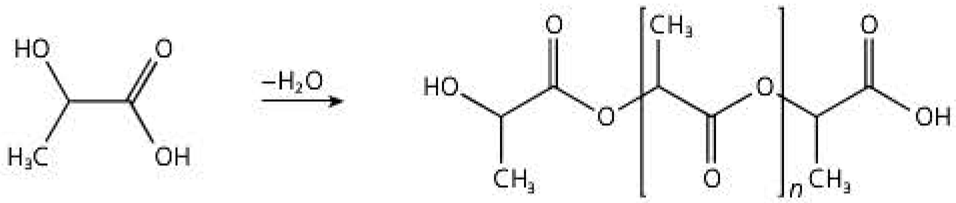


Figure 21.19 Condensation polymerisation of lactic acid

The ester linkages are relatively easily hydrolysed giving the polymer a much shorter life in the environment. This polymer has already been used in a variety of applications such as kitchen film, plastic bags, food packaging and disposable nappies.

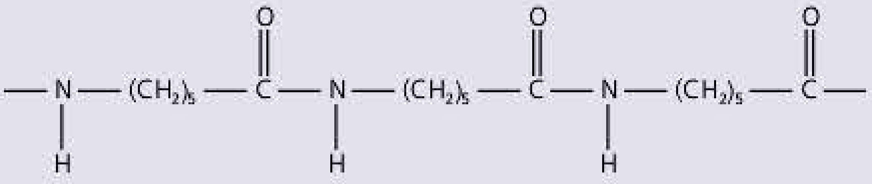
Some common polymers are also degraded by light in the ultraviolet range and this can lead to the failure of materials that use these polymers. The most common examples include polypropene and LDPE, which have tertiary carbon atoms in their chains. Ultraviolet radiation attacks these centres forming free radicals, which then react with oxygen in the atmosphere to form carbonyl groups.

Revision activity

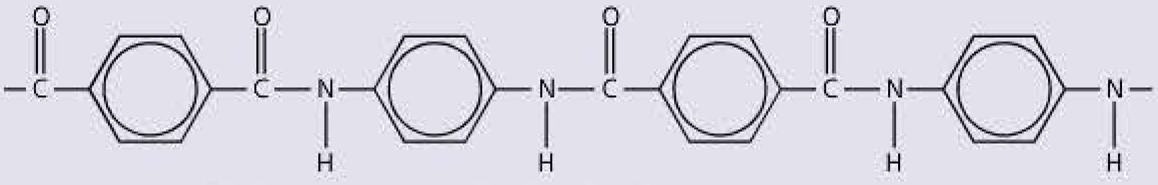
1 Name **two** small molecules that could be eliminated in the formation of a condensation polymer.

2 The two diagrams below show parts of two polymers:

a



b



Deduce what type of polymerisation produced each polymer, explaining your answers.

3 Figure 21.22 shows a length of polymer containing the monomer residue(s). Draw the structures of the original monomer(s).

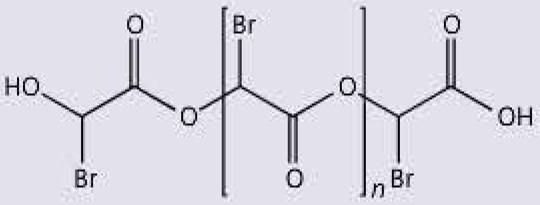


Figure 21.22

4 What form of bonding can exist between condensation polymer strands that does not exist in most addition polymers?

5 Outline briefly the major types of structure that exist in protein molecules.

Answers on p.204

22 Analytical techniques

In this chapter only the section on infrared spectroscopy is needed for AS. The remainder is for A level.

Chromatography

Revised ☐

Chromatography is based on the ability of a solute to dissolve preferentially in one of two solvents. When a solute is shaken with two immiscible solvents, it will dissolve in both. The ratio of the concentrations of the solute in each solvent is called their **partition coefficient**.

The components in a chromatogram can be identified by their separation during the process. 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.

Paper chromatography

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 that are more soluble in the solvent are carried further in a certain time.

The components in a chromatogram can be identified by their **retardation factor**, ***R_f*** (Figure 22.1), which is the ratio of the distance travelled by a particular component compared with the distance travelled by the solvent. Components in a mixture can be identified by running reference samples alongside the mixture or by calculating ***R_f*** values.

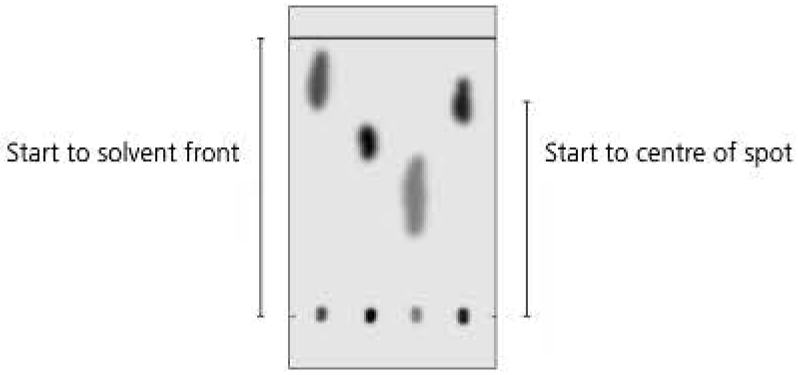


Figure 22.1 Data needed to calculate R_f

A **retardation factor** is the ratio of the distance travelled by a spot to the distance travelled by the solvent.

You are probably familiar with using paper chromatography to separate the dyes in different inks, and have obtained a chromatogram like the one shown in Figure 22.2.

Some mixtures may not give coloured spots. For example, if you try to separate a mixture of amino acids by chromatography the individual amino acids are invisible. To reveal the separation you have to use a 'locating agent', in this case ninhydrin, which turns the spots purple-pink (Figure 22.3).

In Figure 22.3, reference samples of amino acids (1–5) have been run alongside the mixture so there is no need to calculate R_f values.

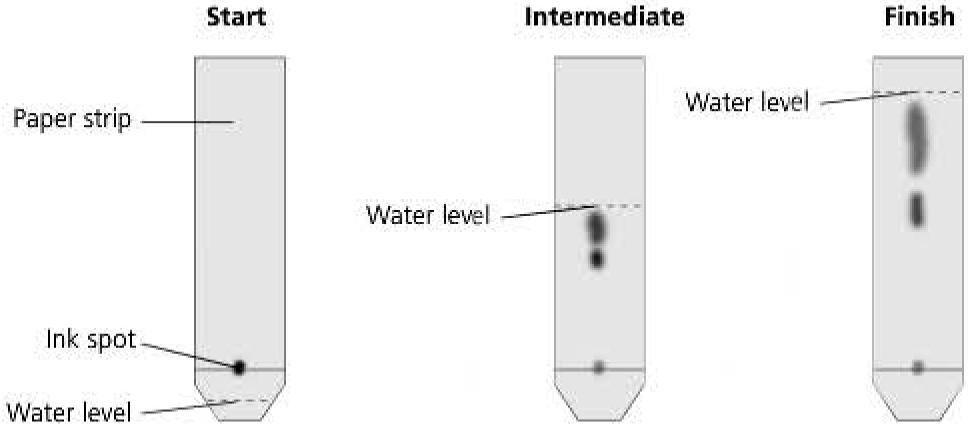


Figure 22.2 Paper chromatography of black ink

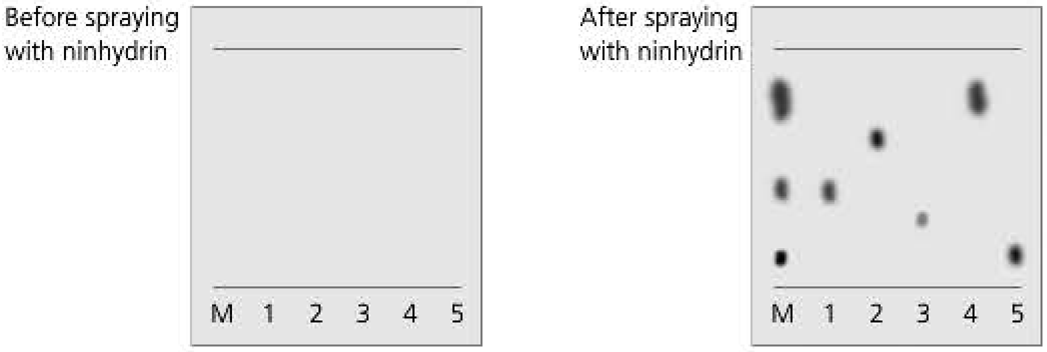


Figure 22.3 Use of a locating agent in paper chromatography

Thin-layer chromatography

This method relies on the adsorption of the solute onto the particles of the thin layer, rather than partitioning between water trapped on the cellulose fibres of the paper and the solvent. Figure 22.4 highlights the differences.

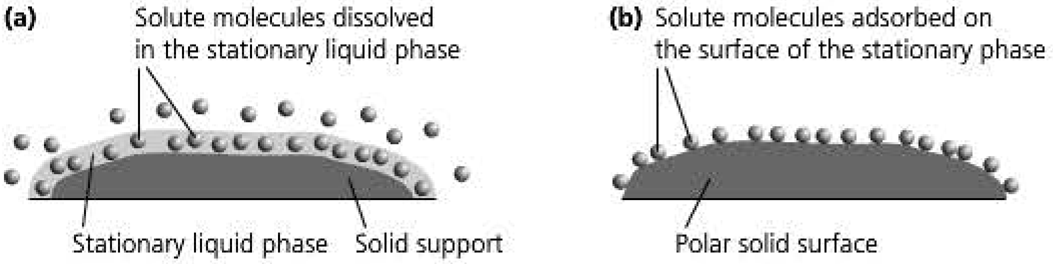


Figure 22.4 Separation by (a) partition; (b) adsorption

Now test yourself

1 What are the differences in the methods of separation between paper chromatography and thin-layer chromatography?

Answer on p.201

Tested ☐

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 that have a 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 at different times and are detected. Sometimes the GLC column is connected to a mass spectrometer (see the next section). 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.

Retention time is the delay between the mixture injected into the column and a given component being detected.

Different components take different times to flow through the columns. Retention times depend on several 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

Retention times are helpful in identifying individual components. By measuring the area under each peak, the proportions of the different components in the sample can be determined (Figure 22.5).

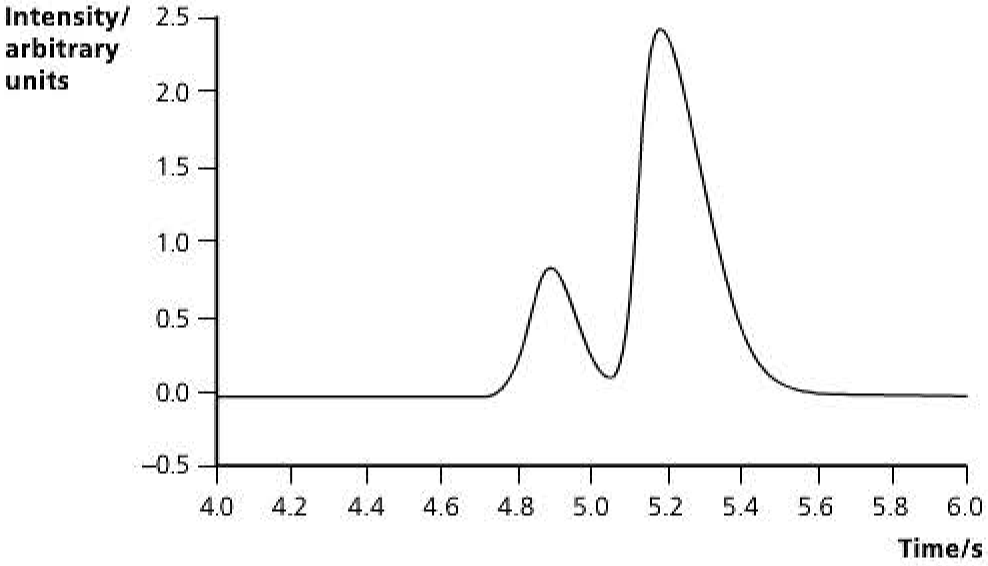


Figure 22.5 Typical GLC output

Now test yourself

2 Using the list of factors that influence retention time above, which are important if the *same* GLC machine is used to compare different samples?

Answer on p.201

Tested ☐

Infrared spectroscopy

Revised ☐

Infrared spectroscopy is useful for detecting bonds and/or functional groups in organic molecules. If you direct a range of infrared frequencies one at a time through a sample of an organic compound, some frequencies are **absorbed** by the compound and some pass through. A detector on the other side of the compound shows that some frequencies pass through the compound with almost no loss, but other frequencies are strongly absorbed. If a particular frequency is absorbed as it passes through the compound being investigated, it means that energy is being transferred to the compound.

Absorptions in infrared spectra are measured at particular wavenumbers. These are 1 cm divided by the wavelength of the energy.

Energies in the infrared region of the spectrum correspond to the energies involved in bond vibrations. These can be bond-stretching or bond-bending vibrations. A typical infrared spectrum is shown in Figure 22.6.

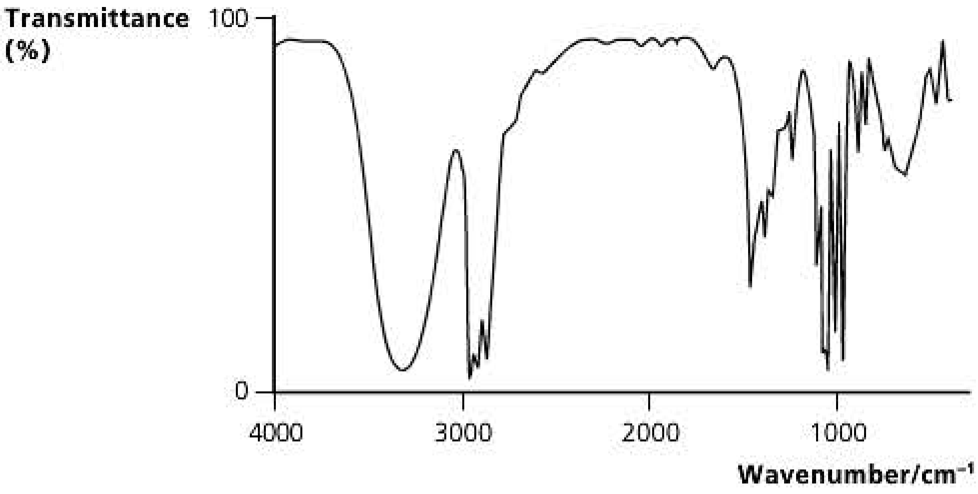


Figure 22.6 The infrared spectrum of propan-1-ol

You need to practise using key absorptions to identify the functional groups present in molecules and deducing the structure of the molecule from its molecular formula. A list of the bonds you need to be able to recognise is given in Table 22.1.

Table 22.1

Bond	Functional groups containing the bond	Absorption range in wavenumbers/cm^{-1}	Appearance of the peak (s = strong, w = weak)
C–O	Alcohols, ethers, esters	1040–1300	s
C=C	Alkenes, arenes	1500–1680	w unless conjugated
C=O	Amides	1640–1690	s
	Carbonyl compounds	1670–1740	s
	Esters	1710–1750	s
C≡C	Alkynes	2150–2250	w unless conjugated
C≡N	Nitriles	2200–2250	w
C–H	Alkanes, CH_2-H	2850–2950	s
	Alkenes and arenes, =C–H	3000–3100	w
N–H	Amines, amides	3300–3500	w
O–H	Carboxylic acids, RCO_2-H	2500–3000	s and very broad
	H-bonded alcohols, RO-H	3200–3600	s
	Free alcohol, RO-H	3580–3650	s and sharp

Now test yourself

Tested ☐

3 If the infrared spectrum of the compound $CH_2=C(CH_3)CO_2H$ was recorded, indicate which bonds would show absorptions in the infrared range, what their appearance would be, and at what wavenumber range you would expect to find them.

Answers on p.201

Mass spectrometry

Revised ☐

The principles on which mass spectrometry is based are simple, and modern mass spectrometers (Figure 22.7) are highly accurate with an accuracy better than 1 part in 100 000.

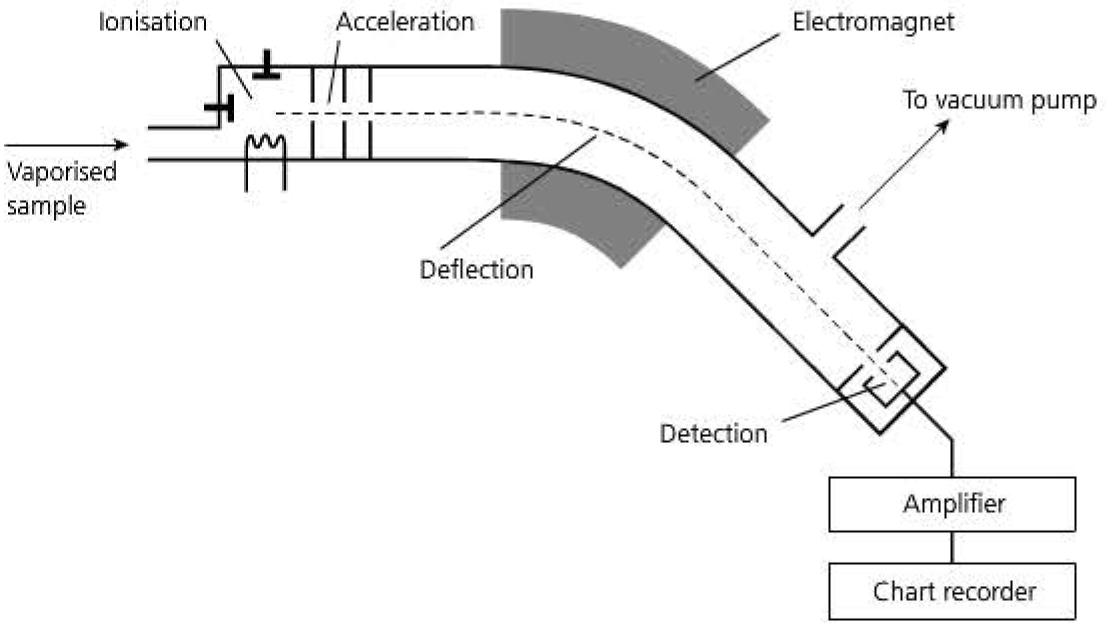


Figure 22.7 A mass spectrometer

In a 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. Lower mass ions are deflected more than those of higher mass.
- The strength of the magnetic field is adjusted to allow the ions to pass through a slit and be detected.

You saw in Chapter 1 how mass spectrometry can be used to determine accurate atomic masses. It can also give useful information about organic molecules. Mass spectrometry can give three different types of information:

- Measurement of the relative heights of the ion corresponding to the molecular mass and the one higher than the molecular mass (*M* and *M*+1) peaks allows us to determine the number of carbon atoms in a molecule. Similar 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 a mass spectrometer may allow the piecing together of the structure of the parent molecule.

Using 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. You 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:

$$n = \frac{100 \times A_{M+1}}{1.1 \times A_M} \qquad n = 100$$

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.

Now test yourself

4 In the mass spectrum of an organic compound the M:M+1 peak height ratio was 8.0:0.43. Calculate the number of carbon atoms in the molecule.

Answer on p.201

Tested ☐

Using the M and M+2 peaks

The halogens chlorine and bromine occur naturally as mixtures of two predominant isotopes. This is shown in Table 22.2.

Table 22.2

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 then it indicates the presence of a bromine atom. If more than one atom of the halogen is present there would also be an *M*+4 peak and you would be able to determine which halogen atoms are present from the ratios.

Using accurate molecular masses

With high-resolution mass spectrometers you can measure the mass to charge (*m*/*e*) ratios to five significant figures (at least 1 part in 100 000). This means that it is not only possible to measure the M_r of a compound accurately, 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-3-en-2-one, C_4H_6O	$CH_2=CHCOCH_3$

Using *accurate* relative atomic masses for hydrogen, carbon and oxygen (H = 1.0078, C = 12.000, O = 15.995) you 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 positive ions 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 22.8 were obtained from propan-1-ol and propan-2-ol.

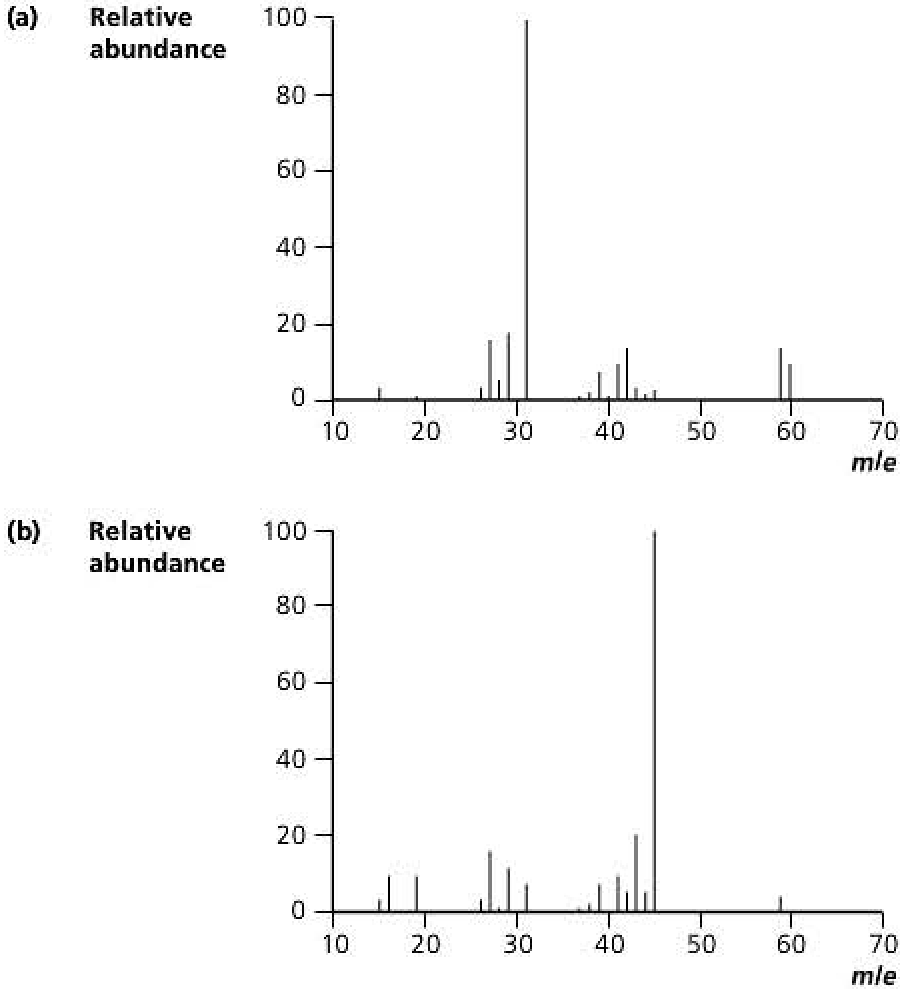
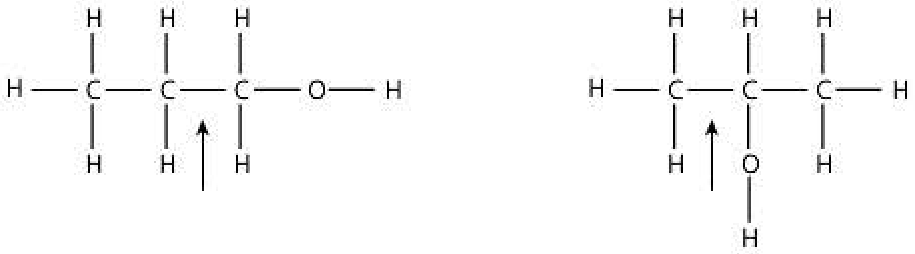


Figure 22.8 Mass spectra of (a) propan-1-ol; (b) propan-2-ol

These mass spectra have different fragmentations. In propan-1-ol the highest 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? Figure 22.9 shows the two isomers.



Propan-1-ol

Propan-2-ol

Figure 22.9

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 22.8. You do not need to be able to explain *why* particular fragments form, just to be able to identify *what* their formulae might be.

Proton (^1H) NMR spectroscopy

Revised ☐

The nucleus of a hydrogen atom spins about an axis. Because 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 22.10 upper).

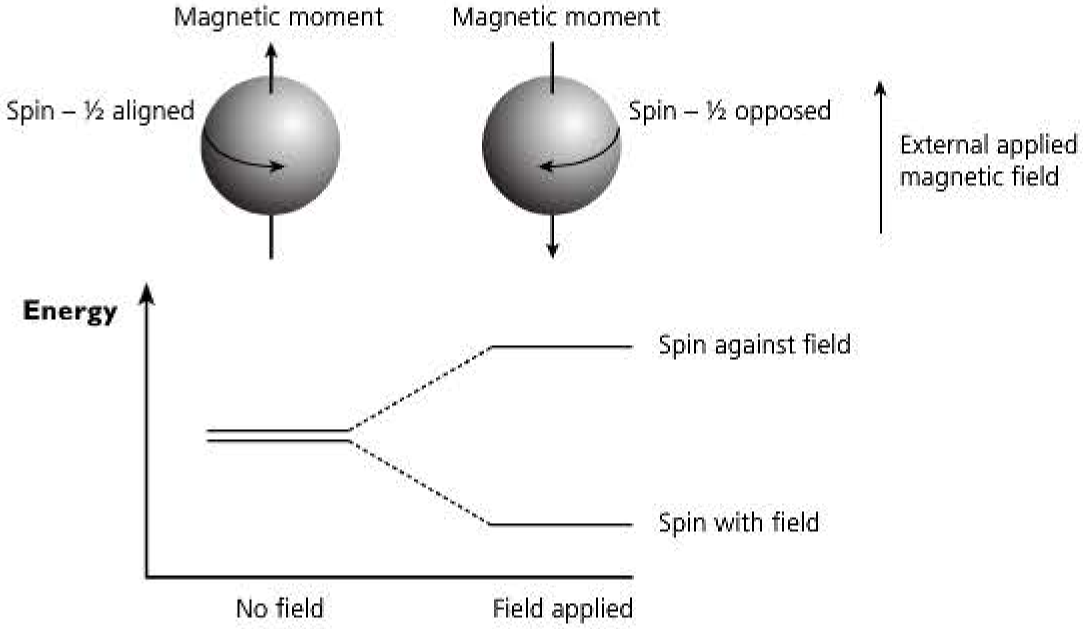


Figure 22.10 Magnetic moments

Another possible state exists where the magnetic moments are aligned against the applied field, but this requires extra energy (Figure 22.10 lower).

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.

Now test yourself

5 What is the effect on the position of the peak produced by a given proton of an electronegative atom?

Answer on p.201

Tested ☐

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. The solvent generally chosen is $CDCl_3$ because it contains no hydrogens. A small amount of tetramethylsilane (TMS) is added to give a zero point.

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 three protons in different environments (Figure 22.11).

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 is to the *left* in an NMR spectrum. The scale, known as chemical shift, and given the symbol δ, is measured in parts per million. A peak at a chemical shift of, say, 3.0 means that the carbon atoms that caused that peak need a magnetic field 3 millionths less than the field needed by TMS to produce resonance. 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 highest area, because it is produced by three protons in an identical chemical environment.

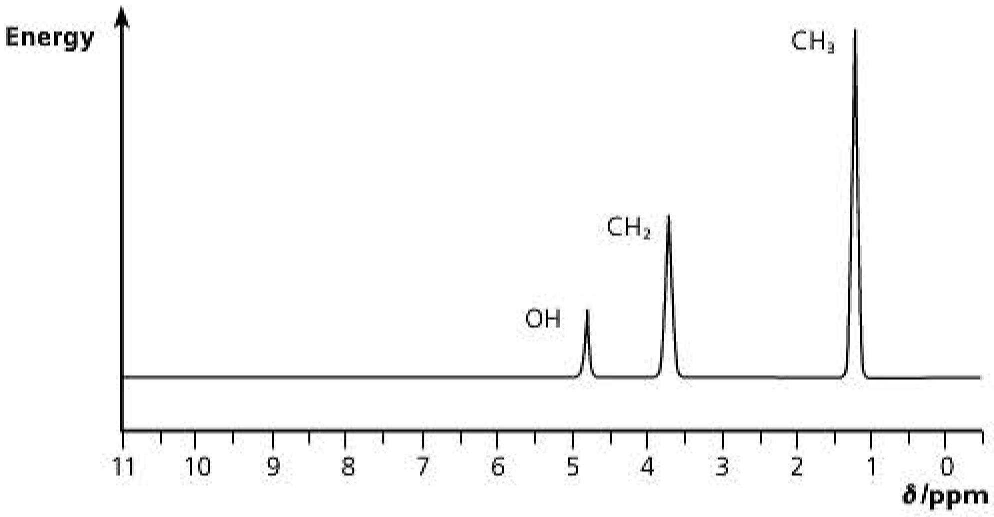


Figure 22.11 Low-resolution NMR spectrum of ethanol

The spectrum for ethanol at high resolution (Figure 22.12) 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**.

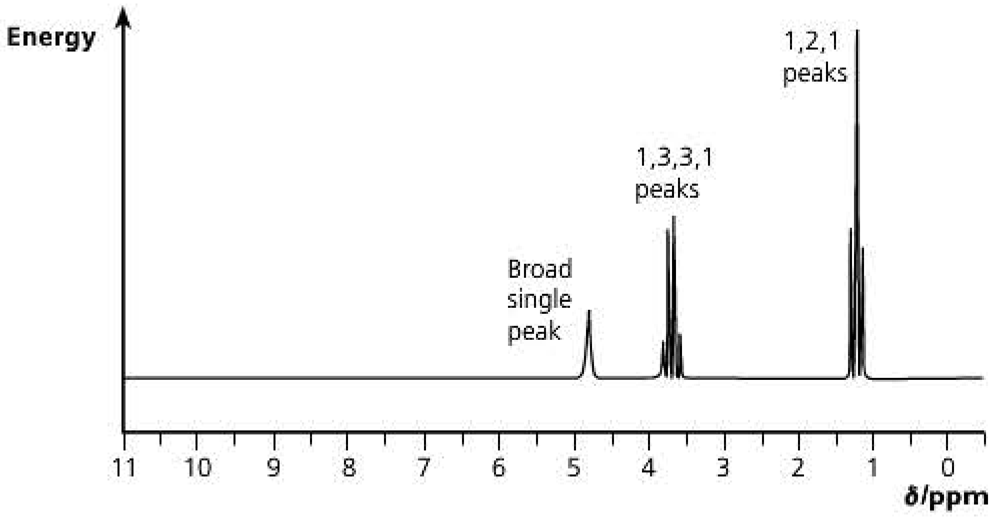


Figure 22.12 High-resolution NMR spectrum of ethanol

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 group absorption being split into three peaks in the ratio shown in Figure 22.13.

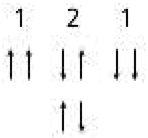


Figure 22.13

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.

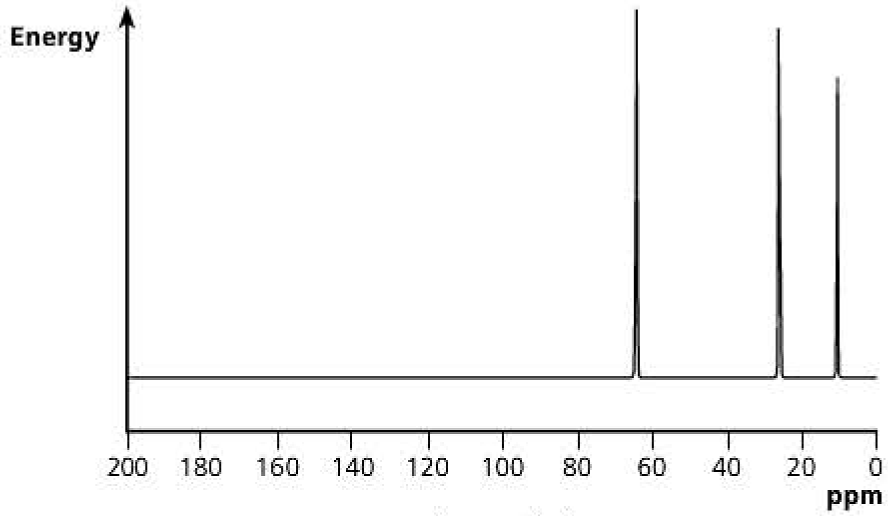
Table 22.3 shows possible splitting patterns produced by protons adjacent to the one being considered.

Table 22.3

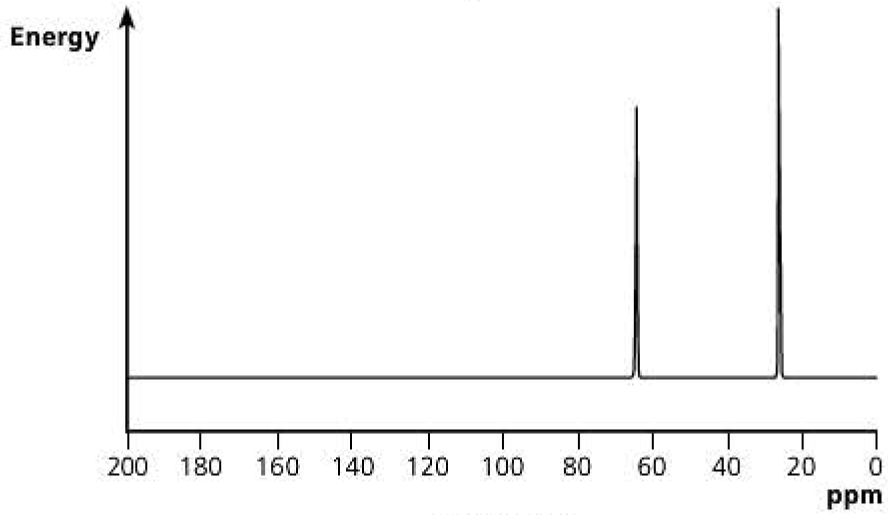
Number of protons adjacent to given proton	Number of lines in multiplet	Relative intensities of lines
1	2	1 : 1
2	3	1 : 2 : 1
3	4	1 : 3 : 3 : 1
4	5	1 : 4 : 6 : 4 : 1

Carbon-13 NMR spectroscopy

The basis for carbon-13 NMR spectroscopy is the same as that for proton NMR spectroscopy — the nucleus of ^{13}C can behave like a tiny magnet (see above). The position of the absorption depends on the electronegativity of the atom attached to a given carbon. The major difference in appearance between ^{13}C and ^{1}H NMR spectra is that the absorptions in a ^{13}C spectrum appear as single lines with no splitting. The spectra shown in Figure 22.14 are those of propan-1-ol and propan-2-ol.



Propan-1-ol



Propan-2-ol

Figure 22.14

Notice that in the spectrum of propan-2-ol there are only two lines because two of the carbon atoms are in identical environments.

As with ^{1}H NMR, TMS is used to give a zero point because it has four carbon atoms in the same environment producing a single strong peak. $CDCl_3$ is used as a solvent — you might think that this would give a confusing peak due to the carbon atom present, but because it is such a large peak (being the solvent) and its absorption is known, it is easily excluded.

Expert tip

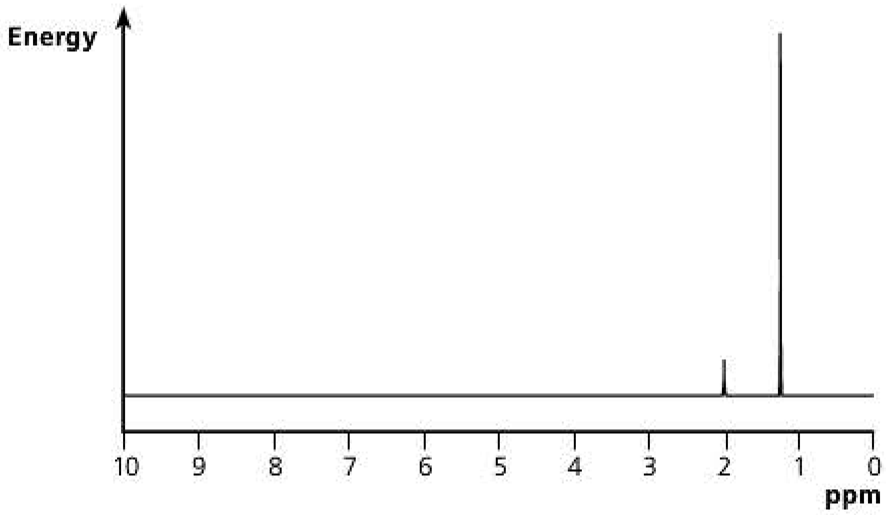
You may be asked to focus on one of these analytical techniques or you may be given data from two or more techniques. Make sure you know which technique gives you what information about a compound.

Now test yourself

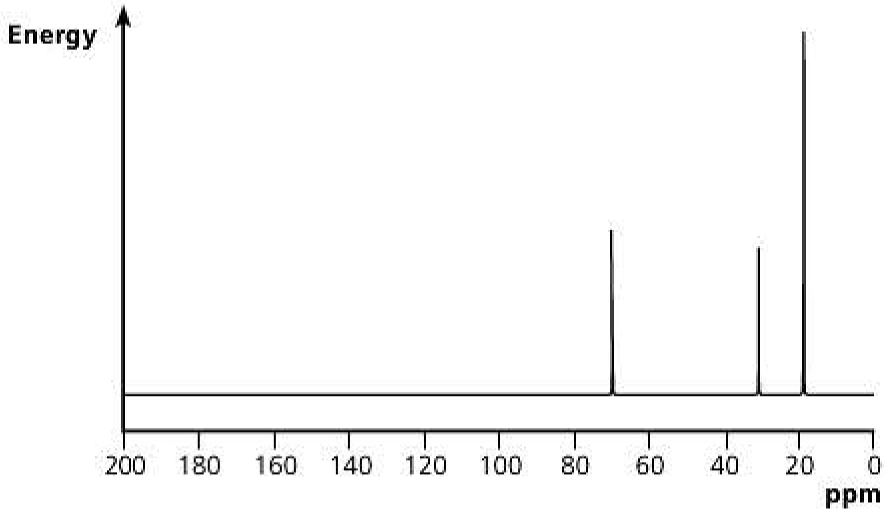
Tested ☐

6 Four isomeric alcohols have the molecular formula $C_4H_{10}O$.

a Draw the structure of the alcohol that produced the ^1H NMR spectrum shown below, explaining your reasoning.



b Draw the structure of the alcohol that produced the ^{13}C NMR spectrum below, explaining your reasoning.



c Draw the structure of the other two isomeric alcohols.

Answers on p.201

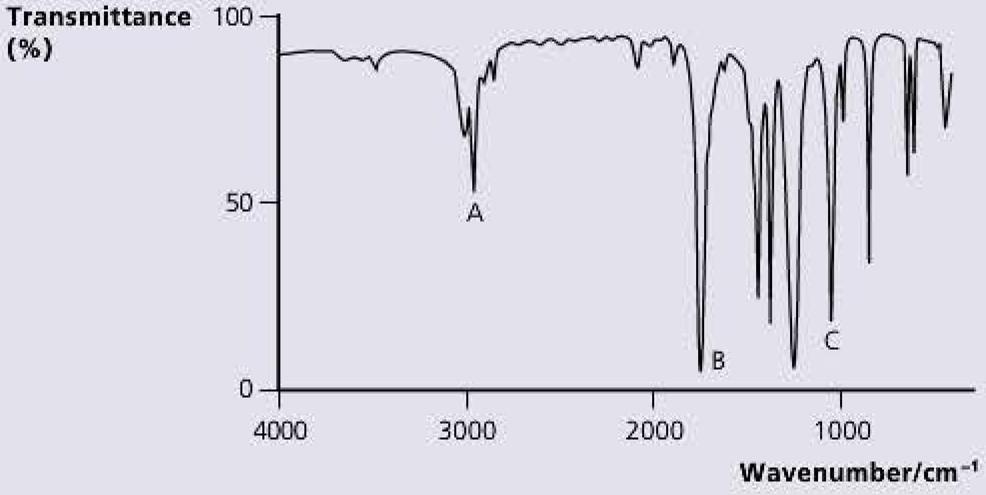
Revision activity

Parts 1, 2 and 3 are for AS and the remainder is for A level.

1 What part of a molecule is responsible for the absorption of infrared energy?

2 Why can two different molecules have very similar infrared spectra?

3 The infrared spectrum of a compound R is shown here:



  a What functional groups are likely to be responsible for the peaks labelled A, B and C?

  b Compound R contains three carbon atoms and has a formula mass of 74. Write a molecular formula for R.

  c Draw a structural formula for R.

4 What is the difference between 'partition' (used in paper chromatography and GLC) and 'adsorption' used in thin-layer chromatography?

5 Suggest the identity of the major fragments and their *m*/*e* values in the mass spectrum of propanone.

6 Using ethanol as an example, indicate the differences between the carbon-13 NMR spectra and the proton NMR spectra of the molecule.

7 In a proton NMR spectrum, what types of protons have their absorptions disappear on the addition of a small amount of D_2O?

Answers on pp.204–5

23 Organic synthesis

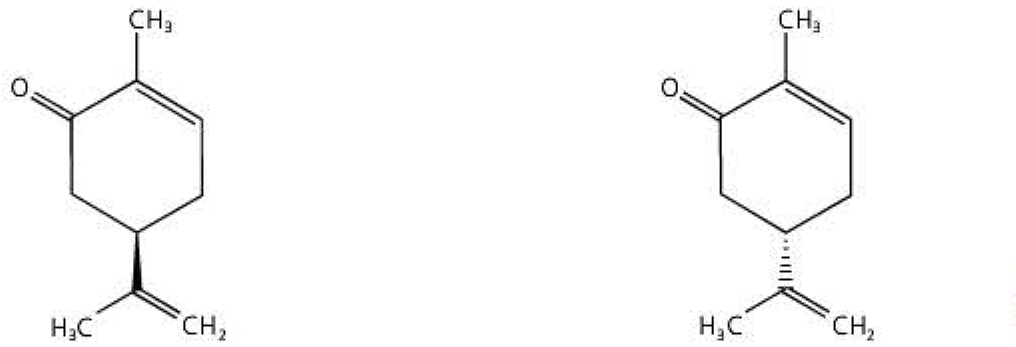
This chapter is needed for A level.

Synthesis of chiral drug molecules

Revised ☐

Drugs have been extracted from plants and other natural sources for hundreds, perhaps thousands, of years. Most of these drugs are active as one optical isomer when chiral carbons are present, which is common in living organisms. There are many examples of different optical isomers having different effects on living organisms.

A simple example is the compound called carvone, which contains a single chiral carbon. The two forms have different effects on the olfactory system giving them different tastes and smells. The R-form smells of spearmint while the S-form smells of caraway.



(R)-(−)-carvone from spearmint oil

(R)-(+)-carvone from caraway seed oil

Figure 23.1 The two optical isomers of carvone

Expert tip

Different conventions are used for optical isomers — depending on the textbook you use, you will come across pairs of optical isomers referred as D/L, +/− or R/S. You do not need to worry about which convention you use — all are acceptable.

The reason for the different smells of the two optical isomers is that the olfactory receptors in the body also have chiral centres that allow them to react more strongly to one form than the other.

Table 23.1 shows the percentage of the different carvone isomers in some natural sources.

Table 23.1

Source	R-carvone/%	S-carvone/%
Spearmint	60–75	0
Caraway	0	50–80
Dill	0	40–60
Gingergrass	20–30	20–30

This shows that, with the exception of gingergrass, which produces both isomers, plants produce carvone in one particular isomeric form.

In the 1950s scientists were looking for a drug to alleviate 'morning sickness' in pregnant women. The drug produced was called 'thalidomide', and it was also a mild sleeping tablet.

Unfortunately, soon after it was launched some babies were born with limb malformation. Laboratory tests that were carried out on animals showed that while the S-isomer caused some birth defects, the R-isomer was an effective sedative. The problem was that even if only the S-isomer was taken by the patient, the molecule could lose the hydrogen on the chiral carbon, allowing both isomers to form in the body.

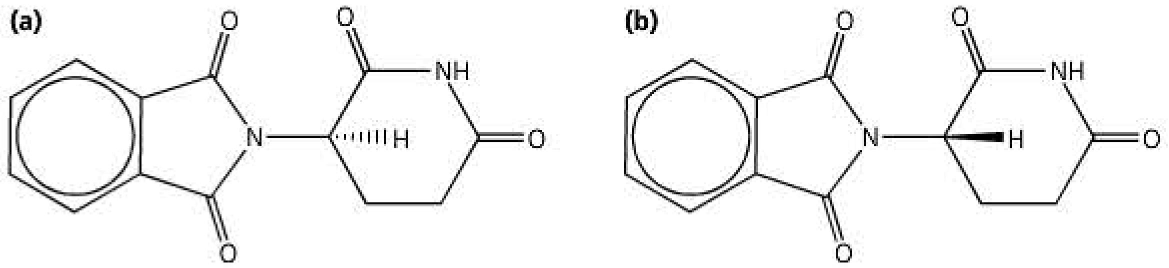


Figure 23.2 Thalidomide isomers

It is likely that the effective isomer fitted a particular enzyme's active site well, while the other interfered with a different active site or possibly with the replication of DNA. It is often the case that one particular optical isomer has bigger therapeutic activity or fewer side effects than the other.

Synthetic routes

Revised ☐

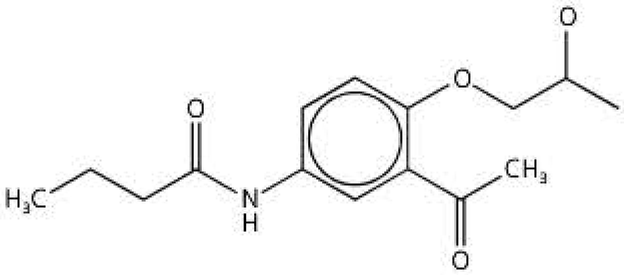
This part of the syllabus draws on the total of your chemical knowledge and consists of three parts:

- For an organic molecule with several functional groups:
  - identify the functional groups using reactions you have come across
  - predict the properties and reactions of the compound.
- Work out a multi-stage synthetic route to prepare a given organic molecule based on reactions you have come across.
- Analyse a given synthetic route in terms of the type of reaction and reagents used for each step and identify possible by-products.

Perhaps the best way to revise this is to look at an example.

Example

Study compound X:



a Identify the functional groups it contains — with the exception of the –O– group.

b Predict how X would react with:

i 2,4-dinitrophenylhydrazine

ii acidified potassium manganate(VII) solution

iii alkaline aqueous iodine solution

Answers

a amide; 2-alcohol/hydroxyl; ketone

b i It would form a yellow-orange precipitate of the 2,4-dinitrophenylhydrazone.

ii The 2-alcohol group would be oxidised to a ketone decolorising the manganate(VII) solution.

iii A yellow precipitate would form as the $CH_3CH(OH)$– group reacts.

Revision activity

1 Butan-2-ol contains a chiral carbon. Draw three-dimensional representations of the two optical isomers of this compound.

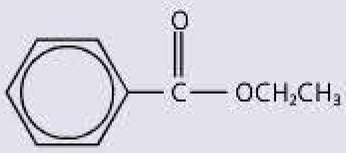
2 Study the structure of the drug molecule *Ultiva*™ shown below. How many chiral carbons does it contain, if any?

3 An unknown organic compound **Y** gives the following reactions.

Reagent	Observation
Sodium metal	No reaction
Acidified potassium manganate(VII)	Solution is decolorised
2,4-dinitrophenylhydrazine	Yellow-orange precipitate formed
Tollens' reagent	Silver mirror formed

Suggest what functional group(s) Y contains.

4 Compound Z is produced naturally in a number of plants. It can also be produced synthetically. It is used in fragrances and in foods and beverages.



Outline a route showing essential reagents and conditions to synthesise compound Z starting from methylbenzene.

Answers on p.205

Experimental skills and investigations

This section is needed for both AS and A level. The AS practical component Paper 3, and the A level practical component Paper 5 are covered separately.

Paper 3: AS practical paper

Revised ☐

Skills tested on this paper are:

- manipulation of apparatus
- presentation of data
- analysis and evaluation

Almost one-quarter of the total marks for AS are for experimental skills and investigations. These are assessed on Paper 3, which is a practical exercise 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 Table 1.

Table 1

Skill	Minimum mark allocation*	Breakdown of skills	Minimum mark allocation*
Manipulation, measurement and observation, MMO	12 marks	Successfully collecting data and observations	8 marks
		Quality of measurements or observations	2 marks
		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 exercise consists of two or three questions. One question is based on 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(s) are quantitative — in other words, involve measurement. 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

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.

A measurement is considered **accurate** if it is judged to be close to the true value.

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 accurate as the *least* accurate measurement.

It is important to understand the difference between accuracy and **precision**. The diagrams in Figure 1 may help.

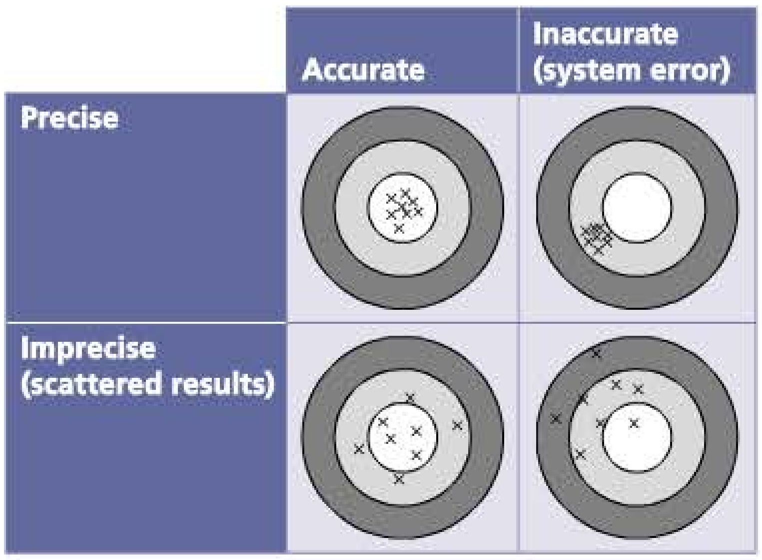


Figure 1

Precision denotes the closeness of agreement between, or consistency of, values obtained by repeated measurements.

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 (Figure 2).

A common mistake is in calculating the average burette reading in a titration. This cannot have a higher degree of accuracy than the burette can produce. So, the average burette reading has to end in '.00 cm^3 or '.05 cm^3'. Anything else is wrong and will be penalised.

Expert 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.

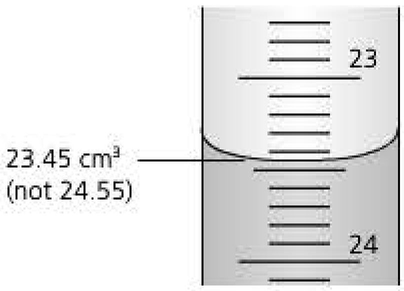


Figure 2

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.

Expert 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.

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.

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.

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.

Expert tip

Examples of students making errors include:

- adding excess reagent when told to add a few drops *followed by* an excess — this often means that an observation carrying marks is missed
- adding reagents in the wrong sequence — this can mean that changes to 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 missed observations

Presentation of data and observations

It is important that, having carried out a practical task, your 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.

Expert 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

Figure 3 shows how to draw a 'line-of-best-fit'. The line is drawn (using a ruler) so that all the points are roughly equidistant from the line, with equal numbers of points on each side.

Expert 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.

Expert 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.

Expert tip

Stir the mixture continuously with a 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.

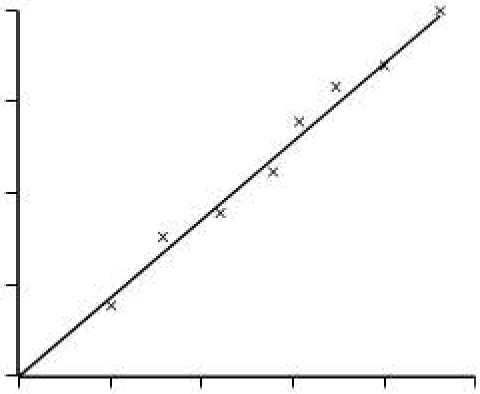


Figure 3

Figure 4 shows what is meant by an 'outlier' — a result which, for some reason, is clearly not part of the data set you want to use.

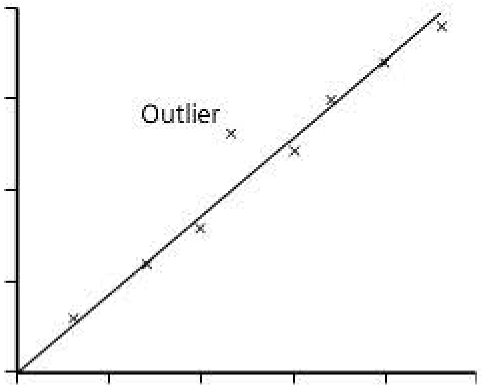


Figure 4

When an experiment generates 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.

Expert tip

The words you use must be clear to an examiner as well as to yourself.

- **Do not use words such as 'see-through' or 'transparent' when you mean 'colourless'. 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 the colour changes such as those that take place when aqueous ammonia is progressively added to a solution containing copper(II) ions.**
- **If a gas is given off, remember that the observation is that 'bubbles are produced' or 'effervescence takes place' — not just 'carbon dioxide is evolved', for example. 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

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 an 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. If there are several inconsistent results then the experiment should be repeated.

You may be asked to draw a graph to display the results because this is an excellent way of showing trends or relationships. A straight-line graph passing through the origin shows a directly proportional relationship between the dependent variable and the independent variable. Sometimes a 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 gradients because this gives a more accurate calculation. Remember that a graph is supposed to provide 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 of doing 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 making a number of readings and averaging them.
- **Systematic errors** affect all the 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. 170.

Expert tip

When you evaluate an experiment you should be able to:

- 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: A level assessment

Revised ☐

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 exercise, but it tests the practical skills you should have developed during your course. Table 2 shows the breakdown of marks.

Table 2

Skill	Minimum mark allocation*	Breakdown of skills	Minimum mark allocation*
Planning	12 marks	Defining the problem	4 marks
		Methods	8 marks
Analysis, conclusions and evaluation	12 marks	Dealing with data	6 marks
		Evaluation	4 marks
		Conclusion	2 marks

* The remaining 6 marks are allocated across the skills in the table and their distribution can vary from paper to paper.

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 exercise consists of two or more questions. One of these will ask you to design an experimental investigation into 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 variable and the dependent variable, or in the form of a graph showing the expected outcome.

There may be questions that contain some experimental data and 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.

Planning

Planning can be a difficult practical skill to master. It relies 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.

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.

Quantitative exercises

You should be able to identify the independent variable and the dependent variable 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 will need processing in some way to enable analysis and evaluation (see later). This also means some discussion of how this processing is to be carried out and this also must go into the plan.

Any recording, graphical and numerical processes to be used should be stated. The steps by which both the experimental procedure and the analysed data will be evaluated should be included.

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, instead relying on an 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 a 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 used 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 an examiner to follow.

Evaluation

This is one of the harder skills to develop because 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 on 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 or excluding an outlier in drawing a line-of-best-fit is shown in Figure 5.

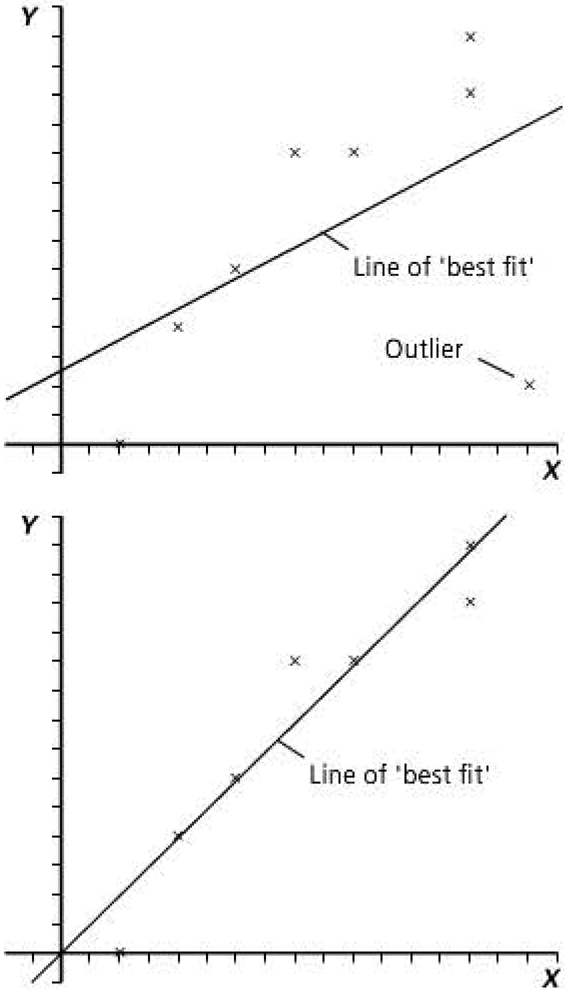


Figure 5 The effects of an outlier

Expert 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.

Expert tip

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
- 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 question the use of a burette to measure different volumes of a liquid. If you use it to measure out 5 cm^3, the error in measurement will be five times bigger than if you use it to measure 25 cm^3.

Expert 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 outweigh the apparatus errors then it is important to identify the flaws in the procedure that 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.

If the errors in the data do not outweigh those due to the apparatus used, you need to suggest how to minimise 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 and answers

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

You have 1 hour and 15 minutes to complete the AS paper. There is a total of 60 marks, so you can spend just over one minute per mark.

You have 2 hours for the A level paper. There are 100 marks, so again you can spend just over one minute per mark. The A level 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 more difficult one(s).

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

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

Some 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 about it carefully, and recall 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 score 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 many marks because they don't read 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 typical examiner's comments. You might like to try answering the questions yourself 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 14 elements are given below.

Element	C	Si	Ge	Sn	Pb
1st IE/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 one mole of atoms ✗ of an element into one 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.*

Candidate A

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

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

Candidate A

c X is in Group 2 of the Periodic Table. ✓

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

Candidate A

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. ✓

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

Candidate B

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

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

Candidate B

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

The equation is correct, as are the state symbols.

Candidate B

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 ✓.

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

Candidate B

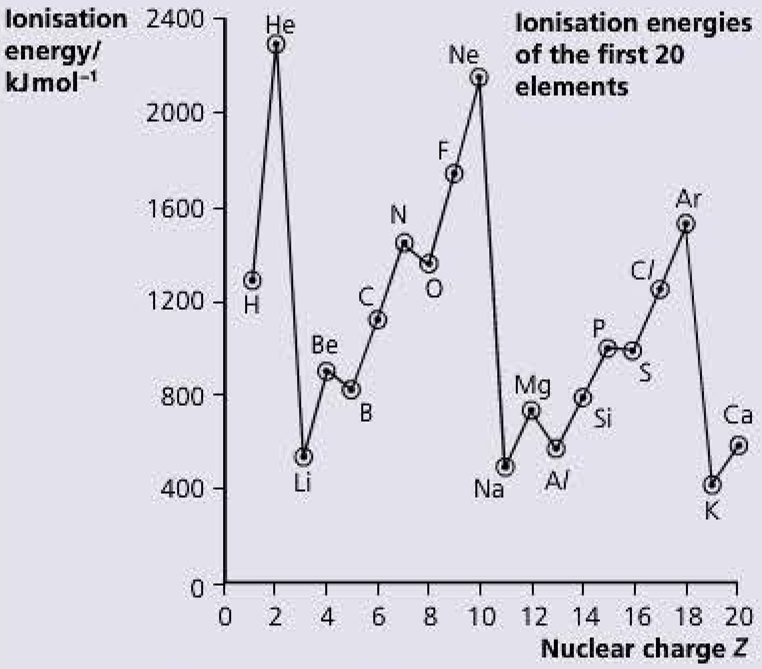
d There are two effects here. First, the atoms are getting bigger so the electrons are further from the nucleus making them easier to remove. ✓ Second, the outer electrons are screened from the nuclear charge reducing its pull on them. ✓

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.



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 Al) 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 gas (Group 18) elements. Suggest why.** **(1 mark)**

(Total: 11 marks)

Candidate A

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

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.

Candidate A

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

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.

Candidate A

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

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.

Candidate A

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

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

Candidate A

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

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.

Candidate A

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

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

Candidate B

a As you 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 ✓.

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

Candidate B

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 ✓.

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.

Candidate B

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 ✓.

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

Candidate B

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

This is correct, no further explanation is needed.

Candidate B

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

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.

Candidate B

e These elements had not been discovered when Mendeleev wrote his table ✓.

This is correct.

Question 3

Ethanol is considered to be 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, $\Delta H_f^{\ominus}$.

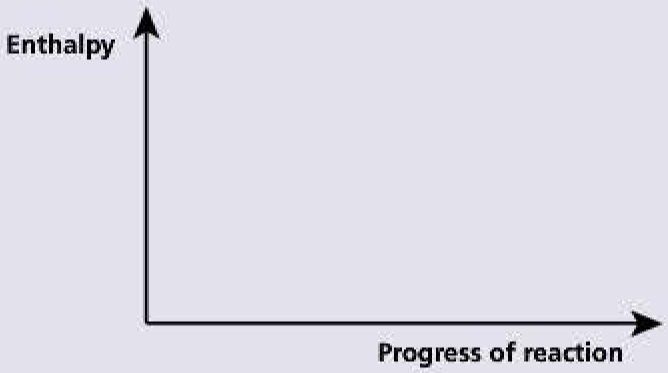
$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \qquad \Delta H^{\ominus} = -1367\,\text{kJ mol}^{-1}$$

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 Copy the axes provided and 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 on the percentage conversion of increasing the pressure. **(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 mole of substance ✓ is formed from its elements. ✓

This definition is not quite complete. The candidate has omitted to mention that it has to be under standard conditions.

Candidate A

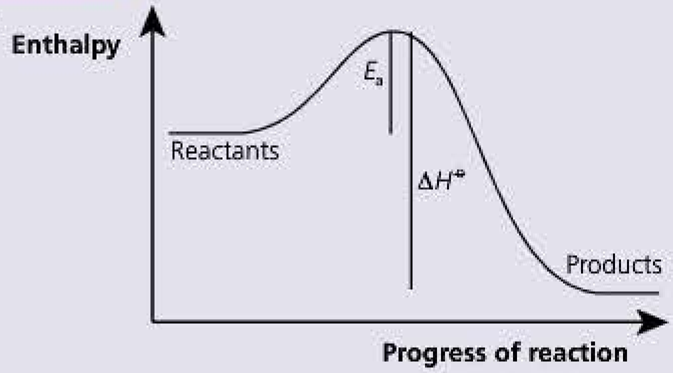
ii To calculate this, I need to reverse the equation and then add the equations for the formation of CO_2 and H_2O. ✗

$+1367 - 394 - 286 = 687\ \text{kJ mol}^{-1}$ ✓ ✓ (ecf)

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.

Candidate A

iii



Shape ✓, E_a ✓, $\Delta H^\ominus$ ✗

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

Candidate A

b i Higher pressure means better conversion. ✓

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

Candidate A

ii It is an exothermic reaction.

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 every examination many candidates lose marks by not reading the question, or by giving an answer to a slightly different question.

Candidate A

iii It pushes the equilibrium to the right. ✓

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 mole of substance ✓ is formed from its elements ✓ under standard conditions. ✓

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

Candidate B

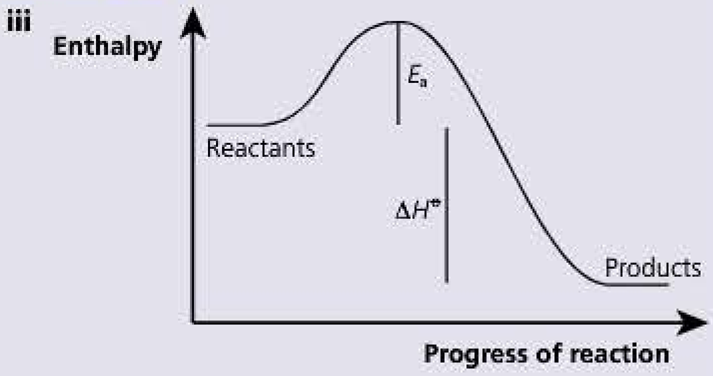
ii Reverse the equation for the formation of ethanol, then add $2 \times \Delta H_f^\ominus$ for CO_2 and $3 \times \Delta H_f^\ominus$ for H_2O ✓.

$+1367 - (2 \times 394) - (3 \times 286) = -279\ \text{kJ mol}^{-1}$ ✓✓

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

Candidate B

iii



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

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 $\Delta H^{\ominus}$.

Candidate B

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. ✗

The first statement here is true, but the second 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.

Candidate B

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. ✓

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.

Candidate B

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

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

Question 4

Group 7 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		
HC*l*	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.

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 write in order to answer the question.

Candidate A

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

This good answer is complete and to the point.

Candidate A

ii HC*l* no effect, HBr some decomposition, HI lots of decomposition. ✓

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

Candidate A

c −1 in Cl^- ✓ and +5 in ClO_3^- ✓

In this correct answer, the candidate does not just state an 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. ✓

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

Candidate B

b i As you 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. ✓

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

Candidate B

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

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

Candidate B

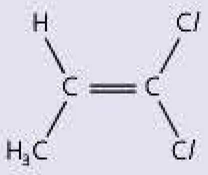
c 1 in Cl^- ✗ and +5 in ClO_3^- ✓

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

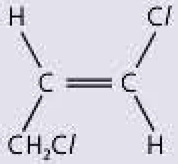
Question 5

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)**

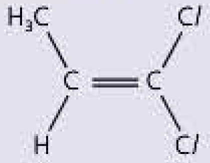
b i Which, if any, of the structural isomers, including isomers 1 and 2 and those that you have drawn, are *cis–trans* isomers? **(1 mark)**

ii Draw the two possible products you could get if the *cis*-isomer was reacted with HBr. **(2 marks)**

(Total: 7 marks)

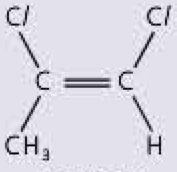
Candidate A

a i



✗

Isomer 3



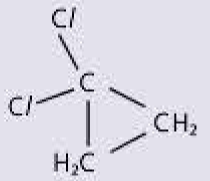
✓

Isomer 4

Isomer 3 is the same as isomer 1, but rotated 180° around the double bond.

Candidate A

ii



✓

This is correct. The candidate did well to spot that this has to be a cyclic compound if it isn't an alkene.

Candidate A

iii Two ✗

This candidate is not sure about isomers of compounds that contain a double bond. The candidate has also not been logical because both isomers 3 and 4 contain a methyl group, as does isomer 1.

Candidate A

b i 3 and 4 ✗

The candidate again shows confusion about cis–trans isomerism. For this to exist, the atoms or groups have to be at opposite ends of a double bond.

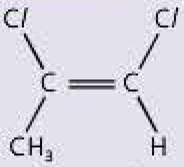
Candidate A

ii $CH_3CClBr–CH_2Cl$ ✓ and $CH_3CHCl–CHClBr$ ✓

Apparently the candidate does know what cis- means. These are good answers, but would have been clearer if the formulae had been displayed.

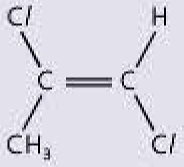
Candidate B

a i



✓

Isomer 3



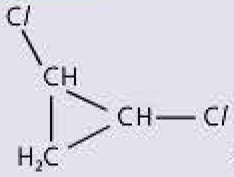
✓

Isomer 4

Both isomers are correct.

Candidate B

ii



✓

This is a different cyclic isomer from that given by Candidate A, but is still correct.

Candidate B

iii Three ✓

This leads from a sound understanding of isomerism and the correct answer in (a)(i).

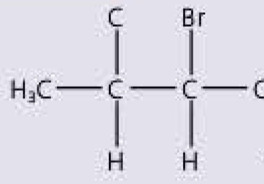
Candidate B

b i 4 and 5 ✓

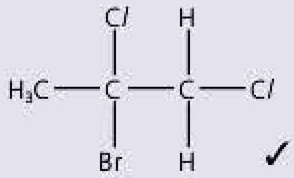
Good! This is once more made simple after a correct answer to (a)(i). This candidate's answers illustrate how a good grasp of the basic principles can lead to much better marks.

Candidate B

ii



✓ and

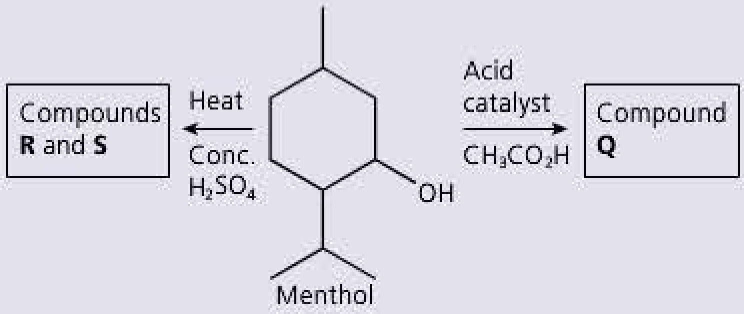


✓

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.



a i The structure of menthol is shown in skeletal form. What is its molecular formula? **(1 mark)**

ii Is menthol a primary, a secondary or a 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 $C_{10}H_{17}O$ ✗

The candidate seems to have assumed that the cyclohexane ring is a benzene ring and has miscalculated the number of hydrogen atoms.

Candidate A

ii Secondary ✓

This is correct.

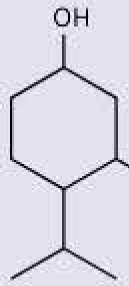
Candidate A

b i Making an ester ✓

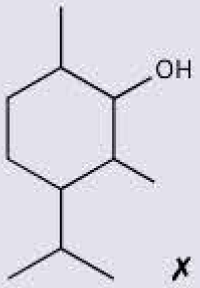
Good, the candidate recognises that the reaction is between an organic acid and an alcohol.

Candidate A

ii



✗



✗

There is confusion here. The candidate seems to think that the –OH group is not removed but can migrate to different ring positions.

Candidate A

iii The bromine would turn colourless. ✓

This is not a perfect answer, but it is close enough to earn the mark.

Candidate A

c i Heat ✓ with potassium manganate(VII) ✗

The candidate uses the correct substance, but to earn both marks acidified aqueous manganate(VII) should be specified.

Candidate A

ii The purple solution would turn pink ✗

This is not sufficiently accurate. The correct answer is 'very pale pink' or 'colourless'.

Candidate B

a i $C_{10}H_{20}O$ ✓

This is correct.

Candidate B

ii Secondary ✓

This is correct.

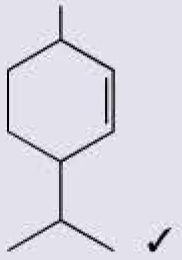
Candidate B

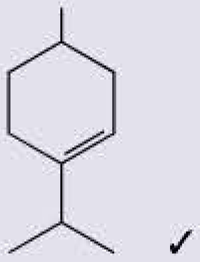
b i Esterification ✓

Good, this candidate recognises that the reaction is between an organic acid and an alcohol to form an ester.

Candidate B

ii





This is a 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.

Candidate B

iii The orange colour of the bromine would disappear. ✓

This is a full and correct answer. Compare it with that of Candidate A.

Candidate B

c i Heat with acidified ✓ potassium dichromate(VI) solution. ✓

Both the correct reagent and conditions are given, for 2 marks.

Candidate B

ii The dichromate solution would be decolorised. ✗

To earn the mark, the initial colour and the change should be given. The orange dichromate solution is not decolorised — it turns green.

A level 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° 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° 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)

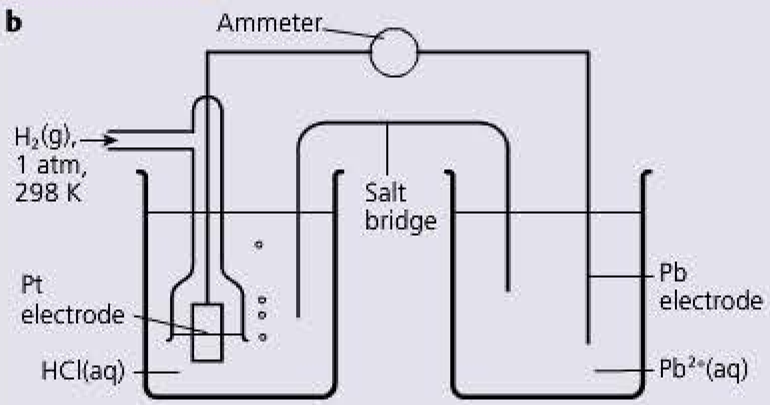
Candidate A

a The standard electrode potential is the potential of the electrode measured under standard conditions ✓ using molar solutions. ✓

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.

Candidate A

b



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.

Candidate A

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 signs show that the elements are oxidising agents. ✓ The larger the value of $E^\ominus$ the stronger the oxidising agent ✓.

This is a well-reasoned answer.

Candidate A

d i The two half-equations are:

$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$ $E^\ominus = -0.17\,V$

$Br_2 + 2e^- \rightarrow 2Br^-$ $E^\ominus = +1.07\,V$

To work out the equation I need to add these:

$SO_2 + 2H_2O + Br_2 \rightarrow SO_4^{2-} + 4H^+ + 2Br^-$ ✓

$E^\ominus_{cell} = -0.17 + 1.07 = +0.90\,V$ ✓

This is a good, well-laid-out and easy-to-follow answer.

Candidate A

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)

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.

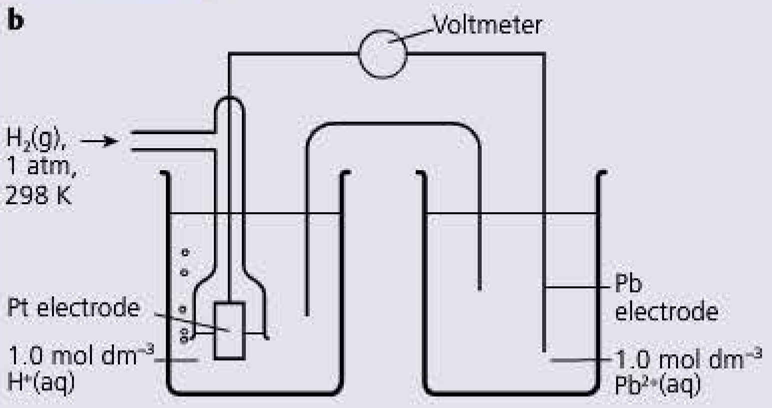
Candidate B

a The standard electrode potential is the potential of the electrode measured under standard conditions ✓ against a standard hydrogen electrode. ✓

This definition is almost correct, but does not mention that the solutions need to be 1 mol dm^{-3}. 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.

Candidate B

b



This is a nice clear diagram with just one mistake — the salt bridge is not labelled.

Candidate B

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. ✓

This is a well-reasoned answer that uses slightly more precise language than Candidate A used.

Candidate B

d i The two half-equations are:

$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$ $E^\ominus = -0.17\,V$

$Br_2 + 2e^- \rightarrow 2Br^-$ $E^\ominus = +1.07\,V$

Because the electrons balance, to work out the equation I need to just add the half-equations:

$SO_2 + 2H_2O + Br_2 \rightarrow SO_4^{2-} + 4H^+ + 2Br^-$ ✓

$E^\ominus_{cell} = -0.17 + 1.07 = +0.90\,V$ ✓

This is a good answer that is well laid out and easy to follow.

Candidate B

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.

$2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$

$5H_2O_2 \rightarrow 5O_2 + 10H^+ + 10e^-$

$2MnO_4^- + 16H^+ + 5H_2O_2 \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$

$E^\ominus_{cell} = 1.52 - 0.68 = +0.84\,V$ ✓

This is very good. The answers are 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, halide ions absorb a photon each and release an electron. This electron then reduces the silver ion to metallic silver:

$$\mathrm{Br^- + h\nu \rightarrow Br + e^-}$$

$$\mathrm{Ag^+ + e^- \rightarrow Ag}$$

a **Predict whether more energy or less energy is needed for this process for $\mathrm{AgC}l$ than AgBr. Explain your answer.** **(1 mark)**

b **Write a chemical equation to represent the lattice energy of $\mathrm{AgC}l$.** **(1 mark)**

c **Using the following data, calculate the lattice energy of $\mathrm{AgC}l\mathrm{(s)}$.** **(3 marks)**

First ionisation energy of silver	+731 $\mathrm{kJ\,mol^{-1}}$
Electron affinity of chlorine	–349 $\mathrm{kJ\,mol^{-1}}$
Enthalpy change of atomisation of silver	+285 $\mathrm{kJ\,mol^{-1}}$
Enthalpy change of atomisation of chlorine	+121 $\mathrm{kJ\,mol^{-1}}$
Enthalpy change of formation of $\mathrm{AgC}l\mathrm{(s)}$	–127 $\mathrm{kJ\,mol^{-1}}$

d **How might the lattice energy of AgBr(s) compare with that of $\mathrm{AgC}l\mathrm{(s)}$? 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 $1.3 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$.**

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 $\mathrm{C}l^-$ to $\mathrm{C}l$. ✓

The logic here is fine, even if it is not precise.

Candidate A

b $\mathrm{Ag^+(g) + C}l^-\mathrm{(g) \rightarrow AgCl(s)}$ ✓

Although the AgCl is ionic, charges do not have to be shown because it is a solid.

Candidate A

c To find the lattice energy use a Born–Haber cycle:

$+285 + 121 + 731 + 349$ ✗ $+ \Delta H^{\circ}_{L} = -127$

$\Delta H^{\circ}_{LE} = -127 - 285 - 121 - 731 - 349$ ✓

$= -1613\,\mathrm{kJ\,mol^{-1}}$ ✓ (ecf)

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.

Candidate A

d The value of the lattice energy of AgBr differs from that of $\mathrm{AgC}l$ because of two factors — the enthalpy change of atomisation and the 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. ✓

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.

Candidate A

e **i** $K_{sp} = [\mathrm{Ag^+(aq)}][\mathrm{C}l^-\mathrm{(aq)}]$ ✓

This is correct.

Candidate A

ii $K_{sp}(\mathrm{AgC}l) = (1.3 \times 10^{-5}) \times (1.3 \times 10^{-5})$
$= 1.69 \times 10^{-10}\,\mathrm{mol\,dm^{-3}}$ ✓ ✗

The calculation is correct but the units are wrong.

Candidate A

f $\mathrm{Ag^+C}l^- + 2\mathrm{NH_3} \rightleftharpoons [\mathrm{Ag(NH_3)_2}]^+ + \mathrm{C}l^-$ ✓

This is correct.

Candidate B

a Bromine forms $\mathrm{Br^-}$ less easily than chlorine forms $\mathrm{C}l^-$, so the reverse reaction should be easier. ✓

This is correct.

Candidate B

b $\mathrm{Ag^+(g) + C}l^-\mathrm{(g) \rightarrow Ag^+(s)C}l^-\mathrm{(s)}$ ✗

This is incorrect. It is the AgCl that is a solid, not the individual ions.

Candidate B

c To find the lattice energy I need to use a Born–Haber cycle.

$EA(Ag) + EA(Cl) + 1st\ IE(Ag) + EA(Cl) + LE(AgCl)$
$= \Delta H_f(AgCl)$

$+285 + 121 + 731 - 349 + LE(AgCl) = -127$

$\Delta H^{\ominus}_{LE} = -127 - 285 - 121 - 731 + 349$
$= -915\ kJ\ mol^{-1}$ ✓ ✓ ✓

This is completely correct. The answer is well laid out and easy for an examiner to follow.

Candidate B

d When you consider AgBr rather than AgCl, three values in the Born–Haber cycle change — EA(Cl), EA(Cl) and $\Delta H_f(AgCl)$. 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. ✓ ✓

This very good complete answer scores both marks.

Candidate B

e i $K_{sp} = [Ag^+]\,[Cl^-]$ ✓

This is correct.

Candidate B

ii $K_{sp}(AgCl) = (1.3 \times 10^{-5}) \times (1.3 \times 10^{-5})$
$= 1.69 \times 10^{-10}\ mol^2\ dm^{-6}$ ✓ ✓

Both the calculation and the units are correct.

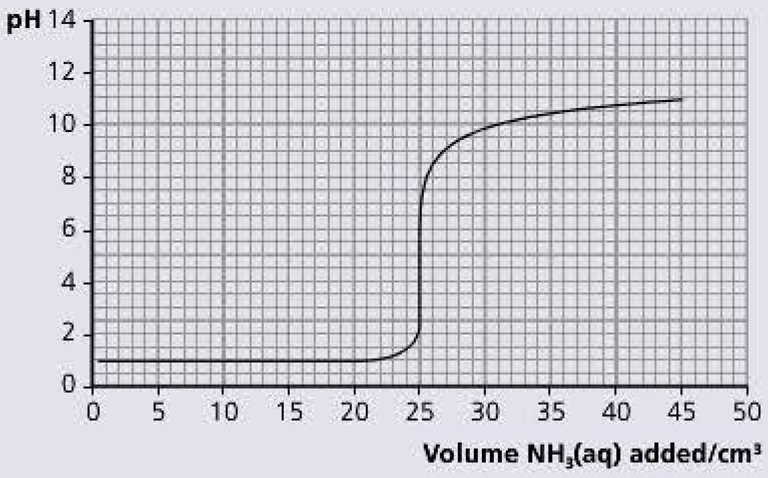
Candidate B

f $Ag^+Cl^- + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + Cl^-$ ✓

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 here.



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)**

iv The pH ranges of four indicators are given in the table. Explain which of these indicators would be most suitable to use for this titration. **(1 mark)**

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

b A buffer solution was made by mixing 50 cm^3 of 0.100 $mol\ dm^{-3}$ sodium ethanoate solution with 50 cm^3 of 0.100 $mol\ dm^{-3}$ ethanoic acid solution. K_a for ethanoic acid is $1.8 \times 10^{-5}\ mol\ dm^{-3}$. 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 H_3O^+ ions **(1 mark)**

ii OH^- ions **(1 mark)**

(Total: 8 marks)

Candidate A

a i pH 5 ✓

This is correct.

Candidate A

ii The curve ends below pH 14. ✓

Although this is true, it does not provide evidence that ammonia is a weak base.

Candidate A

iii 1.0 mol dm^{-3} ✗

This is incorrect. If pH = 1, then [H$^+$] = 1 × 10^{-1} = 0.1 mol dm^{-3}.

Candidate A

iv Methyl red, because it changes colour during the vertical portion of the curve. ✓

This is a good answer.

Candidate A

b $\text{pH} = -\log(1.8 \times 10^{-5}) + \log\frac{0.100}{0.100}$ ✗

$= -\log(1.8 \times 10^{-5}) + \log 1$

$= -\log(1.8 \times 10^{-5})$

$= 4.7$ ✓

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.

Candidate A

c i On adding H_3O^+ ions these will combine with $CH_3CO_2^-$ ions shifting the equilibrium to the left. ✓

This is a good answer.

Candidate A

ii On adding OH^- ions, these will react with H_3O^+ ions shifting the equilibrium to the right. ✓

Another good answer.

Candidate B

a i pH 5 ✓

This is correct.

Candidate B

ii The curve does not reach pH 14. It flattens out around pH 11.5. ✓

This is a correct statement based on the data from the titration curve.

Candidate B

iii Because the starting pH is 1, −log[H$^+$] = 1 and hence the concentration of the acid must be 1 × 10^{-1} = 0.1 mol dm^{-3} ✓

This is correct and well explained.

Candidate B

iv Methyl red because the mid-point of its pH range is close to the mid-point of the vertical portion of the curve. ✓

This is another correct and well-explained answer.

Candidate B

b $\text{pH} = -\log(1.8 \times 10^{-5}) + \log\frac{0.05}{0.05}$

$= -\log(1.8 \times 10^{-5}) + \log 1$

$= -\log(1.8 \times 10^{-5})$

$= 4.7$ ✓ ✓

Both the calculation and the units are correct.

Candidate B

c i When H_3O^+ ions are added, they will combine with $CH_3CO_2^-$ ions, shifting the equilibrium to the left. ✓

This is a good answer.

Candidate B

ii When OH^- ions are added they will react with H_3O^+, shifting the equilibrium to the right. ✓

This is another good answer.

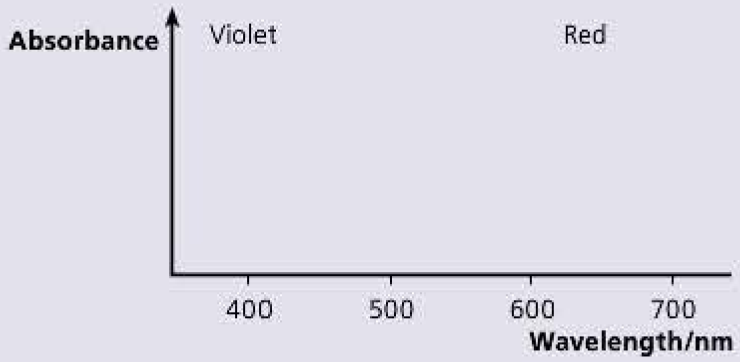
Question 4

The metals in Group 2 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. ✗

The first two properties are chemical in nature, but the third is physical.

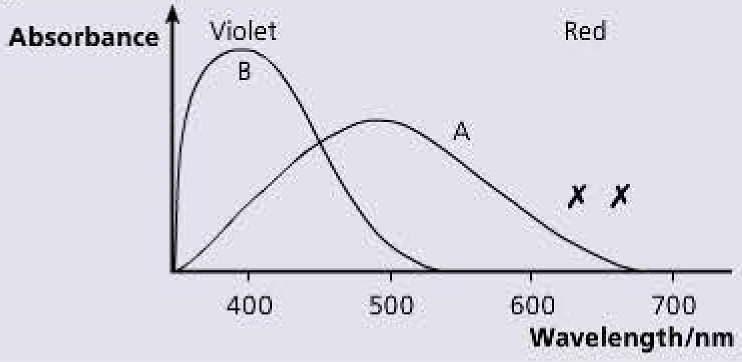
Candidate A

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)

The candidate points out correctly that colour in transition metal compounds is a result of the d-orbitals splitting into two groups of different energies. 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.

Candidate A

c



The candidate has drawn two emission spectra rather than absorption spectra.

Candidate A

d $3d_{x^2-y^2}$ and $3d_{z^2}$ ✓

This is correct.

Candidate A

e **i** $2MnO_4^- + 3SO_2 + 2H_2O \rightarrow 2MnO_2 + 3SO_4^{2-} + 4H^+$ ✗ ✓ (ecf)

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'.

Candidate A

ii The manganese is all precipitated as MnO_2. ✗

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. ✓

Three correct differences in chemical properties are given.

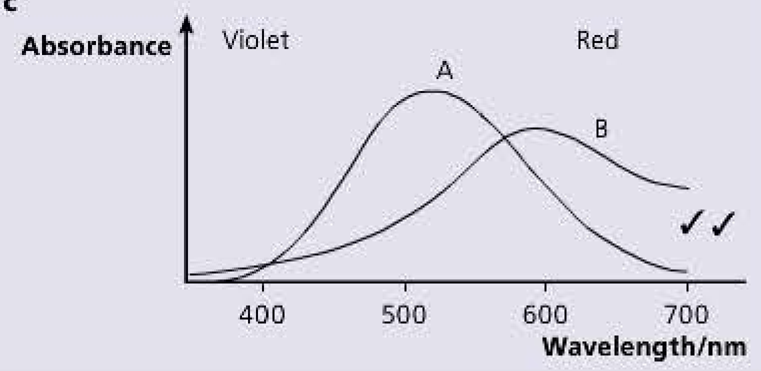
Candidate B

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. ✗

The candidate points out correctly that colour in transition metal compounds is a result of the d-orbitals splitting into two groups of different energies 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.

Candidate B

c



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.

Candidate B

d $3d_{x^2-y^2}$ and $3d_{z^2}$ ✓

This is correct.

Candidate B

e i $2MnO_4^- + 5SO_2 + 2H_2O \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$ ✓ ✓

This is the correct equation, correctly balanced.

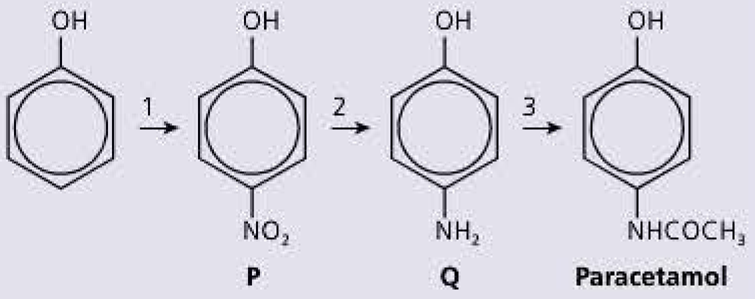
Candidate B

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. ✓

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)**

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 ✗

The candidate has given the reagents for nitration of benzene. Nitration of phenol takes place under milder conditions (see Candidate B).

Candidate A

ii Hydrogenation ✓

Although most textbooks would refer to this as a reduction reaction, hydrogenation would probably be allowed here.

Candidate A

iii Tin and concentrated hydrochloric acid, ✓ heat ✓

The correct reagents and conditions are given, for 2 marks.

Candidate A

iv CH_3CO_2H ✗

The candidate does not seem to have recognised that an amide has been formed.

Candidate A

v Alcohol ✗ and amide ✓

The candidate has forgotten that the –OH group is attached to a benzene ring and is, therefore, a phenol group, not an alcohol.

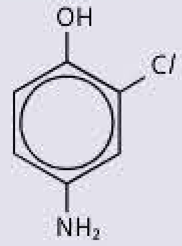
Candidate A

b i A white precipitate forms. ✓

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. So the candidate scores only 1 of the 2 marks.

Candidate A

ii



This is incorrect. HCl does not react to give substitution in the ring.

Candidate A

iii Substitution ✓ (ecf)

Although this is an incorrect answer, it correctly describes what the candidate believed to be true in (ii) and so scores an 'error carried forward' mark.

Candidate B

a i Dilute nitric acid ✓ on warming. ✓

This is a good answer with reagent and conditions correct.

Candidate B

ii Reduction ✓

This is correct.

Candidate B

iii Lithium aluminium hydride ✓ in ether ✓

This is another good answer with both reagents and conditions correct.

Candidate B

iv Ethanoyl chloride ✓

This is correct.

Candidate B

v Phenol ✓ and amide ✓

Both groups are correct.

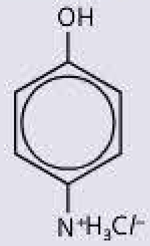
Candidate B

b i Bromine is decolorised ✓ and a white precipitate is formed. ✓

Both observations are correct.

Candidate B

ii



✓

This is correct.

Candidate B

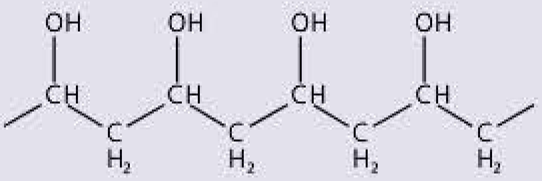
iii Neutralisation ✓

Yet another correct answer.

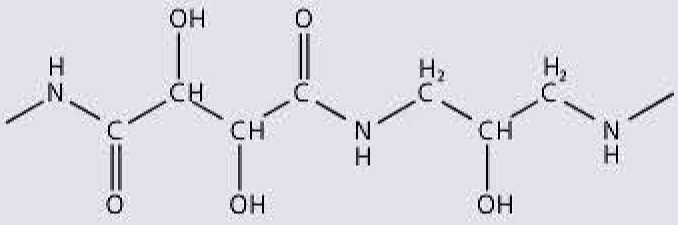
Question 6

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.

L



M



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)**

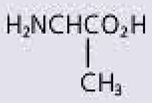
c i **The polymer chains in L can be cross-linked using a small molecule containing two functional groups. Draw the structure of such a molecule.** **(1 mark)**

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.

$H_2NCH_2CO_2H$

Glycine (gly)



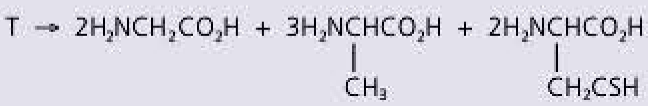
$H_2NCH(CH_3)CO_2H$

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:



$$T \rightarrow 2H_2NCH_2CO_2H + 3H_2N\underset{CH_3}{\underset{|}{C}}HCO_2H + 2H_2N\underset{CH_2CSH}{\underset{|}{C}}HCO_2H$$

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 ✗

This is too vague an answer to score the mark.

Candidate A

b Monomer of L: $H_2C{=}CHOH$ ✓

Monomers of M: $CO_2HCH(OH)CH(OH)CO_2H$ ✗

and $NH_2CH_2CH(OH)CH_2NH_2$ ✓

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-.

Candidate A

c i $CH_2{=}CH_2$ ✗

This is incorrect and ignores the point in the question that the molecule has to have two functional groups.

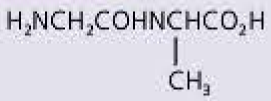
Candidate A

ii Covalent bond ✗

This is not sufficient to score the mark — see Candidate B's answer.

Candidate A

d i



$$H_2NCH_2COHN\underset{CH_3}{\underset{|}{C}}HCO_2H$$

✓

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.

Candidate A

ii It is not optically active. ✓

This is correct.

Candidate A

e i Seven ✗

No. Seven amino acids are linked by six peptide bonds.

Candidate A

ii 575 ✓

This is correct.

Candidate A

iii Refluxed with acid ✓

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 ✓

This is correct.

Candidate B

b Monomer of L: $H_2C{=}CHOH$ ✓

Monomers of M: $HO_2CCH(OH)CH(OH)CO_2H$ ✓

and $H_2NCH_2CH(OH)CH_2NH_2$ ✓

This is a very good answer. All the monomers are identified correctly and their structures are shown accurately.

Candidate B

c i $HO_2C{-}CH_2{-}CO_2H$ ✓

This is correct.

Candidate B

ii Covalent ester linkage ✓

This is correct.

Candidate B

d **i**

$H_2NCH_2\overset{\overset{\displaystyle O}{\|}}{C}—\underset{\underset{\displaystyle H}{|}}{N}CH(CH_3)CO_2H$ ✓

This good answer shows both the dipeptide gly–ala and the peptide bond in displayed form.

Candidate B

ii Glycine is not chiral ✓

This is correct.

Candidate B

e **i** Six ✓

This is another correct answer.

Candidate B

ii 565 ✗

This is an unfortunate miscalculation.

Candidate B

iii Reflux ✓ with concentrated hydrochloric acid. ✓

The answer is correct and complete.

Question 7

a **Study the reaction below, which is second order with respect to NO and first order with respect to H_2.**

$2NO(g) + 2H_2(g) \rightarrow 2H_2O(g) + N_2(g)$

Write the rate equation for the reaction. **(2 marks)**

b **Using the reaction in part a, the rate of the reaction at 1000 K was found to be 0.00267 mol dm^{-1} s^{-1} when $[H_2(g)] = 0.0020$ mol dm^{-3} and $[NO(g)] = 0.0040$ mol dm^{-3}.**

i **Calculate a value for the rate constant at 1000 K giving its units.** **(2 marks)**

ii **Predict the effect on the rate constant of decreasing the temperature to 750 K.** **(2 marks)**

c **A reaction between substances U and V, which is first order with respect to both, has an initial rate of 1.6×10^{-3} mol dm^{-3} s^{-1} at 300 K. The reaction rate doubles when the temperature rises by 10 K.**

Explain which one of the following changes will have the biggest effect on the reaction rate:

- **increasing [U] from 2.00 mol dm^{-3} to 2.06 mol dm^{-3}**
- **increasing the temperature by a further 10 K**

(4 marks)

(Total: 10 marks)

Candidate A

a Rate = $[NO][H_2]$ ✗✗

The candidate has forgotten that the reaction is 2nd order with respect to NO and has also omitted the rate constant.

Candidate A

b **i** $0.00267 = k \times 0.004 \times 0.002$

$k = 334$ ✓; units are mol dm^{-3} ✗

The candidate wrote an incorrect rate equation, but correctly substituted in this equation. The candidate has correctly evaluated the value of k but the units are incorrect.

Candidate A

ii It would decrease because the temperature has decreased ✓ ✗

Although the answer is correct, the candidate has not referred to the rate decreasing, which in turn means that the rate constant is smaller.

Candidate A

c Rate = $k[U][V]$ ✓

Increasing [U] from 2.00 to 2.06 is a 6.00% increase ✗

This is correct, but the percentage increase has been calculated incorrectly.

Candidate A

c Increasing the temperature by 10 K doubles ✓ the rate so this change has the greater effect. ✓

This is correct.

Candidate B

a Rate = $k[NO]^2[H_2]$ ✓✓

This is correct.

Candidate B

b **i** $0.00267 = k \times (0.004)^2 \times 0.002$ ✓

$k = 8.34 \times 10^4$; ✓ units are mol^{-2} dm^6 s^{-1} ✓

This is correct.

Candidate B

ii The rate would decrease because the temperature has decreased. ✓ This in turn would reduce the rate constant. ✓

This is correct and fully explained.

Candidate B

c Rate equation is rate = k[U][V]. ✓ Increasing [U] from 2.00 to 2.06 is a 3% increase would increase the rate by the same factor. ✓

This is correct and fully explained.

Candidate B

c Increasing the temperature by 10 K doubles ✓ the rate so this has the greater effect. ✓

This is correct and fully explained.

Question 8

Modern instrumental techniques play an increasingly important role in determining the structures of organic compounds.

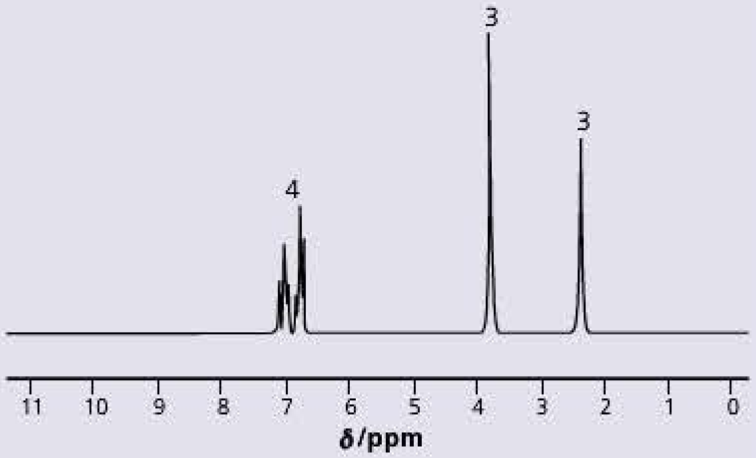
a An aromatic compound R has a mass spectrum in which the M and M+1 peaks are in the ratio 10 : 0.9. The M peak is at *m*/*e* 122. Analysis of the compound gave the following composition by mass: C, 78.7%; H, 8.2%; O, 13.1%.

Showing your working:

i use the data to determine the empirical formula and molecular formula of compound R (3 marks)

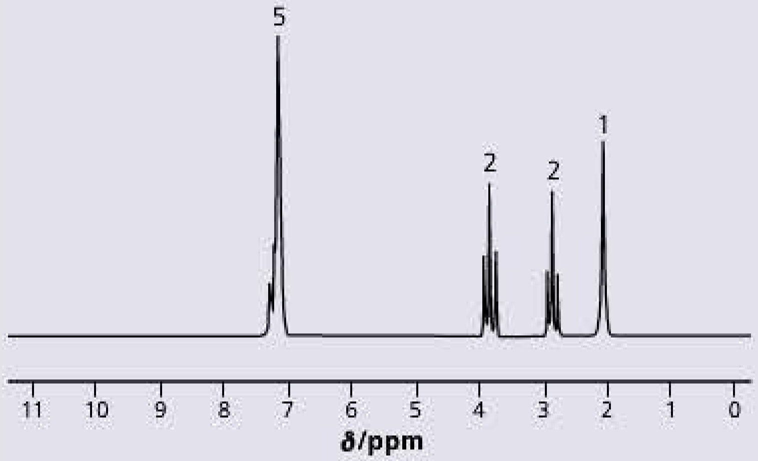
ii use the M and M+1 data to confirm how many carbon atoms are present in compound R (2 marks)

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 shown 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

	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 you know that R has a mass peak at 122. This suggests you need to double the ratio to give $C_8H_{10}O_2$. ✓ (ecf)

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 of the question because there should only be one oxygen in the formula.

Candidate A

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

$$n = \frac{100 \times 0.9}{1.1 \times 10} \checkmark = 8.2 \text{ or } 8 \checkmark$$

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.

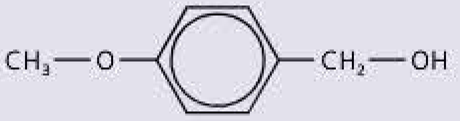
Candidate A

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:

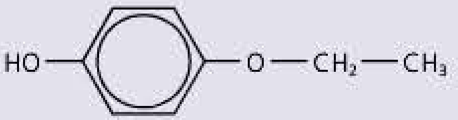


✗

The assignment of the δ values to 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.

Candidate A

c **i** The structure of S is:



✗✗

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.

Candidate A

ii This proton must be an –OH proton that exchanges with D, which does not show in an NMR spectrum ✓.

This is correct.

Candidate B

a **i**

	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 because this has an M_r of 122, this must also be the molecular formula. ✓

This calculation has been carried out correctly. The empirical formula matches M_r and hence the empirical and molecular formulae are the same.

Candidate B

ii Number of carbon atoms is $n = \frac{100 \times 0.9}{1.1 \times 10}$ ✓ = 8.2

or 8 carbons ✓

The calculation of the number of carbon atoms from the M : (M + 1) peaks confirms that deduced in part (i).

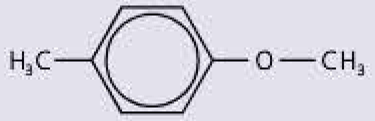
Candidate B

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:

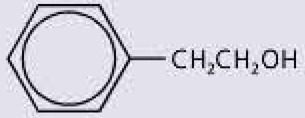


✓

The assignment of δ values to correct hydrogen atoms means that the structure shown for R matches the NMR spectrum.

Candidate B

c **i**



✓✓

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

The structure shown for S is an isomer of R, and the explanation of the NMR spectrum is consistent with this structure.

Candidate B

ii This proton must be an –OH proton that exchanges with D, which does not show in an NMR spectrum. ✓

This is correct.

Question 9

Entropy can be thought of as the number of ways that particles can be arranged, and the number of ways that energy can be shared out between the particles.

a Explain as completely as you can whether the following show an increase or a decrease in entropy.

i $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$

ii $I_2(s) \rightarrow I_2(g)$

iii $N_2O_4(g) \rightarrow 2NO_2(g)$ **(5 marks)**

b Use the data in the table to calculate the entropy change for the reaction:

$Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$

Substance	**Entropy/J K^{-1} mol^{-1} (standard conditions)**
Mg(s)	32.7
$\frac{1}{2}O_2(g)$	102.5
MgO(s)	26.9

(3 marks)

(Total: 8 marks)

Candidate A

a **i** Decrease because two molecules have formed one molecule. ✓✗

ii Increase because a solid has become a gas. ✓✗

iii No change because they are both gases. ✗

i — this is a weak answer because although it is true no mention has been made of the fact that the solid has a more ordered structure.

ii — again although the answer is correct no mention has been made that gases have more disorder and hence higher entropy, but with the first answer probably worth 1 mark.

iii — this is incorrect. The number of particles has doubled and hence also the number of ways that energy can be distributed resulting in an increase in entropy.

Candidate A

b $\Delta S_{system} = S_{Mg} + S_{½O2} - S_{MgO}$

$= 32.7 + 102.5 - 26.9$

$= 108.3$ 37 J K^{-1} mol^{-1} ✓

The problem with this answer is that the candidate has subtracted the entropy of the products from the entropy of the starting materials, rather than vice versa. This is, however, worth a mark because the arithmetic is correct. The units are correct.

Candidate B

a **i** Decrease because two molecules have formed one molecule which, because it is a solid, has more order. ✓✓

ii Increase because a solid has become a gas, which has more disorder ✓✓

iii Although both gases, the number of particles has increased, increasing the entropy. ✓

This candidate shows good understanding of entropy with each answer fully explained.

Candidate B

b $\Delta S_{system} = S_{MgO} - S_{Mg} + ½S_{O_2}$

$= 26.9 - (32.7 + 102.5)$

$= -108.3$ ✓✓ J K^{-1} ✗

This candidate has calculated the value of the entropy change correctly, but loses a mark for quoting the wrong units.

Now test yourself answers

Chapter 1

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 cm^3 of O_2; 75 cm^3 of CO_2

9 1.59 g

10 1200 cm^3

11 0.110 mol dm^{-3}; 6.19 g dm^{-3}

12 0.15 mol dm^{-3}

Chapter 2

1 **A** $^{23}_{11}Na^+$; **B** $^{23}_{11}Na$; **C** $^{23}_{11}Na^-$; **D** $^{24}_{12}Mg$; **E** $^{25}_{12}Mg$; **F** $^{26}_{12}Mg$

2 Group 3; there is a large jump in energy after the third electron is removed.

3 Addition of a second electron to an atom that has already had one electron added.

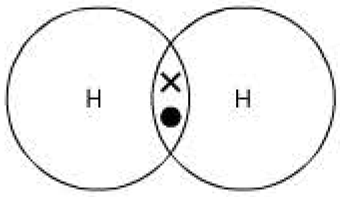
4 For example oxygen, sulfur (any non-metallic element that forms stable X^{n-} ions where *n* is >1).

Chapter 3

1

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	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6$

2 **a**



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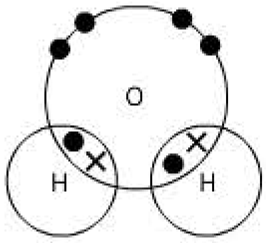

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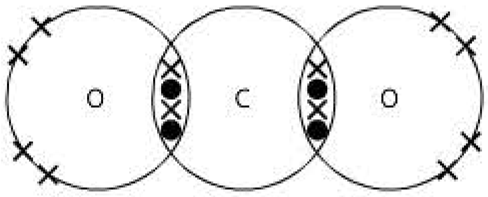

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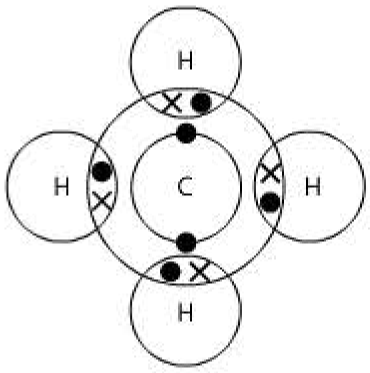

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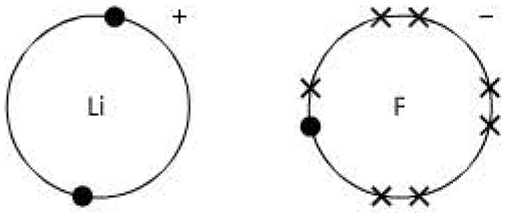


3

Material	Intermolecular force
Methanol, CH_3OH	Hydrogen bonding
Magnesium oxide, MgO	Ionic
Iodine chloride, IC*l*	Dipole–dipole/van der Waals
Argon, Ar	Van der Waals
Aluminium, A*l*	Metallic

Chapter 4

1 Diamond has a giant molecular structure with strong covalent bonds throughout the structure and a tetrahedral arrangement of carbon atoms. Buckminsterfullerene has a simple molecular structure consisting of C_{60} spheres with sp^2 hybridised carbon atoms and weak bonds between the spheres.

2 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. So the data suggest that X has covalent bonds in its molecules, and probably van der Waals forces or dipoles between molecules — for example, paraffin wax.

Chapter 5

1 **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.

2 **a** Entropy increases on melting because the particles are held less rigidly and have more disorder or more ways they can be arranged.

b Entropy decreases as steam condenses because the particles become more ordered or have fewer ways they can be arranged.

3 **a** −ve: fewer particles in product

b −ve: fewer particles in product

c +ve: more gaseous particles in products

Chapter 6

1 **a** +3

b 0

c +6

2 $KMnO_4$: Mn is +7; MnO_2: Mn is +4; K_2MnO_4: Mn is +6

3 **a** $+0.80 + (+0.76) = 1.56\,V$

b $-0.13 + (+2.38) = 2.25\,V$

c $+0.80 + (-0.34) = 0.46\,V$

4 **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 $+1.36 + (-1.07) = 0.29\,V$

Chapter 7

1 **a** **i** The reaction is exothermic, the equilibrium will move in the direction which absorbs energy, i.e. to the left.

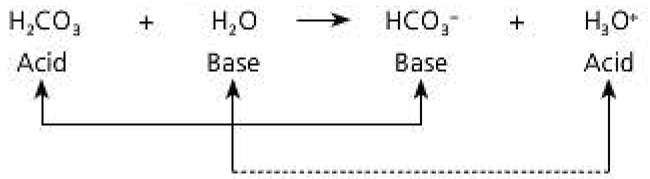
ii The reaction has fewer molecules on the right than on the left, increasing the pressure will favour a shift to the right.

b **i** The reaction consumes CH_3CO_2H in moving left to right, so this is favoured if the acid concentration is increased.

ii The reaction produces water in moving from left to right, the removal of water will favour a shift in this direction.

2 $K_c = \dfrac{[Sn^{4+}][Fe^{2+}]^2}{[Sn^{2+}][Fe^{3+}]^2}$

3 $K_p = \dfrac{p(PCl_3)\cdot p(Cl_2)}{p(PCl_5)}$

4 

$$\underset{\text{Acid}}{H_2CO_3} + \underset{\text{Base}}{H_2O} \longrightarrow \underset{\text{Base}}{HCO_3^-} + \underset{\text{Acid}}{H_3O^+}$$

5 **a** 5

b 3.5

c $K_w = 10^{-14}$, so solution contains $10^{-8.5}\,mol\,dm^{-3}\,H^+$, so its pH is 8.5

6 **a** $K_{sp}(MgF_2) = [Mg^{2+}][F^-]^2$

b $mol^3\,dm^{-9}$

Chapter 8

1 **a** A higher proportion of the molecules have energies greater than E_a.

b E_a is now lower, so a higher proportion of the molecules have energies greater than E_a.

2 The step that takes the longest time dictates how long the whole reaction takes.

3 Because the only compound present in the rate equation is $(CH_3)_3Br$, the second mechanism is correct.

4 **a** A heterogeneous catalyst is in a different physical state to the reactants; a homogeneous catalyst is in the same physical state as the reactants.

b A heterogeneous catalyst is usually a solid; a homogeneous catalyst is usually in solution.

5 Hydrogen bonds and dipole-dipole interactions, e.g. van der Waals forces

Chapter 9

1 **a** The higher the nuclear charge, the stronger the attraction for the electrons.

b The further an electron is from the nucleus, the weaker the force of attraction.

2 The oxidation number matches the group number as far as phosphorus. For sulfur, a chlorine atom is too big to fit six of them round the sulfur atom. Phosphorus also shows a +3 oxidation state.

3 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.

$Si + O_2 \rightarrow SiO_2$

$Si + 2Cl_2 \rightarrow SiCl_4$

$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$

Chapter 10

1 The increase in nuclear charge is counteracted by the increase in the number of inner electrons. The outer electrons are further from the nucleus, which reduces the electronegativity.

2 The small cation at the top of the group has a high charge density; so it can polarise the nitrate anion more.

Chapter 11

1 As you descend the group the van der Waals forces between the molecules get stronger, and the halogens change from gases to a liquid and then to solid elements.

2 There would be no reaction because the H–F bond is stronger than the H–C*l* bond.

3 Any suitable example in which an element in a compound is both oxidised and reduced.

e.g. $2KMnO_4 + MnO_2 + 4KOH \rightarrow 3K_2MnO_4 + 2H_2O$

Chapter 12

1 **a** Scandium has a low density and only forms the +3 oxidation state (it also has a larger atomic radius).

b Zinc has a relatively low melting point and only forms the +2 oxidation state (it also has a high first ionisation energy).

2 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. So, the element is vanadium.

3 $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$

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:

$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$

4 Assume that chromium is in the same oxidation state in each complex. Because the complexes are octahedral they must be of the type $[CrLig_6]^{n+}$. 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.

5 $[CoCl_4]^{2-}$

Chapter 13

1 The bond energy for nitrogen is almost twice as high as that for oxygen (944 kJ mol⁻¹ against 496 kJ mol⁻¹).

2 CH_4 is 109.5°; NH_3 is 107°; H_2O is 105°. The tetrahedral angle is distorted by the one lone pair on the nitrogen atom in ammonia and the two lone pairs on the oxygen in water. Lone pairs occupy a bigger volume in space than bonded pairs of electrons.

3 All nitrates are soluble in water. Whatever nitrate fertiliser is used there is a risk that nitrates will be washed into streams causing eutrophication and/or getting into drinking water supplies.

4 **a** $Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$

b $CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$

Chapter 14

1 2-hydroxypropanoic acid

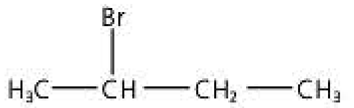
2 **a** 1-chlorobutane

b 2-hydroxypropane or propan-2-ol

c Hexanoic acid

d 3-methylbutylamine

3 **a**



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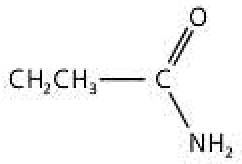

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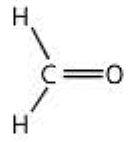

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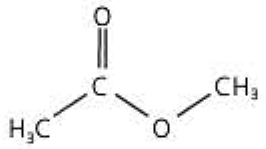


4 **a** $CH_3CH_2CH_2CHO$ (or $CH_3CH_2COCH_3$)

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*.

5 **a** 10

b There are 3 pairs

Chapter 15

1 Free radical substitution

2 **a** $CH_3CH_2CH{=}CH_2 + HBr \rightarrow CH_3CH_2CHBrCH_3$

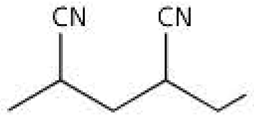
b 2-bromobutane

3 **a** 1,2-dihydroxypropane

b Ethanoic acid and carbon dioxide

4 If aqueous bromine is used, both Br and OH can add to the double bond forming CH_2BrCH_2OH.

5



6 Adding bromine would disrupt the stable π system over the ring.

7 In the 2- and 4- positions

Chapter 16

1 $(CH_3)_2CHBr + OH^- \rightarrow (CH_3)_2CHOH + Br^-$

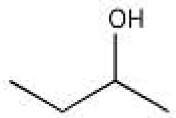
or $(CH_3)_2CHBr + OH^- \rightarrow CH_3CH{=}CH_2 + Br^-$

2 It adds a carbon atom extending the carbon chain.

3 The C–F bond is much stronger than the C–Br bond (467 kJ mol⁻¹ against 276 kJ mol⁻¹).

Chapter 17

1 **a**



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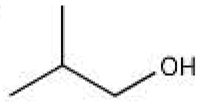

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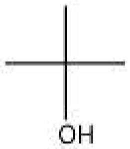

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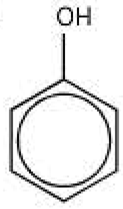


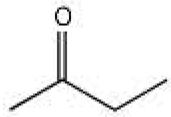
2 **a** secondary

b primary

c tertiary

d secondary

3 **a**



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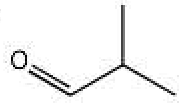


c None

4 **a** ethyl propanoate

b propyl methanoate

c methyl butanoate

d propyl ethanoate

5 In phenol the lone pairs of electrons on oxygen overlap with the ring electrons. When phenol loses a proton, the negative charge can be delocalised over the whole π system, stabilising the anion.

Chapter 18

1 Potassium cyanide plus a little sulfuric acid (HCN is too toxic to use)

2 $CH_3CH_2CH_2CH(OH)CN$

3 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. So K must be $CH_3CH_2CH_2CHO$ and J could be butan-1-ol, $CH_3CH_2CH_2CH_2OH$, or 2-methylpropan-1-ol, $(CH_3)_2CHCH_2OH$.

Chapter 19

1 ethanol; ethanol; acetonitrile (CH_3CN)

2 They are used in perfumes, flavourings, solvents and soaps.

3 $K_a = \frac{[H^+][OH^-]}{[HA]}$

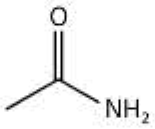
The number before the decimal point in the pK_a represents the $-\log_{10}$ of K_a. So trichloroethanoic acid is about 10^4 times more ionised than ethanoic acid.

4 **a** esters

b phenylesters

c N-substituted amides

5



6 In an acid, the water and acid push the equilibrium reaction towards the alcohol and ethanoic acid. An alkali is more efficient forming the sodium salt of ethanoic acid rather than an equilibrium reaction.

Chapter 20

1 $LiAlH_4$ and H_2 with a platinum, palladium or nickel catalyst. ($NaBH_4$ does not work.)

2 For $LiAlH_4$ the reaction takes place in ethoxyethane solution. With catalyst and H_2 the amine is heated with H_2 in the presence of the metal.

3 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.

4 Asp has an extra $-CO_2H$ group and Lys has an extra $-NH_2$ group.

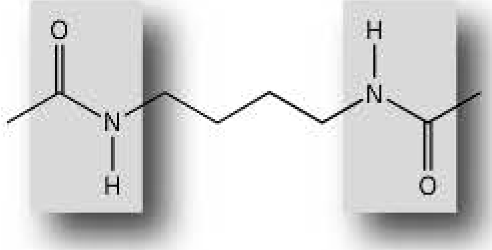
5 $HO_2CCH_2CH_2CH(NH_3^+)CO_2H$

Chapter 21

1 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.

2 **a**



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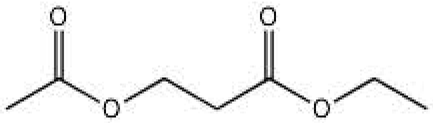


3 In polyethene the forces between the chains are instantaneous dipole–induced dipole interactions. In Kevlar® they are hydrogen bonds between the carbonyl and $-NH_2$ groups.

4 A and T form two hydrogen bonds with each other; C and G form three hydrogen bonds with each other.

5 Disulfide bonding is the 'odd one out' because it is a covalent bond and much harder to break.

Chapter 22

1 Paper chromatography relies on partition; thin-layer relies on adsorption to separate mixtures.

2 Although the temperature of the column and the flow rate of the carrier gas can be adjusted it is the volatility of the sample and the interactions between the components of the sample with both the mobile and stationary phases that are critical.

3 C–O at 1040–1300 cm^{-1} strong; C=C at 1500–1680 cm^{-1} weak; C=O at 1710–1750 cm^{-1} strong; O–H at 2500–3000 cm^{-1} strong and broad

4 $n = \frac{100 \times A_{M+1}}{1.1 \times A_M} = \frac{43}{8.8} = 4.88$, so 5 carbon atoms are present.

5 The peak is shifted to the left in the ^{1}H NMR spectrum.

6 **a** $CH_3C(CH_3)_2OH$ (2-methylpropan-2-ol) because the ^{1}H NMR spectrum shows two peaks in a 9 : 1 ratio.

b $(CH_3)_2CHCH_2OH$ (2-methylpropan-1-ol) because in the ^{13}C NMR spectrum all the carbons are sp^3 and the peak heights are in the approximate ratio 1 : 1 : 2.

c The other alcohols are $CH_3CH_2CH_2CH_2OH$ and $CH_3CH_2CH(OH)CH_3$.

Revision activity answers

Chapter 1

1 7.1 g

2 12.5 cm^3

3 25.0 cm^3

Chapter 2

1 19p, 21n, 18e

2 X has 2 more neutrons and 1 fewer electron than potassium — it must be the cation of an isotope of potassium.

3 First ionisation energy

4 It would be larger because the second electron is being removed from a complete inner shell.

Chapter 3

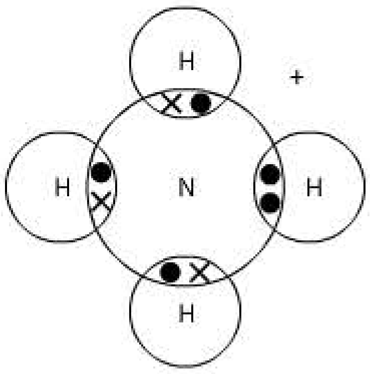
1 In a covalent bond the electrons are shared between the two atoms; in an ionic bond one (or more) electrons are transferred from one atom to the other.

2 van der Waals < permanent dipole–dipole < hydrogen

3 120°

4 In NH_3 the lone pair of electrons on nitrogen occupy a greater volume of space than the bonded electrons, reducing the H–N–H angle from the tetrahedral angle of 109.5°.

5



Chapter 4

1 **a** Use $\frac{V_1}{T_1} = \frac{V_2}{T_2}$. So, $\frac{100}{298} = \frac{V_2}{398}$ and $V_2 = \frac{100 \times 398}{298}$ $= 134\ \text{cm}^3$ (to 3 s.f.)

b Use $p_1V_1 = p_2V_2$. So, $1 \times 100 = 10 \times V_2$, and $V_2 = 10.0\ \text{cm}^3$ (to 3 s.f.)

c Use $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$. So, $\frac{1 \times 100}{298} = \frac{10 \times V_2}{398}$, and $V_2 = \frac{100 \times 398}{10 \times 298} = 13.6\ \text{cm}^3$ (to 3 s.f.)

2 Real gases can be liquefied, indicating that forces must exist between the particles.

3 *Simple molecular*: buckminsterfullerene;
giant covalent: diamond, graphite, graphene

4

Substance	Melting point	Solubility	Electrical conductivity
Potassium bromide	High	Good	Good when molten or in aqueous solution
Aluminium	High	Insoluble	Very good in solid and molten states

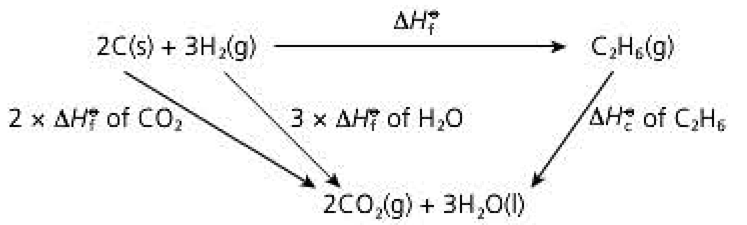
Chapter 5

1 **a** Enthalpy change of formation

b Enthalpy change of atomisation

c Enthalpy change of solution

2



3 $-1559.7\,kJ\,mol^{-1}$

4 You would expect it to be less exothermic because only two molecules of water are formed, but you also have to consider the enthalpy of formation of ethene — it is not a simple comparison.

Chapter 6

1 +1, −1, +5

2 $ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$ reduction;
$ClO^- + 4OH^- \rightarrow ClO_3^- + 2H_2O + 4e^-$ oxidation

3 **a** $Mg(s)/Mg^{2+}(aq)$ $E^\circ = 2.38\,V$, $Cu^{2+}(aq)/Cu(s)$ $E^\circ = -0.34\,V$
$E^\circ_{cell} = -2.38 - 0.34 = 2.04\,V$

b $Fe^{2+}(aq)/Fe^{3+}(aq)$ $E^\circ = -0.77\,V$, $\frac{1}{2}Br_2(l)/Br^-(aq)$ $E^\circ = 1.07\,V$
$E^\circ{}_{cell} = 1.07 - 0.77 = 0.30\,V$

4 You need to use $E = E^\circ + \frac{0.059}{z}\log\frac{[\text{oxidised species}]}{[\text{reduced species}]}$

In this case $E^\circ = 0.43 + \frac{0.059}{1}\log\frac{1.0}{0.01} = 0.43 + 0.059 \times 2$

$= 0.548\,V$

Chapter 7

1 **a** $K_c = \frac{[X_2Y]}{[X]^2[Y]}$

b The reaction is endothermic, so increasing the temperature will shift the equilibrium to the right increasing $[X_2Y]$, so K_c increases.

c Increasing [Y] will have no effect on K_c.

d Adding a catalyst will have no effect on K_c

2 $K_p = \frac{p(NH_3)^2}{p(H_2)^2p(N_2)}$

$1.45 \times 10^{-5} = \frac{p(NH_3)^2}{0.928^3 \times 0.432}$

$p(NH_3) = \sqrt{(1.45 \times 10^{-5}) \times 0.928^3 \times 0.432} = 2.24 \times 10^{-3}$

3 **a** *Acids*: H_3PO_4, HCO_2H, H_2S; *Bases*: PH_3, NH_3

b Strong — H_3PO_4; all the others are weak

4 $K_a = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$

$\frac{[H^+]^2}{0.01} = 1.45 \times 10^{-3}$, so $[H^+]^2 = 1.45 \times 10^{-3} \times 0.01$ and

$[H^+] = 3.81 \times 10^{-3}$

So pH = 2.42

5 Use $pH = pK_a + \log\frac{[\text{salt}]}{[\text{acid}]}$

Mixing the two solutions means that the total volume is $75\,cm^3$ so the concentrations are reduced to ⅔ and ⅓ respectively,

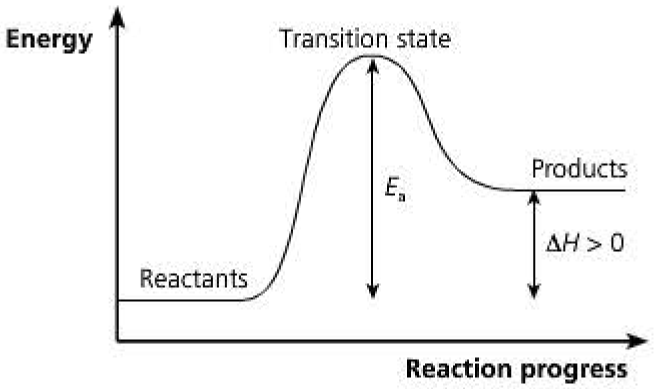
$pH = \log(1.80 \times 10^{-5}) + \log\frac{\frac{2}{3} \times 0.200}{\frac{1}{3} \times 0.200}$

$= \log(1.80 \times 10^{-5}) + \log 2$

$= 5.05$

Chapter 8

1



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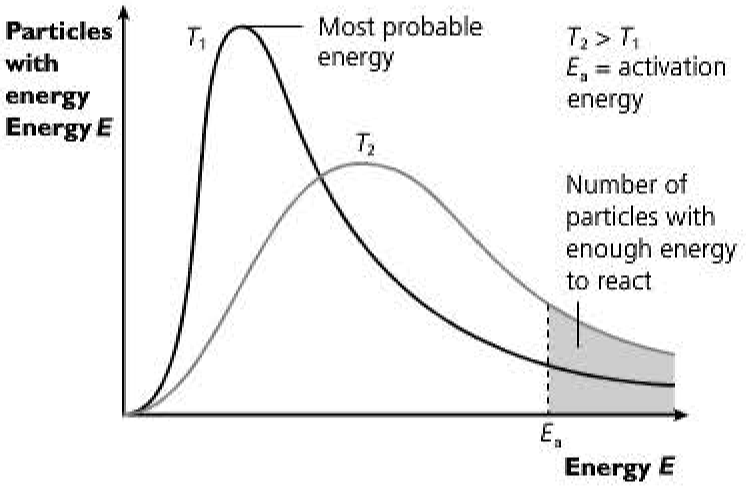


3 When [A] is doubled (runs 2 and 3) the initial rate is doubled, but when [B] is doubled there is no change in initial rate. So the rate equation is rate = k[A].

4 **a** Platinum, rhodium and palladium are commonly used.

b NO_x is converted into N_2 and O_2; CO is converted into CO_2; hydrocarbons are converted into CO_2 and H_2O.

5 **a** The usual answer here is Fe^{2+}/Fe^{3+} catalysing the iodide–peroxodisulfate reaction, but equally acceptable would be the reaction of chlorine radicals with ozone.

b For Fe^{2+}:

$S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$

$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

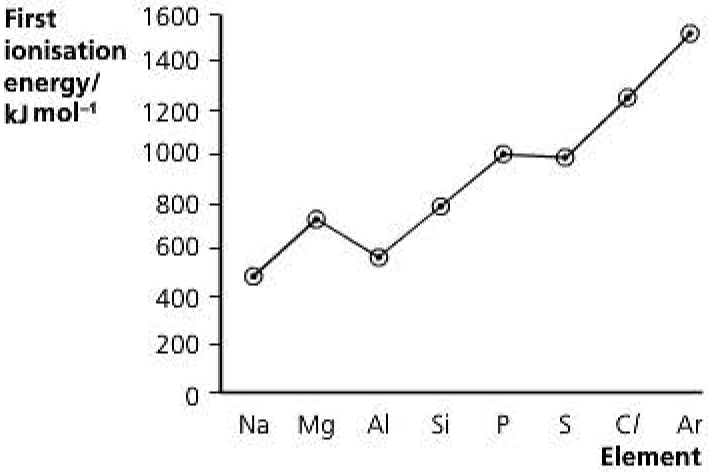
For $Cl\cdot$:

$Cl\cdot + O_3 \rightarrow ClO\cdot + O_2$

$ClO\cdot + O_3 \rightarrow Cl\cdot + O_2$

Chapter 9

1



2 **a** Al_2O_3, SiO_2

b phosphorus

c silicon

d magnesium

3 $Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$

$Al_2O_3 + 2OH^- + 3H_2O \rightarrow 2Al(OH)_4^-$

Chapter 10

1 The reactions are similar, but the elements are less reactive.

2 To form the Group 2 ion, two electrons have to be removed from the atom; this requires more energy.

Chapter11

1 A reaction in which an element is both oxidised and reduced

2 e.g. $Cl_2(aq) + 2OH^-(aq) \rightarrow Cl^-(aq) + ClO^-(aq) + H_2O(l)$

3 **1** Add silver nitrate solution. A chloride will give a white precipitate, a bromide a cream precipitate and an iodide a pale yellow precipitate.

2 Add concentrated sulfuric acid to the solid. A chloride will give steamy fumes, a bromide a mixture of steamy and orange-brown fumes and an iodide a mixture of steamy and purple fumes.

3 Add chlorine water to solutions of the compound and shake with cyclohexane. A chloride will show no reaction, a bromide will produce an orange colour in the cyclohexane, an iodide will produce a purple colour in the cyclohexane.

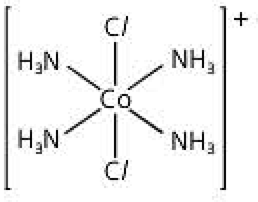
Chapter 12

1 Calcium has no 3d-electrons and is unable to form more than a +2 oxidation state.

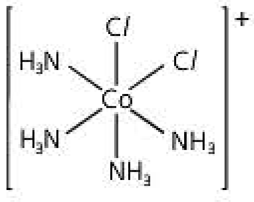
2 Chromium produces complex ions, can form coloured compounds and has multiple oxidation states.

3 Geometrical and optical isomerism.

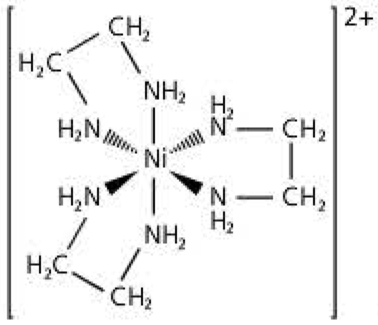
4

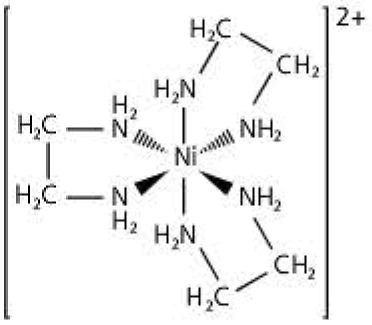


Trans-$[Co(NH_3)_4Cl_2]^+$



Cis-$[Co(NH_3)_4Cl_2]^+$





Chapter 13

1 The N≡N bond energy is very high and the bond requires a lot of energy to be broken.

2 In NH_3 the lone pair of electrons on nitrogen occupy a bigger volume than the bonded electrons, reducing the H–N–H angle from the tetrahedral angle of 109.5°.

3 NO_x is believed to play a part in the reactions that form sulfuric acid in the atmosphere. For example:

$2NO_2(g) + H_2O(g) \rightarrow HNO_2(l) + HNO_3(l)$

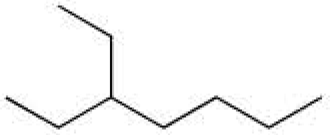
$SO_2(aq) + HNO_3(l) \rightarrow NOHSO_4(l)$

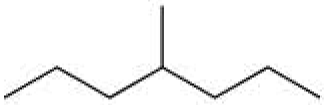
$NOHSO_4(l) + HNO_2(l) \rightarrow H_2SO_4(l) + NO_2(g) + NO(g)$

$SO_2(aq) + 2HNO_2(l) \rightarrow H_2SO_4(l) + 2NO(g)$

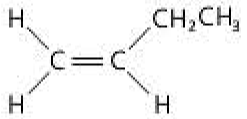
Chapter 14

1

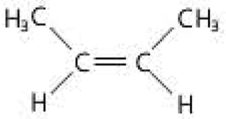




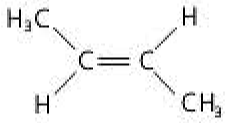
2 **a**



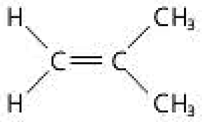
b



c



d



Structures **b** and **c** are *cis–trans* isomers.

3 An electrophilic reagent attacks negatively charged centres; a nucleophilic reagent attacks positively charged centres.

4 In an alkane all the carbon atoms are saturated with four single bonds formed.

Chapter 15

1. Breaking them into smaller fragments produces compounds that are commercially more 'useful'.
2. Alkenes
3. Vegetable oils
4. $CH_3CH(OH)CH_3$
5. They are not biodegradable. They are a source of hydrocarbons that can be re-used (or burned as fuels, but are fossil fuels).
6. It reacts with bromine in a substitution reaction rather than an addition reaction.
7. Methylbenzene can undergo ring- or side-chain substitution.

Chapter 16

1. Carbon and halogens have different electronegativity values and so have different attraction for the electrons in the bond.
2. A C–C*l* bond is much stronger than a C–I bond.
3. $(CH_3)_2CHBr > CH_3CH_2Br > CH_3CH_2Cl > C_6H_5Br$

Chapter 17

1. **a** primary
   b secondary
   c tertiary
   d two secondary
   e primary (left), secondary (right)
   f secondary (left), tertiary (right)
2. Both primary and secondary alcohols cause the acidified potassium dichromate(VI) solution to turn green. On warming the mixture the primary alcohol is oxidised to the carboxylic acid. The smell of this is quite different to the ketone produced by the secondary alcohol. The tertiary alcohol shows no reaction.
3. When the O–H bond is broken, the negative charge on the phenoxide delocalises over the benzene ring.
4. The reaction with phenol requires milder conditions.

Chapter 18

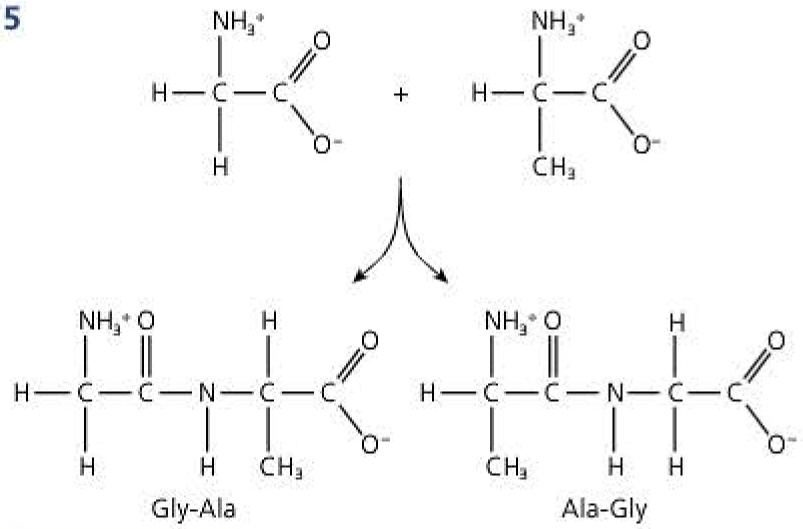
1. Oxidation of the secondary alcohol to an acid would require a C–C bond to be broken.
2. **a** Nucleophilic
   b Addition (across the C=O bond)
3. The iodoform reaction also gives a positive result with ethanol.

Chapter 19

1. (Primary) alcohols, aldehydes and acyl halides
2. Alcohols, esters and acyl halides (plus salts)
3. Any three from: perfumes, flavours, margarine, soap, solvents
4. The highly electronegative chlorine atoms attract electrons from the O–C–O group making it easier to lose the hydrogen ion.
5. HC*l* is a gaseous product making it easier to produce a pure ester.
6. By reacting the acid with PCl_3, PCl_5 or $SOCl_2$

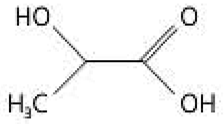
Chapter 20

1. acetonitrile (cyanomethane)
2. diazotisation (coupling)
3. amines
4. They undergo internal ionisation
5.



Chapter 21

1. Water and hydrogen chloride
2. **a** Condensation: an ester group is formed
   b Addition: the backbone consists of C–C bonds
3.



4. Hydrogen bonding
5. *Primary*: the sequence of amino acids in the polypeptide chain

   Secondary: hydrogen bonds resulting from the folding of the main chain e.g. α-helix or β-pleated sheet

   Tertiary: side-chain interactions as a result of folding, e.g. van der Waals forces, hydrogen bonding, ionic interactions or disulfide links

Chapter 22

1. The bonds in the molecule
2. If they contain the same bonds they will have similar spectra.
3. **a** A ($2950\,cm^{-1}$) is due to alkyl; B ($1740\,cm^{-1}$) is due to C=O; and C ($1050\,cm^{-1}$) is due to C–O
   b The molecular formula is $C_3H_6O_2$; the structural formula is $CH_3CO_2CH_3$

4 *Partition* relies on the different solubilities of the material in two solvents, *adsorption* on the attraction of the material to a solid.

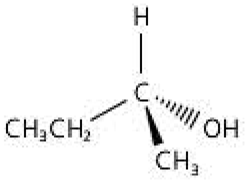
5 CH_3^+ *m/e* 15; $^+C{=}O$ *m/e* 28

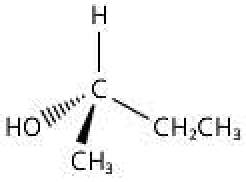
6 In a ^{13}C NMR spectrum there will be two lines corresponding to the two carbon atoms. In a ^{1}H NMR spectrum there will be three groups of lines corresponding to protons in three different chemical environments. These will consist of a single peak, a group of peaks with heights 1, 3, 1 and a group of peaks with heights 1, 2, 1.

7 Protons attached to oxygen or nitrogen that can exchange with deuterium atoms

Chapter 23

1





2 None

3 Aldehyde (cannot be an alcohol because sodium does not react; cannot be a ketone because MnO_4^- is decolorised)

4